Vibrational relaxation theories and measurements

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The rapid progress in research on chemical lasers has led to increased interest in the development of theoretical models of molecular relaxation processes. In this review, recent applications of various theories of nonreactive collisions between diatomic molecules, from semiclassical to quantal, are surveyed in light of experimental data. The intention is to provide the theoretician with a background of those features of the collision problems that require more accurate treatments, and to provide the experimentalist with a spectrum of models available for handling his data.

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I. INTRODUCTION

In a recent compilation of the literature dealing with chemical lasers only, Arnold and Rojeska (1973) list approximately 240 reported laser systems, of which about 190 involve the hydrogen halides (mainly HF). Hydrogen halide chemical lasers are attractive for numerous industrial, academic and military applications because of high power densities at shorter wavelengths and large (about 15%) chemical efficiency. The potential of chemical lasers in general, for probing the details of molecular dynamic reactions, and for related basic and applied research has been discussed in a recent review by Bernstein (1971).

Various studies of the performance characteristics of chemical lasers show that collisional deactivation of the hydrogen halides by various partners is an important criterion in the choice of the reagent mixtures. For example, studies of *cw* transverse flow lasers suggest that the large rates for self-deactivation and vibrational energy transfer in H(D)F molecules are among the reasons why *cw* devices operate under conditions of partial rather than the total inversion characterizing pulsed lasers (Rosen *et al.* 1973). Collisional energy redistribution, rather than specific chemical reactions, has been postulated as the more important performance limiting factor. In a recent investigation and modelling of an atmospheric pressure pulsed HF chemical laser, Chen *et al.* (1974) concluded that the major collisional loss process was due to V–T, R self-relaxation of upper ($v > 2$) vibrational levels of HF and that the v dependence of these rates was a critical model parameter. They also drew attention to the lack of data on processes contributing to rotational relaxation and nonequilibration.

Similar conclusions are obtained in analyses of chemical transfer lasers [e.g., hydrogen halide-CO_2, see Cool (1973)]. Here, identification of the major pumping mechanism depends largely on the degree to which intermolecular V–V and V–R coupling is responsible for the energy transfer rate. Cool suggested that anharmonicity effects and multiquantum transitions could be more important than had been originally expected.

The performance of pulsed electrical lasers [(e.g., CO, see Jacobson and Kimbell (1970, 1973)] seems also to be strongly determined by the details of vibrational self-deactivation. This, together with deactivation in collisions with O and O_2, controls the operation of a transversely spark-initiated CO laser based on ignition of a CS_2/O_2 mixture (Graham *et al.* 1970). According to the above cited compilation by Arnold and Rojeska, this is the technique which has yielded the highest power reported, up to the date of their paper, in a pulsed CO laser. The presence of He or H_2 in nearly all of the chemical systems used for both pulsed and *cw* CO lasers implies that rates for processes CO–X and CO–X_2 are also of interest. This point has also been made by Graham (1970) who, in his investigations of the pulsed electrical lasers at low temperature, considered several mechanisms for establishing population inversion, including cascading, population inversion via collisional excitation, and successive deexcitation due to the anharmonicity of the CO molecule (McKenzie, 1972). In this case, an exact knowledge of the excitation rates is needed to establish the mechanisms responsible for limitations of the laser, expecially at lower temperatures. The reason for this is that when the excitation rates of the upper levels become comparable with the V–V decay rate, overpopulation of the lower levels leads to current saturation and limits the power outputs.

The preceeding examples illustrate the diversity of molecular collision systems of active current interest in laser studies as well as the increasingly emerging suggestion of the importance of those aspects of molecular collision dynamics that, until a few years ago, were not even considered—e.g., vibration–rotation and V–R–T coupling; interplay of strongly attractive and short range repulsive forces; violations of selection rules (Cool, 1972); multiquantum transitions and anharmonicity effects (Dillon and Stephenson, 1972; McKenzie, 1972). The phenomenon that has attracted the greatest amount of attention is the surprisingly fast vibrational relaxation rate of HF, first reported by Airey and Fried (1971), and since confirmed in numer-

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ous experiments (e.g., Hancock and Green, 1972; Stephens and Cool, 1972; Bott and Cohen, 1973; Bott, 1972; Bresheers and Bird, 1973; Hinchen, 1973a; and Ahl and Cool, 1973). Hancock and Green reported a self-relaxation rate two orders of magnitude faster than that predicted by extrapolation of shock tube data, and a similar temperature inversion for HF quenching by D_2 and CO_2, but *not* by N_2. These and other results are discussed in Sec. III.

To summarize, the most important performance-limiting factors in molecular lasers are determined by the various energy transfer processes for self-deactivation and vibrational energy transfer of the constituent gases. Yet, there is a near consensus among all the experimentalists studying these processes that there exists no theory that adequately explains or predicts the variety of their observations. The small sampling of information collected in this review, when viewed under one cover, strengthens both conclusions. The review was primarily guided by the objective of isolating the topics that could be of value in defining criteria for a possible development of a general molecular reaction rate computer code for use in laser modelling studies. This explains its bias toward the halides and the somewhat selective presentation of the experimental data and theoretical methods that appear most promising from this viewpoint and that seem to best bring out the salient features of diatomic molecular collision problems.

The first two sections contain an outline of some major problems and of a few experimental results. In the remaining sections (IV–VII) examples of the methods that have been developed for modelling molecular collisions are arranged in order of increasing sophistication, i.e., semiclassical, classical, Monte Carlo, and quantal.

By and large, the selected bibliography is representative of the state-of-the-art as of early 1974. It is by no means as comprehensive as the subject matter warrants and the author apologizes to those whose work was overlooked or not adequately discussed. Readers interested in pursuing particular problems or ideas are urged to consult the original articles and the several excellent reviews (Rapp and Kassal, 1969; Taylor and Bitterman, 1969; Levine, 1969, 1972; Polanyi, 1971, 1972; Gordon, 1971, 1973; Secrest, 1973; Moore, 1972, 1973; George and Ross, 1973, to cite but a few) dealing in various ways with the fascinating basic problems in this field.

II. PRELIMINARIES

The relaxation processes considered in this review are mainly those that determine the performance of numerous molecular lasers. For example, in the case of the HF chemical laser, the primary reactions

$$F + H_2 \rightarrow HF^* + H \tag{1}$$

$$H + F_2 \rightarrow HF^* + F \tag{2}$$

liberate sufficient energy to populate vibrational levels of HF up to $v = 3$ by reaction (1), and up to $v = 10$ by reaction (2). It has been estimated (Jonathan, *et al.* 1971a) that approximately 70% and 50% of the reaction energies of 31.6 and 98.0 kcal/mole are initially available in the vibrational modes to HF produced by reactions (1) and (2), respectively. In the analogue of reaction (2) for systems $H + Cl_2$ and $H + Br_2$ the values are 45% and 55% (Anlauf *et al.* 1967). Johnathan *et al.* (1971b) showed that the maximum vibrational energy level populations for reactions (1) and (2) were obtained for $v = 2$ and $v = 5$, respectively, and suggested that this provided the explanation as to why these levels showed the strongest lasing action in the H_2–F_2 laser, as reported by Basov *et al.* (1971).

The rates of formation of excited HF and other diatomics, while of great interest, properly belong to the study of reactive collisions and are outside the scope of this review. Many detailed experimental studies of such rates (the theoretical work is referred to in Sec. VI) have been described ever since the suggestion by Polanyi (1961) and the demonstration by Kasper and Pimentel (1964) of the possibility of laser action based on the vibrational population inversion produced in exoergic chemical reactions (see for example Polanyi and Tardy 1969; Parker and Pimentel 1969; Schaefer *et al.* 1970 and Polanyi 1971). Results of measurements of initial distributions of vibrational, rotational and translational energies in product molecules for reaction (1) and its D_2 analogue, including effects of rotational relaxation, have been described by Polanyi and Woodall (1972), and for reaction (2) by Polanyi and Sloan (1972). The last two papers contain references to most of the earlier work, while similar studies in other halide systems are discussed in the companion papers (e.g., Maylotte *et al.* 1972). More recently, Coombe and Pimentel (1973) reported the first investigations of the temperature dependence of the rates for reaction (1). They found the population inversion increasing and decreasing with decreasing temperature for $F + H_2$ and $F + D_2$ respectively.

The excited product molecules formed in reactions (1) and (2) will decay by a variety of processes according to the diluent gas present in the laser. Information on the mechanisms causing the deactivation of these excited molecules and their possible re-excitation is obtained by studying non-reactive collision processes typified by the reactions

$$HF^* + XY \xrightarrow{k_{vv}} HF + XY^* + \Delta E_1, \tag{3}$$

$$HF^* + HF \xrightarrow{k_{11}} 2HF + \Delta E_2 \tag{4}$$

$$HF^* + X \xrightarrow{k_{12}} HF + X + \Delta E_2, \tag{5}$$

$$X^* + HF \xrightarrow{k_{21}} X + HF + \Delta E_3 \tag{6}$$

$$X^* + X \xrightarrow{k_{22}} 2X + \Delta E_3. \tag{7}$$

Reaction (3) represents V–V exchange between HF and XY; reactions (4)–(7) represent various V–R and V–T (and V–R, T) processes. In reactions (3)–(7), XY and X denote any (*hetero*)homonuclear diatomic system, and X can also denote an atom. In reaction (3) if ΔE is zero, or small, the process is said to be resonant or near resonant. Vibrational relaxation in systems governed by such processes has been recently discussed by Moore (1973).

The experimental techniques for the determination of relaxation rates depend on measurement of a relaxation time in a gas disturbed from equilibrium (see for example, Cottrell and McCoubrey 1961). The rate k_{ij} for energy transfer in a collision between X and Y by a process such as T–V from a state i to a state j of X is obtained from

$$X_i + Y \underset{k_{ji}}{\overset{k_{ij}}{\rightleftarrows}} X_j^* + Y \tag{8}$$

and is defined by the number of transitions per second per molecule from state i to state j. If, as is frequently the case, we are only concerned with excitation and de-excitation between the ground to the first excited states, then $i = 0$, $j = 1$, and we can write

$$[X_0] + [Y] \underset{k_{10}}{\overset{k_{01}}{\rightleftarrows}} [X_1] + [Y] \tag{9}$$

where the square brackets denote concentrations.

If we now assume that the probability of excitation of X is independent of the state and concentration of its collision partner Y, and that the disturbance of $[X_1]$ from equilibrium is small so that $[X_0]$ is constant and $[X_0] \gg [X_1]$, the rate equation

$$(d/dt)[X_0] = k_{01}[X_0]^2 - k_{10}[X_1][X_0] \tag{10}$$

can be integrated to give

$$\Delta[X_1(t)] = \Delta[X_1(t = 0)] \exp(-t/\tau), \tag{11}$$

where $\Delta[X_i(t)] = [X_i(t)] - [X_i^0]$, $[X_i^0]$ being the equilibrium concentration.

$$\tau = \frac{1}{k} = \frac{1}{k_{10}' + k_{01}'}, \tag{12}$$

and

$$k_{ij}' = k_{ij}[X_0].$$

If P_{10} is the average transition probability for the process $1 \to 0$ in a single collision and V_c the collision frequency per molecule, we have

$$k_{10}' = P_{10}V_c[X_0]$$

and, for a gas near equilibrium

$$[X_0/[X_1] = (g_0/g_1) \exp(\Delta E/kT), \tag{13}$$

where ΔE is the 0–1 level separation, and the g_i's are the statistical weights of the levels.

Hence,

$$P_{01}/P_{10} = (g_1/g_0) \exp(-\Delta E/kT) \tag{14}$$

and so

$$\tau^{-1} = P_{10}v_c[X_0][1 + g1/g_0 \exp(-\Delta E/kT)]. \tag{15}$$

Strictly speaking, Eqs. (12) and (15) are valid only if a binary rate can be defined, and if only a single process contributes in Eq. (8). In practice, the rate must be considered an average over various inelastic transitions because of the processes connecting any two states to other states in any real system. Hence (12) is more correctly written (Levine and Bernstein, 1972)

$$k < k_{10} + k_{01} \tag{15a}$$

which for a two state system, in the limit of weak coupling and for collinear collisions only, becomes (Herzfeld and Litowitz, 1957)

$$k \simeq k_{10} - k_{01}. \tag{15b}$$

Because of increasing evidence (cf. Sec. III) that relaxation phenomena in many diatomic molecules at low temperatures violate the assumptions leading to Eq. (15b), some remarks on recent treatments of the relationship between rate constants and collision cross sections may be worthwhile.

The basic problem was first attacked by Coulson and Levine (1967) who used the scattering formalism of Lippmann (1966) to introduce the concept of a yield operator such that its average over any ensemble is the effective rate constant. Although the main thrust of their interest was in reactive collisions, the results, with minor modifications, apply to nonreactive collisions as well. Contact with multichannel collision theory is made by relating the yield function to the S matrix, i.e.,

$$Y(E) = \sum_{nn'} | S_{nn'} |^2 \tag{16}$$

which guarantees symmetry and detailed balance, while the relaxation rate constant is defined as the Laplace transform of Y, i.e.,

$$k(T) = (hQ)^{-1} \int_0^\infty Y(E) \exp(-E/kT)\, dE, \tag{17}$$

where Q is the partition function per unit volume for the center of mass motion and all internal degrees of freedom of the collision system. An important result obtained by Coulson and Levine was that, even for systems characterized by perturbations consisting of pair interactions only, the restriction of possible processes in the ensemble to unimolecular or bimolecular only, could be lifted.

Subsequently, Levine and Bernstein (1972) used these ideas to examine the near threshold behavior of vibrational excitation cross sections and were able to suggest a way toward a possible correlation of the departures in the temperature dependence of some relaxation rates from the conventional Landau–Teller (1936) predictions. To discuss vibrational relaxation they investigated the temperature dependence of the rate constant—determined by Eq. (17)—by analogy with the empirically determined dependence for the conventional bimolecular rate constant P_T defined by $P_T = kT/k(T)$, and obtained

$$\ln k(T) = \ln a - 5/2 \ln kT + \ln \left\{ \int_0^\infty Y(E) \exp(-E/kT)\, dE \right\}, \tag{18}$$

where E is the translational energy.

Evaluation of (18) by the method of steepest descent results in

$$\ln Y(E) - E/kT = -A - BT^{-1/3} + 0\ln(T) \tag{19}$$

and allows a single parameter fit for the exponential variation of the yield function

$$\ln Y(E) = -(E_m/E)^{1/2},$$

with $E_m = k(4/27)B^3$. Typical values of E_m taken from their paper are given in Table I. Levine and Bernstein suggested that departures from linearity of the Landau–Teller plots of vibrational relaxation times could be attributed to the (usually neglected) terms of $0\ln(T)$ in Eq. (19). Note, in passing, that a connection between this parameterization of the yield function and the apparent uniqueness of the ratio [well depth/kx (temperature of deviation from Landau–Teller behavior)] pointed out by Miller and Millikan (1970) could perhaps be established. For additional considerations of this subject the interested reader is referred to the original articles, as well as the papers of Gerjuoy (1958), Smith (1962, 1972) and the monograph by Levine (1969).

TABLE I. Typical values of E_m for systems studied by shock tube methods.[a]

System	$E_0/k \equiv \theta_{\mathrm{vib}}$ (°K)	B(°K$^{1/3}$)	E_m/k(°K)
H_2	6.0×10^3	100	1.5×10^5
$H_2 + Ar$	6.0×10^3	101	1.5×10^5
D_2	4.3×10^3	125	2.9×10^5
$D_2 + Ar$	4.3×10^3	125	2.9×10^5
$D_2 + Kr$	4.3×10^3	125	2.9×10^5
N_2	3.4×10^3	235	1.9×10^6
$N_2 + H_2$	3.4×10^3	81	0.8×10^5
O_2	2.24×10^3	126	3.0×10^5
$O_2 + H_2$	2.24×10^3	36	0.6×10^4
$O_2 + D_2$	2.24×10^3	63	0.4×10^5
$O_2 + He$	2.24×10^3	60	0.3×10^5
$O_2 + Ar$	2.24×10^3	161	6.2×10^5
CO	3.08×10^3	160	6.1×10^5
CO + He	3.08×10^3	87	1.0×10^5
CO + Ne	3.08×10^3	142	4.2×10^5
CO + Ar	3.08×10^3	182	8.9×10^5
CO + Kr	3.08×10^3	188	9.8×10^5

[a] From Levine and Bernstein (1972).

Returning to our main topic, if experimental observations are carried out in a gas mixture wherein the molecule being studied may relax by two processes, a shifted relaxation time can be defined

$$\tau^{-1} = (1 - n_Y)\tau_{Y'} + n_Y\tau_Y, \tag{20}$$

where n_Y is the concentration (mole fraction) of Y in Eq. (20) which is now assumed to contribute to the deactivation of A by some process. For this case, observations of a double exponential decay permits the determination of the individual rates. (An example of three exponential decays in DCl–CO–DBr–Ar mixtures has been quoted by Zittel and Moore 1973a). Examples of this are given in Sec. III.

In the general case of a mixture of two diatomic gases and a diluent, for example DF, D_2, Ar, the explicit form of Eqs. (4)–(7) for the relaxation of the system becomes (Bott, 1974)

$$\mathrm{DF}(v=1) + D_2(v=0) \underset{k_{vv}}{\overset{k_{vv}}{\rightleftarrows}} \mathrm{DF}(v=0) + \mathrm{D}_2(v=1) + \Delta E = -83\ \mathrm{cm}^{-1} \tag{21}$$

$$\mathrm{DF}(v=1) + \mathrm{DF}(v=0) \overset{k_{11}}{\rightleftarrows} 2\mathrm{DF}(v=0) + \Delta E = 2907\ \mathrm{cm}^{-1} \tag{22}$$

$$\mathrm{DF}(v=1) + \mathrm{D}_2(v=0) \overset{k_{12}}{\rightleftarrows} \mathrm{DF}(v=0) + \mathrm{D}_2(v=0) + \Delta E = 2907\ \mathrm{cm}^{-1} \tag{23}$$

$$\mathrm{D}_2(v=1) + \mathrm{D}_2(v=0) \overset{k_{22}}{\rightleftarrows} 2\mathrm{D}_2(v=0) + \Delta E = 2990\ \mathrm{cm}^{-1} \tag{24}$$

$$\mathrm{D}_2(v=1) + \mathrm{DF}(v=0) \overset{k_{21}}{\rightleftarrows} \mathrm{D}_2(v=0) + \mathrm{DF}(v=0) + \Delta E = 2990\ \mathrm{cm}^{-1} \tag{25}$$

$$\mathrm{DF}(v=1) + \mathrm{Ar} \overset{k_{1\mathrm{Ar}}}{\rightleftarrows} \mathrm{DF}(v=0) + \mathrm{Ar} + \Delta E = 2907\ \mathrm{cm}^{-1} \tag{26}$$

$$\mathrm{D}_2(v=1) + \mathrm{Ar} \overset{k_{2\mathrm{Ar}}}{\rightleftarrows} \mathrm{D}_2(v=0) + \mathrm{A}_2 + \Delta E \quad \Delta E = 2990\ \mathrm{cm}^{-1} \tag{27}$$

Moore (1967) has discussed the extraction of V–V and V → R, T rates from laser induced fluorescence measurements for such a system and his prescription has been applied by several researchers to their analyses of the data of the experiments quoted in the next section, (e.g., Chen and Moore 1971a, and Stephenson and Moore 1972). The excited species will, in general decay according to, for the example of Eqs. (21)–(27),

$$[\mathrm{DF}^+] = C_1\exp(-t/\tau_f) + C_2\exp(-t/\tau_s) \tag{28a}$$

$$[\mathrm{D}_2^+] = C_3\exp(-t/\tau_f) + C_4\exp(-t/\tau_s), \tag{28b}$$

where τ_f and τ_s are the fast (V–V) and slow (V–R, T) rates respectively and are given by

$$2(1/p\tau_i) = a_1 + b_2 \pm [(a_1 - b_2)^2 + 4a_2b_1]^{1/2}, \tag{29}$$

where the + or − sign is taken according as $i = f$ or s and the constants a and b are functions of the mole fractions of the decaying species and the rate constants (k_{ij}) in Eqs. (21)–(27). Again, in a typical experiment single and double exponential decays can be observed and k_{vv} or ($k_{12} + k_{vv}$) and k_{11} are usually determined, provided values for the other k's are known or can be estimated. The results of such analyses can lead to significantly different interpretations of the data than those obtained on the basis of Eqn. (20) alone. An example of this is provided by the data of the HF–N_2 system as discussed in the next section.

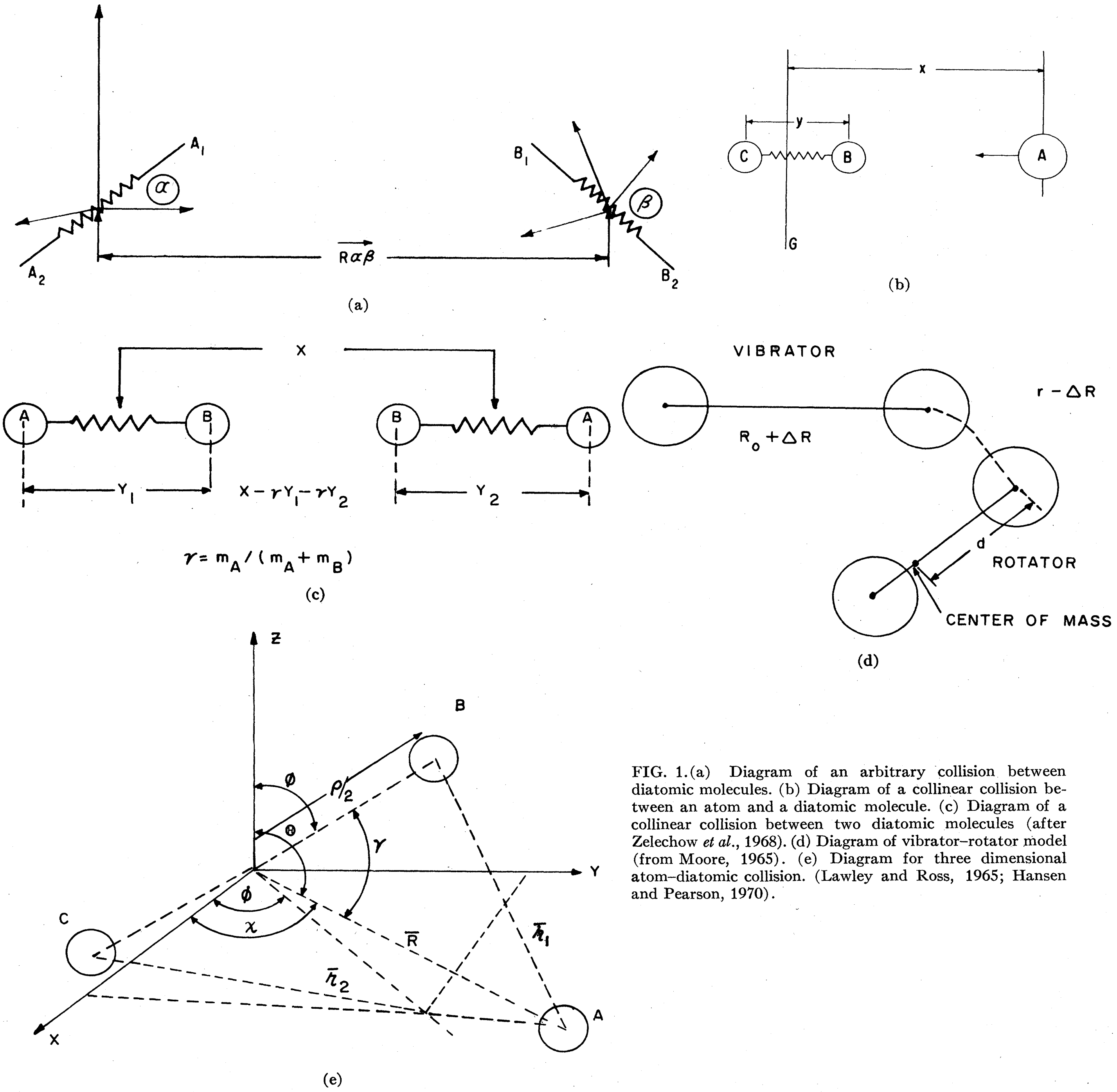

FIG. 1. (a) Diagram of an arbitrary collision between diatomic molecules. (b) Diagram of a collinear collision between an atom and a diatomic molecule. (c) Diagram of a collinear collision between two diatomic molecules (after Zelechow *et al.*, 1968). (d) Diagram of vibrator–rotator model (from Moore, 1965). (e) Diagram for three dimensional atom–diatomic collision. (Lawley and Ross, 1965; Hansen and Pearson, 1970).

An analogous prescription for the determination of V–V transfer rates from shock wave relaxation profiles of two diatomic gases in the presence of an inert monoatomic gas has been recently discussed by Sato *et al.* (1969). This prescription was used by Breshears and Bird (1971) in their determination of V–V rates in the HI–N_2 and DI–N_2 systems, and more recently by Sentman and Solomon (1973) in their analysis of the HF–N_2 shock tube data of Blauer *et al.* (1971).

To treat the energy transfer processes indicated in reactions (4) through (7) with a general computational molecular collision model,[1] we can write the Schroedinger wave equation for two interacting diatomics α, β, see Fig. 1(a).

$$(\hbar^2/{}^2\mu)[V_{R_{\alpha\beta}}{}^2 + V(\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_{\alpha\beta}) - E]\Psi(\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_{\alpha\beta}) = 0 \tag{30}$$

where μ is the reduced mass of the system

---

[1] See also Gioumousis and Curtiss (1958), Hunter and Curtiss (1973 and references therein).

$$\mu = \mu_\alpha \mu_\beta / (\mu_\alpha + \mu_\beta),$$

and μ_α, μ_β are the reduced masses of the diatomics.

The very concept of an intermolecular force implies that the collision complex can be characterized by a set of quantum numbers that do not change during the collision. A general expression for the potential $V(\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_{\alpha\beta})$ can be written by combining Rose's (1958) multipole expression with a short range term, i.e.,

$$V(\mathbf{R}_\alpha, \mathbf{R}_\beta, R_{\alpha\beta}) = \sum_{n=1}^{\infty} \sum_{l_\alpha=0}^{n-1} \sum_{m=-l<}^{l<} \frac{(-1)^{l_\beta}(n-1)!Q_{l\beta m}(\alpha)Q_{l\beta -m}(\beta)}{[(l_\alpha - m)!(l_\alpha + m)!(l_\beta - n)!(l_\beta + m)!]} \times \frac{1}{R_{\alpha\beta}{}^n}$$
$$- A(\mathbf{R}_\alpha, \mathbf{R}_\beta) \exp(-B(\mathbf{R}_\alpha, \mathbf{R}_\beta) \cdot \mathbf{R}_{\alpha\beta}), \tag{31}$$

where the Q's are the irreducible tensorial components of the electrostatic multipole operators for the molecules (Stogryn and Stogryn, 1966; Hirschfelder and Meath, Buckingham 1967) and the coefficients A, B can be determined by requiring that V and its derivative be continuous at, e.g., distances where exchange effects can be neglected (Riera and Meath 1972; Riera 1973). A method for deriving short-range interactions in terms of effective polarizabilities based on treating the atomic electrons as three dimensional coupled harmonic oscillators has been developed by Kim and Gordon (1974, see also Gordon and Kim 1972). An important advantage of their model is that short range forces are not added independently to the long range potential so that the effect of overlap at small distances in the mechanism that causes the long range forces is taken into account.

In the Born–Oppenheimer approximation, the molecular wavefunction can be written (Michels 1972, Harris 1972),

$$\psi_{\gamma_\alpha}(\mathbf{R}_\alpha) = \psi_{n_\alpha \gamma_\alpha s_\alpha}{}^{\mathrm{el}}(R_\alpha) \psi_{n_\alpha \lambda_\alpha s_\alpha v_\alpha}{}^{\mathrm{vib}}(R_\alpha)$$
$$\times Y_{k_\alpha M_{k\alpha} \lambda_\alpha}(R_\alpha) \psi_{s_\alpha M_{s\alpha}}{}^{\mathrm{sp}}(\sigma_\alpha) \tag{32}$$

and similarly for β. (The electronic coordinates $\mathbf{r}_\alpha$ in γ^{el} have been suppressed). This function satisfies the equation

$$[H_\alpha / R_\alpha) - W_\alpha(R_\alpha)] \psi_{\sigma_\alpha}(R_\alpha) = 0. \tag{33}$$

Let Γ denote a state of the collision system. Then

$$\psi^\Gamma(\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_{\alpha\beta}) = \sum_{I'} \chi^{\Gamma'}(\mathbf{R}_\alpha, \mathbf{R}_\beta, \hat{R}_{\alpha\beta}) F^{\Gamma\Gamma'}(R_{\alpha\beta}) / R_{\alpha\beta}, \tag{34}$$

where the expansion coefficients χ are now defined in terms of basis functions given by Equation (32). The definition of the set of quantum numbers Γ depends on our choice of the constants of motion. We devide Γ into three subsets $\lambda_1, \lambda_2, \lambda_3$: i.e., $\Gamma \equiv \lambda_1 \lambda_2 \lambda_3$ where λ_1 denotes those quantum numbers that change in the collision (i.e., the collision channel indices), λ_2 those that define the intermediate coupling necessary to specify the expansion coefficients χ and λ_3 are the constants of motion. If we choose a representation in which the total angular momentum and spin are conserved and construct the expansion coefficients from the wavefunctions, Eq. (32), we obtain in the usual way $\lambda_3 \equiv LSM_L M_S \Pi$, and

$$\Psi_\Gamma(q; \mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_{\alpha\beta}) = \sum_{\lambda_2 \lambda_2} \bar{C}_m \times \psi_{\sigma_\alpha}{}^{\mathrm{el}} \times \psi_{\sigma_\beta}{}^{\mathrm{el}} \times \psi_{\sigma_\alpha}{}^{\mathrm{vib}}$$
$$\times \psi_{\sigma_\beta}{}^{\mathrm{vib}} \times \mathrm{Y}_{k_\alpha M_{k\alpha}}(\hat{R}) \times \mathrm{Y}_{k_\beta M_{k\beta}}(\hat{R}_\beta) \times \mathrm{Y}_{l m_l}(\hat{R}_{\alpha\beta})$$
$$\times F_{\Gamma \lambda_1 \lambda_2}{}^{\mathrm{LS}}(R_{\alpha\beta}) / R_{\alpha\beta}, \tag{35}$$

where we have symbolically denoted by $\bar{C}_m$ the product of all the Clebsch–Gordan coefficients necessary to form the total state function, and the label σ_α represents the collection of quantum numbers

$$\sigma_\alpha \equiv n_\alpha v_\alpha \lambda_\alpha k_\alpha s_\alpha M_{k\alpha} M_{s\alpha}$$

and similarly for σ_β.

With Eqs. (32) and (35) in (30) we obtain with standard manipulation (e.g., Smith, 1971), the usual close coupling equations

$$[d^2/dR_{\alpha\beta}{}^2 + k_\Gamma{}^2 - (l_\Gamma l_\Gamma + 1)/R_{\alpha\beta}{}^2] F_{\Gamma\Gamma'}(R_{\alpha\beta})$$
$$= (2\mu/h^2) \sum_{\Gamma'} V_{\Gamma'\Gamma''}(R_{\alpha\beta}) F_{\Gamma'\Gamma''}(R_{\alpha\beta}), \tag{36}$$

where

$$k_\Gamma{}^2 = (2\mu/h^2)[E - W_\alpha'(R_\alpha) - W_\beta'(R_\beta)]. \tag{37}$$

Here $W_{\alpha(\beta)}'$ denotes $W_{\alpha(\beta)}$ corrected for the nuclear motion (Michels 1972, Lester and Schaefer 1973a).

Further development of this model depends on the explicit selection of the functions in Equation (32).[2] The prescription outlined recently by Smith (1973) is based on the separated atom approximation (*SAA*) and still remains to be tested numerically. The arguments usually advanced (Parr, Lowdin 1964) that molecular wave functions constructed from single atomic orbitals tend to underestimate the charge distributions at large separations (especially so for many-electron systems) and that atomic orbital expansions do not adequately allow for correlation effects, suggest that the *SAA* approximation may turn out to be inadequate. However, the relevance of all these arguments to collision problems has not yet been established [See, however, Tully (1973)]. The alternative possible prescription, based on using configuration interaction molecular wave function obtained from solutions of Eq. (33), still remains to be developed. Examples of applications to special cases have already appeared in the literature (Lester and Schaefer 1973). In the remainder of this review we examine the experimental and theoretical evidence which could provide clues as to the proper choice. (The development of the general computational algorithms or codes hinges on the conclusions that can be drawn from these clues).

The energy transfer modes typified in reactions (4)–(7) are summarized in Table II. Of these, V–T processes are

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[2] For an example of transitions for which Eqn. (32) is *not* appropriate see Andreev *et al.* (1973).

TABLE II. Matrix of energy transfer processes.[a]

		Atom or Molecule		
		T	V	R
Atom	T	A	A	B
or	V	A	B	B
Molecule	R	B	B	C

[a] The letters denote how well the processes are now known A = good; B = moderate; C = weak.

currently the best understood, followed closely by V–V and V–R. Information of R–R energy transfer is still scarce.

Studies of these processes in the halides are complicated for several reasons. First, the halides are characterized by large amplitudes of vibrations which are comparable with the range of the repulsive forces between them. This implies that distorted wave type methods in which separation is made between the interaction potentials in the initial and final states are unlikely to be adequate because the matrix elements representing the initial and final state interactions will differ substantially from each other. Secondly, the effective mass for the interaction will vary according as the collision is considered to proceed primarily with the lighter hydrogen atom or the heavier halide atom. The light mass of the hydrogen atom leads to very efficient coupling with translation and rotational motion and, in general, favors collisions with the lighter end of the diatomic molecule. This observation forms the basis of most V–R energy transfer theories and has received some confirmation in experiments and even in classical model calculations in which this effect has been taken into account (cf. Sec. V). Thirdly, multiple quantum transitions typically depend on the ratio of diagonal matrix elements which can be of the order of unity. This will be so regardless of the potential (i.e., harmonic or anharmonic) used to represent the oscillator. The effect of multiquantum transitions on vibrational relaxation in the CO molecule has been recently demonstrated in the elegant calculations of Dillon and Stephenson (1972, 1973). Lastly, the large vibrational amplitudes of the light hydrogen atom manifest themselves as the chemical affinity for some systems between the incident molecule and the hydrogenic end of the target, leading to the phenomenon of polymerization (Chen and Moore 1971a, b). The consequence of this affinity are that both the separability of the total wave function [cf. Eq. (32)] and the approximation of the dominant interaction by a simple potential (Eq. 31) may be of questionable validity.

The halides considered in this study are characterized by large dipole and quadrupole moments (see Table III). In addition to large rotational level spacing, e.g., 237 cm^{-1} for HBr at 300°K, and small moments of interia which result in high rotational velocities, the halides exhibit hydrogen bonding tendencies. Thus, attractive forces will be prominent in hydrogen halides collisions and prescriptions for calculating transfer rates for e.g., HF–HF, using intermolecular potentials without various (i.e., *d-d*, *q-d*, *q-q* and *q-o*) multipole contributions, cannot be expected to lead to realistic results. Also, for deactivation processes involving inert gases (e.g., He), the high polarizability of the incident atom may require making allowance in the description of its interaction with the target molecule for the eccentricity effect, i.e., the displacement in the effective center of charge from the center of mass. The importance of this effect, which gives rise to R^{-7} terms in the potential in the case of line broadening of infrared spectra of HCl, has been demonstrated by Herman (1963) (see also Margenau and Kestner 1970). The effect is not accounted for in simple models using variants of Morse or Lennard–Jones potentials. It remains to be verified whether the 4–8 potential recently used by Shin (1971d) in his studies of HF de-excitation has led to tolerable results because, in his study, this 4–8 potential simulates the R^{-7} attraction. On the other hand, eccentricity and distortion effects may not be significant in systems where quadrupole interactions dominate.

We conclude this section with two comments. Values for relaxation times or transition probabilities reported in the literature are frequently compared to predictions of the SSH theory (Schwartz *et al.* 1952, Schwartz and Herzfeld, 1954). In drawing conclusions from these comparisons it is important to recognize the sensitivity of the theory to the method of determining the fit of the interaction potential to the Lennard-Jones potential. In method A (Herzfeld and Litovitz, 1959), the two functions are fitted in both magnitude and slope at the distance of closest approach, while in method B the fit is made at the potential corresponding to the distance of closest approach and also at the point of zero potential on the Lennard-Jones function. As has been stressed by Callear (1965, see also McClaren and Appleton 1970), order of magnitude differences between the collision probabilities calculated by the two methods can be expected and especially so at low temperatures. This sensitivity is but another manifestation of the assumption of a hard repulsive core made in many models of molecular collisions and frequently leads to interesting numerical problems (cf. Sec. VI, Gordon 1971, etc.).

Second, the effect of vibration to rotation transfer at low temperature is often tested by studying isotope effects. Deuterization of the colliding species has two consequences: the vibrational frequency is lowered, leading to an increase in the collision induced vibrational deactivation probability, and the moment of inertia is increased, leading to a decrease in this probability. Moore (1969) pointed out that the interplay of these effects could lead to erroneous relax-

TABLE III. Molecular dipole and quadrupole moments[a]

Molecule		Dipole moment $\mu \times 10^{18}$ e.s.u. cm	Quadrupole moment $\theta \times 10^{26}$ e.s.u. cm^2
Homonuclear	H_2	0	+0.662
	D_2	0	+0.649
	O_2	0	−0.39
	F_2	0	+0.88
	Cl_2	0	+6.14
	N_2	0	−1.52
Heteronuclear			
(A) Hydrogen halides	HF	1.736	+2.6
	HCl	1.07	+3.8
	HBr	0.788	+4.0
	HI	0.382	+6.0
(B) Others	CO	0.112	−2.5
	NO	0.158	−1.8
	LiH	5.882	−5.0
	BF	···	−4.5

[a] From D. E. Stogryn and A. P. Strogryn (1966).

TABLE IV. Summary of some typical relaxation measurements.

Molecule	Deactivating partner(s)	Process(es)	Temp. or temp. range (°K)	Authors
A. Shock Tube				
1. Hydrogen and deuterium fluorides				
HF	HF, F, Ar	V–V, V–R, T	600–2400	Blair *et al.* (1973)
HF	HF, DF, N_2, O_2, F, Cl	V–R, T	1400–4100	Blauer *et al.* (1972a)
HF	HCl, NO, H_2O, D_2O	V–V, V–R, T	1000–4100	Blauer *et al.* (1972b)
HF	F	V–T	2500	Blauer and Solomon (1973)
HF	HF, He, Ne, Ar, N_2	V–R, T	1350–4000	Bott and Cohen (1971a)
HF	F	V–T	1890–3310	Bott and Cohen (1971b)
HF	HF	V–V, V–R, T	295, 460–1030	Bott (1972)
HF	HF, HCl, HBr, DF, H_2, D_2, N_2, O_2, CO, NO	V–T, V–R, T	295, 450–1000	Bott and Cohen (1973b)
HF	N_2	V–V	1500–3500	Sentman and Solomon (1973)
HF	HF, Ar	V–T	1400–4100	Solomon *et al.* (1971)
DF	DF, HF, N_2	V–R, T	1400–4100	Blauer *et al.* (1972a)
DF	NO	V–V, V–R, T	1000–4100	Blauer *et al.* (1972b)
DF	H_2, N_2, F, Ar	V–R, T	800–4000	Bott and Cohen (1973a)
DF	CO_2	V–V, V–R, T	295, 468–920	Bott and Cohen (1973c)
DF	HCl, HBr, DBr, O_2, N_2, O_2, CO, NO	V–V, V–R, T	295–800	Bott (1974)
2. Other halides and deuterides				
HCl	HCl, He	V–R, T	1100–2100	Bowman and Seery (1969)
HCl	HCl	V–R, T	700–2100	Breshears and Bird (1969a)
HCl	He, HCl, Ar, Kr	V–T	800–4100	Seery (1973)
HBr	HBr	V–R, T	800–1800	Kiefer *et al.* (1969)
HI	HI, N_2	V–V, V–R, T	1000–2700	Breshears and Bird (1971)
HI	HI	V–R, T	800–1800	Kiefer *et al.* (1969)
DCl	DCl	V–R, T	700–2100	Breshears and Bird (1969a)
DBr	DBr	V–R, T	700–2000	Breshears and Bird (1970)
DI	DI	V–R, T	700–2000	Breshears and Bird (1970)
DI	DI, N_2	V–V, V–R, T	1000–2700	Breshears and Bird (1971)
3. Miscellaneous				
D_2	D_2, Ar	V–R, T	1100–4000	Kiefer and Lutz (1966)
Cl_2	Cl_2, CO, HCl, DCl	V–R, T	400–1400	Breshears and Bird (1969b)
F_2	F_2, H_2	V–T, V–V	750	Diebold *et al.* (1974)
CO	O	V–T	1800–4000	Center (1973)
CO	N_2, Ar	V–T	2200–4000	McLaren and Appleton (1970)
CO	CO	V–V	300	Powell (1973)
CO	O_2, CO	V–V	1750–2300	Sato *et al.* (1969)
N_2	CO	V–V	2200–4000	McLaren and Appleton (1970)
N_2	CO	V–V	1750–2300	Sato *et al.* (1969)
N_2	CO	V–V	960–2200	Von Rosenburg *et al.* (1972)
B. Laser Induced fluorescence				
1. Hydrogen and deuterium fluorides				
HF	HCl, HBr, HI, DF	V–R, T; V–V, R	300, 350	Ahl and Cool (1973)
HF	HF, H_2, Ar	V–R, T	350	Airey and Fried (1971)
HF	CO_2	V–V, V–R, T	R.T.	Chen *et al.* (1968)
HF	HF, N_2, SF_6, F_2, Ar	V–R, T	275–730	Fried *et al.* (1973)
HF	HF, CO, NO, O_2	V–V, V–R, T	295 ± 2	Green and Hancock (1973a)
HF	HF, H_2, D_2, N_2, Ar, H_2O, D_2O, CO_2	V–V, V–R, T	294 ± 2	Hancock and Green (1972a, b)
HF	DF, H_2, Ar, He	V–V, V–R, T	295	Hinchen (1973a)
HF	DF	V–R, T	300–1000	Hinchen (1973b)
HF	CO_2	V–V, V–R, T	295–670	Lucht and Cool (1974)
HF	HF	V–V, V–R, T	290	Osgood *et al.* (1973)
HF	HF, DF, CO_2	V–V, V–R, T	350	Stephens and Cool (1972)
DF	HF, H_2, D_2, N_2, He, Ar	V–V, V–R, T	295	Hinchen (1973a)
DF	HF	V–R, T	300–1000	Hinchen (1973b)
DF	CO_2	V–V, V–R, T	295–670	Lucht and Cool (1974)
DF	DF, CO_2	V–V, V–R, T	350	Stephens and Cool (1972)

TABLE IV. Summary of some typical relaxation measurements.—(*Continued*)

Molecule	Deactiviting partner(s)	Process(es)	Temp. or temp. range (°K)	Authors
2. Other halides and deuterides				
HCl	CO_2, HF	V–V, V–R, T	R.T.	Chen *et al.* (1968)
HCl	HCl, DCl, H_2, He, Ne, Ar	V–R, T	295 ± 2	Chen and Moore (1971a)
HCl	HBr, HI, D_2, N_2, CO, CH_4	V–V, (R, T)	295 ± 2	Chen and Moore (1971b)
HCl	HCl	V–V	R.T.	Gorshkov *et al.* (1971)
HCl (v = 1)	HCl (v = 2)	V–V, R	R.T.	Hopkins and Chen (1972b)
HCl	HCl	V–R, T	R.T.	Margottin-Maclou *et al.* (1971)
HCl, DCl, DBr, DI, CD_4	O_2, CO, NO, O_2, He	V–V, V–T, R	R.T.	Zittel and Moore (1973a)
HCl	HCl, He	V–R, T	144–584	Zittel and Moore (1973b)
HBr	HBr, HCl, He, Ne, Ar, p-H_2, n-H_2	V–R, T	295 ± 2	Chen (1971a)
HBr	D_2, N_2, CO, O_2	V–V	295 ± 2	Chen (1971b)
HBr	HBr, DBr	V–V	R.T.	Chen and Chen (1972)
HBr	HBr	V–R, T	144–584	Zittel and Moore (1973b)
DCl	DCl, HCl	V–R, T	295 ± 2	Chen and Moore (1971a)
DBr	DBr, HBr	V–R, T	295	Chen and Chen (1972)
HD	HCl	V–V, V–R, T	296	Hopkins and Chen (1972a)
3. Miscellaneous				
D_2	HCl, H_2, HD	V–V, V–R, T	296	Hopkins and Chen (1972a)
D_2	D_2, ^{3}He, ^{4}He	V–R, T	R.T.	Hopkins and Chen (1973)
CO	CO, HF, N_2	V–V, V–R, T	295 ± 2	Green and Hancock (1973a)
CO	H_2, D_2, N_2, O_2, Cl_2, He, Ar, CH_4, CF_4, SF_6	V–V, V–R, T	298	Green and Hancock (1973b)
CO	CO	V–R, T	R.T.	Margottin-Maclou *et al.* (1971)
CO	He	V–T	100–300	Miller and Millikan (1970)
CO	DCl	V–V	R.T.	Zittel and Moore (1972)
NO	NO	V–R, T	295 ± 2	Green and Hancock (1973a)
N_2	CO, DCl	V–V	R.T.	Zittel and Moore (1972)
CO_2	HCl, HBr, HI	V–V	298–510	Stephenson *et al.* (1972)

ation times being extracted from experimental data and emphasized the danger of neglecting hydride impurities in deuterated samples. A very thorough and detailed experimental study of relaxation of mixtures involving deuterium halides has been reported by Stephenson, Finzi and Moore (1972).

III. EXPERIMENTAL

In this section we outline the major results of some typical recent measurements of hydrogen halide relaxation rates that provide the information on the mechanisms that should be accounted for in any general theory or in analytical and computational schemes for use in either collision or laser modelling studies. As shown in Table IV, two groups of experiments are surveyed under the headings "shock tube" and "laser fluorescence" according to the means of formation of the excited molecules under study. The results obtained by the recently developed hybrid technique consisting of shock heating followed by monitoring laser induced fluorescence (Bott, 1972) are included under the former heading. Results of molecular beam experiments which, in combination with laser excitation, provide the means for both the preparation and analysis of the collision partners in specific quantal states (see for example, Ross, 1966; Bernstein, 1971; Kinsey, 1972) are only referred to when needed. The deactivation processes measured in the experiments surveyed and the interactions and mechanisms that have been advanced to explain the variety of observed effects are listed in Table V. This information is not exhib-

TABLE V. Summary of main measurements, energy transfer mode and suggested explanations[a]

A. Measurements
1. Self-relaxation
2. Relaxation by isotopic partner
3. Relaxation by atoms[b] (a) *H*; (b) *X*; (c) inert gas; (d) other
4. Relaxation by molecules (a) halides; (b) deuterides; (c) homopolar diatomic; (d) heteropolar diatomic; (e) polyatomic

B. Principal Transfer Modes Discussed in Current Literature
1. V–T, V–R, T
2. Resonant (near resonant) V–V
3. Intermolecular V–R and/or V–V
4. Intramolecular V–R and/or V–R
5. Multiquantum V–V
6. Multiquantum V–R

C. Interactions (isotropic and anisotropic) and Mechanisms
1. Short range repulsion
2. Multipolar interactions (a) dipole-dipole; (b) dipole-quadrupole; (c) dipole-octupole; (d) other
3. H atom abstraction
4. X atom abstraction[b]
5. H bonding
6. Polymerization
7. Orbiting
8. Complex formation (resonances)
9. Collisional interference

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[a] The rates for the processes (and their temperature dependence) listed under (A) provide information on the principal modes of energy transfer (B) and can sometimes be interpreted by invoking one or more of the interactions and mechanisms (C). These lists are by no means exhaustive. For the most current assessment of resonant and near resonant processes see Moore (1973).

[b] X denotes a halogen.

ited in adjacent columns, as it ideally should be, because, so far, no satisfactory causal connections have been established, although some patterns are beginning to emerge.[3]

A. Shock tube measurements

In shock tube experiments advantage is taken of the fact that the translational and rotational temperatures in a shock heated gas are initially higher than the vibrational temperatures and, with time, as the equilibrium is established, the gas density in the hot zone increases. The relaxation time is obtained by measuring the rate of density change or by following the population of the excited level by absorption or emission spectroscopy. Direct measurement of vibrational temperature by atomic line reversal can also be used. Shock tube measurements provide an extensive set of data on many of the diatomics considered in this study over broad temperature ranges from 5000°–300°K.

1. Hydrogen and deuterium fluorides

The earliest shock tube studies of vibrational relaxation of HF were those of Bott and Cohen (1971a, b) and of Solomon *et al.* (1971). In their first paper on HF the former authors reported measurements of 2.7 μ emission in shock heated mixtures of HF and Ar as well as those containing N_2, D_2, and He. Their value for HF self-relaxation time (0.28 μsec·atm) at 1400°K was in agreement with that of Solomon *et al.*, but they noted a discrepancy with these authors of a factory of 2–5 at 4000°K. Slightly longer times for HF–Ar and shorter for HF–He and HF–D_2 were reported. The HF–HF $P\tau$ was a factor of 20 higher than that reported by Airey and Fried (1971) from measurements at 350°K (0.014 μsec·atm). Their Landau–Teller plots for the probabilities for self-relaxation of the hydrogen halides are shown in Fig. 2. Bott and Cohen inferred that V–T processes were more dominant in HF than in the other halides and, on the basis of estimates obtained using a variant of Shin's model (1970a, 1971a) (see their Fig. 1), suggested that strongly attractive forces could perhaps account for the observed temperature dependence of the relaxation rates.

Subsequently (1971b), these authors reported measurements from shock heated mixtures of HF, SF_6 and Ar of HF deactivation by F. Their rate of 3×10^{13} cm³/mol·sec (i.e., relaxation times $\simeq 5.9 \times 10^{-3}$ μsec·atm) at 2000°K for the process given by Eq. (4), also agreed well with the value of 2.9×10^{13} cm³/mol·sec obtained by Solomon *et al.* (1971) from data on shock heated mixtures of HF, F_2, and Ar. The mixture compositions are noted because it appears to affect the self-relaxation rates deduced in other experiments to be discussed below (Sec. III.B). These values imply that fluorine is about 20 times more efficient than HF in deactivating HF. However, more recent experiments yield values substantially lower, i.e., relative factors of 6 (Blauer and Solomon 1972) and 2–5 (Blair *et al.* 1973).

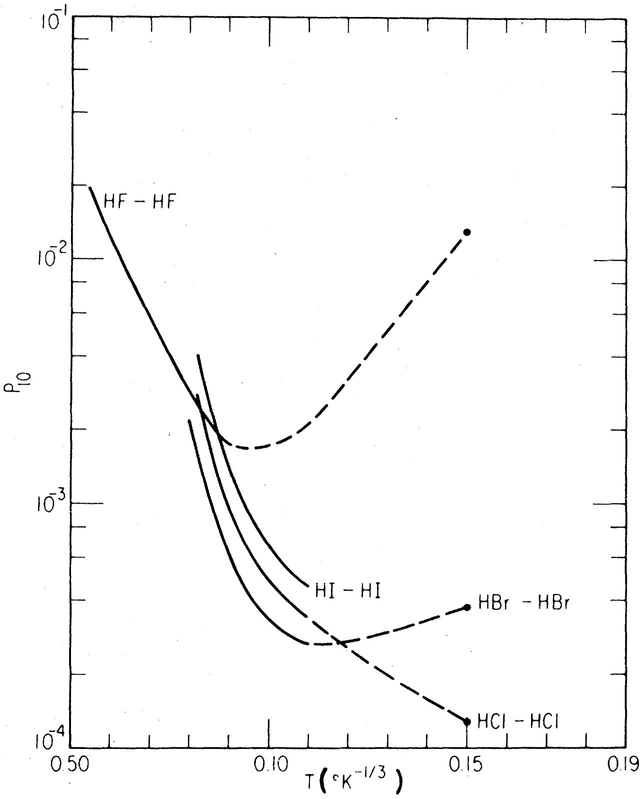

FIG. 2. P_{10} vs $T^{-1/3}$ inferred from measured relaxation times of the hydrogen halides. Dotted lines indicate interpolated values (figure from Bott and Cohen 1971a).

Because results of shock tube HF relaxation at higher temperatures did not agree (on extrapolation) with laser induced fluorescence data at room temperature, Bott (1972) suggested and carried out an experiment combining the two techniques so as to make possible lower temperature determination of relaxation rates from shock heated mixtures. This hybrid technique (illustrated schematically in Fig. 3) was used to obtain the room temperature rate of 2.2×10^{13} cm³/mol·sec in agreement with that obtained in a furnace heated laser induced fluorescence measurement by Fried *et al.* (1973). This is shown in his figure with the predictions obtained with the theory of Shin (1970, 1971a, b) modified by adjustments for the attractive potential of HF with the values indicated for temperatures below 1200°K. Bott conjectured that the results were indicative of fast V–V processes which would explain the large population of excited ($\nu > 3$) HF levels detected in flow tube experiments even though initial reactions populated only the $\nu = 3$ level (see Parker and Pimentel, 1971, and Sec. II above). He also pointed out that if such fast V–V processes were indeed taking place it was not possible to estimate, from his data, the V dependence of the V, R–T rates.

More recently, Bott and Cohen (1973a) reported measurements of vibrational relaxation of DF in the temperature range 800–4000°K by monitoring the 3.5-μ infrared emission. They obtained relaxation times for mixtures of DF in Ar, N_2, H_2, and F and analyzed their results by comparison with the predictions of several theories. A partial summary of their data is shown in Fig. 4 taken from their paper.

In the case of N_2 the departure from the Landau–Teller linearity can already be seen at about 2000°K, thereby ruling out the applicability of the SSH (V–T) theory at lower temperatures. In addition, the SSH theory predicts DF relaxation rates by Ar, N_2, or DF to be substantially faster than the corresponding rates for HF, i.e., DF relaxation by Ar and N_2 should be faster by a factor of 8 at 4000°K,

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[3] Some of the measured rates are summarized in Table VIII, given, for convenience, later in this section.

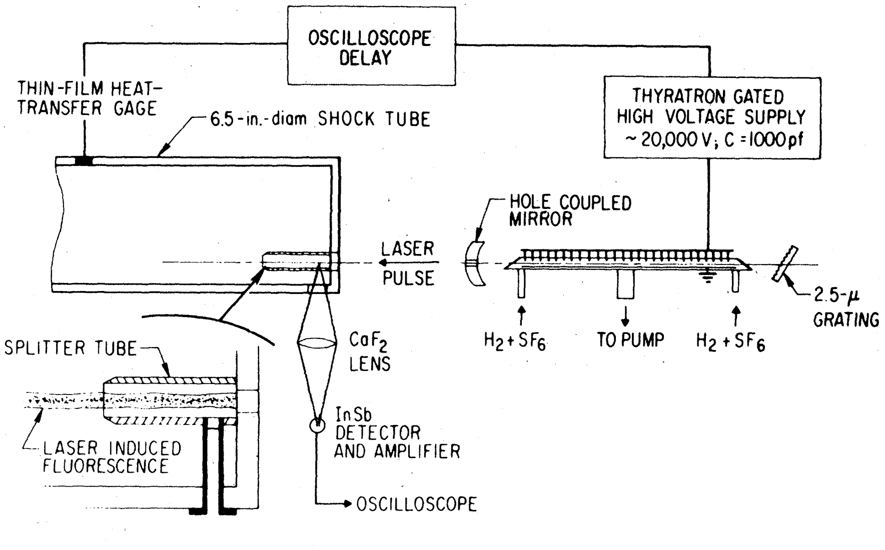

FIG. 3. Schematic of shock tube and pulse laser for the measurement of vibrational relaxation times (figure from Bott, 1972).

and a factor of 40 at 1000°K, while relaxation by DF should be about three times faster than that for HF at the high temperature end of the range, and ten times faster for temperatures below 1000°K. As shown in Fig. 4(a), those predictions are at variance with the experiments. Because predictions of both the absolute magnitudes and of the relative relaxation rates for the isotopic pairs disagreed with their data, Bott and Cohen concluded that the SSH theory could not be used at all to describe relaxation processes in hydrogen halides.

These authors next attempted to interpret the measure ments in terms of Moore's (1965) V–R theory which, at that time, had been shown to be in fair accord with experiment for HCl, HBr, and HI (see Sec. III.B below). For temperatures above 4000°K, their calculated values were within a factor of 2 of those measured for both HF and DF self-relaxation, but they found the temperature dependence to be too large by a factor of 2.5 for DF, and by a factor of 4 for HF. They pointed out that use of Moore's theory for HF relaxation by N_2 resulted in two sets of predictions according as to whether the vibrational energy transfer was to the rotational energy of the halide or of N_2. Calculations based on the former assumption indicated that energy transfer was insensitive to the nature of the chaperone molecule. The second mechanism yielded transfer rates several orders of magnitude smaller than those observed. The net conclusion was that the V–R theory alone did not explain why DF relaxed slower than HF in the presence of Ar and N_2 at the higher temperatures.

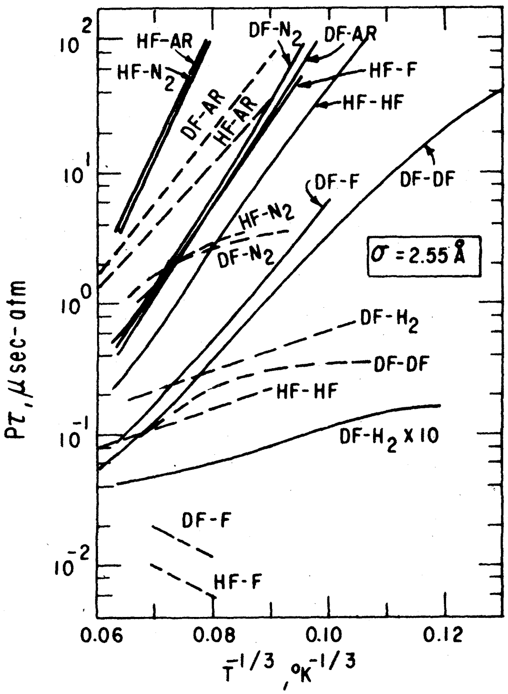

FIG. 4. Comparison of SSH predictions with HF and DF data: —, theoretical; - - - -, experimental (from Bott and Cohen 1973).

Finally, Bott and Cohen compared their results with the predictions of Shin's model in which V–R transfer is handled by making explicit, albeit in a rather ad hoc manner, allowance for long range attractive forces (see Sec. IV). Just like in the case of HF, they found that this model, when adjusted by inclusion of a 3.5 kcal/mole attractive potential led to a tolerable qualitative agreement with both the shock tube relaxation data and with the laser fluorescence measurement of Stephens and Cool (1972). It should be pointed out that the validity of the long range mechanism has been recently questioned (Hinchen 1973a; Zittel and Moore, 1973b).

Bott and Cohen also observed that the temperature dependence of DF was substantially smaller than that for the other deuterated halides in contrast with the results of Breshears and Bird (1969) who found relaxation rates for the halides to be within a factor of 2 of each other and the differences with the deuterated halides to be less than 10% throughout the temperature range (700°–2000°K) of their experiments. Their comparison of the HF and DF relaxation data is shown in Fig. 5.

The extremely fast self-relaxation rate of HF and the very efficient deactivation of both HF and (although by a factor of 2 slower) of DF by fluorine, led Bott and Cohen

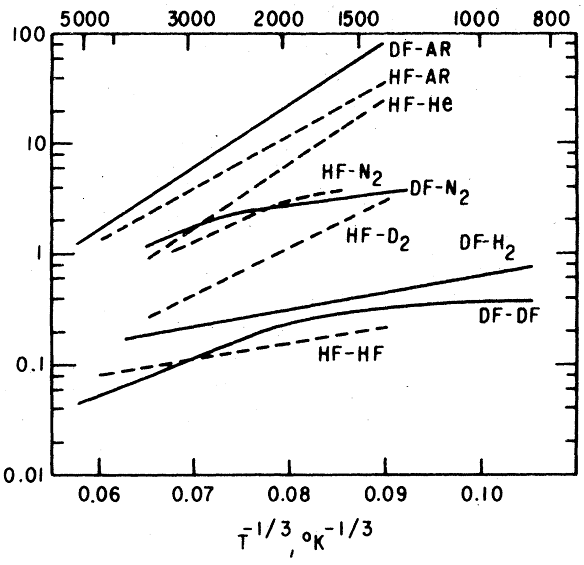

FIG. 5. Comparison of experimental relaxation times of DF with those of HF (from Bott and Cohen, 1973).

to speculate whether chemical action could not be responsible for these rates. The suggestion of, for example, Cl atom exchange via the reaction

$$\mathrm{Cl}' + \mathrm{HCl}'' \rightarrow \mathrm{HCl}' + \mathrm{Cl}'' \tag{38}$$

being responsible for the fast deactivation of HCl, has been made earlier by Ridley and Smith (1971) on the basis of their infrared chemiluminescence measurements in the HI–Cl system, and for HF and F, where it is more probable, by Solomon *et al.* (1971). However, Bott and Cohen (1973b) stressed that verification of such chemical reaction mechanism required knowledge of the relative rates for the reactions $F + HF \rightarrow FH + F$ and $F + DF \rightarrow FD + F$ which were not available.

A final point about these author's analysis of both the HF (1971) and DF (1973a) results concerns the reduction of their data under the assumption of no V–V coupling. Bott and Cohen pointed out that different relaxation times would have been obtained if very fast V–V rates were assumed so that the two relaxation mechanisms (V–V, V–R, T) would be coupled. They noted, however, that in the case of mixtures containing N_2 this assumption would reduce the relaxation times by over a factor of 20 thereby making the efficiency of DF deactivation by N_2 greater than the DF self-relaxation rates—a result contrary to the experimentally indicated trend. Also, if V–V coupling were important, the rates for N_2 relaxation of HF and DF could be expected to differ significantly because of the energy discrepancy (1050 cm^{-1}) between the two molecular pairs—again, not in agreement with the experimental trend, see Fig. 5.

The conjecture that fast V–V transfer to N_2 could be the controlling mechanism in the relaxation of HF(DF)–N_2–Noble gas mixtures has since been examined by Sentman and Solomon (1973). Following the suggestion by Sentman (1973)—see Sec. V for an outline of his model—the former authors reinterpreted the HF–N_2 shock tube data of Blauer *et al.* (1972) in the 1500–3500°K temperature range using the analysis of Sato *et al.* (1969) to separate the V–V and V–R–T contributions. Assuming, in light of Sentman's results, that vibration to vibration transfer [cf. Eq. (3)] was the rate controlling process, these authors obtained tolerable agreement with Sentman's calculation and concluded that HF* deactivation proceeded primarily by V–V transfer to N_2 with the N_2^* decaying subsequently by fast V–R–T exchange with HF. The possibility of such V–V participation in this relaxation process is supported by Hinchen (1973a) whose analysis of the deactivation of the analogous DF–N_2 system at 350°K is consistent with this interpretation (see Sec. III.B, below).

Most recently Bott (1974) has extended the DF relaxation measurements into the temperature range 295°–800°K. For the DF–N_2 system, his measurements, which essentially

TABLE VI. Vibrational relaxation of the hydrogen halides by HF and DF at $T = 295°K$ (from Bott, 1974).

Molecule 1	Molecule 2	k_{21} (μsec·Torr)$^{-1}$ [a]	P_{21} [b]	$k_{vv} + k_{12}$ (μsec·Torr)$^{-1}$ [d]	$P_{vv} + P_{12}$ [a]	Reference
DF	HCl	$(1.6 \pm 0.3) \times 10^{-2}$ [c]	2.7×10^{-3}	$(4.0 \pm 0.4) \times 10^{-1}$	6.8×10^{-2}	Bott, 1974
DF	HBr	$(1.0 \pm 0.2) \times 10^{-2}$	1.8×10^{-3}	$(7.1 \pm 0.7) \times 10^{-2}$	1.26×10^{-2}	Bott, 1974
DF	DBr	$(2.3 \pm 0.7) \times 10^{-2}$	4.1×10^{-3}	$(5.4 \pm 1.0) \times 10^{-3}$	9.5×10^{-4}	Bott, 1974
DF	DF	$(2.1 \pm 0.2) \times 10^{-2}$	4.2×10^{-3}			Bott and Cohen, 1973c
HF	HCl	$(1.5 \pm 0.2) \times 10^{-2}$	2.5×10^{-3}	$(1.7 \pm 0.1) \times 10^{-2}$	2.8×10^{-3}	Bott and Cohen, 1973b
HF	DF	$(3.5 \pm 0.5) \times 10^{-2}$	7.0×10^{-3}	$(7.7 \pm 0.4) \times 10^{-2}$	1.5×10^{-2}	Bott and Cohen
HF	HBr	$(0.9 \pm 0.1) \times 10^{-2}$	1.6×10^{-3}	$(7.5 \pm 1.0) \times 10^{-3}$	1.3×10^{-3}	Bott and Cohen
HF	HF	$(5.6 \pm 0.5) \times 10^{-2}$	11×10^{-3}			Bott, 1972
HCl	HBr	$(1.315 \pm 0 + 14) \times 10^{-3}$	2.3×10^{-4}	$(3.4 \pm 0.3) \times 10^{-2}$	6.0×10^{-3}	Chen, 1971a
HBr	HBr	$(5.7 \pm 0.5) \times 10^{-4}$	1.2×10^{-4}			Chen, 1971a
HBr	DBr	$(3.5 \pm 0.6) \times 10^{-4}$	7.5×10^{-5}	$(1.96 \pm 0.20) \times 10^{-4}$	4.22×10^{-4}	Chen and Chen 1972
DBr	DBr	$(1.7 \pm 0.3) \times 10^{-4}$	3.66×10^{-5}			Chen and Chen
HCl	HCl	$(8.3 \pm 0.8) \times 10^{-4}$	1.27×10^{-4}			Chen and Moore 1971a

[a] k_{21} is the deactivation rate of molecule 2 by molecule 1.

[b] $k_{21} - k_{21}/k_{\mathrm{gas\ kin}}$. At $T = 295°K$, $k_{\mathrm{gas\ kin}} = 2.57 \times d^2/m^{1/2}$ (μsec·Torr)$^{-1}$ with $d = \frac{1}{2}(d_{\mathrm{HX}} + d_{\mathrm{HY}})/2$ in angstroms and m the collision reduced mass in atomic mass units. Collision diameters of 2.5, 3.3, and 3.5 Å have been used for HF(DF), HCl, and HBr(DBr), respectively.

[c] $k_{21} + 0.88k_{12} = (1.6 \pm 0.3) \times 10^{-2}$ (μsec·Torr)$^{-1}$.

[d] k_{vv} is the V–V transfer rate from molecule 1 to molecule 2. The value listed for DF–HCl is k_{vv} and not $k_{vv} + k_{12}$.

yield the combined rate $(k_{vv} + k_{12})$, cf., Eqs. (22), are (on extrapolation) in fair agreement with the earlier (1973a) data. This, according to Bott, implies that if the model of Sentman and Solomon is correct, all the rates measured in the high temperature shock tube experiments were actually V–V transfer rates. The mechanism of HF self-relaxation cannot be considered as settled yet because of the suggestion by Hinchen of possible complex formation (1973a) and because of the evidence for multiquantum transitions obtained in laser induced fluorescence relaxation measurements in other halides as well as in HF (Hopkins and Chen, 1972; Fried *et al.*, 1973; Ahl and Cool, 1973).

Bott's summary of the hydrogen halide relaxation data is given in Table VI and his attempted correlation of all the results is discussed in Sec. III.C below. The other recent results of the Aerospace group on relaxation of hydrogen halides by polyatomic molecules (Bott and Cohen 1973c, 1974) are outside the scope of this review.

In a related experiment spanning the intermediate (600°–2400°K) temperature range and also based on the hybrid technique, Blair *et al.* (1973) reported a maximum in the HF self-relaxation rate at about 1000°K but broader than that inferred on the basis of earlier measurements. Their reported value of 0.1 μsec·atm at 1400°K is considerably lower than that of Bott and Cohen (1971a) and their results at other temperatures are also lower than those of Bott (1972). Because the discrepancies between the various measurements (see Fig. 7 of their paper) are well outside the experimental errors quoted for any experiment, the temperature dependence of the HF rate presents quite a puzzle, especially in the transition (800°–2000°K) temperature range between the various sets of low and high temperature measurements.

2. Other halides and deuterides

In the first shock tube measurements of HCl and DCl vibrational relaxation in the temperature range 700°–2100°K, Breshears and Bird (1969a) reported deviations of the self-relaxation rates (at lower temperatures) from the temperature dependence predicted by the Landau–Teller law, serious disagreement with the SSH theory, and moderate agreement with Moore's (1965) model. The latter gave the correct isotope effect $(P_{\mathrm{DCl-DCl}} > P_{\mathrm{HCl-HCl}})$ and absolute values within a factor of 5 of the data. A suggested maximum in the HCl deactivation probability was speculatively attributed to dipole–dipole attractive forces. Measurements of Cl_2 relaxation over the temperature range 400°–1100°K (Breshears and Bird, 1969b) yielded values consistent with the semiempirical Millikan and White (1963) model for Cl_2–CO but not for the Cl_2–HCl(DCl) system.

More recently shock tube measurements of vibrational relaxation of HCl with a variety of inert gas collision partners were reported by Seery (1973) who measured infrared emission from the HCl fundamental. An important result of his work was the demonstration of a marked decrease in the efficiency of energy transfer for increased reduced mass in excess of that predicted by present theories, even if the data were interpreted on the assumption that the reduced mass corresponded to a halide-hydrogen gas collision rather than HCl-inert gas. His results indicate a less steep dependence on the temperature of the Ar–HCl relaxation than predicted by Sorensen (1972, Sec. IV). Seery found that at the lowest temperature recorded, i.e., 1166°K, the effect of Ar on relaxing HCl was about a factor of 60 smaller than that of He. Significantly, although for temperatures below 1000°K HCl the self-relaxation rate appears to be temperature independent, relaxation by inert gases still seems to follow the Landau–Teller law approximately. Seery also concluded that the results supported Moore's (1969) conjecture that the halide vibrational relaxation at lower temperatures was governed by V–R energy transfer, but stressed the absence of any satisfactory theoretical predictions. Some of his results are shown in Fig. 6.

3. Miscellaneous diatomics

Shock tube measurements of V–V energy transfer in N_2–CO collision for several N_2–CO–Ar mixtures at temperatures ranging from 2000° to 4000°K have been reported by McLaren and Appleton (1970). Their results were in reasonable agreement with the predictions of the SSH model at temperatures of about 4000°K, but were more than an order of magnitude below the model predictions at 2000°K. Both Ar and N_2 were found to be equally efficient partners for T–V relaxation of CO, but Ar was about 2 to 3 times less efficient than N_2 for vibrational relaxation of N_2.

McLaren and Appleton pointed out that interpretations of these results were uncertain because V–V transfer rates for the N_2–CO system were not known with precision. Measurements over a moderate temperature range (1750°–2300°K) by Sato *et al.* (1969) suggested that V–V transfer in this system followed the SSH theory. However, McLaren and Appleton pointed out that their own calculations, also based on the SSH theory showed great sensitivity to the matching of the molecular potential slopes at the distance of closest approach, and implied that the values of V–V exchange rates reported by Sato (1969) were too low by almost a factor of 10 over the temperature range of their experiment. As can be seen in Fig. 7 measurements over the higher temperature range are in reasonable agreement at the intermediate (around 2500°K) temperatures, where they overlap with the results of Sato *et al.* and appear to extrapolate well into the results of measurements over the lower temperature range reported by von Rosenburg *et al.* (1972). Despite the considerable scatter of all the data seen in this figure, the results of all measurements shown lie uniformly below the predictions of the SSH theory—by nearly a factor of 10 at 2000°K, and by several orders of magnitude at lower temperatures. McLaren and Appleton stated that their conclusion that Ar was less efficient than N_2 in T–V relaxation of N_2 was in conflict with previous estimates, that no explanation for this discrepancy was immediately apparent, and that the difference could be due to the combined uncertainties in all measurements. They stressed that the departure from the SSH prediction was consistent with that previously reported by Taylor and Bitterman (1969) who found all measured V–V exchange probabilities to be significantly lower than the SSH predictions over the temperature range 1000°–2500°K. As seen in Fig. 7, the scatter in the data at lower temperature, especially below 1000°K, precludes any speculations as to whether a minimum comparable to that observed in other systems (cf. Sec. II) is present.

The shock tube method has been used for the determination of vibrational relaxation of pure fluorine and fluorine–Ar mixtures in the range 500°–1500°K by Diebold *et al.* (1974)

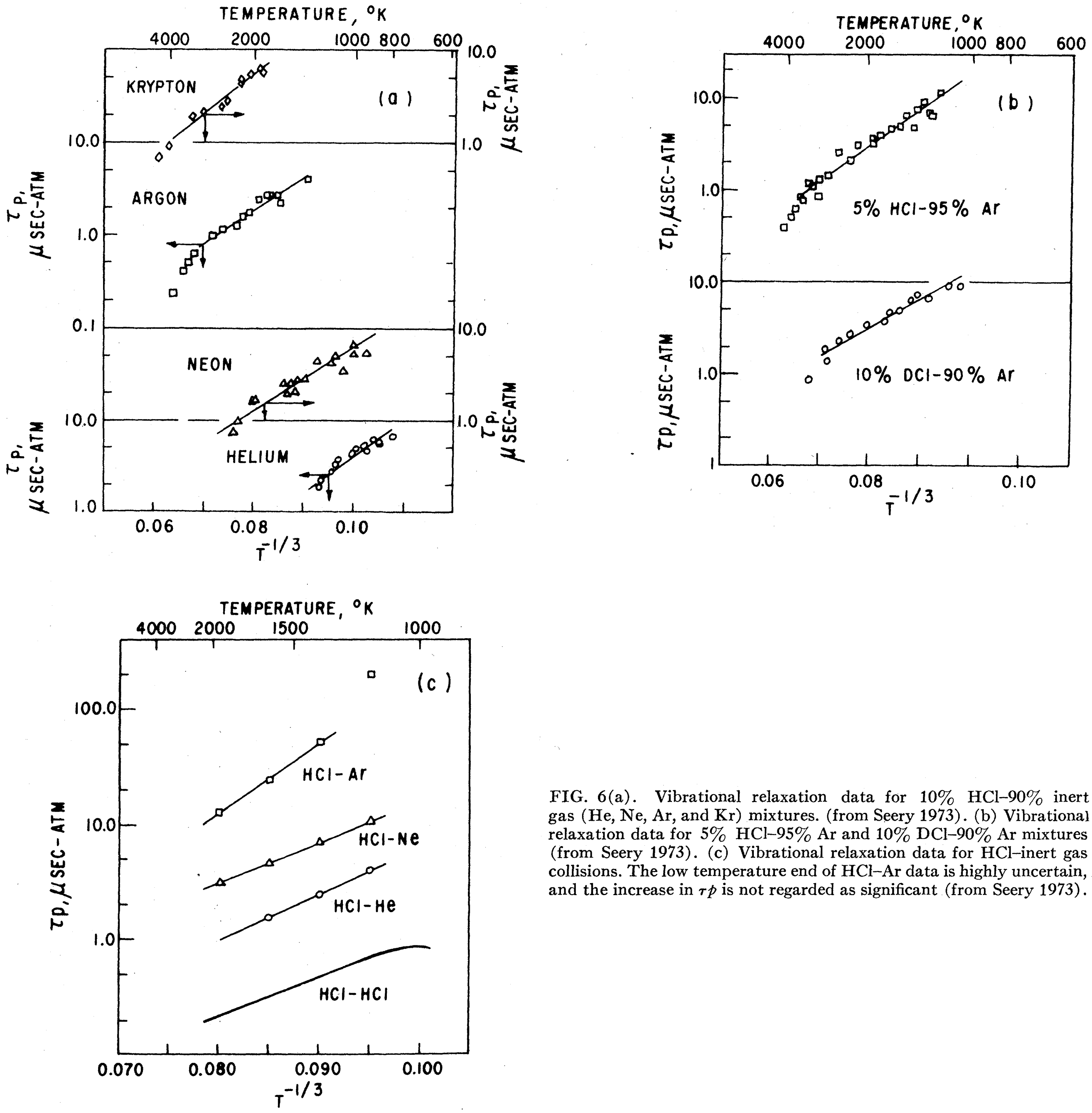

FIG. 6(a). Vibrational relaxation data for 10% HCl–90% inert gas (He, Ne, Ar, and Kr) mixtures. (from Seery 1973). (b) Vibrational relaxation data for 5% HCl–95% Ar and 10% DCl–90% Ar mixtures (from Seery 1973). (c) Vibrational relaxation data for HCl–inert gas collisions. The low temperature end of HCl–Ar data is highly uncertain, and the increase in τp is not regarded as significant (from Seery 1973).

whose paper contains numerous references to earlier work. The relaxation times for both pure fluorine and fluorine infinitely diluted in argon were found to follow the Landau–Teller plots, the relative relaxation rates differing by a factor of 3 at the higher, and over an order of magnitude at the lower end of the temperature range. Diebold *et al.* compared their results with the predictions of the SSH theory based on method A and with the correlation scheme of Millikan and White (1963) with the results shown in Fig. 8. As can be seen, even though the general temperature dependence of the rates is satisfactorily given by both models, neither set of the absolute values, nor the relative relaxation rates are correctly predicted by either theory. Diebold *et al.* noted that their results confirmed the general tendency of the Millikan and White correlation scheme to underestimate (overestimate) relaxation times for diatomics colliding with monoatomic (diatomic) partners.

The evidence for strong attractive intermolecular forces in vibrational relaxation of diatomic molecules is not restricted to the halide data. In shock tube measurements of vibrational relaxation of CO by O in the range 1800°–4000°K, Center (1973) obtained collisional probabilities for V–T transfer of the order of 10^{-2} and pointed out that these were two to three orders of magnitude larger than the probabilities for CO self-relaxation and relaxation by

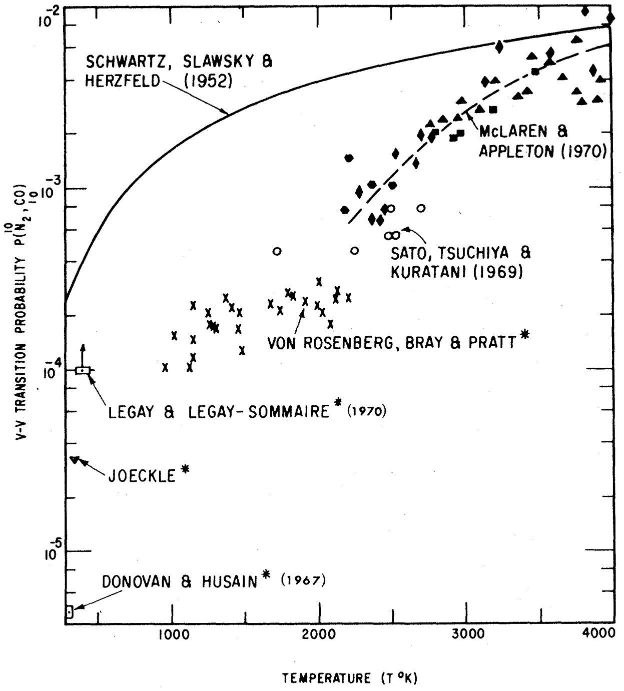

FIG. 7. Vibration–vibration exchange in N_2–CO (from McLaren and Appleton 1970). See original reference for other data.

Ar. He found a weak temperature dependence of the O–CO rate which he extrapolated to obtain 2 μsec·atm at 300°K. Center pointed out that this relaxation mechanism could be significant in CO chemical lasers and suggested that, just as in the case of O_2 and N_2 vibrational relaxation by O, his result, which is not predicted by conventional theories, could be interpreted in terms of chemical effects.

B. Laser fluorescence

In laser induced vibrational excited fluorescence measurements use is made of the large power densities in narrow spectral widths and the high degree of collimation of a laser operating on a given vibrational transition to excite the same transition in a gas sample outside the active laser medium. When the radiative lifetimes of the excited vibrational states are long in comparison to the collisional deactivation times, as in the case in the halides [eg., ~5 msec for HF ($\nu = 1$)], the measured fluorescence decay rates can be directly related to the collisional relaxation rates. Because these measurements have become a classic of a kind, a typical experimental layout and a diagram explaining the basis for them are shown in Fig. 9 taken from Chen (1971a). Detailed discussions have been given by Moore (1967, 1973).

1. Hydrogen and deuterium fluoride

In an experiment that contributed most to the recent increase in interest in the mechanisms of hydrogen halide relaxation, Airey and Fried (1971) reported a self-relaxation rate of 0.095 $\mu\text{sec}^{-1}\ \text{Torr}^{-1}$ at 350°K for HF and a comparably fast deactivation rate of HF by H_2. Though no values were quoted they attributed the latter process to near resonant V–V exchange.

An exhaustive study of vibrational deactivation of HF in pure HF and in additive mixtures was subsequently reported by Hancock and Green (1972a, b). These authors concentrated on measurements at room temperature and considered the relaxation of HF by Ar, H_2, D_2, N_2, CO_2, H_2O, and D_2O, as well as deactivation of H_2 and CO_2 (00^01) by HF ($\nu = 0$). They found that deactivation by Ar was the slowest of the processes studied by them, with the fastest (HF–H_2O) being nearly 5 orders of magnitude greater. Their results are summarized in Table VII.

In analyzing their data, Hancock and Green noticed that the self-relaxation rate for HF in pure HF was nearly a factor of 2 slower than that deduced from HF diluted in Ar. They carried out several measurements to clarify whether this discrepancy could be due to formation of highly excited HF molecules ($\nu = 2$), incomplete rotational thermalization, or polymerization. They concluded that the discrepancy was due to rotational thermalization in HF in the presence of Ar which, from line broadening studies, is known to be about 10% more effective than HF in promoting V–R transfer.

The formation of highly excited HF was discounted because of the observation of single-exponential fluorescence decays in HF–Ar mixtures (cf. Fig. 10) with relaxation times linear with pressure and results independent of J line excitation frequency or power density. Polymerization was eliminated because dimer concentration, being a function of HF pressure, would lead to deviations from linearity in HF additive studies and such deviations were not observed. Also, the presence of Ar would not be expected to affect the monomer–polymer equilibrium. On the other hand, in the absence of Ar, the high rate of V–V transfer in pure HF was of the order of magnitude of rotational relaxation and thus suggestive of rotational nonequilibrium.

The differences in the self-relaxation rates of HF obtained with and without diluents such as Ar, which is generally agreed to be an inefficient deactivation partner, appear to be at present a subject of some debate. According to Hinchen (1973a) who carried out experiments to explicitly test the Ar dilution effect, the self-relaxation rates are the same in either case—a conclusion which must be considered puzzling given the generally high quality and self-consistency of his other results (see below). Blair *et al.* (1973) suggested that the dilution effect, if real, is absent at temperatures above 1500°K.[4] However, in a more recent study, Hancock and Green (1973a) confirm their previous finding and quote deactivation rates from HF–O_2, CO, and NO mixtures (see Table VIII) as being also indicative of the diluent effect. They further point to the consistency of their (proposed) rotational thermalization and *V-R* transfer mechanism with the results of Dillon and Stephenson (1973 and Sec. VII) for DF–CO_2, that energy transfer is most favorable for small energy defects accompanied by large ΔJ changes. Note that the occurence of such (large ΔJ) V–R transfers is also indicated in the experiments of Ahl and Cool (1973), the theoretical studies of Rabitz and coworkers, Sec. IV, and of Thompson (Sec. VI), and the results on the CO–CO system of Lev-On *et al.* (1974).

Hancock and Green pointed out that the usual approximations of the Moore (1967) relaxation equations were not

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[4] See, however, Bott and Cohen (1971a) for a discussion of Ar efforts at higher temperatures.

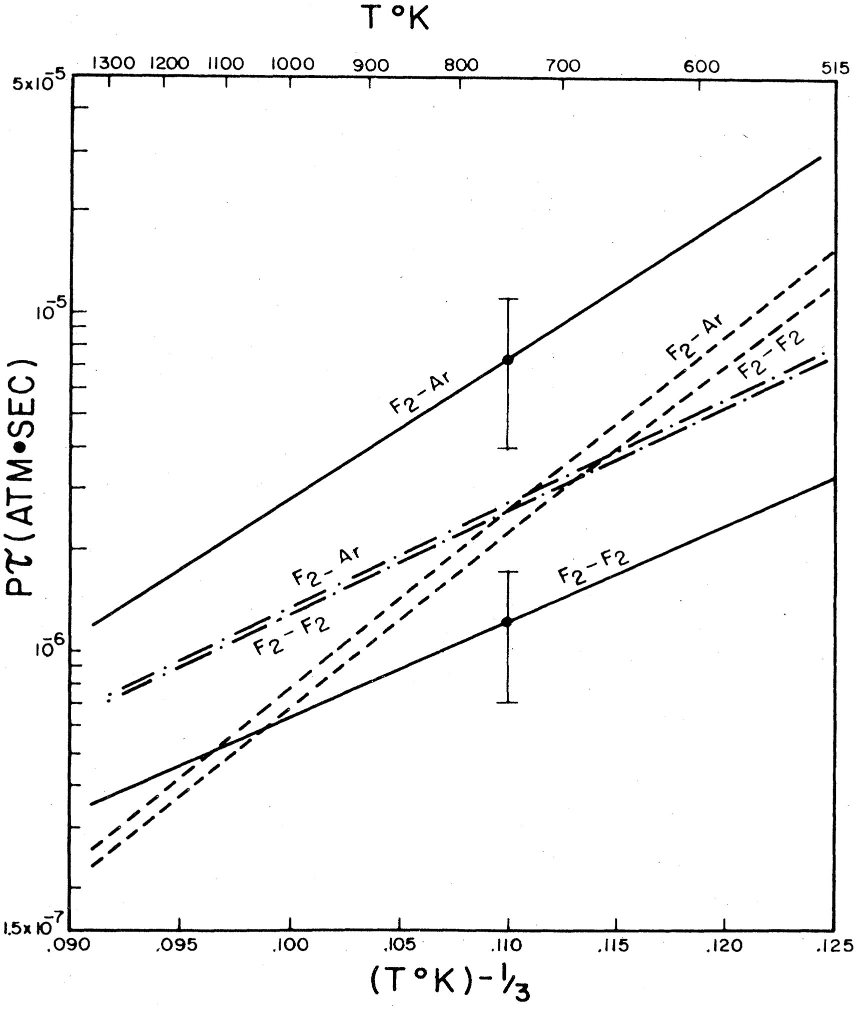
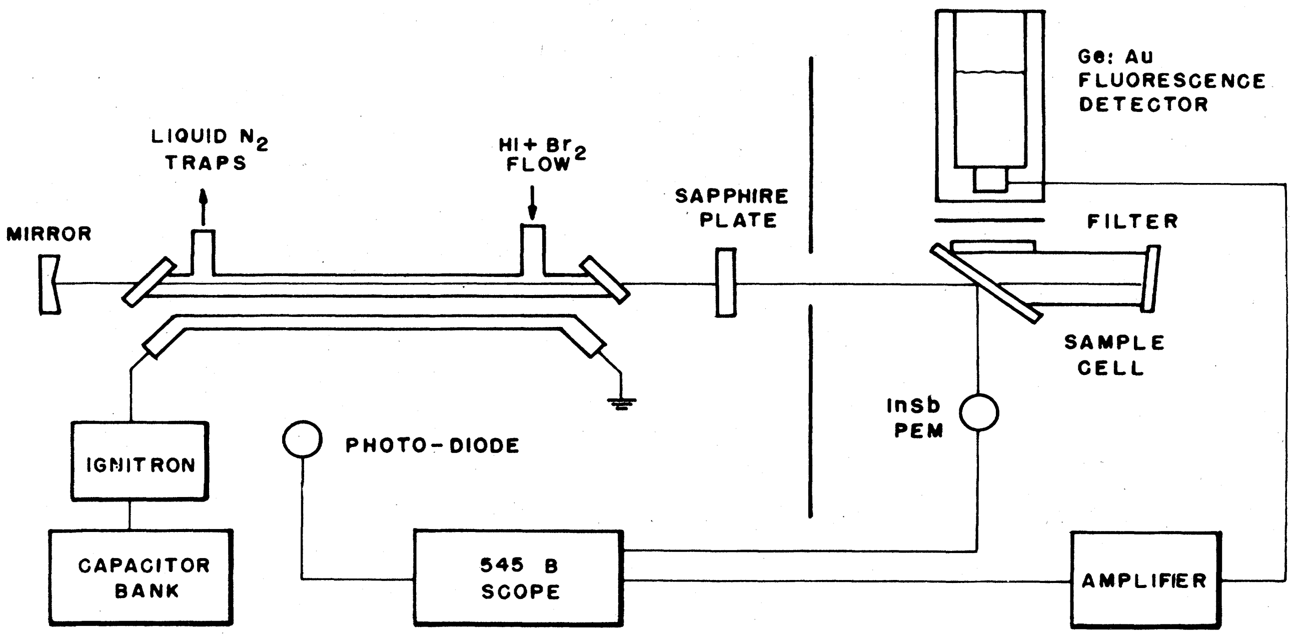


FIG. 8. Landau–Teller plots for vibrational relaxation of F_2 by F_2 and Ar; –•–, SSH; ----, Millikan and White; —, measured. (from Diebold *et al.* 1974).

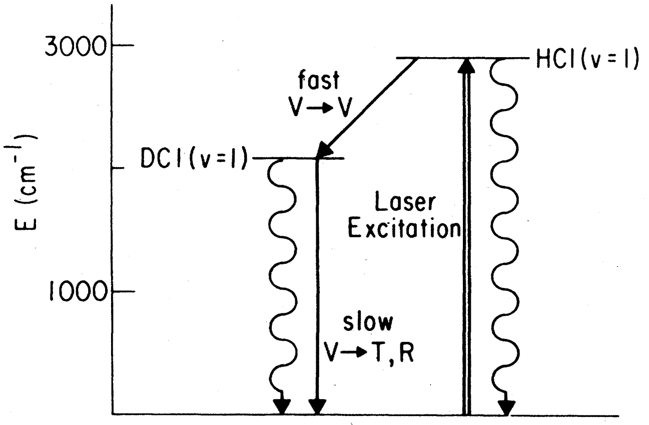
valid for their experiment and analyzed some of their results for HF additive mixtures in terms of two limiting cases corresponding to large and small energy defects between HF and the diluent gas, cf., Table VII. In the former case, e.g., relaxation by N_2, they quoted a combined rate (k_{vv} + k_{12}—see Table VIII) of 125 ± sec^{-1} Torr^{-1} and suggested that unless a two quantum exchange was occurring, the participation of V–V transfer could not be definitely established. In a comparative study with D_2–Ar mixtures their value for the combined V–V and V–R, T process of $(3.7 \pm 0.4) \times 10^3$ sec^{-1}•Torr^{-1} was a factor of 30 larger than that in N_2. Because the energy defect for V–V exchange in D_2 is slightly over one-half of that in N_2, cf. Table VII, Hancock and Green suggested that the 30-fold increase in the HF–D_2 and HF–N_2 deactivation rates could probably reflect a V–V energy transfer mechanism.

At the other extreme, they considered HF–H_2 relaxation where the small energy defect makes the reaction given in Eq. (3) nearly resonant. In this case a double exponential decay is expected and is observed (cf., Fig. 11) thereby permitting the determination of two relaxation times corresponding to the fast and slow processes, cf. Equations (28a) and (28b). Their analysis of this process yielded a value for k_{vv} of $(1.12 \pm 0.2) \times 10^5$ sec^{-1} Torr^{-1}, i.e., 35% larger than that obtained from HF–Ar mixtures, was considered to be outside the experimental error, and could not be explained.

As can be seen from Table VII extremely fast rates, corresponding to nearly gas kinetic values, were obtained for HF relaxation in H_2O and D_2O. Because discussion of triatomics lies outside the scope of this review, we refer the reader to the original paper for details and only note that the equality of these two rates and qualitative consideration of the CO_2–$H_2O(D_2O)$ systems (cf., Widom and Bauer, 1953) led Hancock and Green to suggest that their results could perhaps be interpreted in terms of chemical affinity resulting in "sticky" collisions and associated complex formation. In support of this they noted the fact that ab initio molecular orbital calculations (Kollman and Allen, 1970) indicated a bond energy of approximately 10 kcal/mole for HHO•••H–F, i.e., much stronger than the 6 kcal/mole hydrogen bond strength estimated for the HF dimer. Such a deep attractive well could be used to model strong collisions (i.e., rapid V–T transfer) in the repulsive region of the potential which, except for small differences due to reduced mass effects, would result in near equality of the rates observed in their experiment. The net conclusions of this study were that V–R transfer was responsible


LIQUID N₂ TRAPS
HI + Br₂ FLOW
MIRROR
SAPPHIRE PLATE
Ge: Au FLUORESCENCE DETECTOR
FILTER
SAMPLE CELL
InSb PEM
IGNITRON
CAPACITOR BANK
PHOTO-DIODE
545 B SCOPE
AMPLIFIER

(a)


3000
1000
E (cm⁻¹)
HCl (v = 1)
DCl (v = 1)
fast V→V
Laser Excitation
slow V→T,R

(b)

FIG. 9(a) HBr laser excited vibrational fluorescence apparatus. (From Chen, 1971). (b) Kinetic diagram for laser–excited vibrational fluorescence in HCl–DCl mixtures. HCl is vibrationally excited by a laser pulse. Vibrational energy is transferred rapidly from HCl to DCl by V–V energy transfer. Subsequently, DCl decays more slowly by V–T energy transfer. The concentrations of excited species are proportional to the observed fluorescence initially, but the optical transition rates make a negligible contribution to the observed kinetics (from Chen and Moore 1971).

TABLE VII. Vibrational deactivation rates in HF–additive mixtures at 294°K.[a]

Vibrationally excited molecule	Collision partner	Energy defect (cm^{-1})	Rate constant ($sec^{-1} \cdot Torr^{-1}$)	(Collisions per deactivation)	Collision Diameters (Å)
HF	HF	3961	$(8.74 \pm 0.1) \times 10^4$	57	2.5
HF	Ar	3961	60>	$<1.0 \times 10^4$	3.4
HF	N_2	1630	$(1.25 \pm 0.6) \times 10^2$	5.6×10^4	3.7
HF	D_2	968	$(3.7 \pm 0.4) \times 10^3$	2.7×10^3	2.9
HF	H_2	−201	$(2.4 \pm 0.3) \times 10^4$	5.7×10^2	2.9
H_2	HF	201 [245]	$(6.3 \pm 0.4) \times 10^4$	2.2×10^2	···
HF	CO_2	1612 [352]	$(5.9 \pm 0.2) \times 10^4$	1.2×10^2	4.1
CO_2	HF	(intramolecular $V \rightarrow V$)	$(5.3 \pm 0.2) \times 10^4$	1.4×10^2	···
HF	D_2O	1173	$(4.1 \pm 0.5) \times 10^6$	1.3	2.6
HF	H_2O	205	$(4.1 \pm 1.0) \times 10^6$	1.3	2.6

[a] Table from Hancock and Green (1972b).

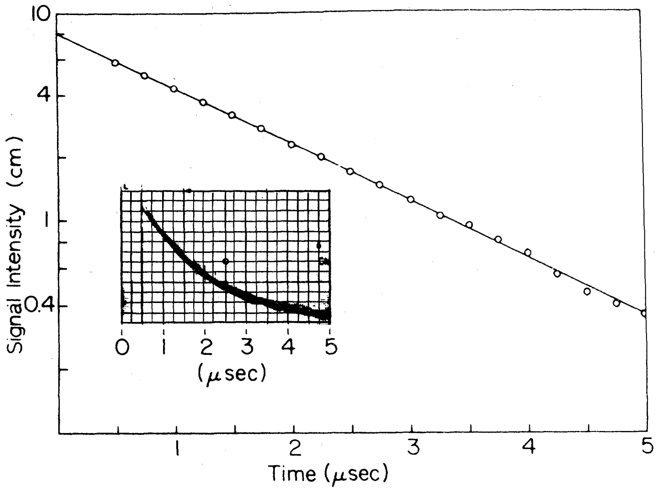


FIG. 10. Laser-excited vibrational fluorescence at 2.4 μ from an HF–Ar mixture; gas pressures were HF = 7.51 Torr, Ar = 49.9 Torr, with τ_{obs} = 1.51 μsec (from Hancock and Green, 1972b).

for the fast halide self-relaxation rates, V–V mechanisms probably dominated energy transfer to homonuclear diatomics (H_2, D_2 and N_2) and to CO_2, and that attractive forces and V–R, T transfer mechanisms could not entirely explain the observed enhancement of all the rates at the lower temperatures.

The predominance of vibration to rotation coupling in the hydrogen halide relaxation has since been confirmed in other laser fluorescence measurements such as those of HF and DF by Hinchen (1973a, b). His results are included in Table VIII. His result for $k_{HF-HF}/k_{DF-DF} = 2.5$ is consistent with the values of 3.3 and 3.4 for the HCl and HBr systems (see below) but not with the prediction of the V–T theory which gives $k_{HX-HX}/k_{DX-CX} \ll 1$, nor with the prediction of Shin's (1971a) theory which, according to Hinchen, yields a value of 8 for this ratio. The relationship in the rates $k_{HF-HF} > k_{DF-HF} > k_{DF-DF}$ indicated by Hinchen's data is similar to that found for HCl and HBr, and adds further evidence for the V–R mechanism. However, in contrast to HBr and HCl relaxation with H_2 where rotational participation by H_2 is discounted, Hinchen points out that the fast rates for the relaxation of HF by D_2 (0.37×10^4 sec^{-1} Torr^{-1}) and DF by H_2 (0.44×10^4 sec^{-1} Torr^{-1}) suggest that these deactivation processes may proceed via V–R transfer to rotational levels in $H_2(D_2)$ in analogy with the V–R deactivation of CO_2 by H_2 discussed by Kolker (1971).

For relaxation by N_2, Hichen obtains 0.20×10^4 sec^{-1} Torr^{-1}, a value an order of magnitude larger than that reported by Hancock and Green (1972, see above), and two orders of magnitude larger than the HF(DF) relaxation rates by Ar and He also obtained by these authors. His limits of <60 sec^{-1} Torr^{-1} for k_{HF-Ar} and k_{HF-He}, and of <30 sec^{-1} Torr^{-1} for k_{DF-Ar} and k_{DF-He}, indicate rates much slower than the H(D)F self-relaxation rates and are

TABLE VIII. Representative low temperature hydrogen and deuterium halide relaxation rates (in units of $10^4 \times$ sec$^{-1}\cdot$Torr^{-1})[a]

		A. Self-Deactivation Rates (K_{11})[a]						
Authors	Temp.[b] (°K)	HF	HCl	HBr	HI	DF	DCL	DBr
Ahl and Cool (1973)	350	4.95 ± 0.4[d] (HF–HCl)	0.09 ± 0.02	0.06 ± 0.02	0.032 ± 0.10[e]	1.8 ± 0.3		
Ahl and Cool (1973)	300	7.00 ± 1.0[d] (HF–HCl)	0.12 ± 0.03	0.06 ± 0.02	0.48 ± 0.10[e]	2.6 ± 0.4		
Airey and Fried (1971)	350	9.5						
Bina and Jones (1973)	300	6.0						
Blair *et al.* (1973)	R.T.	8.7						
Bott (1972)	295	5.6 ± 0.5						
Bott and Cohen (1973b)	295	5.6	0.85 ± 0.10	0.08 ± 0.01				
Bott and Cohen (1973c)	295							
Chen *et al.* (1968)	R.T.				0.0375 (from HI–CO_2)			
Chen and Moore (1971a)	296 ± 2		0.083 ± 0.008				0.025 +0.003 −0.009	
Chen (1971a)	296 ± 2			0.0571 ± 0.005				
Chen and Chen (1972)	295			0.0571 ± 0.005				
Fried (1963)[c]	295	6.7						0.017 ± 0.003
Fried *et al.* (1973)	294	10.0						
Hancock and Green (1972)	294	8.74 ± 0.1 (Ar)						
Hancock and Green (1972)	294	4.4 ± 0.3 (pure)						
Hinchen (1973)	295	6.1 ± 0.4 (pure)						
Hinchen (1973)	295	6.4 ± 0.6 (Ar)				2.1 ± 0.2		
Hinchen (1973)	295	5.8 ± 0.7 (He)						
Green and Hancock (1973)								
Lucht and Cool (1974)	295	8.4 ± 0.7 (HF–CO_2)				2.7 ± 0.3 (DF–CO_2) (at 299)		
Stephens and Cool (1972)	350	5.25						
Zittel and Moore (1973a)	296 ± 2						0.022 ± 0.003	

TABLE VIII. (*Continued*)

B. V–V and V–R, T Rates[a]

Molecule	Deactivating partner (Authors)	Temp. °K	K_{vv}	$K_{vv}+K_{12}$	K_{12}	K_{21}
HF	HCL					
	Ahl and Cool (1973)	350	1.2–2.5	2.2 ± 0.4	<1.2	
	Ahl and Cool (1973)	300	1.6–3.2	2.9 ± 0.3	<1.6	
	Bott and Cohen (1973b)	295		1.7 ± 0.1		1.5 ± 0.2
HF	HBr					
	Ahl and Cool (1973)	350	0.28–0.55	0.35 ± 0.20	<0.28	
	Ahl and Cool (1973)	300	0.47–0.95	0.75 ± 0.20	<0.47	
	Bott and Cohen (1973b)	295		0.75 ± 0.1		0.9 ± 0.1
HF	HI					
	Ahl and Cool (1973)	350	1.45 ± 0.25[g]	0.20 ± 0.15		
	Ahl and Cool (1973)	300	1.95 ± 0.25[g]	0.35 ± 0.20		
HF	DF					
	Ahl and Cool (1973)	350	4.1–11.3	9.8 ± 1.5	$<3.3\pm0.5$	
	Ahl and Cool (1973)	300	7.1–14.3	13.3 ± 1.0	$<4.5\pm0.7$	
	Bott and Cohen (1973b)	295		7.7 ± 0.4		3.5 ± 0.5
	Hinchen (1973a)	295		6.7 ± 0.5		3.4 ± 0.3 (Direct DF excitation) 2.05 (Slow decay in HF/DF mixtures)
HF	N_2					
	Bott and Cohen (1973b)	295		0.0152 ± 0.0015		
	Fried *et al.* (1973)	295			2 ± 1	
	Green and Hancock (1973)	294	0.0125 ± 0.006			
HF	H_2					
	Bott and Cohen (1973b)	295		1.7 ± 0.1		
	Hancock and Green (1972)	294		2.4 ± 0.3	<0.1	6.3 ± 0.4
	Hinchen (1973a)	295		2.39 ± 0.6		
HF	D_2					
	Bott and Cohen (1973b)	295		0.31 ± 0.06		
	Hancock and Green (1972)	294		0.37 ± 0.04		
DF	N_2					
	Bott (1974)	295		0.91 ± 0.09		
	Hinchen (1973a)	295		2.0 ± 0.5		

C. Deactivation by Atoms (in units of $\sec^{-1}$ Torr^{-1})

Author	Temp. (°K)	Molecule	Deactivating atom		
			He	Ne	Ar
Ahl and Cool (1973)	300 and 350	HF			<100 (50 used)
Fried *et al.* (1973)	350	HF			<100
Green and Hancock (1973)	294	HF	<40		
Hancock and Green (1972)	294	HF			<60
Hinchen (1973a)	295	HF	<60		<60
Hinchen (1973a)	295	DF	<30		<30
Zittel and Moore (1973b)	296 ± 2	DCl	2.15 ± 0.2	<0.6	<0.3
Hopkins and Chen (1973)	R.T.	D_2	$0.78\pm0.08(^3He)$ $0.63\pm0.07(^4He)$		

[a] The rates quoted are those reported in the literature and identified in Sec. II, Eqs. (21)–(27).

[b] When no explicit temperature is stated we follow current usage (see Moore, 1973) of using R.T. for room tmeperature

[c] Quoted by Hinchen (see Footnote 7 in Hinchen, 1973a).

[d] Comparable values are obtained from other mixtures.

[e] The discrepancy between these values and that of Chen *et al.* leads to the suggetsion of multiquantum V–V, R transfer as given under HF–HI in Table VIII.B (see Ahl and Cool, 1973).

[f] The dilution effect is confirmed in Green and Hancock (1973a).

[g] For HF($v=1$) → HI($v=2$) cf., (e) above.

in line with the trends for HF–noble gas deactivation shown in Fig. 5.

To study V–V exchange in HF–DF mixtures, Hinchen performed simultaneous measurements of fluorescence at 2.4 μ from HF and at 3.3 μ from DF. His illustration of the immediate buildup and fast falloff of the 2.4 μ fluorescence and of the slow increase in the 3.3 μ emission as the 2.4 μ intensity drops is shown in Fig. 12(a), and that of the double exponential decay which suggests V–V mechanism in DF–D_2 relaxation in Fig. 12(b). The value of 2.05×10^4 $\sec^{-1}$ Torr^{-1} for k_{21} derived from measurements of the slow (3.3 μ) decay is only in fair agreement with that of 3.4×10^4 $\sec^{-1}$ Torr^{-1} obtained from measurements with direct laser excitation of DF in DF–HF mixtures.

In a subsequent paper (1973b), Hinchen examined the temperature variation of the HF(DF) self-relaxation rates

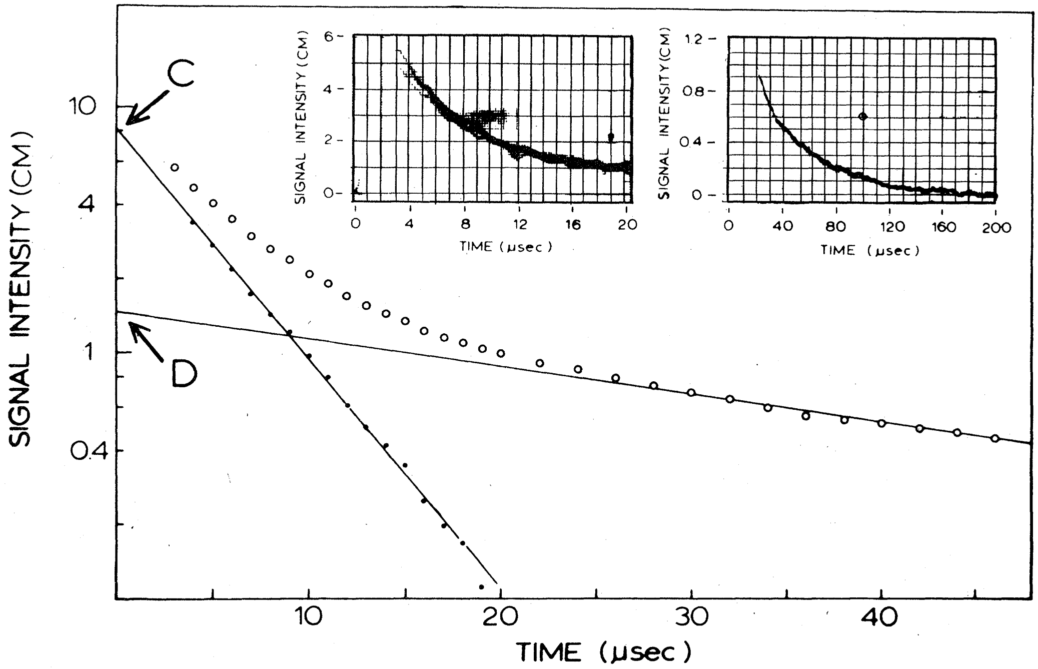


FIG. 11. Fluorescence decay curve analysis in HF–H_2–Ar mixtures. A coupling of the nearly resonant ($v = 1$) vibrational energy levels in HF and H_2 results in double-exponential behavior from which two lifetimes can be extracted. Partial pressures are HF = 0.84 Torr, H_2 = 3.09 Torr, and Ar = 40.0 Torr; measured relaxation times are $\tau_{\mathrm{fast}} = 5.1$ μsec, $\tau_{\mathrm{slow}} = 44.0$ μsec. Additional information is obtained from the ratio of intercepts C/D. The enhanced signal-to-noise obtained from the slower relaxation time results from decreasing the amplifier band pass from 10 Hz–1.0 MHz to Hz–100 kHz. (from Hancock and Green 1972b).

in the range 300°–1000°K. He obtained good matching with higher temperature shock tube data and very good agreement with Bott's (1974) shock tube laser-induced fluorescence measurements at temperatures below 1000°K as shown by his summary of the experimental results in Fig. 13. Hinchen also presented a comparison of his results with the predictions of three theoretical models (Shin 1970a, b, 1971a, b, c; Berend and Thommarson 1972, 1973) which we discuss in Sec. V after the models themselves have been considered. Although he observed no double fluorescence decay over the partial pressure range P_{N_2}(3–42 Torr), Hinchen suggested the fast DF–N_2 relaxation rate could be accounted for by either complex formation between N_2 and DF, or weak V–V transfer.

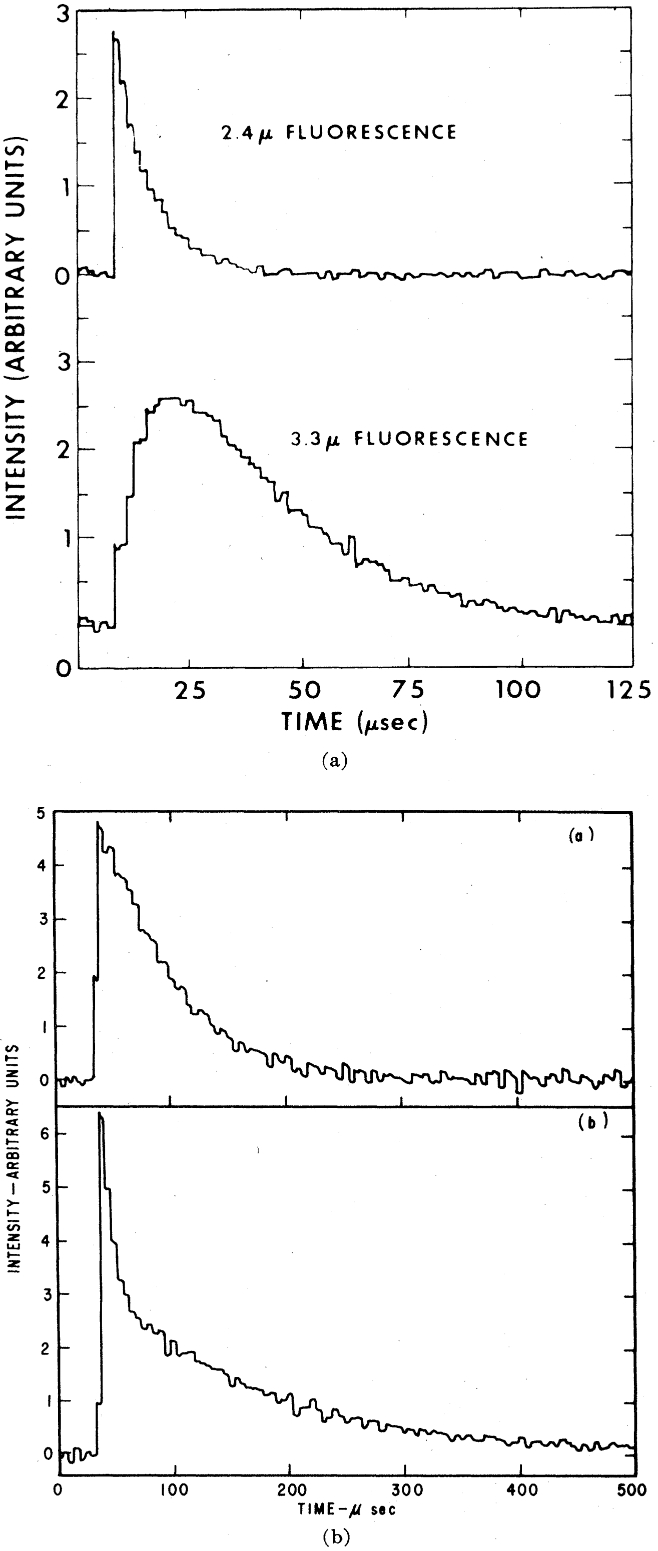
2. Other halides and deuterides

Following the initial investigations of Chen, Stephenson, and Moore (1968) of vibrational energy transfer rates in HCl–CO_2, HCl–HF and HF–CO_2 mixtures, Chen and Moore (1971a, b) applied this technique to the determination of V–R, T transfer rates in HCl with a variety of collision partners. The starting point for their work was the result of early shock tube experiments (Breshears and Bird, 1969a, b; Bowman and Seery, 1969) that neither the relaxation rates nor the isotope effect in H(D)Cl were compatible with V–T transfer theory but could perhaps be interpreted in terms of V–R transfer mechanisms predicted to dominate the hydrogen halide relaxation rates (Moore 1965 and Sec. IV). By selecting appropriate mixtures of the reacting gases, Chen and Moore made use of the fluorescence decay analysis (Moore 1967) to separately study the V–R, T (1971a) and the V–V (1971b) relaxation processes in HCl. Some of their room temperature results are included in Table VIII.

The most important result of their paper was the confirmation of the deviation of the vibrational relaxation probabilities from the conventional Landau–Teller linearity already noticed by Breshears and Bird (1969a), because the fluorescence measurements yielded values for HCl(DCl) deactivation probability approximately 16 times larger than that obtained by extrapolation of shock tube data–see Fig. 14. Their value for DCl self-relaxation of 2.5 + .3, −9 (μ sec·Torr)$^{-1}$ has since been confirmed in the more recent experiments of Zittel and Moore (1973a) who quote 2.2 ± 3 (μ sec·Torr)$^{-1}$.

Chen and Moore discussed their results qualitatively in terms of three vibration to rotation collision models depicted in Fig. 15 and argued that the correct relaxation process could probably be represented by a distribution of collisions represented by these (and intermediate) collision geometries. We include their model here because it is often referred to in current experimental papers (e.g., Hinchen 1973a; Bott 1974).

As depicted in Fig. 15, in model I, where the hydrogen atom of the collision partner does not participate in the collision, the self-deactivation probability of both HCl and DCl is equal to the deactivation probability of each molecule by the other, i.e., $P_{\mathrm{HX-HX}} = P_{\mathrm{HX-DX}}$ and $P_{\mathrm{DX-DX}} = P_{\mathrm{DX-HX}}$. In model II, the rotational velocity of the vibrator molecule does not contribute to the impact and the entire collisional velocity is that of the collision partner. This gives $P_{\mathrm{DX-HX}} \gg P_{\mathrm{HX-HX}} \gg P_{\mathrm{HX-DX}}$ and $P_{\mathrm{HX-HX}} \geq P_{\mathrm{DX-DX}}$.



(a)

(b)

FIG. 12. (a) Fluorescence signals from a mixture of HF (0.48 Torr) and DF (0.72 Torr). Note decay of HF fluorescence at 2.4 μ concurrent with the buildup of DF fluorescence at 3.3 μ (from Hinchen 1973a). (b) Fluorescence signals: (a) Pure DF showing single exponential decay. (b) DF with D_2 showing the fast exponential decay for DF ($v = 1$) + D_2 ($v = 0$) $\rightarrow$ DF ($v = 0$) + D_2 ($v = 1$) followed by the slow rate after attainment of equilibrium (from Hinchen 1972).

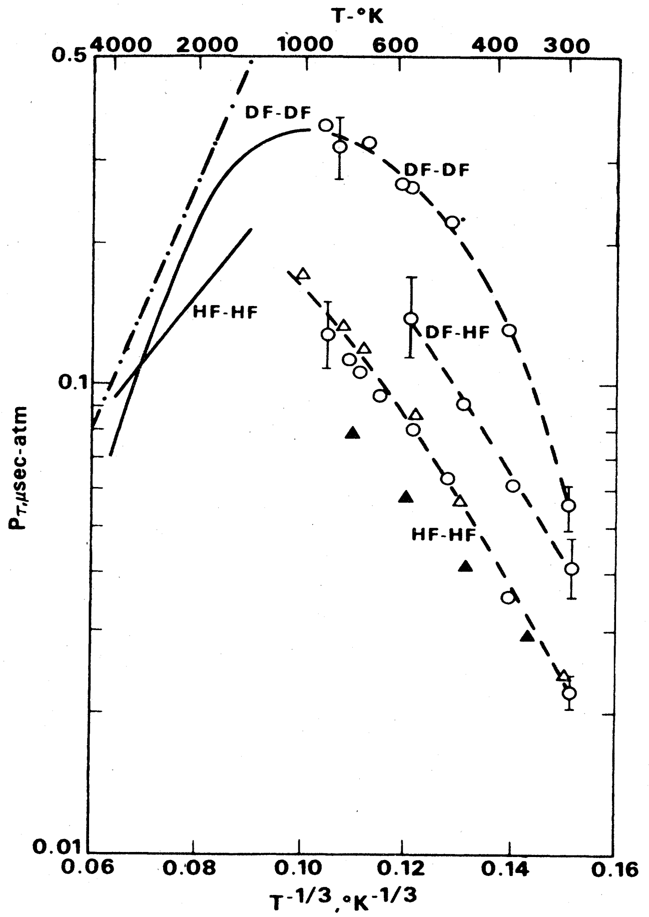


FIG. 13. Relaxation times for DF–DF, DF–HF, and HF–HF at various temperatures: (○, Hinchen 1973b; △, Bott 1972; ▲, Fried, cited in Hinchen 1973b; —, Bott and shock tube; - - -, Blauer, shock tube DF, 1972. (from Hinchen 1973b).

In model III, which is a mix of I and II, the predictions are intermediate: $P_{\mathrm{DX-HX}} > P_{\mathrm{DX-DX}}$ and $P_{\mathrm{HX-HX}} > P_{\mathrm{HX-DX}}$ and, roughly, $P_{\mathrm{HX-DX}} > P_{\mathrm{DX-DX}} > P_{\mathrm{HX-HX}} \geq P_{\mathrm{DX-HX}}$. Chen and Moore noted that the self-relaxation rates they obtained were consistent with model I predictions, but their result of $P_{\mathrm{HCl-HCl}} \geq P_{\mathrm{DCl-HCl}}$ was incompatible with the model II prediction. They concluded that unless rotation–translation coupling occurred late in the collision, the vibrational energy was transferred mostly to rotation of the vibrator molecule, some to rotation of the collision partner and very little to translation. They supported this conclusion with estimates based on a model of vibrational transition probabilities with allowance for rotational anisotropy of the intermolecular potential due to Kapralova *et al.* (1968). They also suggested that the hydrogen bonding interaction between the two HCl molecules offered a plausible explanation for these results.

Because the HCl relaxation rates obtained with *n*-H_2 and *p*-H_2 were the same within the 20% uncertainty limits, Chen and Moore concluded that transfer to rotation of H_2 was not important. They also suggested that because the HCl self-relaxation rates were much larger than those of HCl by either H_2 or the rare gases, the HCl–HCl interaction

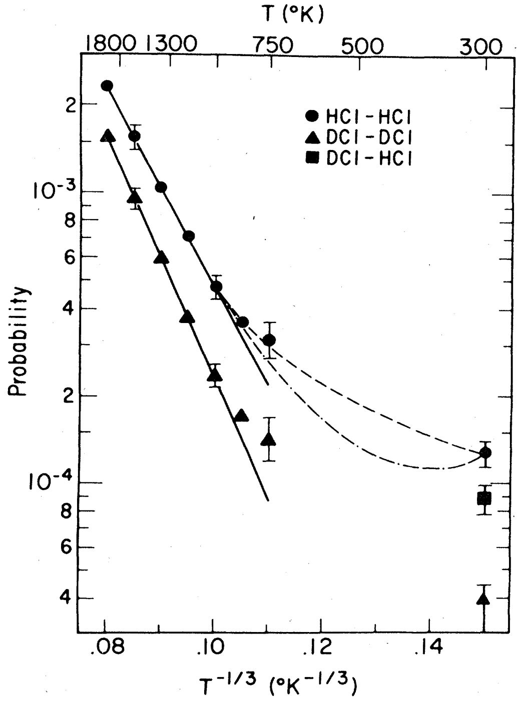


FIG. 14. Probability of vibrational deactivation in hydrogen chloride per kinetic collision vs $T^{1/3}$. Linear extrapolation of shock tube data between 1000 and 2000°K gives P a factor of 16 ± 6 smaller than observed for room temperature. This deviation from linearity is already quite noticeable in the shock tube data between 1000 and 700°K. $P_{\mathrm{DCl-HCl}}$ is for vibrational deactivation of DCL by an HCl collision partner: -•-•, interpolation by $P(T) = A\ T^{-1/6} \exp[(\frac{1}{2}h\nu + \epsilon)/kT \times \exp[\beta T^{-1/3}]$; - - -, arbitrary but equally possible interpolation (from Chen and Moore 1971a).

potential had to be much stronger than in the HCl–H_2 and HCl–rare-gas systems.

In their following paper (Chen and Moore 1971b) these authors investigated the V–V transfer mechanisms in HCl mixtures by selecting the concentrations to derive either k_{vv} or $k_{vv} + k_{12}$ directly from the data—see Table VIII. The essential result was that for near resonant processes [i.e., $\Delta E \leq 100\ \mathrm{cm}^{-1}$ in Eq. (3)] the energy transfer probabilities were about an order of magnitude larger than those reported up to that date for other diatom–diatom systems and that these probabilities decreased slowly with increasing ΔE for the HCl–hydrogen halide systems. Their measured cross sections for HCl–HBr and HCl–D_2 were quoted to be greater than those obtained by transition dipole and dipole-quadrupole calculations respectively. They noted that the probability of energy transfer from CO to O_2 (with $\Delta E = 587\ \mathrm{cm}^{-1}$) was of the order of 10^{-7}, whereas that of the hydrogen halides was four orders of magnitude larger and attributed this dramatic difference to strong attractive forces and the large amplitude of the H-atom stretching vibrations. They also pointed out that H-atom bonding could be expected to be less important in V–V than in V–R, T transfer because coupling caused by it required collinear H atom to H atom collisions rather than those in the hydrogen bonded orientation. A suggestion that V–V transfer in HCL ($v = 2$) relaxation was caused by short range forces has been recently made by Hopkins and Chen (1972b).

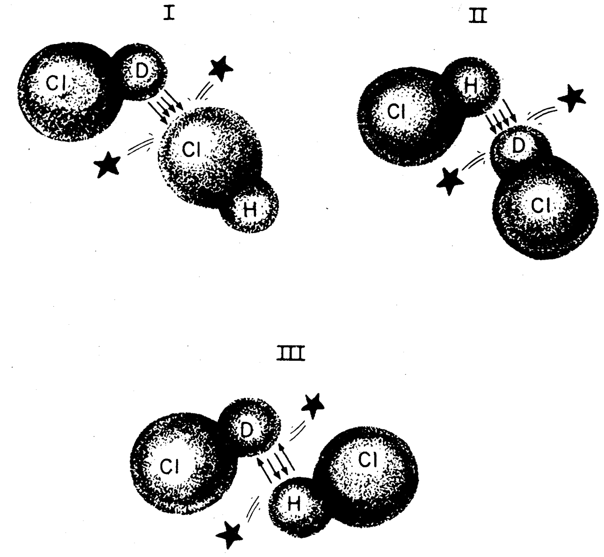


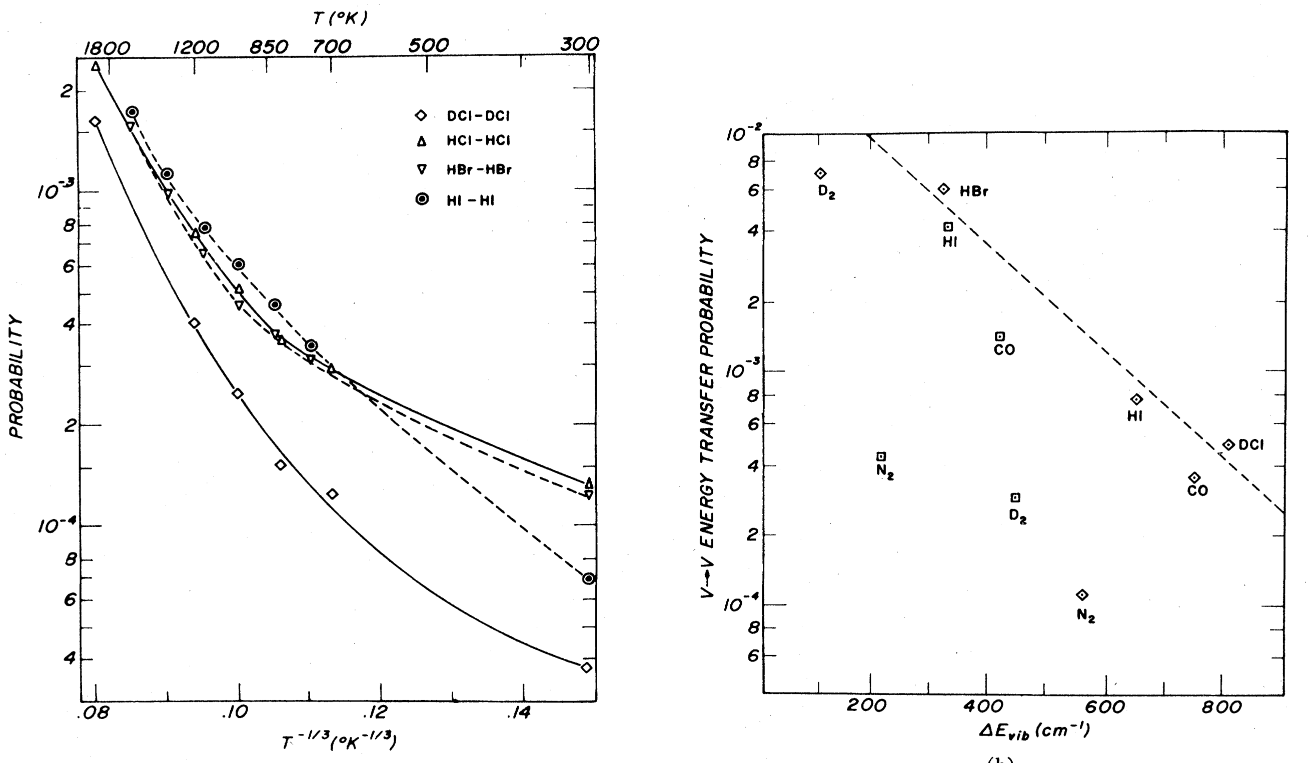
FIG. 15. Collision models for vibration-to-rotation energy transfer in hydrogen chloride. Deactivation of excited DCl by an HCl collision partner is illustrated. In Model I the velocity of impact of the vibrating D atom with the collision partner is predominantly D atom (vibrator) rotation. Energy is transferred to rotation of the vibrator and no rate change on isotropic substitution of collision partner H by D is expected. In Model II impact velocity is taken to be entirely rotation of the collision partner H atom and reduction of this velocity by substitution of D would decrease the probability by a large amount. Energy is transferred into collision partner rotation. Model III is a compromise between I and II. Experiment indicates that Model I plays the dominant role for HCl–HCl and DCl–DCl collisions.

An analogous study of relaxation in HBr mixtures was subsequently reported by Chen (1971a, b). By comparing his results with the rates for other hydrogen halides, Chen deduced that the HCl–HCl potential had a deeper attractive well and a steeper repulsive part than was the case for either the HBr–HBr or the HI–HI systems. From the equality of rates for n-H_2 and p-H_2 relaxation and the similarity of the vibrational–relaxation rates in different rare gases, Chen concluded that neither rotational transfer to H_2 nor transfer to translation were significant. Chen's results for both the V–R, T and the V–V processes he studied are included in Table VIII and his summary of the self-relaxation rates and possible correlation with energy discrepancy is shown in Fig. 16.

Vibrational relaxation rates in HCl have also been measured by Gorshkov *et al.* (1971). They used two lasers placed on a common optical axis and deduced the vibrational relaxation rate from analysis of the mixture gain between the time of the flash photolysis initiated reaction in one and the laser pulse formation in the second. Their results for the relaxation constants (only three of which are independently determined) among several vibrational levels at room temperature for the reaction

$$\mathrm{HCl}(v = m) + \mathrm{HCl}(v = n) \rightleftarrows \mathrm{HCl}(v = m - 1) + \\ + \mathrm{HCL}(v = n + 1)$$

are given in Table IX. The V–V and V–T rate constants were computed from the SSH theory and the influence of variations in the V–V rates on the duration and magnitude



(a) (b)

FIG. 16. (a) Probability of vibrational deactivation in hydrogen halides per kinetic collision vs $T^{-1/3}$ (from Chen 1971a). (b) Probability of vibration ⟶ vibration energy transfer between HBr ($v = 1$) and AB ($v = 0$) levels vs energy discrepancy ΔE: ◇, data for process HCl ($v = 1$) + AB ($v = 0$) $\rightleftarrows$ HCl ($v = 0$) + AB ($v = 1$); ⊡, data for process HBr ($v = 1$) + AB ($v = 0$) $\rightleftarrows$ HBr ($v = 0$) + AB ($v = 1$); both presented in the exothermic direction (from Chen 1971b).

of the population inversion in the transition $V = 2 \longrightarrow V = 1$ was studied. Gorshkov *et al.* (1971) found that the best match to the experimental decay rates could be obtained if the computed rate constants were decreased by a factor of about 2.[5]

Zittel and Moore (1972) reported fluorescence measurements in N_2–CO, CO–DCl and N_2–DCl mixtures at 295°K. They reported a fast V–V rate at this temperature, in agreement with the SSH dependence predicted from shock tube data by Sato *et al.* (1969). They interpreted this result as indicative of the role of dipole-quadrupole forces first considered by Hancock and Smith (1971), as perhaps responsible for the near resonant exchange between these heavy diatomics.

In a more detailed investigation of relaxation processes in DCl systems, Zittel and Moore (1973b) discuss V–T, R relaxation of HCl(DCl) by He; nearly resonant single quantum V–V exchange in CO–DCl, ^{13}CO–DCl and $CD_4(v_3)$; nearly resonant multiquantum V–V exchange in HCl, $^{16}O_2$, $^{18}O_2$, and nonresonant V–V exchange for various DCl(HCl)–CO, NO, O_2, and other mixtures–see their Table III. They pointed out that for the latter case, the rates though quoted as k_{vv} [cf. Eq. (3)], actually represented sums of several V–V and V–T, R rates. These authors also measured the self-relaxation rates of HCl and HBr in the temperature range 144°–584°K and found well defined minima between 300° and 400°K. They pointed out that the near equality of these rates (see Fig. 17) in molecules with quite different dipole moments (cf., Table III) cast doubts on the validity of the dipole–dipole attractive potential correction (Shin 1971a, c) involved in discussions of the HF(DF) data (Bott and Cohen 1971b, 1973a; Hinchen 1973a). They argued instead that theoretical models involving strong attractive forces to describe effects like multiple collisions (Clark and Smith, 1970), long lived bimolecular complexes (Airey and Smith 1972, Berend and Thommarson 1973b), and close, large impact parameter repulsive collisions were probably necessary to explain the magnitude and temperature dependence of halide relaxation data. Their comparison of the HF–HCl self-relaxation probabilities with those for the HCl–He, CO–He systems is shown in Fig. 18. Note that the data suggest a minimum in the HCl–He probabilities—the first one reported for this system.

TABLE IX. Values of relaxation constants and molecular collisions (From Gorshkov *et al.*, 1971).

Experimental relaxation constant (cm³/mole sec) ($K_{m,m\pm1}{}^{n,n\pm1}$)	Number of collisions
$K_{10}{}^{12} = (1.5\text{–}3) \times 10^{12}$	40–80
$K_{01}{}^{21} = (0.91\text{–}1.82) \times 10^{12}$	66–132
$k_{10}{}^{23} = (0.64\text{–}1.28) \times 10^{12}$	95–190
$k_{01}{}^{32} = (0.24\text{–}0.47) \times 10^{12}$	256–512
$k_{21}{}^{23} = (4.5\text{–}9) \times 10^{12}$	13–26
$k_{12}{}^{32} = (2.7\text{–}5.4) \times 10^{12}$	22–44

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[5] For more recent measurement for $m = n = 1$ see Hopkins and Chen (1972) and Osgood *et al.* (1973) for the analogous results in HF.

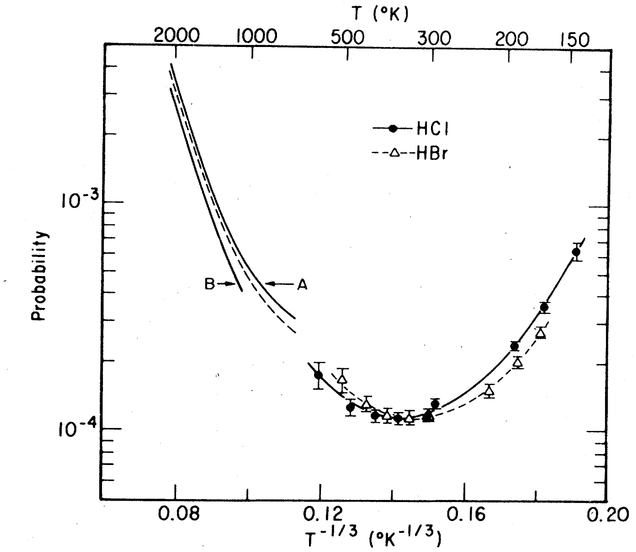


FIG. 17. Probability for HCl and HBr deactivation (from Zittel and Moore, 1973b).

3. Miscellaneous

Room temperature measurements of vibrational relaxation in CO, HCl (and CO_2 and N_2O) have also been reported by Margottin–Maclou *et al.* (1971) using the laser fluorescence method. These authors investigated the relative contribution to the net relation rate β (defined by $\beta = K + \delta + \pi P$) of the three processes of diffusion and wall excitation (δ), quenching collisions (K) and spontaneous emission (πP). For the latter, the effect of self-absorption due to radiation trapping, which results in lowering of the spontaneous emission rate, was taken into account. The vibrational thermalization constants were determined as a function of pressure and size of the excitation cell and, in turn, were used to determine the variation of the total relaxation constant β. Because the vibrational thermalization constant for CO is low, the net relaxation rate is determined by the radiative contribution over a large range of pressures. For room temperature, in the range 0.1–1 atm, these authors obtained relaxation constants roughly agreeing with the shock tube data of 0.1 $sec^{-1} \cdot atm^{-1}$ and the SSH prediction of 0.3 $sec^{-1} \cdot atm^{-1}$.

In HCl, collisional relaxation is more effective than in CO, and radiative relaxation contributes only a small part to the net rate. To study the process, the authors used population inversion obtained by forming HCl directly in a vibrationally excited state in a pulse discharge in a flowing mixture of H_2 and NOCl. Measurements were taken for a range of pressures between 0.02–200 Torr, for different cell sizes and with different laser lines used for excitation. From the high pressure measurements, the vibrational thermalization constant of $K/P = 700$ sec^{-1} $Torr^{-1}$ was obtained, corresponding to a deexcitation probability of 10^{-4}, a value slightly smaller than that reported by Chen and Moore (1.2×10^{-4}). From the low pressure measurements, the authors deduced that the diffusion coefficient for HCl was equal to the kinetic self-diffusion coefficients, just like the case of CO. For both the NO and CO_2 molecules excited into the (001) vibrational level, the radiative relaxation constant was taken equal to the spontaneous emission coefficients corresponding to all transitions from this level, except for those corresponding to the (001)–(000) transitions for which self-absorption of the fluorescence radiation had to be taken into account. For NO, the authors used the values of self-broadened half-width calculated on the basis of the Anderson (1949) theory. They estimated the precision of their measurements to be ±25% for HCl, ±10% for CO.

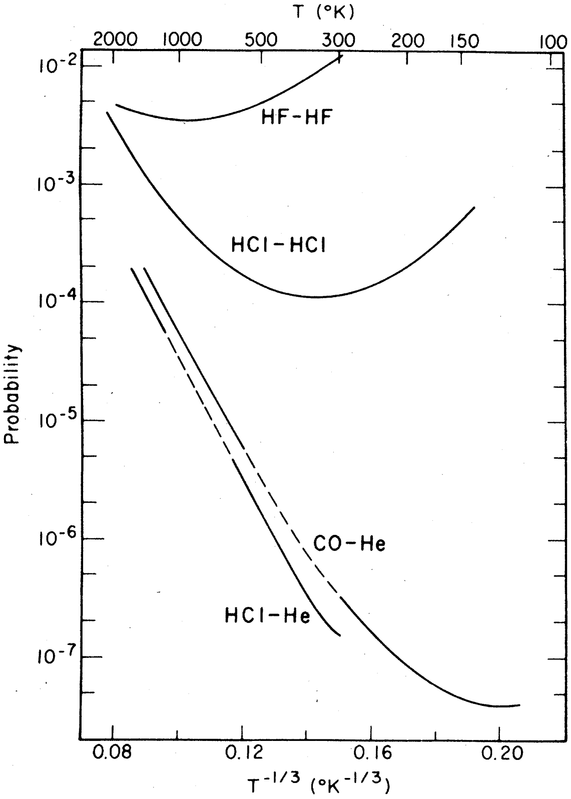


FIG. 18. Comparison of probabilities for self-deactivation and deactivation by He. (from Zittel and Moore 1973b).

Laser excited vibrational fluorescence method has also been used by Stephenson and Moore (1970) to investigate intermolecular V–V transfer in gaseous CO_2 for a variety of polyatomic collision partners at temperatures in the range 300°–800°K. All deactivation cross sections except those for CO_2 and CH_4 were found to decrease with increasing temperature and those for the rare gases depended only weakly on the reduced mass. The authors pointed out that a simple form of calculating transition probabilities as functions of velocity and intermolecular potentials used in most theories of V–V transfer did not account for the results. They noted that their observations of equal cross sections for both n-H_2 and p-H_2 implied that the energy transfer into rotation of H_2 was not taking place. Subsequently, Stephenson *et al.* (1972) investigated V–V transfer in CO_2 hydrogen halide mixtures. They obtained large deactivation cross sections for V–V exchange between $CO_2(00^01)$ and HCl($v = 1$), those for HCl and DCl being of the order of 0.5 Å^2 and decreasing slightly with increasing temperature in the range 298°–510°K. Stephenson *et al.* noted that existing theories of vibrational energy transfer

TABLE X. Vibrational energy transfer rates in NO and CO at $T = 298 \pm 1$°K (from Stephenson, 1974).

M	$k_{\text{NO-M}}$ ($\sec^{-1}\cdot\text{Torr}^{-1}$)	$k_{\text{CO-M}}{}^{a}$ ($\sec^{-1}\cdot\text{Torr}^{-1}$)
H_2O	$59\,000 \pm 7000$	6400 ± 1600
D_2O	650 ± 130	440 ± 60
CH_4	$6\,100 \pm 500$	297 ± 20
C_2H_4	$11\,900 \pm 900$	3800 ± 250
C_2H_6	$6\,500 \pm 600$	3200 ± 300
C_4H_{10}	$8\,500 \pm 700$	6400 ± 300
NO_2	$66\,000 \pm 5000$	145 ± 30
N_2	29.3 ± 6^{b}	440 ± 40^{b}

[a] Rate constants from J. C. Stephenson and E. R. Mosberg, J. Chem. Phys. **60**, 3567, 1974, except for the NO_2 rate.

[b] Rate constants for VV exchange in the exothermic direction.

due to long range multipolar forces did not qualitatively explain their data, although for CO_2–HBr, CO_2–HCl and CO_2–HI, multipolar contributions were estimated to be possibly significant. They suggested that energy transfer among vibrations of CO_2 was aided by attractive forces and transfer to rotation in $CO_2(00^{\circ}1)$-hydrogen halide collisions.

Among the more recent applications of the laser excited vibrational fluorescence method is that by Stephenson (1974) who reported rates for deactivation of NO($v = 1$) by H_2O, D_2O, NO_2, CH_4, C_2H_4, C_2H_6, and C_4H_{10} as well as of N_2 ($v = 1$) and of CO ($v = 1$) by NO_2 and N_2O_4. Stephenson found that only bimolecular collisions contributed to the relaxation rate over the temperature range of 100°–300°K, and established an upper possible limit for the termolecular rate constant $K_3 < 8 \times 10^{-35}$ cm^6 sec$^{-1}\cdot$mol^{-2}. Stephenson's results showed a typical temperature inversion in energy transfer (exothermic) from CO to NO, and a dramatic, nearly 100 times greater efficiency, of N_2O than D_2O in de-excitation of NO. His results for the activation of both NO and CO by a variety of collision partners are summarized in Table X. Although the internal states of the collision partners were not determined so that no information as to the combination of V–V or V–T processes causing the deactivation of NO could be obtained, Stephenson suggested that the V–V transfer process

$$\mathrm{NO}(1) + \mathrm{H_2O}(000) \rightarrow \mathrm{NO}(0) + \mathrm{H_2O}(010) + \Delta E = 300\ \mathrm{cm}^{-1}$$

would probably be a most likely candidate. The efficiency of deactivation of NO by NO_2, which he found to be about 450 times greater than that of CO, was ascribed by him to the V–V transfer process

$$\mathrm{NO}(1) + \mathrm{NO_2} \rightarrow \mathrm{NO}(0) + \mathrm{NO_2}(001) + \Delta E = 255\ \mathrm{cm}^{-1}$$

and possibly to the chemical reaction

$$\mathrm{NO} + \mathrm{NO_2} = \mathrm{N_2O_3} + \Delta H = 9.7\ \mathrm{kcal/mole}.$$

Vibrational relaxation of D_2 in ^{3}He and ^{4}He mixtures has been measured by Hopkins and Chen (1973) who suggested that transfer of vibrational energy into both rotation and translation was taking place. No comparison with any theory was reported.

C. Correlations

An early systematic correlation of relaxation data was formulated by Millikan and White (1963)—see Fig. 19.

$$\log_{10}(P\tau_v) = 5 \times 10^{-4}\,\mu^{1/2}\theta^{4/3}\left[T^{-1/3} - 0.015\,\mu^{1/4}\right] - 8.00 \qquad (39)$$

where $\theta = h\nu/k(°K)$, P is the pressure (atm), μ the reduced mass and τ_v the relaxation time in seconds. This equation was found to reproduce the measured times to within 50% for a variety of systems such as N_2–I_2 and O_2–H_2. In the case of carbon monoxide the predictions of the empirical relation differed from experimental values by factors of 3 and 5 at 5000°K and 2000°K, respectively. Millikan and White showed that the empirical relation frequently resulted in values of transition probabilities nearly as accurate as those obtained by detailed calculations using the SSH theory. This empirical relation was subsequently verified qualitatively by White (1968) who measured the vibrational relaxation of N_2–He, N_2–CH_4 and N_2–C_2H_2 mixtures. His results were in reasonable agreement with the predictions of the empirical model, provided the assumption was made that only T–V processes were operative and the dominant V–V processes could be ignored. However, for N_2–He mixtures, empirical estimates were up to two orders of magnitude off.

Benson and Berend (1966) pointed out that the Millikan and White correlation did not include data for the light

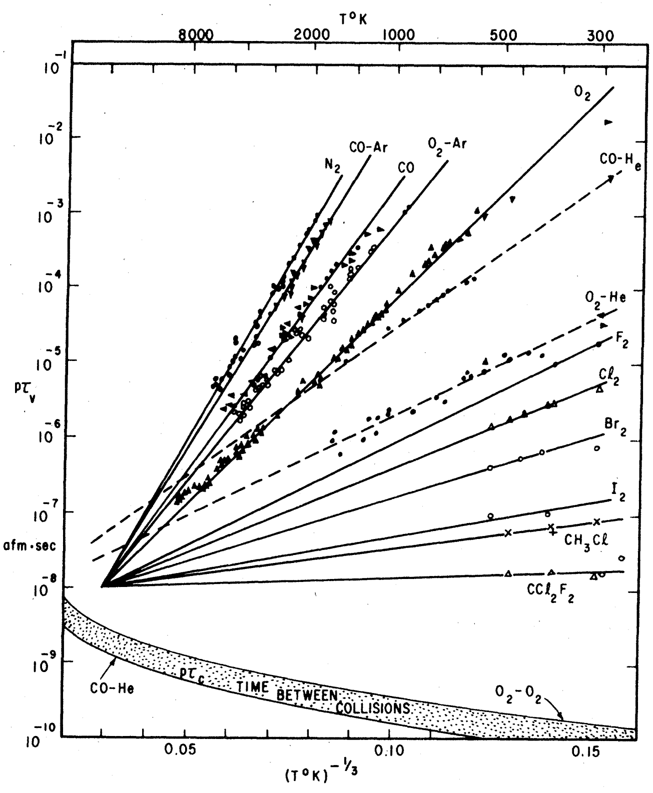


FIG. 19. Correlation of vibrational relaxation times for diatomic molecules (from Millikan and White 1963). For the sources of the data points, especially for O_2 which are not distinguished here, see the original reference.

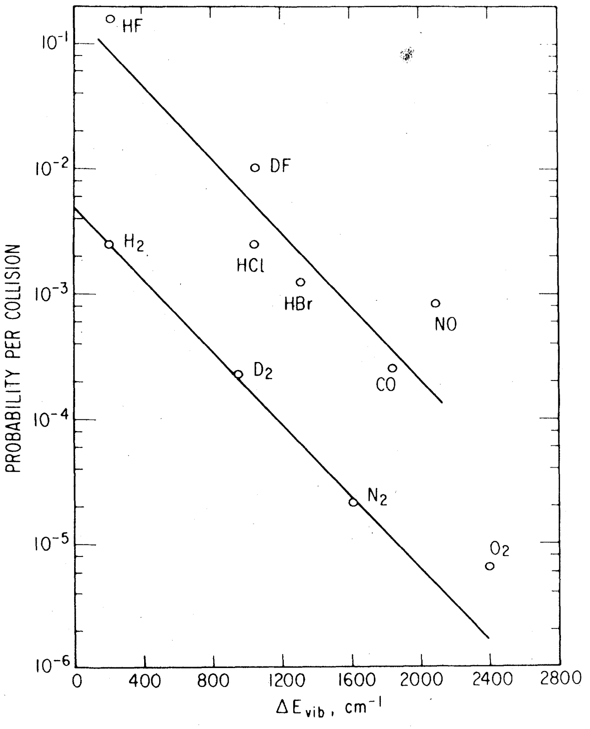


FIG. 20. Energy transfer probabilities from HF to various molecules at room temperature versus ΔE_{vib}. Data point for H_2 represents the exothermic transfer probability from $H_2(1)$ to HF(0). (from Bott and Cohen 1973b).

diatomics, which deviated from the correlated curves by as much as factors of 100. For the data that did fall on the correlation diagram, the most severe discrepancies were approximately of a factor of 5. Callear (1967) pointed out that the Millikan and White correlation did not take into account the effect of large amplitude of vibration of the light molecules and, hence, would not be applicable to the halides such as HCl and HF. An attempt to correlate the halogen relaxation data has been recently described by Diebold *et al.* (1974).

Because no really satisfactory correlation of the halide relaxation data has yet been established, it may be worthwhile to outline some of the more recent attempts to do so. As we have seen the trend toward relaxation times shorter than those predicted by Eq. (39) was originally reported for HI and HCl (Chen *et al.* 1968) and has since been confirmed in extensive measurements on HF, HCl, and HBr, some of which were discussed above.

The most frequently used correlation technique consists of a plot of the logarithm of the transition probability for a given process and the (vibrational) energy defect between the colliding molecules as shown for example in Fig. 16(b). This correlation was first suggested by Lambert and Salter (1957) for V–T energy transfer in polyatomic molecules and, as has been discussed by Callear (1967), it follows from the assumption of an exponential interaction potential in either the classical Landau–Teller or the distorted wave Jackson–Mott expressions for probability transfer. Because of the indications that the halide relaxation mechanisms stem from quite complex interactions, the failure of this simple prescription is not surprising.

Bott and Cohen (1973b) exhibited the HF–diatomic data as shown here in Fig. 20 and pointed out that the homonuclear and heteronuclear molecules fell along separate lines. They suggested that the dipole-dipole attractive forces could perhaps be responsible for the differences shown. More recently Bott (1974) on the basis of his measurements ofthe temperature dependence of DF ($v = 1$) relaxation in several diatomics, concluded that transfer rates to homonuclear diatomics exhibited positive temperature dependence characteristic of short range repulsive forces, while transfer rates to heteronuclear diatomics had inverse temperature dependence typical for attractive interactions. This is shown in Fig. 21. He pointed out, however, that according to the long range interaction resonant energy transfer model of Mahan (1967) the predicted temperature dependence of the DF–HCl rate was T^{-1} whereas his data indicated a $T^{-2.5}$ dependence. Zittel and Moore (1973b) also collected their results in a correlation diagram, shown here as Fig. 22(a). As can be seen the relaxation probabilities involving only heavy atom diatomics are small and more strongly dependent on ΔE than those involving the hydrogen halides or a hydrogen halide–heavy atom-diatomic. Because existing theories do not account for the various ΔE dependencies shown, nor for the large differences for systems with similar interaction potentials, Zittel and Moore suggested that coupling of the hydrogen halide rotational motion would be responsible for the observed V–V rates. The possibility of special potential features characteristic of hydrogen halide heavy atom interactions was also suggested by these authors on the basis of a similar correlation plot for such systems, here shown as Fig. 22(b).

IV. SEMICLASSICAL

Semiclassical treatments of molecular energy transfer fall into two categories: those employing perturbation techniques and those which do not. Typically, in the semiclassical treatment, the translational motion is treated classically, the target molecule is allowed to have quantized vibrational levels and is represented by simple harmonic or Morse oscillators. In models of diatom–diatom collisions, the structure of the incident molecule is also sometimes suppressed. We outline a few of the more frequently used approaches.

In time-dependent perturbation methods, the Schroedinger equation for the collision system is written as (Rapp and Kassal, 1969)

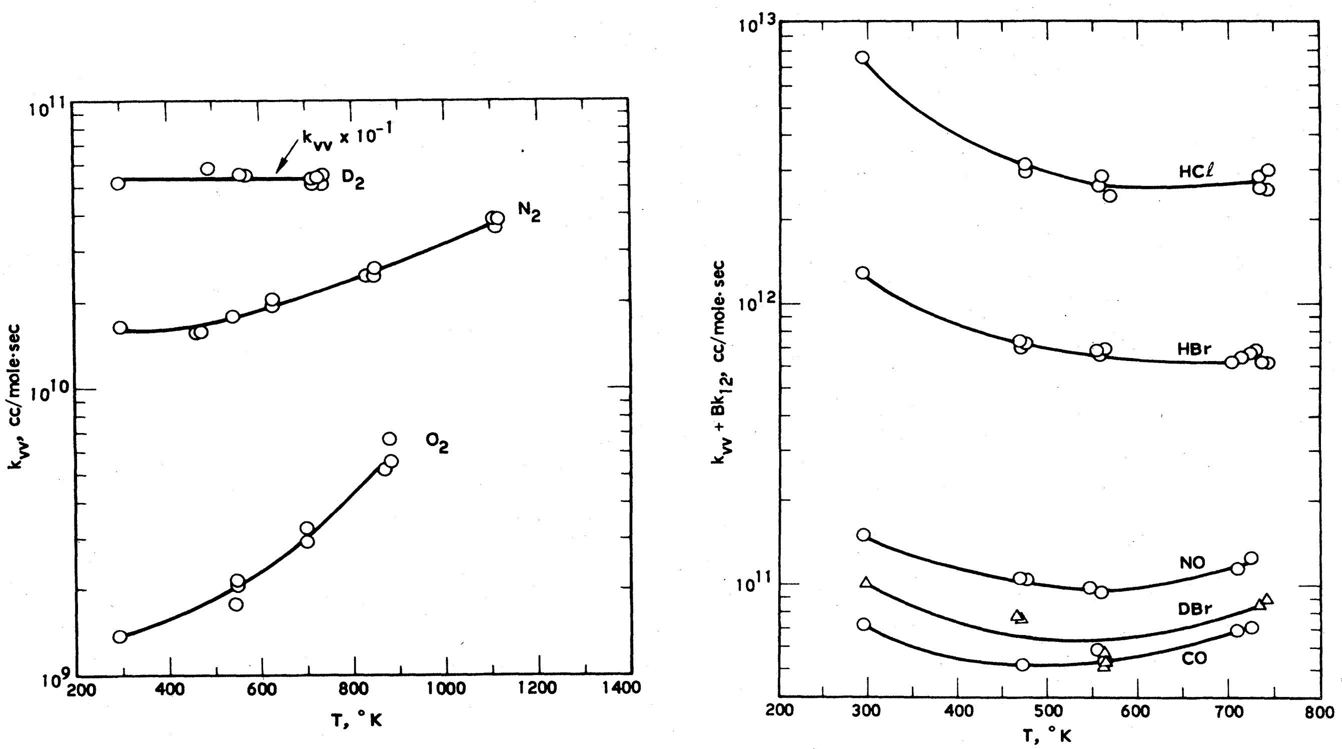
$$\{H_0 + V(t, R)\}\,\psi = \hbar i(\partial\psi/\partial t) \tag{40}$$

and the wavefunction is expanded

$$\Psi(t, R) = \sum_n a_n(t) H_n(R) \exp(-i\omega_n t). \tag{41}$$

Then, since $H_0 H_n(k) = \zeta_n H_n(R)$, $\hbar\omega_n = \zeta_n$

$$V_{jn}(t) = \int_{-\infty}^{+\infty} V(t, Y) H_j(Y) H_n(Y)\, dY \tag{42}$$



(a) (b)

FIG. 21. (a) Energy transfer rates from DF ($v = 1$) to D_2, N_2, and O_2. Data for DF–D_2 are converted to exothermic rate for V–V transfer from D_2 ($v = 1$) to DF. (b) Energy transfer rates from DF ($v = 1$) to several heteronuclear diatomics. $B = 0$ for HCl; $0.64 < B < 0.79$ for HBr; and $B = 1$ for NO, DBr, and CO.

and the expansion coefficients $a_n(t)$ satisfy the equations

$$da_j/dt = (1/i\hbar) \sum_n a_n(t) V_{jn}(t) \exp(i\omega_{jn}t) \tag{43}$$

from which the transition probability $P_{k-l} = |a_l(\infty)|^2$ follows since $a_k(-\infty) = 1$ and $a_l(-\infty) = 0$ for $k \neq l$, where k is the initial state.

A. Collinear models

The above approach can be, and has been, successfully used to discuss collisions in which (at high velocities) the transition probabilities are not small, and when an appreciable fraction of the molecules in the high velocity tail of the distribution account for most of the energy exchange. In the calculations of Rapp and Sharp (1963) a combined repulsive-attractive form for the potential was assumed with a parametric representation determined by several known potential functions. The cross sections obtained by integration over the classical trajectory were shown to be sensitive to the form of this potential.

Zelechow *et al.* (1968) used this method to calculate V–V and V–V–T energy transfer between two diatomic molecules. They used a model based on a collinear collision of harmonic oscillators with an exponential repulsion between the center atoms. The resultant Schroedinger equation was solved by the method of Kerner and Treanor (Kerner 1958, Treanor 1965, 1966) using a linearized potential in the oscillator coordinates, i.e., for the system shown in Figure 1(c), the interaction is first written as

$$\begin{aligned} V'(X, Y_1, Y_2) &= E_0 \exp[-(X - \mu Y_1 - uY_2)/\alpha] \\ &= E_0 \exp(-X/L) \times [1 + \mu(Y_1 + Y_2)_\alpha \\ &\quad + \mu^2(Y_1 + Y_2)^2/2\alpha^2 + \cdots], \end{aligned} \tag{44}$$

where the coordinates are defined in Figure 1(c), v_0 is the relative initial velocity of the diatomics; $E_0 = \frac{1}{2}(m_A + m_B)v_0^2$ the initial relative kinetic energy and $X = x - x_T$, where x_T is the distance at the classical turning point. Here α is a range parameter characterizing the interaction, and higher order terms in (44) are neglected if the vibrational amplitudes are small compared to α. The classical equations of motion are next solved for $X(t)$ using the perturbation energy $V'(X) = E_0 \exp(-X/\alpha)$ and neglecting the effect of vibrations on the motion in X. The resultant function of time substituted into equation (44) yields the time-dependent perturbation energy acting on the oscillators, in the form

$$\begin{aligned} V'(t, Y_1, Y_2) &= F(t)[(\alpha/\mu) + Y_1 + Y_2 \\ &\quad + (\mu/2\alpha)(Y_1 + Y_2)^2 + \cdots] \end{aligned} \tag{45}$$

with

$$F(t) = (\alpha/\mu) E_0 \operatorname{sech}^2(v_0 t/2u) \tag{46}$$

The first term on the rhs of Eq. (44) does not affect vibrational transition probabilities and is neglected, the terms in Y_1, Y_2 are the perturbation that cause V–T transfer while the cross term $Y_1 Y_2$ is responsible for V–V transfer.

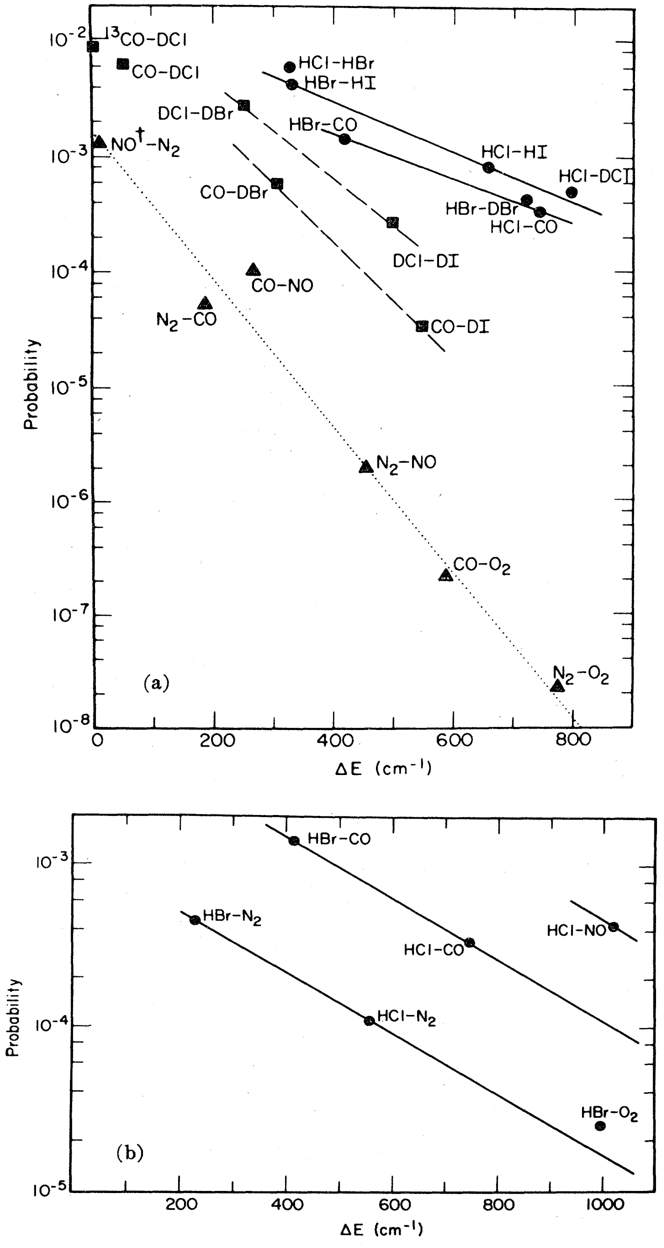


FIG. 22.(a) Plot of V–V relaxation probability against energy discrepancy, ΔE (from Zittel and Moore 1973a). (b) V–V relaxation probabilities for hydrogen halides with various heavy-atom diatomics plotted against energy discrepancy (from Zittel and Moore 1973a).

The time-dependent Schroedinger equation

$$\{(-h^2/2\mu)[(\partial^2/\partial Y_1^2)] + \tfrac{1}{2}k(Y_1^2 + Y_2^2) \\ + F(t)[Y_1Y_2 + \mu/2\alpha(Y_1 + Y_2)^2\}\Psi = hi\,\partial\psi/\partial t \qquad (47)$$

is next transformed to normal coordinates, so that it becomes separable yielding two differential equations: one for a harmonic oscillator with the force constant of k the molecule AB, and the other for a harmonic oscillator with a time varying force constant $k_s(t) = k + k'(t)$ driven by a force $(2)^{1/2}F(t)$. The essence of Kerner–Treanor method is the observation that the solution of the Schroedinger equation for a simple harmonic oscillator driven by a force $F(t)$

$$(-h^2/2\mu)(\partial^2\psi/\partial x^2 + [\tfrac{1}{2}kx^2 - xF(t)]\Psi = ih(\partial\psi/\partial t)$$

is given by

$$\psi_m(x,t) = N_m \exp\left[(i/h)\left(\mu \dot{u} x - \int_{t_0}^{t}(\delta + E_m)\,dt\right) \right. \\ \left. - \beta^2(x-u)^2\right] \times H_m[\beta(x-u)], \qquad (48)$$

where H_m is the mth Hermite polynomial, $\beta^2 = 1/\hbar(\mu k)^{1/2}$, and $\delta = \frac{1}{2}\mu\dot{u}^2 - \frac{1}{2}ku^2$, and the probability density $\psi^u\phi$ is that of any stationary state of the oscillator moving according to $u(t)$—i.e., the oscillating wave packet does not spread with time. In general, if $\psi(x)$ is a solution for a potential $V(x)\cdot$, then $\phi(x_1t) = \psi(x-u)\exp\{(i/h)[2\mu_i - \omega(t)]\}$ is a solution for a potential

$$V(x,t) = V(x-u) - x\mu u - \tfrac{1}{2}\mu u^2 + \omega(t),$$

where u and ω are arbitrary functions of time.

Zelechow *et al.* applied this prescription to the above problem and as an illustration calculated several transition probabilities for N_2–N_2 collisions. The results showed that the probability for a V–V–T process changed much more rapidly with velocity than the probability for a V–V process. For V–V–T transfer to an adjacent level, processes involving transfer of a single quantum were shown to be more probable than processes involving transfer of several quanta. The model is discussed in greater detail by Rapp and Kassal (1969).

Essentially the same formulation was used by Rapp and Englander–Golden (1964) in their calculations of probabilities for resonance and near-resonance V–V exchange. Their predicted values for N_2–N_2, N_2–CO, and CO–NO V–V exchange at room temperature were found to be in fair agreement with Callear's (1963) values. More recently, Locker and Wilson (1970) have extended this model by removing the united atom constraint, i.e., they allow the target diatomic to oscillate as the intermolecular coordinate is traced out. For a discussion of the results we refer the reader to their paper and the references cited therein.

Yet another study of the collinear collision model, which relies on the phase averaging procedure (Kelley and Wolfsberg, 1966), has been described by Heidrich *et al.* (1971). Starting with earlier calculations of Rapp and Kassal (1969), these authors investigated collisions for an exponential repulsive potential between an atom and harmonic oscillator. The authors carried out extensive comparisons between quantum, semiclassical and classical treatments of the collinear model. The quantal results used for comparison were those of Secrest and Johnson (1966), further discussed in Sec. VII. Heidrich *et al.* concluded that both the classical and semiclassical phase average approximation yielded results remarkably close to those of exact quantal calculations and suggested generalizations to arbitrary nonexponential repulsive potentials. They also suggested extension of the model calculations to noncollinear collisions with simultaneous vibrational and rotational transitions, and to real collision systems. Results of such extensions could be of interest because of the simplicity of their models and the rapidity of the calculations.

Jeffers and Kelley (1971) carried out calculations of vibration transfer in CO–CO collisions with allowance for both long and short range interactions and assuming a collinear, nonrotating molecular collision model. They used the Jackson–Mott (1932) and Rapp and Englander–Golden (1964) probabilities for V–V transitions to obtain thermally averaged probabilities for short range interactions, and the contributions from the long range interactions from the Sharma–Brau (1967, 1969) theory. Over a temperature range of 100°–700°K they obtained agreement within 25% with the data of Hancock and Smith (1971) by adding the contributions from the two interactions for different values of the vibrational quanta N. Their results at 300°K indicated that the short range interactions dominated the transition probability for vibrational energy defects greater than 210 cm^{-1}, while the long range interactions dominated for smaller defects. They suggested that for systems characterized by moderately strong long range forces due to dipole–dipole and dipole–quadrupole interactions and small energy defects, the long range forces could dominate the transition probabilities even at moderate temperatures. Their prediction that the V–V transfer rates would peak at $v = 3$ has since been confirmed by Powell (1973). The general conclusions to be drawn from their treatment of short-range forces have, however, been cast in doubt by the recent work of Dillon and Stephenson (1973b).

B. Intuitive models

The two semiclassical models in this subsection were, until quite recently, the only ones apart from the SSH theory to be frequently used in interpretation of the various (halide) relaxation data. Although far from rigorous (hence the above heading), they have been quite fruitful in providing insight into the basic mechanisms involved in the relaxation processes. In fact, Moore's theory has been the starting point for the large volume of work based on the recognition of the importance of vibration to rotation coupling, while Shin's model has been the only one with which the temperature inversion in the HF(DF) relaxation rates, for example, could be simulated (Bott and Cohen, 1971a, b).

In deriving his theory of vibrational and rotational transfer Moore (1965) followed the suggestion of Cottrell that V–R transfer was more likely in molecules with large translational velocity (i.e., such that $I/d^2 \ll M$, where I is the moment of inertia of the rotating molecule, M the reduced mass of the vibrational normal coordinate, and d the distance from the axis of rotation to the peripheral atom—see Fig. 1(d). Under the assumption that the relative translational motion was slow in comparison with the rotational velocity, Moore modified the semiclassical time-dependent V–T theory of Cottrell and McCoubrey (1961) by substituting ωd for the translational relative velocity and I/d^2 for the reduced mass. He obtains for the probability of V–R transfer

$$P_{10} = (16\pi^3 I^2 \nu / hM\alpha^2 d^4) \exp(-4\pi^2\nu/\alpha\omega d), \tag{49}$$

where ν is the vibrational frequency, and M the reduced mass of the vibrational normal coordinate; α is the usual potential energy range parameter. In deriving this expression, Moore assumed that the potential between an atom of the rotator and the nearest neighbor atom of the vibrator was given by

$$V = V_0 \exp(-\alpha r)(1 + \alpha \Delta R). \tag{50}$$

Where r is the distance between the colliding atoms for zero vibrational displacement (ΔR). This choice for the potential was made by Moore with the restriction that the range parameters would have to be altered as the internuclear separation decreased as, otherwise, the repulsive potential would be too steep resulting in a too steep temperature dependence of the transfer probability. This prediction has been since confirmed (see Sec. III). Moore considered only collinear collisions with the rotational velocity parallel to the normal coordinates and neglected initially the change in velocity due to the quantum of energy transferred during the collision. His final expression, after averaging over the thermal distribution of rotational velocities, is

$$P_{10} = \frac{1}{Z_0} \frac{17.1 I^{13/6} \nu^{4/3}}{d^{13/3} T^{1/6} M \alpha^{7/3}} \exp\left[-1.78 \left(\frac{I\nu^2}{d^2\alpha^2 T}\right)^{1/3}\right] \times \exp \frac{0.7194\nu}{T}. \tag{51}$$

Where the factor Z_0 (>1) is a correction for the decreased energy transfer probability in noncollinear collisions. The second exponential factor is a first order correction for the change in the relative velocity due to the energy transferred. Moore pointed out that further corrections were needed to account for coupling to translation and for the expected decrease in the vibrational transfer probability in molecules with large rotational spacings.[6]

A modification of this treatment with allowance for both the relative translational motion and the rotation of both collision partners, has been described recently by Zittel and Moore (1973a) in connection with their investigations of V–T, R relaxation in the $\mathrm{HCl(DCl)}$–$\mathrm{CH_4(CD_4)}$ systems. The modification consists of introducing an effective reduced mass given by

$$(\mu)^{-1} = m^{-1} + A_1 \mu_{R_1}^{-1} + A_2 \mu_{R_2}^{-1}, \tag{52}$$

where m is the reduced translational mass, $\mu = I/d^2$, d is the distance from the center of mass of the rotator to the rotating peripheral light atom, and A a parameter describing the asymmetry of the rotating molecule and geometry at closest approach—see Fig. 5 of their paper.

A somewhat different and rather successful approach to investigations of the interplay of various interactions, and of the contributions of coupling between different degrees of freedom to a particular relaxation process, has been developed by Shin (1964, ff.). The main step in Shin's prescription is to seek the principal contributions of the integrands in the expressions for a given transition probability by retaining the dominant terms in expansions of these integrands as functions of energy. The integrals for the transition probability are then evaluated by a saddle point method and the resultant expressions examined to determine the relative importance of the contributing effects that have been included in the interaction potential chosen for a particular collision system.

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[6] These corrections have been subsequently studied by Shin in his classical model (see Sec. V).

Thus, in his semiclassical WKB model (the classical version is outlined in Sec. V), Shin starts with the Zener's (1931) distorted wave approximation for the transition probability for spherically symmetric potentials

$$P_{ij}=\frac{8\mu x_{ij}^2}{h^2[E(E+\Delta)]^{1/2}}\left[\int_{-\infty}^{+\infty}\psi(E,r)V(r)(E+\epsilon,r)\,dr\right], \tag{53}$$

where i, j, denote the initial and final quantal states of the model collision system of a collinear, one dimensional structureless particle (atom or molecule) on an oscillator, E is the relative energy, Δ the change in the internal energy of the oscillator, μ the reduced mass of the system, and x_{ij} the matrix elements of x between the unperturbed initial and final states of the oscillator. Shin made use of the Landau-Lifshitz modification of Eq. (53)

$$\begin{aligned}P_{ij}\sim I_{ij}^2=&\left[\int^{+\infty}\exp\{-2\mu/h)^{1/2}\right.\\&\times\left[\iint_{r_2}^{r}[V(r)-(E+\Delta)]^{1/2}\,dr\right.\\&\left.-\int_{r_1}^{r}[V(r)-E)^{1/2}\}]\,dr\right]^2\end{aligned} \tag{54}$$

for WKB wavefunctions and evaluated (54) in the limit $V(r)\longrightarrow\infty$ to obtain

$$\begin{aligned}I_{ij}=\exp\Bigg\{&-(2\mu/h)^{1/2}\Bigg[\int_{E+\epsilon}^{V(r)\to\infty}[V(r)-(E+\Delta)]^{1/2}\\&\times(dr/dV)\,dV-\int_{E}^{V(r)\to\infty}[V(r)-E]^{1/2}\\&\times(dr/dV)\,dV\Bigg]\Bigg\}.\end{aligned} \tag{55}$$

For $V(r)$ very large compared to E, Shin expands the difference between the two integrals in Eq. (55) in a power series of $\epsilon/[V(r)-E]^{1/2}$ to obtain various expressions for I_{ij} according to the choice of $V(r)$. The vibrational de-excitation transition probability is then derived from

$$P=\int_0^{\infty}P_{ij}Z(E)\,dE, \tag{56}$$

where $Z(E)\,dE$ is the number of collisions in the energy range E, $E+dE$, under the condition that the behavior of I_{ij}^2 and of $Z(E)$ is determined by the exponentials ($Z(E)\sim\exp(-E/kT)$), in which case the major contribution to P is obtained by minimizing $2I_{ij}-E/kT$ at an energy E^* defined in the asymptotic limit of $\hbar\longrightarrow0$ as the most probable energy for the transition e.g.,

$$E^*=\chi-\Delta/kT+0(\hbar) \tag{57}$$

for the purely repulsive part of the 12–6 L-J potential, with

$$\chi=\left[\left(\frac{\Gamma(7/12)}{\Gamma(7/12)}\frac{(2\pi\mu)^{1/2}a_0(\Delta)kT}{\hbar}\right]^{12/19}, \tag{58}$$

where the Γ functions arise from the power series expansion which defines I_{ij} (see Shin, 1964). His expression for the de-excitation probability for the (12–6) L-J potentials is

$$P_{10}\sim\exp\left\{-\frac{3\chi'}{kT}+1.48\frac{\chi'^{1/2}\epsilon^{1/2}}{kT}+0.51\frac{\epsilon}{kT}+\frac{\Delta}{2kT}\right\}. \tag{59}$$

Shin showed that allowing for the attractive interaction $[-4\epsilon(a/2)^6]$ via the above prescription resulted in room temperature de-excitation probabilities greater by one to two orders of magnitude than those obtained with the repulsive potential alone. This conclusion was criticized by Rapp and Kassal (1969) who pointed out that it could be an overestimation due to evaluation by Shin of only the exponential factors in P_{10}.

Among the numerous results obtained with this model is Shin's suggestion (1967b) that a satisfactory explanation of the temperature dependence of vibrational relaxation times in polar molecules would require calculations with anisotropic dipole–dipole and dipole–quadrupole interactions, and his prediction (1968b) that in HBr–HBr collisions the dominant contributions to V–T transfer would come from those nearly collinear orientations in which the two H atoms were facing each other.[7] For other applications discussed before 1970, we refer the reader to the original papers and we outline below Shin's treatment of the CO–He data of Miller and Millikan (1970).

The starting point of Shin's calculation (1971c) is a modification of his method for calculation of V–V transfer probabilities by allowing for the effect of potential barrier penetration. For the 1–0 transition probability, in the case of the CO–He system described as interacting via the Morse potential, $V(x)=\epsilon\{\exp[\alpha-x/a]-2\exp[\frac{1}{2}\alpha-(x/2a)]\}$, Shin writes

$$\begin{aligned}P_{10}(E)=&\left(\frac{8\Delta}{M}\right)\left(\frac{\pi\mu a}{\hbar}\right)^2\\&\times\exp\left(-\frac{4a(2\mu\epsilon)^{1/2}}{\hbar}[g(E+\Delta)-g(E)]\right),\end{aligned} \tag{60}$$

where

$$g(E)=(E/\epsilon)^{1/2}\tan^{-1}(E/\epsilon)^{1/2}-\tfrac{1}{2}\ln[1+E/\epsilon]. \tag{61}$$

He now defines the thermal average probability by

$$P_{10}(T)=\frac{1}{kT}\int_0^{\infty}P_{10}(E)\exp(-E/kT)\,dE \tag{62}$$

(Recall the discussion of Equation (17)!) and again assumes that the integral will go through a maximum at some energy E.* Then $E \gg \Delta$ implies $E^* \gg \Delta$ and the exponential part of P_{10} in Equation (62) is expanded in a power series of Δ leading to

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[7] For an experimental verification of Shin's prediction (1969a, b), of the velocity dependence of vibrational transition probabilities in molecular beam measurements of inelastic energy losses (O^+, $O_2^+-O_2$), see Cosby and Moran (1970).

$$P_{10}(T) = (8\Delta/M)(\pi\mu a/\hbar)^2(4\pi/3)^{1/2}(\chi/kT)^{1/2} \times \exp\left(-\frac{3x}{kT} + \frac{4(\epsilon\chi)^{1/2}}{\pi kT} + \frac{16\epsilon}{3\pi^2 kT} + \frac{\Delta}{2kT}\right) \tag{63}$$

with

$$\chi = [(1/2\mu)^{1/2}(\pi a\Delta kT/K)]^{2/3}$$

Shin observed that at low temperature, E can be of the order of vibrational spacing, i.e., no longer large compared to Δ. Under these conditions particles can penetrate the barrier with a probability which Shin writes as

$$T(E) = (\bar{E}/\bar{\Delta})^{1/2} \exp\left\{-\frac{4a(2\mu\epsilon)^{1/2}}{\hbar} \times \left[\bar{\Delta}^{1/2} - \ln\left(\frac{\bar{\Delta}^{1/2} + (1+\bar{E}+\bar{\Delta})^{1/2}}{(1+\bar{E})^{1/2}}\right) - \bar{E}^{1/2}\tan^{-1}\left(\frac{(\bar{\Delta}\bar{E})^{1/2}}{\bar{E} + (1+\bar{E}+\bar{\Delta})^{1/2}}\right)\right]\right\}, \tag{64}$$

where

$$\bar{E} = E/\epsilon, \qquad \bar{\Delta} = \Delta/\epsilon. \tag{65}$$

With this model, Shin obtained a reasonable agreement with the CO–He data of Miller and Millikan (1970), at temperatures above 150°K, for the temperature dependence of the relaxation time and showed that agreement in absolute values would be obtained provided an arbitrary (!) steric factor of one-third was used. He pointed out that there was no satisfactory way of determining the dependence of the steric factor at low (<150°K) temperatures where effects of molecular orientation on the relaxation process could be expected to be negligible. Note in passing that the apparent structures in the data below 300°K are not discussed either by Shin, or by Miller and Millikan, and remain to be confirmed in other experiments. Also, the deviation of the data from Shin's theory at temperatures below 150°K suggests that in this temperature regime the CO–He system is subject to interactions which are more strongly attractive than those allowed for in his model and which could give rise to intermediate complex (resonance) formation in He–CO low energy collisions.

In another paper, Shin (1971a) attempted to account for the observations of Bott and Cohen of fast self-relaxation rates in HF, discussed in Sec. III, by invoking again the WKB approximations with an adjustable attractive potential. This model overestimates the effect of attractive forces at low temperatures because, for example, it predicts vibrational relaxation rates in HF approximately an order of magnitude greater at 294°K than those at 350°K, whereas the experimental results indicate that the difference between the two rates is about a factor of 2 or less. It is not clear whether this discrepancy is to be attributed to the basic assumptions of the model, the arbitrariness in the choice of the potential and other parameters, or, possibly, to the numerical problems associated with WKB functions (Shin, 1968b, 1970).

In subsequent papers Shin (1972b, c) applied this theory to calculations of the temperature dependence of vibrational transition probabilities for O_2, N_2, CO, and Cl_2 at temperatures below 300°K. Shin concluded that, although in the case of O_2, N_2 and CO, the attractive forces were weak, they would be sufficiently strong to increase the efficiency of V–V transfer by one or two orders of magnitude in the 100–300°K temperature range and that the use of purely repulsive potentials for the probabilities for these molecules was inadequate. According to him the simple technique of weakening the repulsive potential by altering the depth of the potential well could not be used to obtain satisfactory results.

For a discussion of a modified model that explains the low temperature HF self-relaxation in terms of intramolecular V–R transfer and a comparison with a previous explanation in terms of intermolecular V–R transfer (1973), see Shin (1974c).

C. Rotational transitions

The need to include V–R coupling mechanisms in vibrational relaxation studies prompts our outline of a few rotational excitation models.

Lawley and Ross (1965a,b) discussed the rotational excitation of a diatomic molecule by an atom using a representation for the total wavefunction in which the rotor functions were quantized along the moving interparticle axis—see Fig. 1(e). For their investigation of alkali–hydrogen halide collisions, these authors restricted the interaction potential to dipole–induced-dipole and dispersion terms involving an anisotropically polarizable dipolar molecule and an atom, i.e., they took

$$V(\theta, \phi; \mathbf{R}) = V_0(R) + V_2(R)P_2(\cos\gamma) \tag{66}$$

with

$$P_2(\cos\gamma) = \sum_m C_{2m}(\theta\phi)C^*_{2m}(\Theta\Phi), \tag{67}$$

where θ, ϕ are the polar coordinates of the diatomic with respect to fixed axes, Θ Φ the coordinates of the relative position radius vector $\mathbf{R}$, and γ is the angle between R and the molecular axis. The rotating set of basis functions is defined by

$$\Psi_{j\mu}(\gamma\zeta) = \sum_m D_{m\mu}{}^j(\Phi, \theta, 0)\psi_{jm}(\theta, \phi) \tag{68}$$

and thus the matrix elements of $P_n(\cos\gamma)$ are independent of Θ and Φ.

Lawley and Ross used a time dependent formulation of the scattering problem wherein the total wave function was expanded in the basis given by Eq. (68) i.e.,

$$\psi(t) = \sum_{j\mu} a_{j\mu}{}^{j_i\mu_i}(t)\Psi_{j\mu}(t)\exp(-iE_jt/h) \tag{69}$$

and solved numerically the differential equations derived by the method of variation of constants with a time dependent potential derived from a classical trajectory. For the isotropic part of the potential they used the Lennard-Jones (12, 6) with parameters for K–HBr, Cs–HBr, and Li–HBr, while the anisotropic part was taken to vary as R^{-6} and to have P_2 symmetry i.e.,

$$V = 4\epsilon\{(\sigma/R)^{12} - (\sigma/R)^6[1 + kP_2(\cos\gamma)]\}. \tag{70}$$

Lawley and Ross investigated the effect of neglecting intermultiplet transitions and estimated that this tended to increase the elastic cross sections by about 50% for large impact parameters. Their results for the $j = 0 \rightarrow 2$ transition are given in Table XI.

TABLE XI. The effect of intermultiplet transitions in a $j = 0 \rightarrow 2$ transition.

	V_{02}	α	θ_d	R_c	P_{02} [a]	$\Sigma_\mu P_{0,2\mu}$ [a]
1.	−14.7	−7.656	0	1.0	1.0×10^{-3}	1.6×10^{-2}
2.	−14.7	−7.656	0	1.5	5.6×10^{-6}	8.0×10^{-5}
3.	−14.7	−7.656	$\pi/2$	1.0	9.0×10^{-4}	1.20×10^{-2}
4.	−14.7	−7.656	$\pi/2$	0.8	1.33×10^{-2}	1.26×10^{-2}
5.	−14.7	−3	0	1.0	3.55×10^{-1}	3.79×10^{-1}
6.	−5.76	−3	$\pi/2$	1.0	2.64×10^{-1}	3.87×10^{-1}
7.	−7.35	−7.656	$\pi/2$	0.8	3.68×10^{-2}	3.64×10^{-2}

[a] The last two columns list the transition probabilities obtained without and with intermultiplet transitions, respectively. Here R_c is the reduced distance of closest approach on the trajectory, and θ_d is the angle of deflection of the hard-sphere trajectory. [from Lawley and Ross (1965)].

The influence of rotational transitions on V–T transfer has been studied in the framework of semiclassical theory by Hansen and Pearson (1970). The starting point for their work was the observation of Calvert and Amme (1966) that for comparison of theoretical models with experiments, it is necessary to know total cross section which can be transformed into probabilities and relaxation rates. Hansen and Pearson pointed out that three dimensional model results were needed to fit the Landau–Teller plots in both the slope and the absolute magnitude, because only the slope could be fit with a one dimensional model. Their prescription for extending one dimensional semiclassical theory of vibrational transitions in homonuclear diatoms to three dimensions is based on small perturbations methods applied to harmonic oscillator rigid rotator wavefunctions. For the interaction potential they take a linear superposition of exponential repulsions between atomic centers i.e., with the collision coordinates in Fig. 1(e),

$$V = A[\exp(-r_1/\alpha) + \exp(-r_2/\alpha)] \tag{71}$$

$r_{1,2} = r \mp \frac{1}{2}\rho \sin\theta \cos(\phi - \chi)$ so that

$$V \approx 2A \exp(-2/\alpha) \cosh[(\rho/2\alpha) \sin\theta \cos(\phi - \chi)] \tag{72}$$

which for the bond length ρ near its equilibrium value ρ_e and for small χ in the region near the turning part, can be written to first order in $(\rho - \rho_e)$ and χ as

$$\begin{aligned} V \approx 2A \exp(-r/\alpha) \{&\cosh(\delta \sin\theta \cos\phi) \\ &+ x\delta \sin\theta \sin\phi \sinh(\delta \sin\theta \cos\phi) \\ &+ [(\rho - \rho_e)/2\alpha] \sin\theta \cos\phi \sinh(\delta \sin\theta \cos\phi)\}, \end{aligned} \tag{73}$$

where $\delta = \rho_e/2\alpha$, and A is determined in terms of the potential $(\bar{V}_0)$ obtained by averaging V over all configurations at the distance of closest approach $(r = \sigma)$ by $\bar{A} = \bar{V}_0 \exp(\sigma/\alpha)$. The final result is

$$\begin{aligned} V = \bar{V}_0 &\exp[-(r - \sigma)/\alpha](\delta/\sinh\delta) \\ &\times \{\cosh(\delta \sin\theta \cos\phi) + \chi\delta \sin\theta \sin\phi \sinh(\delta \sin\theta \cos\phi) \\ &+ [(\rho - \rho_e)/2\alpha] \sin\theta \cos\phi \sinh(\delta \sin\theta \cos\phi)\}, \end{aligned} \tag{74}$$

where the first two terms are functions of the rotational coordinate only and determine the elastic and pure rotational transitions, the term linear in $(\rho - \rho_e)$ determines the vibrational transitions, and the last interference term gives rotational transitions simultaneous with the vibrational, which, as the authors note, cannot be obtained in a one dimensional model. They showed that the effect of this rotational coupling on vibrational transitions could increase the vibrational transition rates by 50% or more. This is consistent with the results of detailed quantum mechanical close coupling calculations recently reported by Lester and Schaeffer (1973). The results of the Hansen and Pearson model for vibrational relaxation of O_2, N_2 and CO in the temperature range 500–5000°K were in good agreement with experiment (cf., Table XII) but they did not obtain satisfactory results for the halogens and suggested that short range forces were, perhaps, necessary to explain the halogen sound absorption data.

Rabitz and Gordon (1970a) derived first- and second-order formulae for the rotational transitions using time-dependent perturbation theory along a linear trajectory as discussed by Mott and Massey (1965). The approximation of the linear trajectory is valid if the energy transfer in rotation $\Delta E(RR) \ll \Delta E(TT)$, i.e., $\Delta E/RT \ll 1$.

TABLE XII. Comparison of experimental and calculated relaxation times [from Hansen and Pearson (1970)].

Species	Collision partner	T(°K)	$T^{-1/3}$	$p\tau$ (atm-sec) Exptl	$p\tau$ (atm-sec) Calc
O_2	O_2	5000	0.058	4.0×10^{-7}	5.8×10^{-7}
		2000	0.079	6.0×10^{-6}	7.2×10^{-6}
		1000	0.1	1.0×10^{-4}	0.98×10^{-4}
		500	0.126	2.5×10^{-3}	2.2×10^{-3}
O_2	Ar	2000	0.079	3.0×10^{-5}	3.1×10^{-5}
		1000	0.1	8.9×10^{-4}	1.2×10^{-3}
O_2	He	1500	0.087	1.0×10^{-6}	0.5×10^{-6}
		300	0.149	4.0×10^{-5}	6.0×10^{-5}
O_2	H_2	1000	0.1	3.8×10^{-7}	3.2×10^{-7}
		300	0.149	2.4×10^{-6}	3.7×10^{-6}
N_2	N_2	5000	0.058	6.6×10^{-6}	9.3×10^{-6}
		2000	0.079	7.4×10^{-4}	5.3×10^{-4}
CO	CO	5000	0.058	1.9×10^{-6}	2.5×10^{-6}
		2000	0.079	6.8×10^{-5}	6.6×10^{-5}
CO	He	1000	0.1	2.9×10^{-5}	2.7×10^{-5}
		300	0.149	2.6×10^{-3}	3.0×10^{-3}
CO	H_2	1000	0.1	2.8×10^{-6}	2.9×10^{-6}
		300	0.149	6.8×10^{-5}	6.8×10^{-5}

TABLE XIII. Molecular parameters and cross sections for specific molecular systems.[a]

Molecule		HF	HCl	HCl:DCl	DCl:HCl	DCl	HBr	OCS	HCN	CICN	BrCN
B (MHz)		616 404	312 991			161 656	250 361	6081	44 316	5971	4120
μ (D)		1.819	1.1085			1.1033	0.788	0.715	2.986	2.80	2.94
Q (D·Å)		2.6	3.6			3.6	4.3	0.786	3.1	3.9	6.0
M (g/mole)		10.01	18.00	18.24		18.50	39.98	30.00	13.51	30.50	52.48
J_1 at $T = 300°\mathrm{K}$		2	3	3	4	4	3	22	8	22	27
σ_T (Å^2)		769	359	288	257	361	280	359	1746	2689	3293
Contribution to σ_T by interaction in percent	μ_1-μ_2 First order	84.0	68.5	57.2	51.6	60.3	56.4	64.4	64.3	61.1	58.1
	μ_1-μ_2 Second order	6.0	9.0	13.9	12.5	13.9	7.0	25.2	27.8	30.9	30.6
	μ_1-Q_2 First order	3.6	6.2	13.4	6.3	7.1	7.5	3.6	2.4	2.5	3.3
	Q_1-μ_2 First order	5.0	10.0	7.4	22.6	12.4	15.8	5.0	4.5	4.5	6.0
	Q_1-Q_2 First order	1.4	6.3	8.1	7.0	6.3	13.3	1.8	1.0	1.0	1.4
Contribution to σ_T by transition in percent	$\Delta J_1 = \pm 1$	87.6	74.7	70.6	57.9	67.5	63.9	68.0	66.8	63.5	62.0
	$\Delta J_1 = \pm 2$	12.4	25.3	29.4	42.1	32.5	36.1	32.0	33.2	36.5	38.0
Cross section ratio $\sigma(2)/\sigma(1)$		0.14	0.34	0.42	0.73	0.48	0.56	0.47	0.50	0.57	0.61
Transition rate K_{J_1} (MHz/mm)		25.5	9.35	8.62	7.65	9.78	4.95	7.89	58.1	61.9	58.1

[a] From Verter and Rabitz (1973). For sources of constants used see original paper.

The theory was applied to transitions for energy transfer in the HCN–HCN and ICN–ICN collisions, leading to reasonable agreement with experimental data for the higher rotational quantum numbers.

The rationale for the Rabitz and Gordon approach rests on a result previously derived by Gross and Gordon (1966), who showed that if rotational energy changes in collisions were smaller than the translational energy changes, the translational motion would be only slightly perturbed so that use of a perturbation theory along a linear trajectory was justified. Rabitz and Gordon stressed that such an approximation was necessitated also by practical consideration given that a coupled equation system for collisions of two rotors with only ten rotational levels would lead to as many as ten thousand channels.

Rabitz and Gordon determined their potential by starting with the expansion of the multipole interaction between two nonoverlapping charge distributions as discussed by Gray, Hirschfelder *et al.* and Rose (Gray 1968; Hirshfelder, Curtiss and Bird 1954; Rose 1958). The expression for the potential is that given by Eq. (31) in Sec. II. The multipole moments are given by

$$Q_{li} = \int \rho(i) r_i^{l_i} P_{li}(\cos\Theta_i)\, dr \tag{75}$$

and since

$$R \gg r_1 + r_2 \text{ (no overlap of charge distributions)}, \tag{76}$$

we have

$$l = l_1 + l_2,$$

and

$$V = \sum_{l_1 l_2 = 0}^{\infty} V_{l_1 l_2}. \tag{77}$$

In a linear trajectory model, the velocity is assumed to be constant along the path. Choosing the motion to be in the $X - Z$ plane and parallel to the Z axis, Rabitz and Gordon take the impact parameter at $t = 0$ as the value of the distance of closest approach, i.e., $Z = -Vt$, and hence parametrize V in terms of t, which they then substitute into the Born expansion, to obtain the scattering matrix elements in the usual way.

Rabitz and Gordon justify use of the Born expansion by noting that for their problem, $x \simeq 0.2$ Å for temperatures in excess of 300°K and reduced masses greater than 30. In their first calculation, Rabitz and Gordon assumed only one term in the potential expansion thereby avoiding any interference terms in the final expression for the cross sections. In a subsequent paper they also investigated the effect of cross terms obtained if several terms were retained in the expression for the potential, Eq. (77). They concluded that, for molecules possessing large enough multipole moments, cross term contributions between the first- and second-order terms could be comparable to the first- and second-order terms. In particular, they observed that such contributions would be important for collisions where the first-order cross terms vanished, even though the second order terms did not.

Verter and Rabitz (1973) have applied this model to a detailed investigation of rotational relaxation cross sections for a large number of molecules (HF, HCl, DCl, HBr, OCS, HCN, ClCN and BrCN). They retained all first-order terms in Eq. (77) involving the dipole and quadrupole moments of both molecules and the second-order term for the dipole–dipole interaction. They discussed the results in terms of the dependence of both the total and partial inelastic cross sections, for first- and second-order processes, on the rotational constants, the dipole and quadrupole moments of the molecules, as well as on the reduced mass of any given collision pair for collisions at 300°K. Verter and Rabitz found the $\Delta J = 2$ transitions strongly dependent on the rotational constant and contributing up to 42% to, for example, the total cross section in the DCl–HCl system. A summary of their results is given in Table XIII. An interesting result, pointed out by Verter and Rabitz, is the difference in the cross section ratios for the DCl–HCl and the HCl–DCl combinations, which, as can be seen, is attributable to the significant quadrupole-dipole contributions for the former system. A more recent theoretical development, based on a model employing an effective Hamiltonian formalism which reduces the dimensionality of the problem caused by the large number of rotational channels (Rabitz 1972, 1973), has been described by Zarur and Rabitz (1973, 1974).

A semiclassical three-dimensional model for vibrational relaxation including intermultiplet transitions to infinite order has been used by Sorensen (1972) to study vibrational relaxation in the He–H_2, Ar–HCl, and Ar–O_2 systems. Simultaneous vibrational and rotational transitions were treated to first order. The basic elements of the Sorensen model are as follows: The potential between the atom–diatomic is expanded in a Taylor series around the internuclear distance, r_{eq}, of the target, i.e.,

$$V(R, t, \gamma) = V(R, r_{\mathrm{eq}}, \gamma) + (\partial v/\partial n) \mid r_{\mathrm{eq}}(r - r_{\mathrm{eq}}) \mid \tag{78}$$

The neglect of the higher order terms implies that the target molecule is taken to be a harmonic oscillator. The relative motion is determined from the average potential

$$\phi(R) = (1/4\pi) \int V(R, r, \gamma) \, d\Omega \tag{79}$$

which leads to the equations of motion

$$dR/dt = V_0[1 - (b/k)^2 - \phi(R)/E]^{1/2}, \tag{80}$$

$$d\Theta/dt = -bV_0/R^2 \tag{81}$$

where b is the impact parameter, V_0 the initial velocity, and $E = \frac{1}{2}\mu V_0^2$, where μ is the reduced mass. The wavefunction for the total system is then expanded as a product of harmonic oscillator and rigid rotator wavefunctions of the unperturbed molecule, i.e.,

$$\begin{aligned}(H_0^{\mathrm{vib}} + H_0^{\mathrm{rot}}) \mid v\rangle \mid jm\rangle \\ = [\hbar w(v + \tfrac{1}{2}) + \hbar^2/2I)j(j+1)] \mid v\rangle \mid jm\rangle,\end{aligned} \tag{82}$$

with

$$\Psi(t) = \sum_{v,j,m} \mid v\rangle \mid jm\rangle \exp[-(i/\hbar)(E_v + E_j)t] C_{vjm,v'j'm'}. \tag{83}$$

Integration of the equation of motion determines the coefficient C and hence the transition probability from an initial (vj) to a final $(v'j')$ vibration–rotation state.

$$P_{vj,v'j'} = (2j+1)^{-1} \sum_{mm'} \mid C_{vjm,v'j'm'} \mid^2 \tag{84}$$

and hence the cross section from

$$\sigma_{vj,v'j'} = 2\int_0^\infty bP_{vj,v'j'}(E, b)\, db. \tag{85}$$

Sorensen used the dumbbell model (cf., Rapp and Kassal) to estimate the intermolecular potentials for Ar/HCl and Ar/O_2, and the Gordon and Secrest (1970) potential for He/H_2. His results showed that for Ar/HCl, V–R coupling dominated the vibrational relaxation and eliminated most of the order of magnitude discrepancy with the SSH prediction. The predicted temperature dependence remained steeper than that suggested by the experiments. For Ar/O_2, V–R coupling was important, leading to increases in the excitation probabilities greater than the 50% reported by Hansen and Pearson (1970). Sorensen attributed this increase to his exact treatment of the intermultiplet transition. He reported negligible V–R coupling effects in He/H_2.[8]

D. Other models

A frequently used approximation for three dimensional calculations is the breathing sphere model described in detail by Rapp and Kassal (1969). Among the more recent reported investigations with this model is that of Wilson and Locker (1972, see also references cited therein) who extended to three dimensions the one dimensional method of Cheung and Wilson (1969) for the calculation of vibration transition probabilities in atom–diatomic molecule collisions.

The Cheung and Wilson method is based on an approximation of the intermolecular potential such that separate solutions to the Schroedinger equations are obtained by separation of variables in each of several regions into which the configuration space of the system is divided. The boundary conditions between the regions lead to systems of linear equations the solutions of which allow transition probabilities to be determined. Various forms of intermolecular potentials can be used.

For their investigation of the atom–diatomic system of reduced mass M, Wilson and Locker chose the interaction potential $V(\mathbf{r}, \boldsymbol{\varrho})$ to be of simple exponential repulsion form, i.e., $V(\mathbf{r}, \boldsymbol{\varrho}) = V(r - \rho) = 5h\nu \exp(-(r-\rho)/a)$ (ν frequency of oscillator, a-range parameter) which they approximated by a set of constant linear segments, and calculated the transition probability over each segment in a manner analogous to the one dimensional energy transfer calculations. Over each segment, Wilson and Locker separate the Schroedinger equation

$$\begin{aligned}[(-h^2/2\mu)\nabla\rho^2 + \tfrac{1}{2}k_e(\rho - \rho_e)^2 \\ - (h^2/2M)\nabla_r^2 + V(\mathbf{r}, \boldsymbol{\varrho}) - E]\Psi = 0\end{aligned} \tag{86}$$

(μ reduced mass of sphere, ρ_e its equilibrium radius, k_e force constant of its oscillatory motion) according to $\Psi = f(\bar{\rho})F(\bar{r})$ and approximate the potential over each segment

$$V(u) = V_i\sigma_i \leq u \leq \sigma_i + 1 \qquad (u = r - \rho). \tag{87}$$

The functions of $(\bar{\rho})$ and $F(r)$, which describe the motion of the oscillator and the incident atom respectively, can be separated into their angular and radial parts in the usual way. For the oscillator, Wilson and Locker obtain the solution in terms of Hermite polynomials

$$f(\rho) = Y_{em}(\rho)(N_{1n}/\rho)\exp(-n^2/2)H_n(n), \tag{89}$$

where $N_{1n} = [c^{1/2}/\pi)^{1/2}(1/2^n n!)]^{1/2}$; $\eta = c^{1/4}(\rho - \rho_e - A/2)$, $A = 2e(e+1)/c\rho_e^3\, C = 31(e+1)/\rho_e^4 + \mu k_e/h^2$ so that the

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[8] See, however, Note added in proof.

TABLE XIV. Comparison of perturbation approximations for the $v = 0 \rightarrow 1$ vibrational transition (from Roberts, 1971).[a]

		$V = c \exp[-\alpha(c - y)]$			$V = c \exp[(-\alpha x)(1 + \alpha y)]$	
m	α	Jackson–Mott DW	Internal average DW	Optical DW	Jackson–Mott DW	Optical DW
0.2	0.114	39%	14%	0%	6%	−5%
0.5	0.114	133%	37%	3%	19%	−8%
1/13	0.1287	10%	2%	−2%	0%	−5%
13/37	0.1287	82%	27%	3%	12%	−7%
5/11	0.1287	116%	34%	3%	17%	−8%
0.5	0.1287	113%	37%	3%	19%	−8%
1.25	0.2973	963%	149%	3%	66%	−14%
2/3	0.3	219%	57%	−1%	22%	−14%

[a] The mass and potential range parameters m and α are defined in Secrest and Johnson, 1966.

effects due to rotation of the sphere are introduced via the 1-dependence of A and C. The separated equation for the incident atom leads to uncoupled second-order differential equations for the radial functions which are solved subject to the usual asymptotic conditions expressed in terms of spherical Hankel functions. With this separation, rotational coupling is suppressed in this model so that only particular cross sections corresponding to constant 1, m, λ, and μ are obtained for each solution. Wilson and Locker pointed out that the uncoupling of the angular momentum of the oscillator and of relative motion constituted probably the most serious approximation of their model. The total inelastic cross section for a particular vibrational transition is obtained from

$$\sigma_{n0\rightarrow n} = \frac{4\mu h^2}{M k_n f} \sum_{\lambda=0}^{\infty} \frac{|C_{n\lambda}|^2}{2\lambda + 1} \tag{90}$$

by summing over all the partial wave contributions.

Because of the large number of λ terms (of the order 10^2 to 10^3) which have to be included in Eq. (90) and the need to evaluate matrix elements of Hankel functions in a harmonic oscillator basis set, Wilson and Locker resorted to the modified wave number method of Takayanagi (1963) which they adjusted for treatment of inelastic scattering by a plane wave and examined the effect of variations in the range term (a) and the reduced mass of the oscillator. They presented results for values of $M = 4$ and 8 amu. The effect of increasing the oscillator mass while holding the reduced mass constant led to an increase in the excitation probability, although that increase was rather slight. On the other hand, softening the potential, i.e., altering the range parameter from 0.1–0.5A., the only values reported by the authors, led to a decrease in the transition probabilities at higher energies. These results are illustrated in Figs. 4 and 6 of their paper. Wilson and Locker reported numerical instabilities characteristic of such model calculations (cf., Gordon 1969, 1971) which led to poor normalization of the transition probability and were found to be a sensitive function of both λ and the reduced mass factors. They discounted the use of the stepwise approximation to the interaction potential as a source of errors because small enough step sizes could be easily chosen so that further refinement produced no significant changes.

Numerical difficulties for certain mass ratios were also reported in earlier applications of the model by Wilson (1970) to the collinear collisions of diatomic molecules represented by harmonic oscillators. Wilson studied the dependence of the vibrational transition probabilities on the incident relative translational energy, atomic masses and the intermolecular interaction potential. He was able to show that V–V transfer was significant but not dominant, and that the matching of vibrational frequencies of the colliding molecules did not appear to be an important factor in such transfer.

A semiclassical treatment for the calculation of direct and multiple transition probabilities for the collinear collision of an atom with a harmonic oscillator has also been developed by Roberts (1970a). The method used was based on a single optimal choice of an effective interaction potential for the entrance and the exit scattering channels. The agreement obtained between the simplified approach and exact quantum mechanical results led Roberts to suggest that extension of the method to more complex processes was possible. In a subsequent paper (1970b), Roberts evaluated the classical trajectory integrals for a Lennard-Jones potential and for the exponential interaction. He used the L-J results for comparison with those of Bernstein and Kramer (1964), and those of Marriott and Micha (1969) for glory quenching in Li–HBr collisions, and the others were compared with exact numerical values. Excellent agreement was obtained in each case.

In a further extension of these ideas, Roberts (1971) considered the problem of improving the perturbation theory for inelastic bimolecular collisions by a suitable choice of an effective distortion potential and averaging over all cases for which exact multistate results were available for comparison—See Table XIV. He was able to reduce the error obtained with a distorted wave calculation from 116% to 5%. Roberts noted that the perturbation approach based on optical formalism could lead to a correct description of elastic scattering, in which case, as suggested by Levine and Johnson (1970), inelastic transitions would also be accurately obtained.

A semiclassical treatment of multichannel problems based on the uniform WKB approximation has been developed by Eu (1972, 1973 and references therein). The method depends on contruction of scattering matrix elements in terms of quadratures involving Airy functions and appears promising, but no results directly applicable to the problems discussed here have yet been reported.

More recently several calculations of vibrational relaxation rates which explicitly invoke different multipole interactions have been reported by Lev-On *et al.* (1973, 1974), Sharma *et al.* (1973), Sharma (1974), as well as by Dillon and Stephenson (1972, 1973, 1974) whose work is discussed in Sec. VII. Lev-On *et al.* (1973) used a first order perturbation approximation with a dipole–dipole perturbing potential to obtain a closed form expression for the (V–V) probability of energy transfer in the limit of high-J values. In their recent investigation of the CO–CO system, Lev-On *et al.* (1974) suggested that the rotational transition involving $\Delta J > 1$ were necessary to explain temperature dependence of the V–V transition probabilities. Sharma (1974) suggested a method for estimating the derivative of the average quadrupole polarizability with respect to internuclear distance from the differences in the deactivation rates of ^{12}CO and ^{13}CO by DCl.

V. CLASSICAL

A survey of the papers dealing with applications of classical mechanics to vibrational relaxation problems leads to a rough identification of four classes of approaches or models. Three of these are defined and illustrated in this section while the fourth (Monte Carlo) is discussed in Sec. VI. We define as "pragmatic" models in which the interactions between real systems are handled by formulating and solving a collision problem with the help of as many approximations and adjustable parameters as are needed to produce an answer. Such models are not rigorous but, not surprisingly, will often lead to tolerable results because realistic approximations and parameters can nearly always be chosen to emphasize a particular aspect of a given collision (relaxation) problem.

Next come "parametric" models, in which the influence of a minimal set of parameters on some feature of the collision system is studied without particular regard as to whether it represents a specific combination of atoms or molecules (though frequently it will do so). Such models are extremely useful because they permit the testing of approximations and establish the relative importance of various physical and numerical parameters which can then be used in real problems. An example of this approach is the exact solution of the one dimensional, atom–diatomic molecule model by Kelley and Wolfsberg (1966) and the more recent work by the same authors described below. Lastly, the most rigorous treatments are the "classical S-matrix" theories which, as Secrest points out in his excellent survey of the field (1973), should more properly be called semiquantal rather than either classical or semiclassical. Because of the complexity of molecular collision dynamics, the most numerous classical calculations of vibrational relaxation rates in diatomic molecules reported to date have, unfortunately, been limited to those carried out only within the framework of the first category of treatments.

A. Pragmatic models

In a detailed investigation based on classical trajectory calculations of transition probabilities between vibrational levels of diatomic molecules, Benson and Berend (1966) obtained interesting agreement with various sets of data. In their work, the interaction between the diatom (described by a harmonic potential function) and the incident particle was represented by a Morse-type potential

$$V = V_0\{[1 - \exp(-ar)]^2 - 1\} \qquad (91)$$

with the range term ('a') chosen to give optimum fit to experimental data. Investigation of the dependence of the results on 'a' showed that, while this dependence was small at very high temperatures, for some molecules at room temperatures a 10% change in 'a' could alter the transition probabilities by an order of magnitude! At lower temperature, this dependence was even stronger, but in two-dimensional calculations the change in magnitude of the room temperature transition probabilities was noted to be only a factor of 4 (Thommarson *et al.* 1971). The results reported in the 1966 paper included satisfactory agreement with experiment at moderate (and, for some systems, even quite high) temperatures. However, at low temperatures the predictions of the model were at variance with experiment. An example of the results for the N_2–N_2 system is shown in Fig. 23 where the very reasonable agreement at temperature above 2000°K is evident.

The Benson *et al.* sequence of papers through 1966 has been critically discussed by Rapp and Kassal (1969) to whom the reader is referred for details. Our outline of their more recent results is subject to the observation that the simple potential and parameter fitting procedures severely limit the predictive value of their method.

In their investigation of the effect of rotational motion in atom–diatom collisions these authors showed that for low rotational energies, rotation to vibration transfer (R–V) could be as effective as translation to vibration transfer (T–V), but at high rotational energies such transfer was

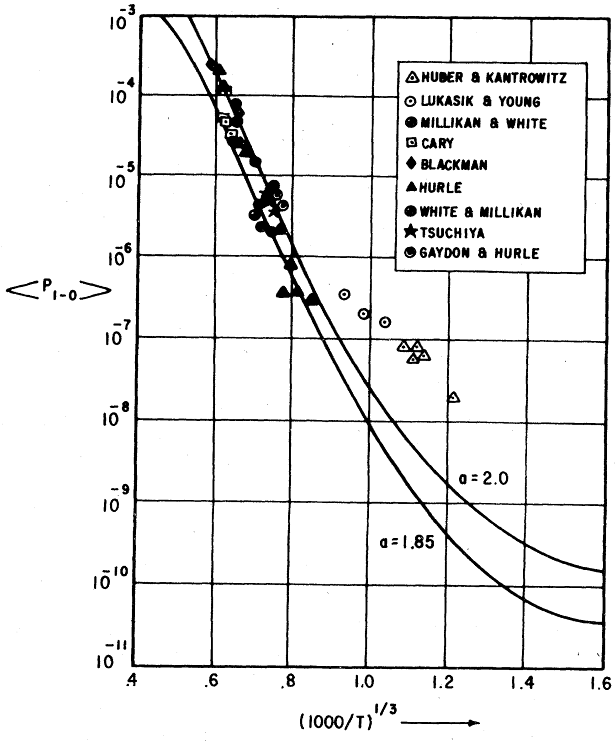

FIG. 23. Transition probabilities N_2–N_2 (from Benson and Berend 1966).

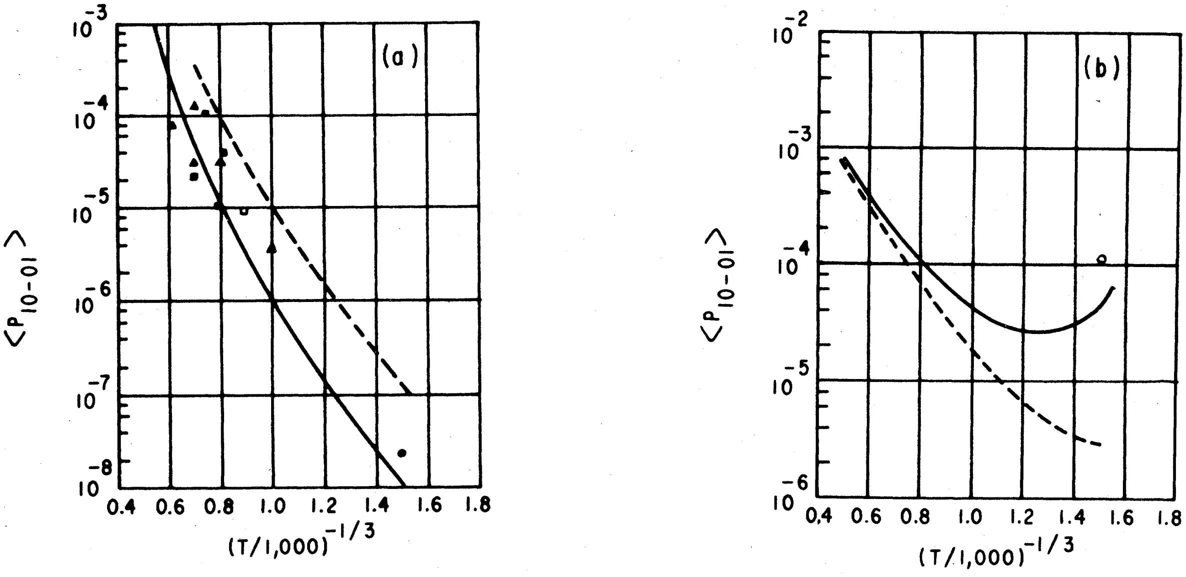

FIG. 24. (a) Vibration–vibration transition probabilities vs temperature for the reactions $N_2^* + O_2 \rightarrow N_2 + O_2^*$: - - -, SSH theory; —, classical theory (for discussion of experimental points refer to original paper) (from Berend *et al.* 1972). (b) Vibration–vibration transition probabilities vs temperature for the reactions $HCl^* + N_2 \rightarrow HCl + N_2^*$: - - -, endthermic; —, exothermic; ○, Chen and Moore 1971b (from Berend *et al.* 1972).

less probable. More recently, Berend *et al.* (1972a) used their model to calculate V–V transfer rates for the N_2–O_2 and N_2–HCl systems. They obtained fairly good agreement with experimental data over the range of temperature 1000°–4000°K.

A two-dimensional collisional model was used with the interaction potentials between the nonbonded atoms taken to be of a Morse-type, i.e.,

$$V = \sum_{i \neq j} v_{ij}^0 \{[\exp(-d_{ij}\Delta r_{ij})]^2 - 1\}, \tag{92}$$

where r_{ij} is the equilibrium internuclear distance obtained from experimental collision diameters using arithmetic-mean combining procedure, v_{ij}^0 is the well depths estimated from heats of vaporization data assuming close packing geometric-mean combination laws (Hirschfelder *et al.* 1954), and d_{ij} is the usual adjustable range term which was varied in an initial T–V calculation to give an optimum fit to experimental T–V data on pure N_2 (Benson and Berend, 1969).

These authors calculated V–V and T–V transition probabilities for the N_2–O_2 system, and at low temperatures V–V transfer was the dominant effect. By varying range terms (taken initially to be 2.05A) they, however, obtained an overestimate of P_{10} by a factor of 8 and still below the predictions of the SSH model—see Fig. 24. They noted that their T–V results were a sensitive function of the range parameter but that their V–V transfer rates could be considered reliable. For the N_2–HCl system at room temperature their V–V transition probabilities were still a factor of 2 below experiment.[9]

Berend *et al.* also investigated the effect of molecular alignment on the V–V transfer rate in N_2–HCl. As discussed in Sec. II vibration to rotation coupling could be expected to contribute strongly because of large tangential velocity of the *H* atom, due to rotation. Hence, on direct impact in light–heavy mass combinations, a large amplitude bond stretching is expected and, thus, large V–R transition probabilities. Berend *et al.* found that the greatest contribution to this energy transfer came from those direct impact collisions in which the H atom was between N and Cl. They argued that the N_2–HCl system was also more sensitive to the effect of attractive terms because of the upward trend in the Landau–Teller plot for the endothermic processes (see Fig. 24). The exothermic rate obtained by detailed balancing gave a negative temperature dependence in the region 300°–500°K. They also obtained a partial correlation between the vibrational level resonance effect and exothermicity. For well matched masses (N_2, CO, N_2, NO), they found that the energy transfer efficiency decreased exponentially with increasing vibrational defect for $\Delta\nu > 200$ cm^{-1} in agreement with calculations based only on a short range interaction (cf., Sharma and Brau, Taylor and Bitterman and Sec. I). On the other hand, for $\Delta\nu < 200$ cm^{-1}, long range effects could also contribute which the authors asserted to be the reason why the correlation of their results with the vibrational resonance defect was less satisfactory. Note that their conclusion that energy discrepancies between colliding molecules was not necessarily a measure of the efficiency of V–V transfer, is consistent with the results previously established by Wilson (1970).

More recently, Berend and Thommarson (1973a) applied the classical 1966 Benson and Berend model to collisions of He with CO in an attempt to explain the low temperature increase in the relaxation rates reported by Miller and Millikan (1970). In light of previous discussions of their model (see Rapp and Kassal, 1969), their conclusions must be viewed with reserve. In particular, they used a well depth for the CO–He interaction of 1.095×10^{-3} eV, ap-

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[9] As has been pointed out by Rapp and Kassal (1969) factors of 2 are not necessarily significant in some model calculations.

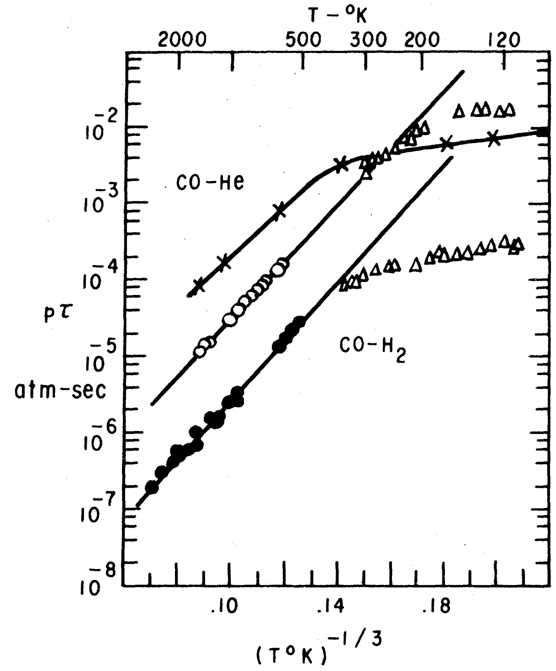

FIG. 25. Vibrational relaxation time for carbon monoxide infinitely dilute in quenching gas at total pressure p. △, vibrational fluorescence technique; ○, shock tube (Millikan 1964); ●, shock tube (Hooker and Millikan 1963); × (Berend and Thommarson 1973a) (from Miller and Millikan 1970).

proximately one-third of that used by Secrest and Eastes (1972) for their exact quantum mechanical calculation of this system. No explanation for their choice is offered but the results obtained with it, cf., Fig. 1 of their paper, show a less steep temperature dependence in the higher temperature range than that reported by Miller and Millikan. The absolute values are also at variance with the data, as shown in Fig. 25 where the Berend and Thommarson curve has been superimposed on the data of Miller and Millikan. An unusual aspect of these calculations, noted by the authors, was that the results were apparently not sensitive to variations of the range factor in the Morse potential. This is in conflict with the strong dependence on the potential parameters demonstrated by Thompson (1968) whose results Berend and Thommarson use as a basis for comparing the effects of varying the well depth in the one and two dimensional versions of their model.

According to Berend and Thommarson, the shallower wells contributed more to the transition probability in the two dimensional results at low energies, but the difference diminished toward higher energies. They interpreted this as being due to the fact that the transition probability maxima were not obtained at collinear collision geometries (contrast the results for the N_2–HCl system) but at impact parameters varying from 0.2 to 0.5 Å. According to the authors, these maxima could be correlated with rotational excitation maxima and were, therefore, interpreted as being indicative of strong R–V coupling. Note that their model leads to a moderate temperature dependence of the transition probability and not to the virtually temperature independent transition probabilities with decreasing temperature indicated by the measurements below 200°K.

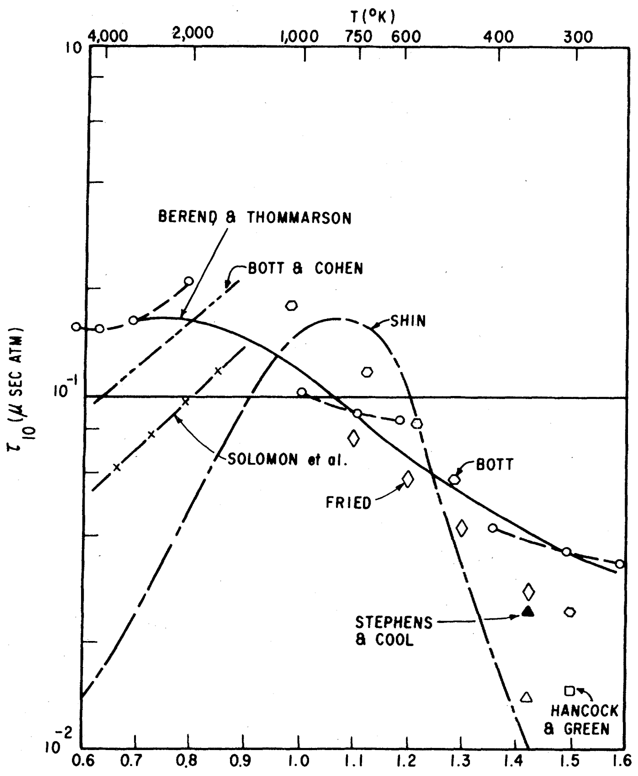

FIG. 26. Vibrational relaxation in HF. (from Berend and Thommarson 1973b).

A more recent application of this model was to the vibrational relaxation of HF and DF (Berend and Thommarson, 1973b). For the interaction potential they took the sum of Morse and Coulombic potential functions. The Morse potentials were accounted for in the usual manner while the Coulombic contribution was formulated by viewing the HF dipole classically as $H^{+\delta}$–$F^{-\delta}$ and adjusting δ for consistency with the experimental dipole moment. For the trajectory calculations at three different temperatures they used initial conditions defined by stipulating that the colliding molecules were in a single most probable rotational state at each temperature. Their results for the HF–HF system are shown in Fig. 26. Note that at lower temperatures this model underestimates the rates in comparison with experiment and does not predict the rapid drop with temperature indicated by the data of Stephens and Cool and Hancock and Green. (Another comparison of this model with experiment and Shin's models is shown in Fig. 27.) In a subsequent paper, Thommarson and Berend (1973) included a broader range of initial rotational states and obtained better agreement with experiment. By simulating dimer formation in their model they obtained results which, they assert, showed that dimer formation played a dominant role in vibrational relaxation below 1000°K. Because of the numerous assumptions made in their model, this conclusion should, for the time being, be viewed with reserve.

A vibration rotation model, consisting of a rotation averaged oscillator and a rigid rotator, has been developed by Shin (1970a, 1971c), who used it to obtain reasonable agreement with experiment for the vibrational relaxation

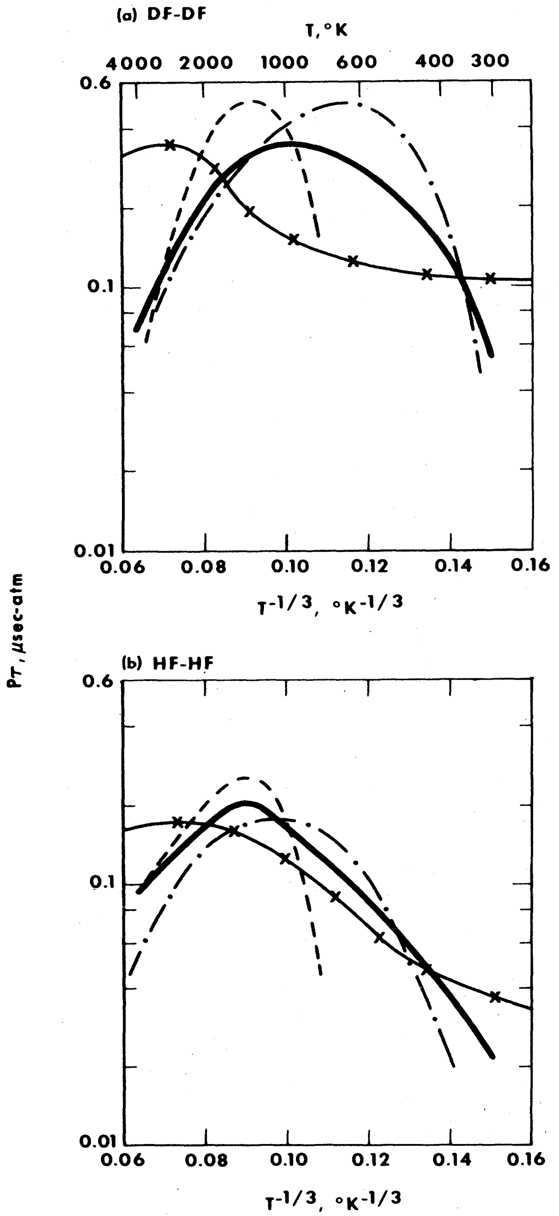

FIG. 27. Comparison of experimental and theoretical vibrational relaxation times for (a) DF–DF and (b) HF–HF: —, experimental data; - - -, Shin, $\sigma = 2.55$; -·-·-, Bott and Cohen modifications; x-x-x, Berend and Thommarson (from Hinchen 1973b).

time in HCl, DCl, HBr and HI. Shin found coupling to the translational motion, which is included in this model, to be most important in HCl, and least in HI.

The interaction potential, represented as a sum of Morse potentials between the atoms

$$V = \sum_{i+1}^{4} \epsilon[\exp(l - r_i/a) - 2\exp(l/2 - r_i/2a)], \qquad (93)$$

where l and a are determined by fitting this to an L–J potential, is averaged over the orientations of the rotating oscillator on the grounds that the rotational velocity of the oscillator must be large compared to the translational velocity for the V–R transfer mechanism to be efficient. Linearization in the vibrational coordinates and use of classical equations of motion permit the evaluation of the probability for vibrational energy transferred to the oscillator, ΔE, from

$$\Delta E = (1/2\mu) \left| \int_{-\infty}^{+\infty} F(t) \exp(i\omega t)\, dt \right|^2$$

and

$$P_{01}(E_r, E_0) = \Delta e/h\omega \qquad (94)$$

where E_0 is the relative translational energy, and E_r the minimum relative rotational energy before excitation of the oscillator. The relaxation rate $P_{01}(T)$ is obtained by thermally averaging $P_{01}(E_0, E_r)$ over a Boltzmann distribution of rotational and translational energies

$$P_{01}(T) = (1/kT)^2 \int\int P_{01}(E_0, E_r) \times \exp[-(E_r + E_0)/kT]\, dr\, dE_0. \qquad (95)$$

In analogy with the semiclassical model, a most probable rotational energy (E_r) for vibrational energy transfer is defined and, after further approximations on E_0, the final expression for the transition probability is written in the form

$$P_{01}(T) = f_{vt} P_{vt}(T), \qquad (96)$$

where the factor f_{vt} represents the effect of the translational motion on the vibrational excitation.

The model was used to obtain reasonable agreement with the self-relaxation data of Breshears and Bird (1969) in the temperature range 600–2000°K. It overestimates the HI data at the lower end of temperature range, is worst for HBr, and best for DCl—see Fig. 29. Inclusion of f_{vt} increases P_{01} by about 25%.

Shin also reported (1974a) an application of this classical V–R energy transfer model to the study of the temperature dependence of the probability of V–V–R transfer in HCl collisions. For this calculation Shin assumed the interaction potential energy to be the sum of four atom-atom interactions of the Morse-type. To evaluate the vibrational matrix elements for V–V transfer with allowance for V–R transfer, he took the dominant perturbations to the interaction as coming from the "nearest-neighbour" H atom interaction during the rotation of the two HCl molecules. With this assumption he calculated the perturbed energy which, following previous treatment, he used to determine the transition probability. By estimating the range parameter in terms of the Lennard–Jones constants in the usual way (Shin, 1964), Shin obtained transition probabilities for the 11–20 process decreasing with temperature in the range 300°–700°K and increasing thereafter (cf. Fig. 1 of his paper). For hydrogen bonding energies of 2.5 Kcal per mole, Shin obtains a general agreement in the temperature dependence of the transition probability in the range 600°–800°K with experimental results of Noter *et al.* (1973). These authors report a drastic decrease in the transition probabilities at temperatures just above 600°K with a leveling off in the range 650–800°K which is not reproduced by Shin's theory. His results do not show the apparent increase in the transition probability in the vicinity of 400° indicated by the experimental data of Noter and suggested in the parameterization of Sharma *et al.* (1973) even though the latter authors obtained absolute values approximately an order of magnitude below the experimental ones. The rapidly decreasing effect of the perturbation due to the molecular attraction with increasing temperature, which leads to the inversion in the temperature dependence of the probability at 700°, remains to be verified experimentally.

Very recently Keizer and Shin (1974) used a classical collinear collision model (Shin 1968) to investigate the effect of coupling of binary adjacent collisions on vibrational energy transfer. They used the "nearest atom" collinear approximation to express the overall potential energy as a sum of two exponentials to calculate the T–V energy, i.e., the vibrational energy of the diatomic from the translational motions (when both projectile particles are taken to be structureless) as

$$\Delta E = (2/M)\pi\mu\omega a)^2\{\exp(-2\omega\tau_{D,1}) + \exp(-2\omega\tau_{D,2}) + 2\cos(\omega t_0)\exp(-\omega\tau_{D,1} - \omega\tau_{D,2}). \quad (97)$$

They showed that, for times between successive collisions shorter than or comparable to the vibrational period of the target molecule, and for increasing density of the collision system, the dependence of the energy transferred to vibration increased with temperature with a (proportionally) greater effect for light projectile particles.[10]

A classical model for V–V and V–R energy transfer between dissimilar molecules has been recently proposed by Sentman (1973). The model is developed for the collisions of two rotating oscillators interacting via a repulsive intermolecular potential and the effect of relative translational motion and of rotation of both molecules on vibrational transitions is taken into account. If the molecular rotation is suppressed the model reduces, in principle, to that of Rapp and Englander–Golden (1964) for V–V transitions, and that of Rapp and Sharp (1963) for V–T transitions but, results supporting this contention have not yet been reported. We refer the reader to Sentman's paper for some details of the analysis and a list of the approximations necessary, and present the reported results in Figs. 28–30.

As can be seen in Fig. 28, the predicted temperature dependence of the HF, DF self-relaxation times is in rough agreement with the high temperature measurements and is better for DF than for HF. Because no long range forces are explicitly included in the model, even qualitative agreement of medium and low temperatures is not expected, though it is not apparent how such a correction would affect the high temperature results or those shown in Figs. 29 and 30. The fluoride cross relaxation times and the self-relaxation times of other halides (Fig. 29) also exhibit the requisite temperature dependence and the correct isotope effect. The discrepancies of the HCl(DCl) results with the data are attributed by Sentman to the failure in these systems of one of the approximations made in evaluating his expressions for the transition probability. Of the other results obtained (Fig. 30), those for the HF(DF)–N_2 system caused the re-examination of the data of Blauer *et al.* (1971) referred to in Sec. III. Note, however, that the possibility of V–V relaxation being the rate limiting process has been anticipated by Bott and Cohen (1973a) and the separation of the V–V and V–R, T processes depends only on the use of the analysis of Sato *et al.* (1969).

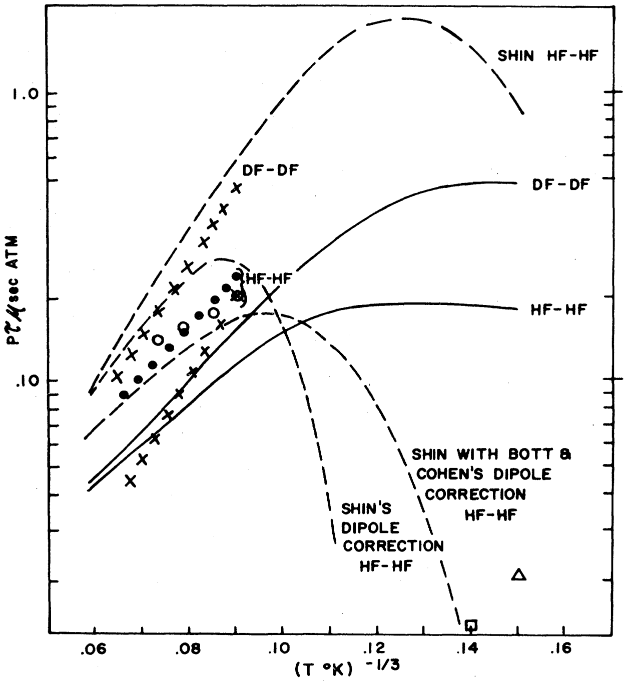

FIG. 28. Relaxation times for HF and DF. x: data of Solomon *et al.* (1972a, b); ●, data for Bott and Cohen (1971a); ○, data of Just (in Sentman 1973); □, HF–HF data of Airey (Airey and Fried 1971); △, HF–HF data of Hinchen (see Sentman 73); —, Sentman (1973); - - -, Shin theory (1971a) using σ = 2.55 Å (from Sentman 1973).

B. Parametric models

The first exact model classical calculations of the energy transfer processes in collinear collisions were carried out by Kelley and Wolfsberg (1966). These authors considered both the harmonic and Morse-type potentials and the interaction between the collision partners as a combination of both exponential repulsion and a Lennard-Jones 6–12 potential. They showed that the energy transferred decreased strongly as the initial energy of the oscillator increased and also that the effect of using a Morse potential was to decrease the energy transfer by as much as an order of magnitude.

Rapp and Kassal (1969) derived an approximate correlation between the ratio of exact and apparent energy transfer and the mass function of the collision system, i.e.,

$$(\Delta E/\Delta E)_{\mathrm{ap}} = R = \exp(1.685m), \quad (98)$$

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[10] Note that this development brings the subject of this review into contact with the theory of intercollisional interference effects for which well-known techniques based on autocorrelation functions have been developed (see Van Kranendonk, 1968). The author is grateful to Dr. J. C. K. Lewis for drawing his attention to the possibility of handling some of the halide relaxation problems in this way.

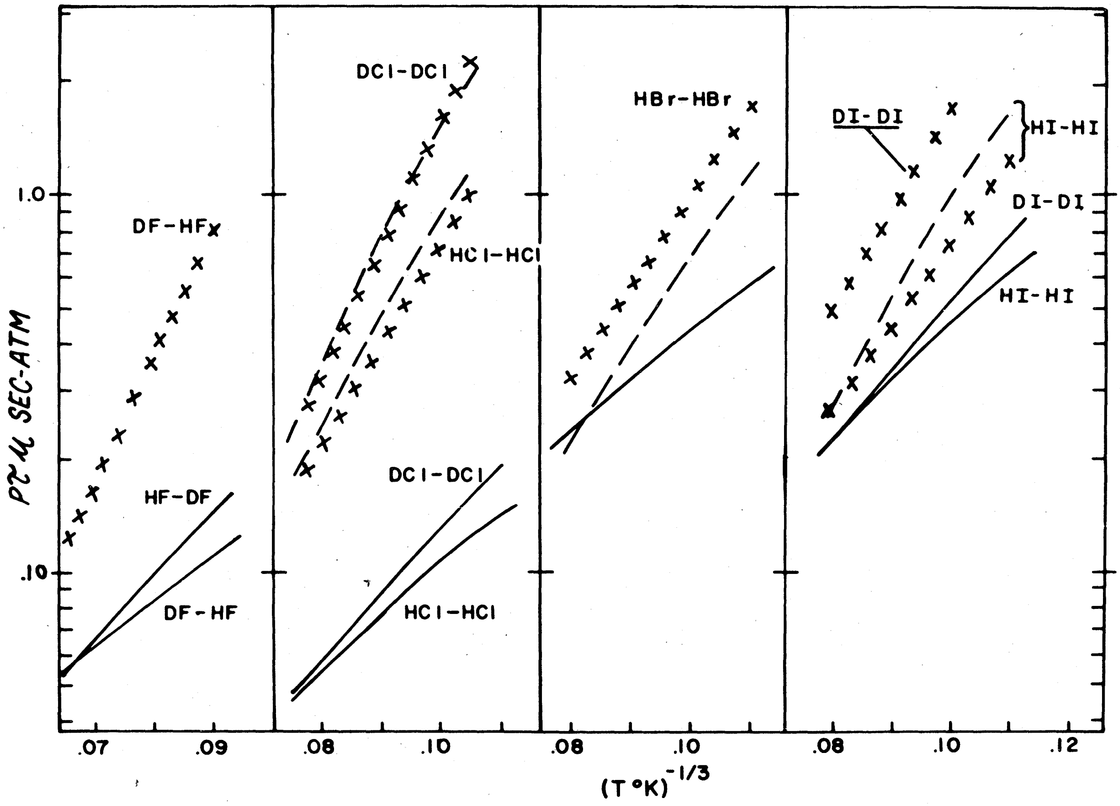

FIG. 29. Relaxation times for various species: x, DF–HF (Blauer *et al.* 1972a); x, HCl–HCl, DCl–DCl (Breshears and Bird, 1969a, b); x, HBr HBr (Kiefer *et al.* 1969); x, HI–HI, DI–DI (Kiefer *et al.* 1969; Breshears and Bird 1970); —, Sentman (1973); - - -, Shin (1971c) (from Sentman 1973).

where the mass transfer functions is given by

$$\bar{m} = (m_A m_C/m_B)(m_A + m_B + m_C)^{-1}. \qquad (99)$$

Rapp and Kassal found the correlation satisfactory for light atoms colliding with heavy homonuclear molecules in the sense that their approximate results were in good agreement with the exact calculation of Kelley and Wolfsberg. No equivalent calculations for halide molecule collisions have yet been reported.

The literature on model molecular collision calculations contains frequent reminders that, for proper comparison of theoretical results with experiment, three dimensional calculations are necessary. In the absence of these, an averaging over all molecular orientation is conventionally carried out via the steric factor concept whereby the steric factor is set equal to some constant smaller than unity, as by Kelley and Wolfsberg (1969), or evaluated by some prescription as by Shin (1968a, 1972b). In their calculations of R–V and V–V transfer, Kelley and Wolfsberg (1970) showed that the steric factor concept is rather invalid. The same conclusion was reached by Wartell and Cross (1971) who investigated a hierarchy of semiclassical approximations to three dimensional model problems and demonstrated the variations in the steric factor with energy and temperature as shown by the examples given in Table XV.

Kelley and Wolfsberg applied their earlier (1969) model to detailed calculations of both T–R and T–V transfer in atom–diatomic molecule collisions. They used exponential repulsive interaction between the collision partners and represented the diatomic molecule by both harmonic and Morse oscillators. Several important conclusions were reached. First, to examine the validity of the steric factor concept for vibrational excitation processes they explicitly incorporated the steric factor in their model. Thus they found that, for average energy transfers, representation of the target as a harmonic molecule led to better results than the use of a Morse potential. Secondly, for collisions with a heteronuclear molecular system, they found that the steric factor procedure led to overestimates of vibrational energy transfer up to several orders of magnitude. This overestimate increased as the mass of the impingent atom decreased. The only situation for which steric factor adjustment gave results not sensitive to the orientation was for the case of an atom of nearly equal mass colliding with a homopolar molecule. Also, for light atoms incident on homonuclear molecules, they found that introduction of rotational excitation energy did not enhance the vibrational energy transfer. Next, Kelley and Wolfsberg demonstrated conclusively that the modified wave number method (Takayanagi, 1963) led to serious overestimates of the energy transfer probability for large impact parameters, a conclusion also arrived at previously by Shin (1967b).

With regard to rotational excitation, Kelley and Wolfsberg established that the average rotational energy transfer was a linear function of the relative collision energy for all

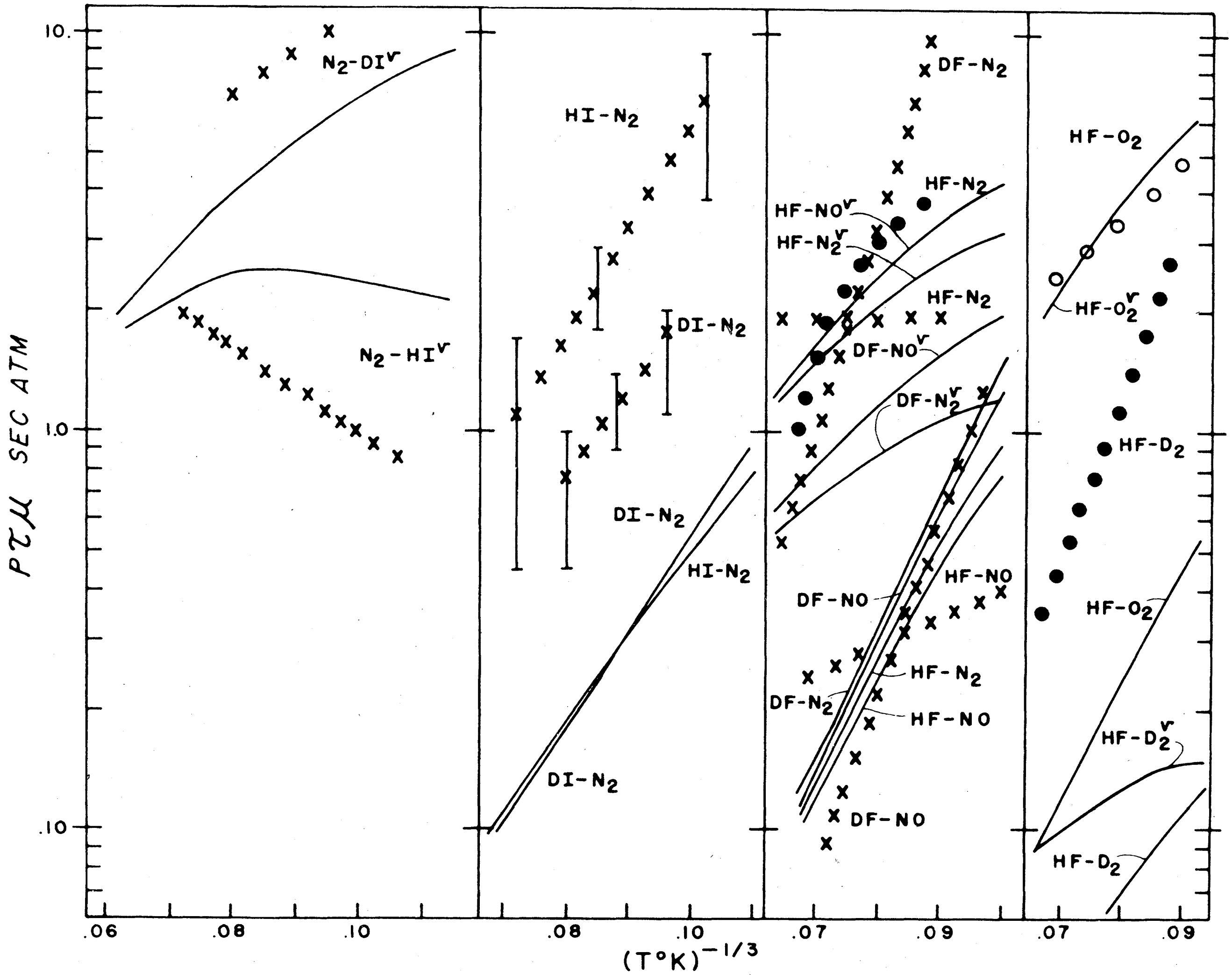

FIG. 30. Relaxation times for various species. x: N_2–DI^v, H_2–HI^v, HI–N_2, DI–N_2 (Bresears and Bird 1971); x: HF–N_2, DF–N_2, HF–NO, DF–NO (Bauler *et al.* 1972a, b); ●: HF–D_2, HF–N_2 (Bott and Cohen 1971a); ○: HF–O_2 (Blauer *et al.* 1972a) —, Sentman (1973). (from Sentman 1973). [See also Sentman and Solomon (1973).]

systems studied by them and concluded that, in their model, such energy transfer processes could be treated adequately by approximating the target molecule as a rigid rotor. Their results for the dependence of the energy transfer on the steric factor led these authors to suggest that conclusions based on calculations for collinear systems should be viewed with caution. In particular, they found that noncollinear collisions were more impulsive than collinear collisions and much more efficient in exciting the molecular vibrations. The only exception to this result were collisions between a heavy atom and a heteropolar molecule consisting of a heavy and light atom, e.g., a heavy halide. Kelley and Wolfsberg pointed out that similar trends had been obtained in the exact quantum mechanical calculations of Johnson and Secrest (1966) and of Secrest (1969)—see Sec. VII.

TABLE XV. Calculated steric factors (from Wartell and Cross, 1971).

	E_{cm} = 4.8 eV		E_{cm} = 12.4 eV	
v'	$P_{v'0}{}^{Av}/P_{v'0}$	$Q_{v'0}{}'/P_{v'0}$ (a.u.^{2})	$P_{v'0}{}^{Av}/P_{v'0}$	$Q_{v'0}{}'/P_{v'0}$ (a.u.^{2})
1.	0.111×10^3	0.604×10^4	0.162×10^3	0.138×10^4
2.	0.127×10^2	0.479×10^3	0.355×10^2	0.840×10^3
3.	0.490×10	0.105×10^3	0.581×10	0.154×10^3
4.	0.164×10	0.286×10^2	0.247×10	0.336×10^2
5.	0.856	0.107×10^2	0.848	0.113×10^2
6.	0.480	0.490×10	0.495	0.426×10
7.	0.318	0.262×10	0.268	0.211×10

In another application of this classical model Kelley (1970) investigated the dependence of impulsive collision trajectories on the effective reduced mass parameter $\bar{m}$ characteristic of the system and defined by Eq. (99). Such sensitivity in the soft interaction collisions with increasing $\bar{m}$ had been previously shown (Kelley and Wolfsberg, 1967) to have important implications in the formulations of approximate T–V energy transfer equations. Because of the different dependence on particle mass and collision energy exhibited by intramolecular de-excitation probabilities,

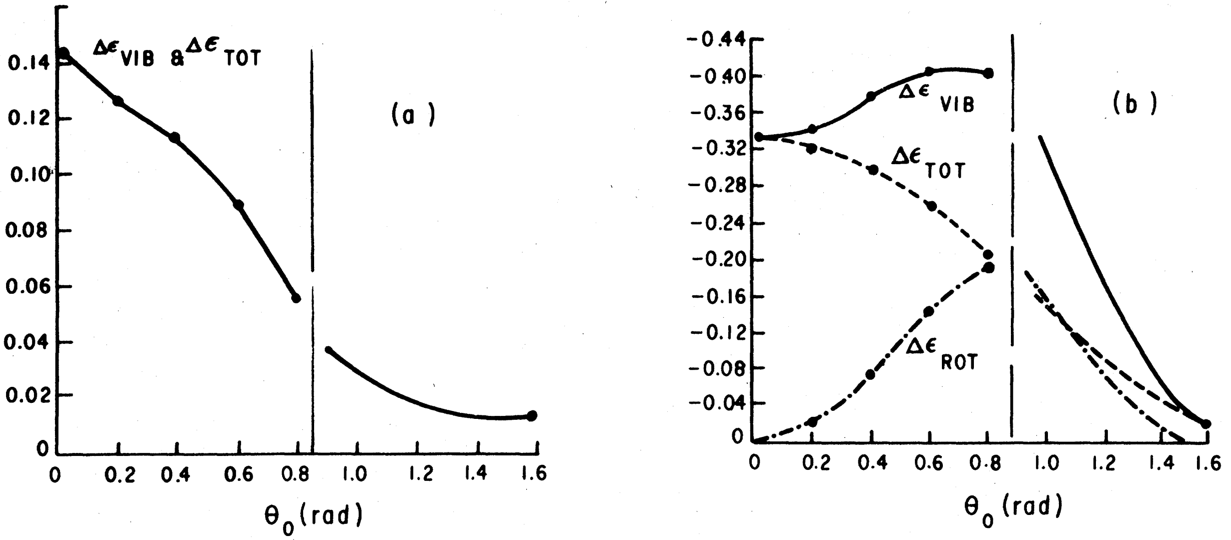

FIG. 31. (a) Vibrational de-excitation of a Morse oscillator as a function of initial relative atom-oscillator orientation; $m_A = 4$, $m_B = m_C = 80$ $E_0 = 0.02$, $\epsilon_0 = 2.0$, and $D = 5$ eV. (from Kelley 1970). (b) Vibrational de-excitation of a Morse oscillator as a function of initial relative atom-oscillator orientation; $m_A = 130$, $m_B = m_C = 1$. $E_0 = 0.02$, $\epsilon_0 = 2.0$, and $D = 5$ eV. (from Kelley 1970).

Kelley suggested that intermolecular excitation probabilities derived from a collinear collision model could frequently lead to erroneous conclusions.

For the model depicted in Fig. 2(a) Kelley considered the solutions of the classical equations describing the motion of a structureless particle (A) with a vibrating but nonrotating oscillator (B–C) where the oscillator was bound by either a Morse or a harmonic potential and the motion of the entire system was restricted to one plane through the interaction. Assuming a hard sphere collision radius large enough so that the separation between the incident atom and the center of mass of the oscillator could be approximated by

$$R_{AB}(t) = R(t) - 2(t)\cos\Theta_0, \tag{100}$$

with

$$R_0 = \sigma_{AB} + \{z_0 + [m_c/(m_B + m_C)\alpha]\ln[\beta(1+\gamma)]\} \times \cos\Theta_0 + \phi[(2E_0/M)(2\pi/\omega)], \tag{101}$$

where $10 < \phi < 1$, and the initial relative atom oscillator momentum vector was directed toward the center of mass $B - C$ (cf. Fig. 2), Kelley calculated the change in the oscillator energy according to

$$\Delta E_{tot} = (P_r'^2 - P_r^{02})/2\mu, \tag{102}$$

where the rotational and vibrational energy changes are, respectively,

$$\Delta E_{rot} = P_{rot}'/2\mu, \tag{103}$$

$$\Delta E_{vib} = \Delta E_{tot} - \Delta E_{rot}, \tag{104}$$

and

$$\mu = m_B(m_B + m_C)/m_C. \tag{105}$$

Kelley reported results for different values of the relative masses obtaining energy changes ($\Delta\epsilon_{vib}$ and $\Delta\epsilon_{rot}$) for various orientations (Θ_0) from the phase average oscillator collision momenta. These he obtained by averaging the momentum parallel to the components along the line of centers given by

$$P_r{}^l = [2\mu(D - \epsilon_0)]^{1/2}[\gamma\sin\omega t_c/(1 - \gamma\cos\omega t_c)]\cos\Theta_0 \tag{106}$$

for a Morse oscillator and by

$$P_r{}^l = [(2\mu\epsilon_0)^{1/2}\cos\omega' t_c]\cos\Theta_0 \tag{107}$$

for a harmonic oscillator.

For his model calculations, Kelley chose the dissociation energy of 5 eV for each system, the initial oscillator vibrational energy as 2 eV and the relative atom oscillator collision energy as 0.02 eV. The increasing importance of intramolecular V–R energy transfer relative to intermolecular V–T transfer in vibrational de-excitation is illustrated in Fig. 31. In the case of the light atoms, heavy oscillator ($\bar{m} = 0.024$) system in Fig. 31(a), the vibrational and rotational energy increments are approximately equal and V–R transfer is negligible; the amount of vibrational de-excitation decreases with increasing deviation of the system from the collinear orientation. On the other hand, for the heavy atom, light oscillator combination ($M = 0.98$), [cf. Fig. 31(b)], the vibrational de-excitation increases with deviations from the collinear orientation to a maximum at which point the intermolecular V–R and intermolecular V–T processes contribute equally. (Note that the $\bar{m}$ value for the latter system is close to the maximum limiting value, unity, for the atom-homonuclear oscillator system). Kelley showed that the increasing mass effect of V–R transfer on vibrational de-excitation led to the de-excitation mass dependence for the collisional orientation different from that for orientations which allowed for rotational participation. [See his Figure 6(b)]. Thus, the vibrational de-excitation for the collinear orientations decreased more rapidly with increasing reduced mass for $\bar{m}$ greater than 0.5, than that for noncollinear orientations. Similar trends were predicted in collision energy dependence for both processes. Kelley concluded that for the collinear model, de-excitation would proceed entirely by the V–T process and that intramolecular V–R transfer dominated at the relative orientation of $\Theta_0 = 0.8$.

For collision energies in the range 0.01–0.1 eV, Kelley found that the V–T energy transfer was nearly constant up to 0.05 eV and then decreased with increasing collision energy, whereas the V–R energy transfer tended to increase with increasing collision energy over the whole range. He concluded that the vibrational excitation in the hard sphere model could not be obtained by the assumption of collinear collisions or by restricting the considerations to V–T processes alone. For collisions of light with heavy heteronuclear oscillators, Kelley found the mass dependent effect more pronounced in harmonic than the Morse case, presumably because, for the latter, a larger fraction of the vibrational period was spent in stretched configurations with low momentum available for transfer. The significant result of this model was the sizeable participation of intramolecular V–R transfer in systems with high $\bar{m}$ values (see also Sec. VI).

C. Classical S-matrix

Over the last few years there has been a revival in the development of rigorous classical theories that simulate the quantum mechanical aspects of both reactive and non-reactive molecular collisions largely because of the conceptual appeal of such simulation, and the fact that new techniques, coupled with modern computers, make many-body classical problems tractable as well as, perhaps, computationally less arduous than fully quantal treatments. Emphasis in such work has been on defining the conditions under which the models could be confidently used (e.g., Gross 1969, Marcus 1970, and Miller 1970a). Two of the more recent results can be mentioned. In a detailed comparison of a rigorous classical treatment of a rigid rotor–atom problem with the essentially exact quantum mechanical solution of Johnson *et al.* (1967), Miller (1971b) established that, provided sums or averages over several quantum states were sought, the classical solution was satisfactory. Bowman and Kupperman (1971), in a similar comparison for vibrational excitation of H_2 by H (Truhlar and Kupperman 1970) also found the expected quenching effect in the classical calculation with an important difference. The effective quantum mechanical threshold for the reaction was lower than the classical threshold by about 50 mV. This effect could be important in the evaluation of low-temperature relaxation rates.

We conclude the sampling of classical methods with an outline of a series of recent and important contributions by Miller and his collaborators (Miller 1969–1973) and by Marcus, Pechukas *et al.* (1965–1973)[11] although these methods could equally well be considered to belong in the section on quantum mechanical models. Miller addressed himself to the central question of determining the conditions under which classical methods could be made to correctly model essentially quantal effects.

In his first paper (1970) Miller showed that an exact numerical solution of the classical equations of motion could be used to construct the classical limit of the quantum mechanical S-matrix which he called the "classical S-matrix". The connection with quantum mechanics is maintained via the principle of superposition—instead of combining the probabilities for a process, Miller adds the probability amplitudes. For the atom–rigid rotor system the classical S matrix is defined, or rather constructed, by writing

$$S_{j_2l_2j_1l_1}(J) = \sum D^{-1/2} \exp(i\phi_{j_2l_2j_1l_1}(J)), \tag{108}$$

where l is the orbital angular momentum of the atom relative to the rotor, l_2 the rotational angular momentum of the atom, and J the total system angular momentum. Subscripts 1 and 2 denote the initial and final states and the phase is determined from the classical trajectory

$$\phi_{j_2l_2j_1l_1}(J) = \pi(l_1 + l_2)/2 - \int_{\infty}^{+\infty} dt(RP + q_l l + q_j j), \tag{109}$$

where q_l and q_j are the coordinates conjugate to l and j; R, P the center of mass coordinate and momentum, and

$$D = (i\pi/2)^2 \det \begin{vmatrix} \partial l_2/\partial q_{l_1} \; \partial l_2 \; \partial q_{j_1} \\ \partial j_2/\partial q_{l_1} \; \partial j_2/\partial q_{j_1} \end{vmatrix}. \tag{110}$$

For a classical Hamiltonian, e.g.,

$$H(P, l, j; Rmq_l, q_j) = (P^2 + l^2/R^2)/2\mu + B_j^2 + V(R, \gamma) \tag{111}$$

$$\cos\gamma = -\cos q_l \cos q_j + [(l^2 + j^2 - J^2/2l_j] \sin q_l \sin q_j \tag{112}$$

the phase is determined by integrating Hamilton's equations with initial conditions defined by the state '1' and conservation of energy.

The cross sections are determined from either

$$\sigma_{1,2}{}^J = \sum_{l_1, l_2} | S_{j_2l_2,j_1l_1}(J) |^2 \tag{113}$$

or from

$$\sigma(j_1l_1 \rightarrow j_2) = \sum_{l_2} | S_{j_2l_2j_1l_1}(J) |^2 \tag{114}$$

according to the degree of averaging (quenching) of quantal effects, like tunneling and interference, one is interested in observing.

In his modelling of the atom rigid rotor system, Miller (1971) showed that a strictly classical approach which neglected interference gave poor agreement with the quantal

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[11] A rather complete list of references to this work is given in the reviews of Secrest (1973) and George and Ross (1973).

TABLE XVI. Rigid rotor–atom transition probabilities (from Miller, 1971).

Transition	Classical	Semiclassical	Uniform	Quantum
2, 4–0, 6	0.161	0.428	0.213	0.176
2, 6–0, 6	0.233	0.509	0.108	0.142
2, 8–0, 6	0.263	0.645	0.263	0.234
2, 6–2, 4	0.130	0.172	0.116	0.109
4, 2–2, 4	0.238	0.560	0.211	0.220
4, 4–2, 4	0.115	0.136	0.071	0.078
2, 8–2, 6	0.260	0.266	0.059	0.063
4, 4–2, 6	0.105	0.109	0.028	0.019
4, 6–2, 6	0.102	0.146	0.109	0.087
4, 8–2, 6	0.080	0.106	0.067	0.107
4, 10–2, 8	0.636	0.20	0.369	0.297
4, 4–4, 2	0.113	0.134	0.070	0.083
4, 6–4, 4	0.121	0.178	0.140	0.111
4, 8–4, 6	0.116	0.130	0.056	0.073

values, but that improving the classical description by what he calls the "uniform averaging procedure" resulted in interference and tunneling effects being rapidly quenched. Thus, examination of the averaging procedure for both linear atom–diatom (vibrational excitation) and rigid rotor atom (rotational excitation) collisions showed that even a summation over a few quantum states is often sufficient to justify a completely classical treatment. An example of these results and the comparison with the exact quantum mechanical calculations of Johnson *et al.* (1967) is shown in Table XVI. Subsequently this method was used by Doll and Miller (1972) to investigate the H/H_2, H/Li_2, and He/H_2 systems. For the latter case these authors obtained excellent agreement with the quantum mechanical results of Eastes and Secrest (1972) for collision energies in the range of 1–2 eV. According to Doll and Miller, their results justified the use of their approximations and, in particular, the addition of the amplitudes instead of the probabilities themselves, even for highly quantumlike systems and for both reactive and nonreactive collisions.

Because the dynamics of the classical formulations does not allow the treatment of forbidden processes, in fact, in such a formulation they cannot occur at all, Miller (1972) proposed an extension of his classical S-matrix method based on analytic continuation. The main idea of this is to combine a Monte Carlo averaging of some degrees of freedom with a semiclassical state-for-state description of other degrees of freedom. This "partial averaging" technique amounts to quantizing only those degrees of freedom that require quantization, e.g., rotation can be treated by Monte Carlo, while vibration is handled in the usual way.

The method was then applied by Miller and George (1972) to the He/H_2 system, using the same potential energy surface as was used by Gordon and Secrest (1970) in their exact quantum mechanical calculations. The results were found to be in agreement with the quantum mechanical results to within a factor of 2 and in very good agreement with the Monte Carlo classical results described by Bunker (1971). The effect of different potentials was studied by representing the diatomic by both a harmonic and a Morse potential for direct comparison with the work of Eastes and Secrest. The results showed that the Morse potential overestimated the transition probability by a factor of about 10 at the higher energies studied. A more recent comparison of the modified classical S-matrix results for the collinear $H + H_2$ reaction (ground state–ground state), which shows excellent agreement with quantal calculations for probabilities ranging over *ten* orders of magnitude, has been described by Hornstein and Miller (1974).

VI. MONTE CARLO

One of the main reasons for the increased use of classical trajectory Monte Carlo methods in molecular dynamics has been the success of early calculations of reactive collisions in correctly predicting product energy distributions (Maylotte *et al.* 1972). The early work in the field has been reviewed by Bunker (1968, 1971) and by Polanyi (1972). Since our main interest here is in nonreactive collisions we refer the reader to the literature cited for discussions of the methods and results and only mention a few. For the halide relaxation problems, Monte Carlo methods are probably among the most fruitful (potentially) because of the increasing evidence that the mechanisms of low temperature collisional relaxation may involve, in part, "nearly reactive" collision processes.

Among the early Monte Carlo calculations for the reaction $F + H_2$ are those of Blais (1971). He reported slight variations with initial energies for cross sections for the reactions leading to different vibrational states of HF. The most probable vibrational state obtained in this calculation was $v = 3$. The interatomic forces chosen to represent the system $F + H_2$ were approximated by the Landau–Teller (1936) equation in which contributions of multiple exchange integrals were neglected and only the Coulomb exchange integrals from the $^1\Sigma$ and $^3\Sigma$ states of the diatomic combinations were taken into account. In addition, he assumed that all the electronic orbitals of the system could be represented as s orbitals. Comparison of these results can be made with the measurements reported by Basov *et al.* (1971) according to which $v = 3$ state was the least preferred vibrational state for the HF molecule, the most preferred being either 1 or 2 depending on how the experimental data was interpreted. Polanyi and Woodall (1972) reported, on the basis of their "arrested relaxation" measurements, $v = 2$ for $F + H_2$, and $v = 3$ for $F + D_2$.

These authors also report measurements of the mean fractions of available energy entering product vibration rotation and translation. For the $F + H_2$ reaction they find their measured value of 66% in the vibrational excitation of HF below the 74% reported by Muckerman (1971) and above the 55% obtained by Jaffe and Anderson (1971). Polanyi and Woodall suggested that these discrepancies could be removed by adjustment of the LEPS (London–Eyring–Polanyi–Sato) energy surface used in the calculations cited.

For the $F + D_2$ system, Polanyi and Woodall obtain 66% in vibration. Blais and Truhlar (1973) reported good agreement with this result. These authors carried out a detailed calculation using valence bond treatment of H_2F surface which treats explicitly the p valence electrons on F. They also give a detailed comparison of their results with those of other workers. Other recent calculations reported are those of Muckerman for $F + HD$ (1973) and Wilkins (1972, 1973).[12]

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[12] For a very sophisticated application of Monte Carlo reactive calculations to the three-body recombination problem, see Whitlock *et al.* (1972, 1973).

The first detailed nonreactive Monte Carlo calculations of vibrational energy transfers in gases were reported by Dubrow and Wilson (1968). They investigated collisions of diatomic molecules with a collinear model of two molecules described by Morse stretching potentials and interacting via a 6–12 Lennard-Jones potential. The results showed that V–V energy transfer was a highly efficient process when translational energy and *both* vibrational energies were large. They found that V–V transfer was also significant when the initial translational energy and the vibrational energies were relatively small, but not important for large differences between the initial vibrational energies at either high or low translational energies. V–V transfer was also found to be significant for large translational energy if the vibrational energy was fairly small. Dubrow and Wilson suggested a nonlinear relationship between the two modes of energy transfer.

Extensive Monte Carlo classical trajectory calculations have been reported by Thompson (1972a, b, c) who studied the vibrational relaxation of HF and DF by F, H, and D atoms over a temperature range of 600–2000°K using classical trajectory methods with "realistic" interaction surfaces. The potential chosen by Thompson was that previously used by Blais (1971), which, in analytic form, is given by (assuming that overlap can be neglected)

$$V = Q_{12} + Q_{23} + Q_{13} - \{\tfrac{1}{2}[J_{12} - J_{23}]^2 + (J_{23} - J_{13})^2 + (J_{13} - J_{12})^2]\}^{1/2} \tag{116}$$

where Q_{ij} and J_{ij} are the Coulomb and exchange integrals respectively which can be written as functions of the internuclear distance of atom pair using the Heitler–London equations

$$Q_{ij}(R_{ij}) = \tfrac{1}{2}[{}^1E_{ij}(R_{ij}) + {}^3E_{ij}(R_{ij})], \tag{117}$$

$$J_{ij}(R_{ij}) = \tfrac{1}{2}[{}^1E_{ij}(R_{ij}) - {}^3E_{ij}(R_{ij})], \tag{118}$$

where the singlet and triplet energies of each atom pair, ${}^1E_{ij}$ and ${}^3E_{ij}$ are given by

$${}^1E_{ij} = {}^1D\{1 - \exp[-\alpha(R_{ij} - R_c)]\}^2 - {}^1D \tag{119}$$

$${}^3E_{ij} = {}^3D\{1 + \exp[\beta(R_{ij} - R_c)]\}^2 - {}^3D \tag{120}$$

and, for $R_{ij} > R_c$, by

$${}^3E_{ij} = C(R_{ij} + A)\exp(-\sigma R_{ij}). \tag{121}$$

Because the potential energy surface parameters may be of interest in other calculations they are collected here in Table XVII.

TABLE XVII. Potential-energy surface parameters [from D. L. Thompson (1972b, c)].

	HF	F_2	H_2
${}^1D$	6.11658 eV	1.650609 eV	6.11658 eV
α	1.1749624 a.u.$^{-1}$	1.5356426 a.u.$^{-1}$	1.1749624 a.u.$^{-1}$
R_e	1.7331 a.u.	2.67968 a.u.	1.7331 a.u.
${}^3D$	3.734952 eV	2.0244014 eV	3.734952 eV
β	1.2834946 a.u.$^{-1}$	2.0902097eV	1.2834946 a.u.$^{-1}$
C	1.133295 × 10^4 eV·a.u.	5.09172 × 10^6 eV·a.u.	1.133295 × 10^4 eV·a.u.
σ	2.715124 a.u.$^{-1}$	4.388149 a.u.$^{-1}$	2.715124 a.u.$^{-1}$
A	−2.567337 a.u.	−2.8192234 a.u.	−2.567377 a.u.
R_c	3.3070845 a.u.	3.3070845 a.u.	3.3070845 a.u.

The significance of Thompson's calculations lies in the fact that he attempted to obtain the correct temperature dependence by overcoming the objection discussed by Rapp and Kassal (1969) to previous classical energy transfer calculations, in the connection between the average energy transferred per classical collision and the real quantum of energy that is transferred in the collision. As discussed by Rapp and Kassal, and emphasized by Thompson, the extent to which a classical approximation can be trusted to account for collisional energy repartitioning is questionable, because of the assumption that every collision in a calculation process possesses some attributes of the real transfer. To correct for this, an average energy transfer per collision must be defined, i.e.,

$$\langle \Delta E \rangle = N^{-1} \sum_{i=1}^{N} \Delta E_i, \tag{122}$$

where N is the total number of collisions in the calculation sample.

Thompson separated the contribution from the classical trajectories according as to whether vibrational gain or loss occurred in the collision and defined the transition probability for a vibrational transition by

$$P_{j\to k} = \langle \Delta E_j^- \rangle / h\nu_{j\to k} \tag{123}$$

with

$$\langle \Delta E_j^- \rangle = N^{-1} \sum_{i=1}^{n-} \Delta E_i^- .$$

He then obtained rate constants from $k_{jk} = P_{jk}C$, where C is the collision frequency. Two types of calculations were carried out. In the first, all variables except vibration were thermally averaged over the Monte Carlo results in an attempt to simulate the experimental conditions. In the second, some initial state variables (vibrational state, rotational state, relative collisional energy) were varied to determine their influence on the energy transfer process. An important point of this calculation was that no adjustments at all were made to the potential energy surface.

Although comparison of Thompson's result with the measurements of both Bott and Cohen and Solomon *et al.* (cf. Table I, Thompson, 1972b) give agreement to within a factor of 5, a closer examination of his results shows a slight temperature dependence and an increasing deactivation rate with increasing temperature. Also, over the range of his calculations (600°–2000°K) the results for HF and DF deactivation by F are approximately equal. The data show a different trend. From Figure 11, the deactivation rate of DF by F is seen to be approximately a factor of 2 smaller than for HF, and decreasing with increasing temperature. Because the data quoted by Bott and Cohen cover the range 2000°–3000°K, while the calculations of

Thompson were only carried out to the lower temperature of this range, no detailed comparison of the temperature dependence of the rate can be made. However, as noted by Thompson, the data reported both by Bott and Cohen and by Solomon *et al.* (1971) show considerable scatter. A hint of an inversion in the rate of DF de-excitation can be seen at about 2500°K. The value quoted by Bott and Cohen at 2000°K of 3.0×10^{13} cm^3/mole sec is approximately a factor 4 times larger than that obtained by Thompson. In a more recent communication Thompson (1974) points out a correction and the good agreement with the measurements of Blauer and Solomon (1973) and Blair *et al.*, (1973).

Also of interest are two other results suggested by Thompson, namely the participation of multiple quantum transitions and the determination of the dominant mechanism for deexcitation in the case of *F* atom collisions with HF and DF. Thompson found that vibrational de-excitation proceeded primarily by vibration to rotation transfer and especially so for de-excitation from the higher lying vibrational levels. Vibrational excitation from the ground state, on the other hand, was shown to proceed primarily via a T–V process. The former of these results is consistent with the interpretation of HF de-activation already discussed (Sec. III), while the participation of multiquantum transitions is in agreement with the trends established for CO deactivation by the recent calculations of Dillon and Stephenson, discussed in Sec. VII. The contributions of the different processes to vibrational energy transfer as a function of the initial vibrational rotational states are given in Table XVIII.

In a subsequent study (1972c) Thompson considered the vibrational relaxation of HF and DF by H and D atoms. He established the importance of multiquantum transitions and noticed that the deexcitation rate from the highly excited vibrational levels deviated from the rule

$$k_{v\rightarrow v-1} \simeq v k_{1\rightarrow 0} \tag{124}$$

For the processes studied, his results were quantitatively in better agreement with expected trends in that vibrational deactivation by D followed the established isotope effect leading to rates lower than the corresponding deactivation by H, and especially so at the higher temperatures. For temperatures below 1500°K, however, the rate for vibrational deactivation of HF by D was slightly higher than that by H. Also, a deviation from linearity in the H + HF process was obtained in the temperature range 900–1700°K and was not explained. In contrast with the results obtained for F relaxation of these molecules, Thompson found that both V–R and V–T processes contributed to vibrational deexcitation.

TABLE XVIII. F + HF Energy transfer as a function of initial vibrational and rotational state [from Thompson (1972)].

v	J	$E_{\text{vib}}\Delta$ (eV)	$E_{\text{rot}}\Delta$ (eV)	$E_{\text{rel}}\Delta$ [a] (eV)	Major process	Minor process
0	4	0.0	0.012	−0.012	T → R	None
0	12	0.0	−0.012	0.012	R → T	None
1	0	−0.003	0.051	−0.048	T → R	V → R
1	4	−0.001	0.013	−0.012	T → R	V → R
1	12	−0.004	−0.009	0.013	R → T	V → T
3	4	−0.003	0.021	−0.018	T → R	V → R
3	12	−0.060	0.034	0.026	V → R	V → T
5	4	−0.027	0.037	−0.010	V → R	T → R
5	8	−0.042	0.015	0.027	V → T	V → R

[a] $E_{\text{rel}} = 0.1949$ eV corresponds to the most probable relative energy at 1500°K.

More recently, Monte Carlo calculations for the deactivation of HF by F have been reported by Wilkins (1973) and by Thommarson and Berend (1974), and we refer the reader to the papers cited for a comparitive discussion of the three sets of results now available for this reaction.

A very accurate comparison of classical trajectory calculations for the rotational excitation of H_2 by Li^+ with the quantal close coupling results of Lester and Schaefer (1973b) has been discussed by LaBudde and Bernstein (1973b).

VII. QUANTAL

Although the principles of detailed quantum mechanical treatments of collision problems have been known for a long time (Jackson and Mott, 1932), extensive applications to molecular systems had to await the advent of digital computers and the development of special numerical techniques. The first step in this direction was taken by Marriott (1964, 1965), who formulated and solved the vibrational excitation problem for CO within the framework of the close coupling approximation. The essential feature of his model was that, in addition to the short range forces of the weak interaction models (Herzfeld and Litowitz, 1959), both long range effects and strong coupling between the initial and final states were taken into account. This constituted a substantial improvement on earlier work in which such coupling was neglected (Takayanagi, 1963). In a series of papers (1964a, b, 1965, 1971) Marriott obtained reasonable agreements with experimental data for vibrational relaxation in several gases. He also studied quantitatively the sensitivity of the results with respect to variations in the intermolecular potential parameters.

In his paper on the vibrational excitation of CO, Marriott (1964a) solved the close coupling equations obtained from the Schroedinger equation for the collision of a structureless particle with a diatomic molecule. In deriving these equations he neglected coupling between rotational and vibrational states and took the interaction potential to be spherically symmetric and separable in vibrational and intermolecular coordinates. The molecular wave functions were also assumed to be separable in terms of electronic, rotational and vibrational coordinates [cf. Eq. (32)], with the vibrational part taken as simple harmonic for each independent mode of vibration. The interaction between the CO molecules was represented by an empirical Lennard-Jones potential. A significant approximation made consisted of representing the coupling terms for all impact parameters by *S*-wave-type terms only. In other words, the effect of the system angular momentum on the matrix elements was ignored. The cross sections for vibrational excitation were obtained from the solutions of the close coupling equations in the usual way. The relaxation rates differed from the experimental values by factors of between 2 or 3 in the temperature range of 1000–4500°K and diverged (on extrapolation) severely from experimental values for temperatures below 1000°K.

Under the assumptions stated, Eq. (30)–(37), given in Sec. II, become

$$[d^2/dr^2 + k_n^2 - l(l+1)/r^2]F_n{}^l(r) = 2m \sum_{m'=0}^{\infty} Fm'^l(r) V_{nm'}(r), \tag{124}$$

with

$$V_{nm}(r) = V_0 V(r) \prod_{p=1}^{j} \phi_n(R_p) V(R_p) \phi_m(R_p)\, dR_p, \tag{125}$$

where

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{126}$$

$$V_p(R_p) = \exp(-A_p R_p), \tag{127}$$

and the ϕ_n are the harmonic oscillator functions.

This constitutes the quantal formulation of the breathing sphere model. When system angular momentum effects are allowed for (cf. below) Eqn. (120) becomes

$$V_{\text{eff}}(r) = V(r) + l(l+1)/2mr^2. \tag{128}$$

In his next paper (1964b) Marriott improved this formalism by adding the centrifugal term to the L-J potential, thus allowing for the previously ignored angular momentum effects. This led to smaller cross sections (Gianturco and Marriott, 1969) in nearly complete agreement with experimental data. Nearly, because the slope of the curve was now altered to suggest, at low temperatures, relaxation times longer than observed! Marriott found the cross sections to be quite sensitive to the L-J potential parameters and especially σ. The convergence of the expansion, Eq. (34) was, however, fairly fast, being usually obtained with three or four states.

Subsequently, Taylor and Gianturco (1969) used this model to investigate the effect of anharmonicity on CO self-relaxation times and reported improved agreement with experiment (see also Tait *et al.* 1969).

Marriott's results showing the effect of including the centrifugal term on the cross sections for the excitation of the first two vibrational states of CO at a collisional energy of 1.5 eV are given in Table XIX. Also shown in the table are cross sections for vibrational excitation of CO by He, calculated with the interaction modified by softening the standard Lennard-Jones repulsive core (Marriott, 1971).

TABLE XIX. Close coupling cross sections for vibrational excitation of CO(πa_0^2) [from Gianturco and Marriott, 1969 and Marriott, 1971).

		CO–CO		He–CO	
		No angular momentum	With angular momentum	With angular momentum	
Collision energy/system				LJ	SC
1.5 eV	Q_{01}	2.2×10^{-2}	1.2×10^{-2}	9.7×10^{-1}	1.13×10^{-1}
	Q_{02}	6.3×10^{-6}	1.7×10^{-6}	···	1.66×10^{-4}

This lowered the cross section considerably, lengthening the relaxation times and reducing the discrepancy with experiment (Hooker and Millikan, 1963). A brief account of Marriott's results for CO_2 and H_2O has been recently given by Fisher (1972).

A different model for exact quantum mechanical calculations of a collinear collision of a point particle with a harmonic oscillator was presented by Secrest and Johnson (1966). In this method the diatomic molecule was treated as a harmonic oscillator and interaction potentials varying from very hard to very soft were considered. The geometry of the model is that of Fig. 1(b). The Schroedinger equation for the collision system is solved by the method of amplitude density functions.

The transition amplitude density method, introduced by Johnson and Secrest (1966), has proven to be very useful because it has provided the basis for a series of exact quantum mechanical calculations that have produced many new results and that are widely used as standards for testing other approximations. In addition it has led to the development of a number of very efficient algorithms and to date, it is the only method with which some numerical instabilities (cf. Sec. IV) which plague many model calculations can be avoided (Eastes and Secrest 1972). The principle of the method is the concept of imbedding (Bellman *et al.* 1960), and its application to potential scattering has been discussed in detail by Calogero (1967) whose explanation of it is given below.

For the simple example of a single channel problem, instead of evaluating the phase shift δ_l produced by a potential $V(r)$, one sets up a family of problems $P(\bar{r})$ consisting of evaluating the phase shift $\delta_l(\bar{r})$ produced by a potential $V(r)\Theta(\bar{r} - r)$ where $\Theta(\bar{r})$ is a unit step function. The real problem of finding the δ_l due to $V(r)$ can be symbolically represented by $P(\infty)$. The function $\delta_l(\bar{r})$, called by Calogero the "phase function" has the following properties: it vanishes at origin, satisfies a first order differential equation

$$(d/d_r)\delta_l(r) = -k^{-1}V(r)[\cos\delta_l(r)\hat{\jmath}_l(kr) - \sin\delta_l(r)\hat{n}_l(kr)]^2 \tag{129}$$

and it yields asymptotically the value of the scattering phase shift, i.e.

$$\lim_{r\to\infty}\delta_l(r) \equiv \delta_l(\infty) = \delta_l. \tag{130}$$

It follows that the solution of the original problem can be obtained by generating sequential solutions to the problems $P(\bar{r})$ in a continuous fashion from $P(0)$ to $P(\infty)$, i.e., integrating the "phase equation" (129), from the origin to infinity.

In the more general case of the scattering equation

$$u''(r) + [k^2 - W(r) - \bar{W}(r)]u(r) = 0 \tag{131}$$

with the boundary conditions

$$u(0) = 0$$

$$u(r) \underset{r\to\infty}{\longrightarrow} \sin(kr + \delta). \tag{132}$$

Calogero takes the two independent solutions $\bar{u}_{1,2}(r)$ of

$$\bar{u}''(r) + [k^2 - \bar{W}(r)]\bar{u}(r) = 0 \tag{133}$$

with the boundary conditions

$$\bar{u}_1(0) = 0$$

$$\left.\begin{matrix}\bar{u}_1(r)\\ \bar{u}_2(r)\end{matrix}\right\} \xrightarrow[r\to\infty]{} \left\{\begin{matrix}\sin\\ \cos\end{matrix}\right. (kr + \bar{\delta}) \tag{134}$$

and defines the "amplitude function" $\alpha(r)$ and the "phase function" $\gamma(r)$ by

$$u(r) = \alpha(r)[\cos\gamma(r)\bar{u}_1(r) + \sin\gamma(r)\bar{u}_2(r)]. \tag{135}$$

Since $\bar{\delta}$ is the S wave phase shift due to scattering by $\bar{W}(r)$, then provided the limits $\alpha(\infty)$ and $\gamma(\infty)$ exist, we have

$$\delta = \bar{\delta} + \delta\gamma(\infty). \tag{136}$$

In the spirit of the preceeding example, δ can now be determined if $\gamma(\infty)$ is known. Advantage can be taken of the arbitrariness in the choice of $\alpha(r)$ and $\gamma(r)$ implied by Eqn. (135). The choice

$$u''(r) = \alpha(r)[\cos\gamma(r)\bar{u}_1{}'(r) + \sin\gamma(r)\bar{u}_2{}'(r)] \tag{137}$$

leads to the phase equation

$$\gamma'(r) = -k^{-1}W(r)[\cos\gamma(r)\bar{u}_1(r) + \sin\gamma(r)\bar{u}_2(r)]^2 \tag{138}$$

i.e., a first-order equation from which $\gamma(r)$ and hence $\gamma(\infty)$ and δ can be determined.

The advantage of this method, stressed by Levine (1969), is that if $V = V_1 + V_2$ and the exact solution for V_1 is known, it is sufficient to truncate V_2 to solve for the scattering by V. This is seen in the above example if we take $\bar{W}(r) = l(l+1)/r^2$ and $W(r) = V(r)$ which implies $\bar{u}_1(r) = \hat{\jmath}_l(kr)$ and $\bar{u}_2(r) = -\hat{n}_l(kr)$, and leads to Eq. (129).

The amplitude density method can now be obtained by generalization of the preceeding to the multichannel case and using the integral representation for the Schroedinger equation (see Johnson and Secrest 1966; Secrest and Johnson, 1966). The important property of the resultant algorithms is that the step by step computation of the amplitude density function can be avoided and the scattering amplitudes are computed directly.

Johnson and Secrest explored in detail the dependence of the transition probabilities on the precise form of the potentials and showed that the transition probability for an oscillator (in its ground state) interacting with an atom depended critically and varied rapidly as the potentials were changed from very hard to very soft. They also established that in some cases double and even triple quantum jumps were important. (We note that this result has also become apparent in the semi-classical treatments, see for example Rapp and Sharp (1963).) Even within this method, the determination of the potential that corresponded most accurately to any actual physical interaction had to be carried out semi-empirically.

Analysis of the results obtained and detailed comparison between the exact quantum treatments, the distorted wave approximation and the semiclassical approximation of Rapp and Sharp (1963) indicated that the distorted wave approximation broke down at high energies and even at very low energies gave results that were consistently too low. Because at these energies the distorted wave approximation would be assumed to yield reasonable results, the authors concluded that the quasiclassical approximation was not a good one. Exact comparison of transition probabilities as a function of the energy for different values of the molecular parameters showed that the distorted wave approximation results differed from the classical results considerably, but they also differed from exact results by nearly a constant factor except in a few cases where the variations were of several orders of magnitude. Comparison of the exact calculations with those obtained by the quasi-classical approximation indicated the same behavior—the variations between the two methods ranging from several orders of magnitude down to factors of about two. The biggest discrepancies were found for cases where the probabilities of double or triple quantum jumps became comparable in magnitude with the probabilities for single quantum jumps, under which conditions the quasi-classical approximation broke down completely. In conclusion it should be pointed out that this treatment, applied to the reaction of the form A + BC, ignored the details of the interaction between A and C, since the collision model was collinear, when the order of interaction was A, B and C.

A different approximation for nonreactive molecular collisions has been proposed by Levine (1968), who neglected the interaction between the open and closed channels and derived the basic equations from the Lippman–Schwinger variational principle. It is shown that the phase shift so obtained is the highest lower bound to the exact phase shift obtainable from a local potential. The basic idea is to apply the approximation to the calculation of the quasibound, i.e., resonance states.

Because no coupling is involved, these states are approximated as ordinary bound states and are then calculated by conventional means. The model assumes that the internal states of the molecule are unchanged during the collision while the resonant state is described as a bound state arising from the attractive mutual interaction between the two excited molecules. Hence, the classification of the bound states, i.e., resonances, can be based on quantum numbers appropriate to the noninteracting molecules. The theory was subsequently extended to the investigation of internal excitation in molecular collisions and of resonances due to rotational excitation (Levine *et al.* 1968[13]). Exact numerical results were presented for the case of a collision of s structureless atom with a rigid homonuclear rotator. The quantitative prediction of the resonance energies obtained required the description of the relative motion in an optimized local potential which had to be specifically described. The main results of the work were the demonstration of occurence of resonances at collision velocities in the thermal energy range, the breakdown of the above mentioned approximation and the feasibility of predicting the position of resonance energies. However, the extent of the influence of off-diagonal coupling parameters on the resonances was not investigated and no specific molecular system was treated.

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[13] For a recent review of resonances in molecular collisions see Levine (1970).

The close coupling approximation has been also applied to the vibration translation energy transfer problem by Chan *et al.* (1968) and by Shipsey (1972). Chan *et al.* also investigated the distorted wave approximation for diatom-diatom collisions and used an integral equation formulation to solve their coupled equations. They reported slow convergence of the eigenfunction expansion, e.g., the results from a two state expansion were consistently below those of three and four state expansion (contrast Marriott's results), or of the distorted wave results, at all low energies.

Chan *et al.* discussed their results in terms of probabilities for nearest neighbor and non-nearest neighbor transitions as functions of energies. An oscillatory behavior of the probability of some selected non-nearest neighbor transitions, as a function of energy, was obtained in the three and four state calculations. Chan *et al.* claimed their method to be faster computationally than the algorithm of Secrest and Johnson (1966).

Eastes and Secrest (1972) used a close coupling expansion to investigate the effect of rotational coupling on vibrational transitions for the He–H$_2$ system. They found that transitions from the ground to the first excited rotational state could be accurately obtained if transitions between excited rotational levels were neglected but those between excited vibrational states were included. At high energies they showed that the transitions not involving those to the states coupled in their expansions could also be neglected. The computational method was essentially that used by Sams and Kouri (1969), modified by the techniques of Johnson and Secrest (1966, 1968).

For their model computation, Eastes and Secrest chose their atom homopolar diatomic molecule model, shown in Fig. 1b. In the center of mass coordinates they write the Schroedinger equation for the collision system as

$$[-\nabla_x^2 + H_y + V(\mathbf{x}, \mathbf{y}) - E]\Psi(\mathbf{x}, \mathbf{y}) = 0, \qquad (139)$$

where E is the total energy of the system, $V(\mathbf{x}, \mathbf{y})$ is the interaction potential of He with the center of mass of H$_2$ and H$_y$ is the Hamiltonian of the free H$_2$ molecule. For the interaction potential they chose the Gordon and Secrest (1970) form

$$V(x, y) = C \exp(-\alpha_0 x + \alpha_1 x \Delta y) \times [(1 + \gamma_0 \Delta\gamma) + \beta(1 + \gamma_2 \Delta y) P_2(\hat{\mathbf{x}}, \hat{\mathbf{y}})] \qquad (140)$$

with the constants given by

$$C = 1127.9, \quad \gamma_0 = -0.07417, \quad \alpha_0 = 0.2792$$

$$\gamma_2 = 0.2298, \quad \alpha_1 = 0.008445, \quad y_0 = 6.0514, \quad \beta = 0.251.$$

To avoid numerical complications for the basis wave functions, Eastes and Secrest approximated the H$_2$ molecule Hamiltonian by

$$\left\{-\frac{d^2}{dy^2} + [l_2(l_2+1)/\langle y^2\rangle_n] + (y - y_0)^2 - E_{nl_2}\right\} \times \phi(nl_2 \mid y) = 0, \qquad (141)$$

where

$$\langle y_n^2\rangle = \int_{\infty}^{\infty} \phi(nl_2 \mid y) y^2 \phi(nl_2 \mid y)\, dy = y_0^2 + n + \tfrac{1}{2}, \qquad (142)$$

and

$$\phi(nl_2 \mid y) = (\pi^{1/2} 2^n n!)^{-1/2} H_n(y - y_0) \exp[-\tfrac{1}{2}(y - y_0)^2], \qquad (143)$$

$$E_{nl_2} = 2n + 1 + l_2(l_2+1)/(y_0^2 + n + \tfrac{1}{2}), \qquad (144)$$

where H_n is a Hermite polynomial.

Because the properties of H$_2$ enter into the problem only in the energy levels and in the $V(x)$, Eastes and Secrest suggested that this simple well-defined model would prove more useful for testing approximations (as indeed it has!).

Following Arthurs and Dalgarno (1960), Eastes and Secrest expand the total wavefunction in a set of basis functions which are eigenfunctions of the total angular momentum (J) and obtain a set of coupled differential equations for the expansion coefficients in the usual way, i.e.

$$\{-(d^2/dx^2) + [l_1(l_1+1)/x^2] - k_{nl_2}{}^2\}\psi^J(nl_1l_2NL_1L_2 \mid x) + \sum_{n'l_1'l_2'} V^J/nl_1l_2n'l_1'l_2' \mid x)\psi^J(n'l_1'l_2'NL_1L_2 \mid x) = 0. \qquad (145)$$

The expansion coefficients ψ^J can be computed from solutions of Eq. (145) once the V-matrix elements defined by

$$V^J(nl_1l_2n'l_1'l_2' \mid x) = \int_0^{\infty} \iint \phi^*(nl_2 \mid y) y^*(l_1l_2JM \mid \hat{\mathbf{x}}, \hat{\mathbf{y}}) V(\mathbf{x}, \mathbf{y}) \times \phi(n'l_2' \mid y) y(l_1'l_2'J'M' \mid \hat{\mathbf{x}}\hat{\mathbf{y}})\, d\hat{\mathbf{x}}\, d\hat{\mathbf{y}}\, dy \qquad (146)$$

are known. For the boundary conditions, Eastes and Secrest write

$$\psi_{x=0}{}^J = 0, \qquad (147)$$

$$\psi_{x\to\infty}{}^J \sim xj_{L_1}(k_{NL_2}x)\bar{\delta}_{\alpha\alpha'} - k_{nl_2}x_{nl_1}(k_{nl_2}x)R^J(nl_1l_2NL_1L_2), \qquad (148)$$

where the last expression is for the open channels only, that for the closed channels being

$$\Psi_{x\to\infty}{}^J \sim i^{-L_1}xj_{L_1}(k_{NL_2}x)\bar{\delta}_{\alpha\alpha'} - k_{nl_2}i^{l_1}h_{l_1}{}^+(k_{nl_2}x)R^J(nl_1l_2NL_1L_2), \qquad (149)$$

where $j_l(kx)$, $n_l(kx)$, and $h_l^+(kx)$ are the spherical Bessel functions defined in the usual way, i.e., solutions of Eq. (139) or (145) with $V^J \equiv 0$. Following Arthurs and Dalgarno, the cross section for the transition from the state (N, L_2) to the state (n, l_2) is given by

$$\sigma(nl_2NL_2) = [4\pi k_{nl_2}/(2L_2+1)k_{NL_2}] \times \sum_{J,L_1,l_1} (2J+1) \mid T^J(nl_1l_2NL_1L_2) \mid^2, \tag{150}$$

and the total cross section $\sigma(nL_2)$, and the partial cross section $\sigma(NL_2)$, are given by

$$\sigma(NL_2) = \sum_{nl_2} \sigma(nl_2NL_2) = \sum_J \sigma^J(NL_2), \tag{151}$$

with

$$\sigma^J(NL_2) = \sum_{nl_2} [4\pi k_{nl_2}/(2L_2+1)k_{NL_2}] \times \sum_{L_1l_1} (2J+1) \mid T^J(nl_1l_2NL_1L_2) \mid^2. \tag{152}$$

The numerical methods for solving Eq. (145) with the boundary conditions (147), (148), (and/or (149)) is that of Sams and Kouri (1969). Writing Equation (145) in a matrix notation

$$[-\mathbf{D}_x^2 + \mathbf{1}(x) - \mathbf{k}^2 + \mathbf{V}(x)]\Psi(x) = 0 \tag{153}$$

$$\Psi(0) = 0\,\Psi_{x\to\infty} = j(x) - \mathbf{k}n(x)\mathbf{R} \tag{154}$$

Equation (103) is converted to the integral equation

$$\Psi(x) = \mathbf{j}(x) + \mathbf{c}\int_0^\infty \mathbf{j}(x_<)\mathbf{n}(x_>)\mathbf{V}(x')\Psi(x')\,dx'. \tag{155}$$

Sams and Kouri showed that if $\Psi_0(x)$ is a solution of

$$\Psi_0(x) = \mathbf{j}(x) + \mathbf{c}\int_0^x [\mathbf{j}(x')\mathbf{n}(x) - \mathbf{j}(x)\mathbf{n}(x')] \times \mathbf{V}(x')\Psi_0(x')\,dx', \tag{156}$$

with

$$\Psi(x) = \Psi_0(x)\mathbf{Q}, \tag{157}$$

where

$$\mathbf{Q}^{-1} = \mathbf{1} - \mathbf{c}\int_0^\infty \mathbf{n}(x')\mathbf{V}(x')\Psi_0(x')\,dx' \tag{158}$$

then, if Equation (156) is solved for $\Psi_0(x)$ then Q can be determined from Equation (158) and $\Psi(x)$ can be computed.

TABLE XX. Total cross section (from Eastes and Secrest, 1972).[a]

Total energy, (E)[b]	Five-state calculation for $\sigma(0\,0)$	One-state calculation for $\sigma(0\,0\,0\,0)$
1.2	9786.7	9788.8
1.3	9440.9	9443.1
1.4	9196.0	9198.3
1.5	9006.5	9001.7
1.7	8722.4	8727.8
2.0	8423.8	8430.3
2.5	8088.4	8095.6
3.1	7815.8	7820.8

[a] Unit of cross section (area), 0.57993×10^{-2} Å^2.
[b] Unit of energy, 0.26881 eV.

Eastes and Secrest arranged the computational method to permit direct calculation of the transition matrix elements. To avoid the numerical instabilities due to the exponential growth of one of the solutions, they used the technique of Johnson and Secrest (1966) of computing the matrix elements at each step of the integration and avoiding the singularity by introduction of an artificial matrix which is guaranteed to make Q nonsingular (cf., above).

By varying the number of terms retained in the expansion, of the function $\Psi(x, y)$, Eastes and Secrest were able to investigate the effect of including highly excited rotational states on selected transitions. Thus, they found that, for transitions from the ground state $(n, l_2) = (0, 0)$, to the first rotational state $(0, 2)$, inclusion of highly excited rotational states such as $(0, 8)$ was not necessary even at total energies at which this state was accessible. On the other hand, they found it necessary to include a few *vibrationally* excited states such as $(1, 0)$ and $(1, 2)$ even though these states are closed and lie above the negligible $(0, 8)$ state. These conclusions were found to be true in the energy range $E = 1.2$ to 3.1 (the unit of energy is 0.269 eV, the vibrational spacing of the H_2 molecule). Their results for the spin average and total cross sections, Eqs. (150) and (151), for the one and five state calculations at several typical energies are given in Table XX, and for several J values at one energy in Table XXI. As can be seen, even though the

TABLE XXI. Total energy $E = 2.5$ (from Eastes and Secrest, 1972).[a]

J	One state $\sigma^J(0\,0)$[b]	Five state $\sigma^J(0\,0)$	One state $\Sigma_j\, Jj_{(0\,0)}$	Five state $\Sigma_j\, Jj_{(0\,0)}$
0	1.5	3.2	1.5	3.2
1	21.5	16.4	23.0	19.6
2	3.8	12.4	26.8	32.0
3	56.7	45.4	83.5	77.4
4	0	11.9	83.5	89.3
5	89.1	80.7	172.6	169.2
6	18.7	18.4	191.3	188.4
[b]7	71.9	85.3	263.2	273.7
8	105.9	80.7	369.1	354.4
9	4.2	30.6	373.3	385.0
10	165.6	155.4	539.0	540.2
11	78.7	61.5	617.7	601.7
12	29.9	63.7	647.6	665.4
13	221.6	203.9	869.2	869.3
14	104.2	83.7	973.4	953.0
15	15.3	50.1	988.7	1003.0
20	317.4	309.7	1866.8	1891.9
25	405.2	398.0	2868.1	2876.2
30	94.5	108.4	3659.8	3666.2
35	550.5	545.1	6023.7	6028.5
40	181.8	181.1	7658.3	7651.0
45	31.8	31.9	8029.3	8021.8
50	4.5	4.5	8086.8	8079.6
55	0.6	0.6	8094.6	8087.3
60	0.1	0.1	8095.6	8088.4

[a] Unit of energy, 0.26881 eV.
[b] Unit of cross section 0.57993×10^{-2} Å^2.

TABLE XXII. Some S-matrix elements for He–H_2 Scattering (from Eastes and Secrest, 1972).

Total energy 4.0 H_2 states included	Total angular momentum $J = 10$				
	$\mid S^{10}(n, 10 - 1_2, 1_2\, 000) \mid^2$ for various $(n, 1_2)$				
	(0, 0)	(0, 2)	(0, 4)	(1, 0)	(1, 2)
(0, 0) (0, 2)	3.4696^{-1}	2.5556^{-1}			
(0, 0 to (0, 4)	2.8987^{-1}	2.2032^{-1}	3.4164^{-2}		
(0, 0) to (0, 6)	2.9068^{-1}	2.1550^{-1}	3.6039^{-2}		
(0, 0) to (0, 8)	2.9071^{-1}	2.1544^{-1}	3.5975^{-2}		
(0, 0) to (0, 6) (1, 0) (2, 0)	3.1869^{-1}	2.1002^{-1}	3.4261^{-2}	9.1549^{-6}	
(0, 0) to (0, 8) (1, 0) (2, 0)	3.1873^{-1}	2.0997^{-1}	3.4203^{-2}	9.1558^{-6}	
(0, 0) to (0, 6) (1, 0) (1, 2) (2, 0)	3.0904^{-1}	2.1551^{-1}	3.1800^{-2}	1.1707^{-6}	2.4346^{-7}
(0, 0) to (0, 6) (1, 0) to (1, 4) (2, 0)	3.1000^{-1}	2.1471^{-1}	3.2178^{-2}	8.5295^{-7}	8.9507^{-8}
(0, 0) to (0, 6) (1, 0) to (1, 4) (2, 0) (2, 2)	3.0994^{-1}	2.1474^{-1}	3.2164^{-2}	7.8138^{-7}	1.4014^{-7}

total cross section in the one state approximation agrees well with the exact five state result, the partial cross sections do not, especially at the low J values. The convergence of the expansion can also be seen from the typical S matrix element shown in Table XXII for the total energy $E = 4.0$ at an angular momentum $J = 10$. The need for including the vibrationally excited states and the possibility for neglecting the rotational levels in the calculation of the (0, 0) to (0, 2) transitions, for example, is clearly seen.

It is to be noted that these results are based on a purely repulsive exponential model which for the He/H_2 system because of the shallow well, is expected to provide a good approximation. However, in the presence of long-range forces, the effect of excited rotational states may be greater. This is illustrated by the result of Schaefer and Lester (1973) for the case of the Li^+/H_2 system discussed below.

In another calculation, Secrest and Eastes (1972) examined the effect of an attractive potential well in the atom–diatomic collinear model. For a square well they found sharp resonances in the transition probability which could be predicted by the simple formula

$$\omega[m(E_{in} - 2i - 1 + d]^{1/2} = (2n + 1)\pi/2, \qquad (159)$$

where 'i', d, and ω are the oscillator state, the well depth, and width respectively. Because no resonances were observed for a soft Morse potential, Secrest and Eastes suggested that, in this case, the vibrational transition probability was determined more by the slope of the potential at the classical turning point than by the presence or absence of an attractive well.[14] A compilation by these authors of the various potential parameters used in their work is given in Table XXIII.

White and Hayes (1972) carried out calculations for the vibrational excitation of H_2 by Li^+ using a collinear model [see Figure 1(b)] for an atom scattered by a harmonic oscillator. Their method of solution consisted of converting the coupled differential equations (cf. Gordon and Secrest, 1966) to a set of Volterra equations which they proceeded to solve by the method of Sams and Kouri (1969, described above). A significant aspect of their model was an investigation into the detailed numerical methods necessary in the handling of coupled equations in the presence of exponentially growing terms in the asymptotically closed channels. In this they followed the suggestions made by Secrest (1971), and discussed in some detail by Gordon (1971), for the stabilization of the solutions. They reported equivalence of several stabilization methods—a result of particular interest in this study in view of the instability problem that has plagued the breathing sphere model computations reported by Marriott and those reported by others (cf., Wilson 1970, Ormonde *et al.* 1972, and Smith *et al.*, 1974).

White and Hayes (1972) reported reasonable agreement with the experimental measurements of vibrational excitation for this system of Held *et al.* (1970), and showed that a maximum excitation was obtained from a bond angle in the Li–H–H system of 60°. However, despite the presence of a shallow potential well in the potential surface they used, they did not find any resonances. By studying other model

TABLE XXIII. Mass ratio and Lennard-Jones parameters for various systems (from Secrest and Eastes, 1972).

System	Mass ratio (m)	Well depth d (eV)	Minimum point r_0(Å)	Well depth (d)	Minimum point (r_0)
H_2He	0.66504	0.001589	3.111	0.005835	50.44
N_2He	0.12501	0.002635	3.511	0.018014	155.46
O_2He	0.11117	0.002928	3.372	0.025179	142.34
Cl_2He	0.05343	0.005204	3.754	0.148624	129.41
Br_2He	0.02443	0.006281	3.841	0.313530	150.34
I_2He	0.01499	0.006460	4.241	0.485671	173.49
COHe	0.09386	0.002889	3.460	0.021476	169.59
NOHe	0.10303	0.003004	3.393	0.020541	166.19
NClHe	0.00281	0.005226	3.301	0.028202	1113.23
H_2Ne	0.90918	0.002971	3.230	0.010904	52.36
N_2Ne	0.41876	0.004924	3.631	0.033666	160.78
O_2Ne	0.38678	0.005472	3.491	0.047047	147.36
Cl_2Ne	0.22157	0.009728	3.874	0.277809	133.55
Br_2Ne	0.11212	0.011736	3.961	0.585773	155.04
I_2Ne	0.07366	0.012072	4.361	0.907597	175.30
CONe	0.31419	0.005401	3.579	0.040146	175.46
NONe	0.35205	0.005617	3.513	0.038402	172.07
NClNe	0.01013	0.009762	3.420	0.052676	1153.35
H_2Ar	0.95196	0.005534	3.584	0.020313	58.10
N_2Ar	0.58780	0.009168	3.984	0.062679	176.43
O_2Ar	0.55547	0.010193	3.844	0.087636	162.19
Cl_2Ar	0.36036	0.018112	4.228	0.517231	145.74
Br_2Ar	0.19997	0.021869	4.313	1.091552	168.84
I_2Ar	0.13599	0.022489	4.714	1.690813	189.47
COAr	0.44129	0.010064	3.933	0.074810	192.74
NOAr	0.49993	0.010460	3.865	0.071515	189.33
HClAr	0.01486	0.018190	3.773	0.098147	1272.59

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[14] Recently, Eastes and Marcus (1973) found very narrow compound state resonances for Morse potential scattering. These resonances caused drastic decreases in the inelastic vibrational transition probabilities.

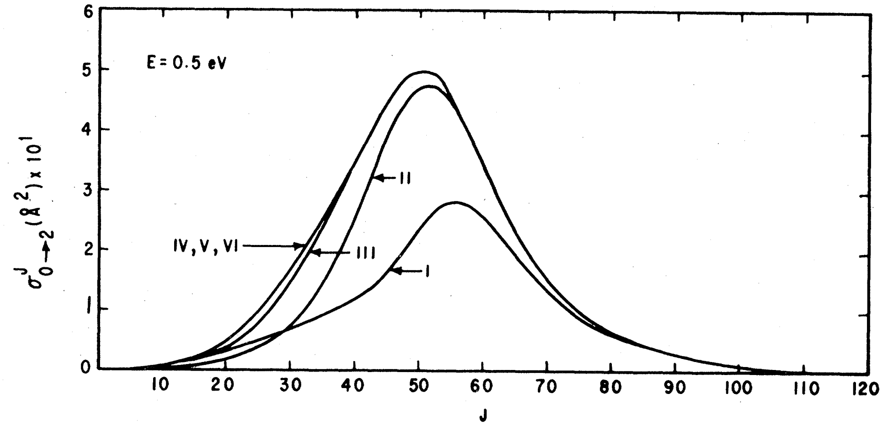

FIG. 32. Partial integral cross sections as a function of basis in the VR model for the $0 \to 2$ transition at 0.5 eV. Basis states (v, j): I—(0, 0) (0, 2); II—(0, 0) (0, 2) (0, 4); III—(0, 0) to (0, 6); IV—(0, 0) to (0, 8); V—(0, 0) to (0, 8), (1, 0) to (1, 6). [from Lester and Schaefer, 1973].

potential energy surfaces they found that the results were sensitive to potential energy shifts of about 1-eV—a sensitivity greater than the expected inaccuracy in the *ab initio* surface, due to Lester (1971), which they used. Their conjecture that inclusion of R–V coupling could significantly alter these results has since been confirmed.

Lester and Schaefer (1973) reported calculations of rotational excitation of H_2 by Li^+. They used the basic theory of Arthurs and Dalgarno (1960) and studied various forms of internal representation of the diatomic, i.e., a rigid rotator (RR)

$$[-(\hbar^2/2M)\nabla_r^2 - \epsilon_j]y_{jm_j}(\hat{r}) = 0, \tag{160}$$

$$\epsilon_j = j(j+1)hcB, \tag{161}$$

an energy corrected rotator (ECRR)

$$\epsilon_j = j(j+1)hcB_0 - [j(j+1)]^2 hcD_0, \tag{162}$$

and a vibrating rotator (VR)

$$[-(h^2/2M)\nabla_r^2 + V_0(r) - \epsilon_{vj}]X_{vj}(r)y_{jm_j}(\hat{r}) = 0. \tag{163}$$

Expanding the total wavefunction Ψ_{vj} (cf., Eqs. (36, 34), Sec. II above) in the basis of total angular momentum functions, they reduce the Schroedinger equation to a set of coupled equations in the usual way. To evaluate the potential coupling matrix element, Lester and Schaefer expand the potential energy surface in a Legendre expansion, (Lester, 1971), i.e.,

$$V(r, R, \Theta) = V_0(r, R) + V_2(r, R)P_2(\cos\Theta) + V_1(r, R)P_4(\cos\Theta) \tag{164}$$

which leads to

$$\langle V'j'l' \mid V \mid V''j''l''\rangle = \sum_\lambda f_\lambda(j'l'j''l''J)\int_0^\infty X_{V'j'}(r)V_\lambda(r,R)X_{V''j''}(r)\,dr.$$

The cross sections are obtained from the solutions of the coupled equations by standard techniques

$$\sigma_{vj\to v'j'} = \sum_J \sigma_{vj\to v'j'}{}^J;$$

$$\sigma_{vj\to v'j'}{}^J = \frac{\pi(2J+1)}{k_{vj}{}^2(2j+1)}\sum_{ll'} | T_{v'j'l',vjl}{}^J |^2, \tag{166}$$

where, in the evaluation of $V_\lambda(r_0, R)$; r_0 is kept fixed at the same value of 1.4 au for both the rigid rotator and energy-corrected rotator models. For the interaction potential these authors used a composite of a self-consistent *ab initio* potential and multipole contributions, i.e.,

SCF for $2 < R < 12$ a.u.

multipole expansion for $R > 12$ a.u.

and $V(\zeta, R) = A(3)\exp(-B(\zeta)R)$ for $R < 2$ a.u.

Analytic expressions for each coefficient in Eq. (165) were obtained and evaluated in the regions $2 < R < 12$ a.u., and $R > 12$ a.u., with the condition that, for the RR and ECRR cases, continuity of V and its derivative was imposed at $R = 2$ a.u. For the vibrating rotator case, the coupling matrix elements were computed numerically from a two-dimensional grid in ζ and R, and expressions for the potential and the vibrational eigenfunction were obtained as solutions of Eq. (163) in which V_0 was taken to be Kolos–Wolniewicz (1964) potential for H_2.

Several important results were obtained in these calculations. First, the convergence of the expansion, in the sense of the number of states needed for no further change in the total cross section, was found to require the inclusion of channels arising from the next two allowed (whether open or closed) states beyond the final state of a given transition. This is illustrated in Fig. 32 taken from their paper. Second, in comparison of the RR and ECRR models, they found that for the smaller energy spacing, the inelastic cross sections were larger. Third, they found that retention of ground rotational states was more important for convergence of a given transition than inclusion of first excited vibrational states, as far as rotational excitation cross sections were concerned. Fourth, for very low incident energies, they isolated significant resonance structures due to the

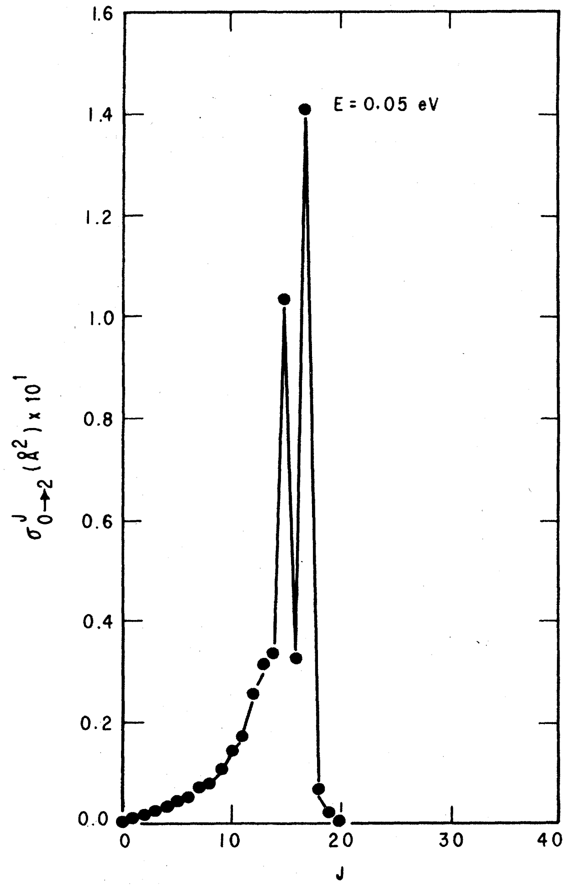

FIG. 33. Partial integral cross section for the 0 → 2 transition at 0.05 eV in the VR model for basis: (0, 0) (0, 2) (0, 4) (0, 6) (0, 8). [from Lester and Schaefer, 1973].

bound states supported in the 0.25 eV potential well in the present system; Fig. 33 illustrates their results. Indications of similar structures in other threshold regions were also obtained. The main conclusion of their work was that for highly anisotropic systems, the accuracy of the scattering wave functions used was as important a consideration as convergence of the coupling expansion, and that ECRR model calculations could be used to obtain quite accurate results with negligible difference from the VR model. An unsatisfactory feature of their calculation was the rather arbitrary choice of r_0 as the equilibrium separation (cf., above). The rather arbitrary procedure in choosing the value of r_0 was noted by these authors, who suggested that a better prescription was needed before their model could be extensively applied to other systems. More importantly, the convergence criteria determined by the anisotropy of the potential energy surface were found to be more stringent than in previous studies of less anistropic systems.

In comparing their results with classical results quoted by La Budde and Bernstein (1973), Lester and Schaefer suggested that the use of a large rotational constant indicated a strong correspondence with their close coupled channel cross sections obtained by retaining only open channels. The smaller rotational constants in classical treatment tended to yield larger cross sections, in agreement with results obtained with quantal calculations which included closed channels.

In another paper (Schaefer and Lester, 1973) these authors explored the effect of rotational excitation on the vibrational cross sections. They found that pure rotational excitation dominated the inelastic scattering at 1.2 eV in the center of mass system and that preparation of H_2 in different nonzero rotational states enhanced the 0–1 vibrational cross sections by approximately an order of magnitude. They attributed this result to the anisotropy of the interaction (cf. above) and, just like for rotational excitation, showed that increased wave function expansions were necessary for convergence of the cross sections in this system. They also showed that, neglecting initial excitation and allowing for vibrational state coupling within the usual breathing sphere approximation, led to results which were within a factor of 2 of the converged close-coupled channel value. The effect of initial rotational excitation on their vibrational cross section is shown in Fig. 34.

Recently Roberts and Diestler (1972) reported exact quantum mechanical calculations for collinear collisions between an atom and a diatomic oscillator. They solved the Schroedinger equation for the collision system in reduced coordinates (cf. Secrest and Johnson, 1966) with the Morse potential given by

$$V(x,y) = D'\{\exp[-2\alpha'(x-y-x_0')] - 2\exp[-\alpha'(x-y-x_0')]\} \qquad (167)$$

using the close coupling approximation with initial value and periodic reorthogonalization technique described by Riley and Kupperman (1968). Roberts and Diestler addressed themselves to the problem of comparing approximate distorted wave and exact transition probabilities for strongly attractive Morse interactions so as to test possible

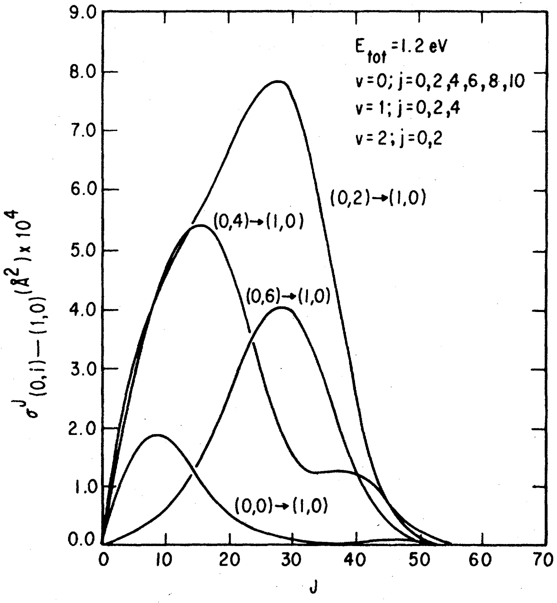

FIG. 34. Partial integral inelastic cross sections for excitation from selected initially excited rotational (0, 1) states to the (1, 0) state. [from Schaefer and Lester, 1973].

simplifications previously developed for atoms with interacting diatomic harmonic oscillators via an exponential repulsive potential. They found that, although the distorted wave approximation yielded transition probabilities that differed by as much as 150% from the exact values, introduction of a correction factor dependent on the total reduced mass of the system led to an average error of 5% only! They found that the correction factor given by

$$F \simeq (1 - \tfrac{4}{3}m)^2 \text{ allowed them to write} \tag{168}$$

$$P_{i\to i+1}{}^{\text{exact}} \simeq F P_{i\to i+1}{}^{\text{DW}}, \tag{169}$$

where

$$P_{i\to i+j} = (j!)^{-1} \sum_{J=1}^{i+j-1} P_{j\to j+1}{}^{0}. \tag{170}$$

The factor F was virtually identical to that obtained by Roberts (1970, 1971) in his earlier investigations of the exponentially repulsive potential. They also compared their results for multiple quantum transitions and found that even for strong attractive forces, transitions involving up to three quanta were in error from the exact results by about only 1%. A typical set of values for the multiquantum transition probabilities taken from their paper is given in Table XXIV.

TABLE XXIV. Multiple quantum transition probabilities (from Roberts and Diestler, 1972)[a]

ϵ_{total}	i	f	$P_{i\to f}{}^{\text{exact}}$	$P_{i\to f}$ [b]	$P_{i\to f}/P_{i\to f}{}^{\text{exact}}$
3.00	0	2	1.54×10^{-5}	1.53×10^{-5}	0.99
4.00	0	2	2.69×10^{-4}	2.68×10^{-4}	1.00
4.00	1	3	4.47×10^{-5}	4.63×10^{-5}	1.04
4.00	0	3	2.09×10^{-7}	2.05×10^{-7}	0.98

[a] $P_{i\to f}$ as a function of energy for $m = 0.5$, $\alpha = 2.5$ Å^{-1}, $h\omega/k = 3000$°K, and $D = 6000$ cal/mole.

[b] $P_{i\to f}$ were calculated using Eq. (170).

Saxon and Light have developed a fully quantum mechanical model for atom–diatomic collisions following the formalism initially proposed by Miller and Light (1971). The model was applied to $H + H_2$ rotational excitation. The results indicated a strong dependence on the assumed threshold for the cross sections. In a comparative study using classical trajectories for the same surface, Miller and Light (1971) obtained results which gave good agreement with the quantum mechanical calculations but showed that at low incident energies, tunneling effects dominated. A significant difference between the quantum mechanical and classical models was the noted asymmetry in both forward and backward scattering (peaking). No backward peak was obtained in the classical result. Further results with the model would be of interest because it allows for both reactive and non-reactive collisions and could also be modified for unsymmetric reactions.

In the comparison of the distorted wave approximation with the exact quantum mechanical calculations of Secrest and Johnson, Thiele and Weare (1968) found that the results of Jackson and Mott (1932) gave consistently high transition probabilities and were dependent upon the repulsive strength of the potential, the incident energy, and the mass parameter. They also found that double and even triple quantum transition could be more important than single quantum transition. The reason for this is that Jackson and Mott's treatment is based on an expansion of the transition amplitudes in which only the first order terms are retained. Hence, no information about second and higher order transition probabilities can be obtained by this method. The higher order terms considered by Thiele and Weare led to reasonably good results for sufficiently light incident atoms and at low kinetic energies. For example, the double quantum transition probability in second order can be related to that in first order through the equation

$$P_{l\to l+2}{}^{(2)} = P_{l\to l+2}{}^{(1)} + 0(P_{l\to l+1}{}^{(1)} \times P_{l+1\to l+2}{}^{(1)}) \tag{171}$$

where l is the initial oscillator state. Thiele and Weare found that the second term was usually greater than the first.

We conclude this review with an outline of a rigorous theory of rotational and vibrational multiquantum processes recently developed by Dillon and Stephenson (1972, 1973, 1974). The basis for the development is to be found in the relaxation theory of pressure broadening due to Fano (1963) and stems from the time dependent formulation of the relaxation operator discussed by Dillon *et al* (1970). The formalism is obtained from an expansion of the scattering operator in a series of rotational tensor operators in a way that guarantees unitarity and permits evaluation of S-matris elements to all orders. The transition probabilities are then evaluated using (for example) classical path approximations.

The starting point of this theory is the series expansion for the scattering operator, S

$$S = \Theta \exp\left(-i \int_{-\infty}^{\infty} \tilde{V}_{12}{}^{T}(t)\, dt\right) = \sum_{n=0}^{\infty} S_n. \tag{172}$$

where $\tilde{V}_{12}{}^{T}(t) = \exp(iH) V_{12}{}^{T} \exp(-iHt)$, and the intermolecular potential $V_{12}{}^{T}$ between molecules, designated as 1 and 2, is expanded in a series of normal modes (transition moments) q_1, q_2 as

$$V_{12}{}^{T} = \sum_{i,j=0}^{\infty} C_{ij} q_1{}^{i} q_2{}^{j}. \tag{173}$$

Using ladder operators

$$q \equiv \gamma(a^{\dagger} + a), \tag{174}$$

which satisfy

$$[a, a^{\dagger}] = 1 \tag{175}$$

$V_{12}{}^{T}$ is expanded to second order to give

$$\begin{aligned} V_{12}{}^{T} = {} & V_{12}{}^{0} + V_{12}{}^{R}(c_0 + a_1{}^{\dagger}a_1 + a_2{}^{\dagger}a_2) \\ & + V_{12}{}^{V-T}[a_1{}^{\dagger} + a_2{}^{\dagger} + c_1(a_1{}^{2} + a_2{}^{2}) + c_2 a_1{}^{\dagger}a_2{}^{\dagger}] \\ & + V_{12}{}^{V-V} a_1{}^{\dagger}a_2 + \text{c.c.}, \end{aligned} \tag{176}$$

where the superscripts on the V's identify the processes to which they give rise and V_{12}^0 determines the collision trajectory.

To evaluate the rate k_{if} for a transition from a state $|\,i\rangle$ to a state $|\,f\rangle$

$$k_{if} \sim \langle|\,\langle i\,|\,S\,|\,f\rangle\,|^2\rangle_{\mathrm{av}} \tag{177}$$

where $\langle\ \rangle_{\mathrm{av}}$ denotes a thermal average over translational degrees of freedom, Dillon and Stephenson introduced an approximation whereby intermediate state energy defects $\omega_{n'n}$ are replaced by a mean value $\bar{\omega}_{if}$ which depends only on the initial and final states, i.e.,

$$\begin{aligned}&\langle i\,|\,\Theta\exp\left[-i\int_{-\infty}^{\infty}\tilde{V}_{12}{}^{T}(t)\;dt\right]|\,f\rangle\\ &\quad\cong\langle i\,|\exp\left[-i\int_{-\infty}^{\infty}\exp(i\omega_{i}ft)\,V(t)\;dt\right]|\,f\rangle.\end{aligned} \tag{178}$$

This approximation amounts to a representation of the resonance function by a step function and can be shown to be exact for correct choices of the $\bar{\omega}_{if}$—a condition that can be satisfied for many cases of practical interest.

In their first paper these authors focused on the fourth term in Eqn. (176)—responsible for V–V exchange—which they take in the form

$$V^{VV} = V_{12}\gamma_1\gamma_2(a_1{}^{+}a_2 + a_1a_2{}^{+}) \tag{176a}$$

and make use of the fact that V_{12} contains rotational operators so that it can be expanded as a sum of spherical tensors

$$V_{12} = \textstyle\sum_n f_n(t)\,T^n, \tag{179}$$

where all the time dependence is contained in the coefficients $f_n(t)$ which do not operate on vibrational or rotational states.

From Eqs. (178) and (179),

$$\langle i\,|\,S\,|\,f\rangle = \langle i\,|\,S(\omega)\,|\,f\rangle, \tag{180}$$

where

$$S(\omega) = \exp\{-i[\textstyle\sum_n K_n(\omega)\,T^n](a_1{}^{\dagger}a_2 + a_1a_2{}^{\dagger})\}, \tag{181}$$

and

$$K_n(\omega) \equiv \gamma_1\gamma_2\int_{-\infty}^{\infty}\exp(i\omega t)\,f_n(t)\;dt, \tag{182}$$

and the energy defect ω is determined by the initial and final states

$$\omega \equiv \omega_{if} = E_0(f) - E_0(i), \tag{183}$$

where $|\,i\rangle = |\,1\ 2\rangle$, $|\,f\rangle = |\,1',2'\rangle$ for two colliding molecules designated by 1 and 2. The basic states of these are expanded in simple products of rigid rotor and harmonic oscillator states

$$|\,1,2\rangle = |\,j_1m_1\rangle\,|\,V_1\rangle\,|\,j_2m_2\rangle\,|\,V_2\rangle \equiv |\,\alpha V_1V_2\rangle, \tag{184}$$

where α is a collective quantum number for the rotational states and, with the use of the commutator properties of the ladder operators, Eqn. (175), new vibrational quantum numbers j, m are defined by

$$J\,|\,\alpha jm\rangle = j\,|\,\alpha jm\rangle \qquad j \equiv \tfrac{1}{2}(V_1 + V_2), \tag{185a}$$

$$J_z\,|\,\alpha jm\rangle = m\,|\,\alpha jm\rangle \qquad m \equiv \tfrac{1}{2}(V_1 - V_2), \tag{185b}$$

where

$$J \equiv \tfrac{1}{2}(a_1{}^{\dagger}a_1 + a_2{}^{\dagger}a_2) \qquad J_z \equiv \tfrac{1}{2}(a_1{}^{\dagger}a_1 - a_2{}^{\dagger}a_2), \tag{185c}$$

so that

$$a_1{}^{\dagger}a_2 + a_1a_2{}^{\dagger} = 2J_x. \tag{186}$$

By analogy with angular momentum operators, this leads to a diagonalization transformation for vibrational operators, whose matrix elements are simply the rotation matrices

$$\langle\,jm'\,|\exp\{-(i\pi/2)J_y\}\,|\,jm\rangle = d_{m'm}{}^{j}(\pi/2) = \Delta_{m'm}{}^{j} \tag{187}$$

which are used to eliminate the vibrational operators from Eqn. (181), to give

$$\begin{aligned}\langle\alpha'jm'\,|\,S\,|\,\alpha jm\rangle &= \langle\alpha'jm'\,|\,S-1\,|\,\alpha jm\rangle\\ &= \sum_{n=-j}^{j}\Delta_{m'n}{}^{j}\Delta_{mn}{}^{j}\langle\alpha'\,|\,S(\omega,n) - 1\,|\,\alpha\rangle\end{aligned} \tag{188}$$

where the operator $S(\omega, n)$ now contains only rotational operators

$$S(\omega,n) \equiv \exp[+i2n\textstyle\sum_i K_i(\omega)\,T^i] \tag{189}$$

For the case of the transition dipole–transition dipole interaction, i.e.,

$$\begin{aligned}V_{12} &= [r^3(t)]^{-1}(\partial\mu/\partial q)_1(\partial\mu/\partial q)_2\\ &\quad\times(\cos\Theta_1\cos\Theta_2 + 2\sin\Theta_1\sin\Theta_2\cos\phi).\end{aligned} \tag{190}$$

Dillon and Stephenson make use of the result established by Dillon *et al.* (1970) who showed that for rotational operators which are simple Legendre polynomials, the scattering operator can be expanded as a sum of Legendre polynomials

$$S = \exp[-iK_1\eta'_n\wp P_n(\cos\chi^0)] = \textstyle\sum_j\tau_j{}^{(n)}\wp P_j(\cos\chi^0) \tag{191}$$

Taking advantage of the invariance of the angle averaged scattering operator under rotations of the collision plane and using the tensor formulation of the dipole–dipole interaction [see e.g. Fano and Racah (1958) Appendix J] the operator $S(\omega, n)$ can be further reduced to

$$\begin{aligned}S(\omega,n) &= \exp[-\tfrac{1}{2}inK(\omega)\,(6)^{1/2}T_{2,0}(1,1)]\\ &= \sum_{l=1}^{\infty}(2l+1)\,i^l(2l+1)^{1/2}j_l[nK(\omega)]\,T_{0,0}(l,l) + \cdots,\end{aligned} \tag{192}$$

where terms which do not contribute to the average over m's have been omitted, and where

$$K(\omega) \equiv 4\left(\frac{\partial\mu}{\partial q}\right)_1\left(\frac{\partial\mu}{\partial q}\right)_2 \gamma_1\gamma_2 \times \int_{-\infty}^{\infty} \exp(i\omega t) P_2(\cos\Theta(t)) R^{-3}(t)\, dt, \tag{193}$$

and j_l is the spherical Bessel function.

The matrix elements of $S(\omega)$ can now be evaluated to give

$$\begin{aligned}(2j_1'+1)(2j_2'+1) &\times \sum_{JJ'MM'} |\langle j_1'j_2'J'M'jm' \mid S(\omega) \mid j_1j_2JMjm\rangle|^2 \\ &= \sum_{n,k=-1}^{j} \Delta_{m',n}{}^{j}\Delta_{m,n}{}^{j}\Delta_{m',k}{}^{j}\Delta_{m,k}{}^{j} \\ &\times \sum_{l>0} j_l[nK(\omega)]j_l[kK(\omega)](2j_1+1)(2l+1) \\ &\times \begin{pmatrix} j_1' & l & j_1 \\ 0 & 0 & 0\end{pmatrix}(2j_2+1)(2l+1)\begin{pmatrix} j_2' & l & j_2 \\ 0 & 0 & 0\end{pmatrix}^2,\end{aligned} \tag{194}$$

where use has again been made of the invariance of the (orientation) averaged scattering operator under rotations of the collision plane.

To obtain the total V–V transition rate, Dillon and Stephenson averaged the probability for vibrational exchange over a Boltzman distribution of initial vibrational states and summed over final states, and then averaged over the translational degrees of freedom in the classical path approximation by integrating over the impact parameter b and the relative speed v. The averaging over the orientation angles of the collision plane α, β, γ, has been carried out by averaging over the initial and summing over the final magnetic quantum numbers in deriving Eqs. (192) and (194) (Cooper 1967).

Dillon and Stephenson applied this formalism to the calculation of vibrational relaxation in CO for processes of the type

$$\mathrm{CO}(v-n) + \mathrm{CO}(n) \to \mathrm{CO}(v-n-\Delta v) + \mathrm{CO}(n+\Delta v) - \Delta E \tag{195}$$

where v is the sum of vibrational excitation in both molecules, Δv the number of vibrational quanta exchanged and $n < v/2$.

A typical set of results is shown in Fig. 35 where the gradual decrease of the probability with vibrational energy defect for $\Delta v = 1$ is compared to the steep drop in corresponding Born approximation result for $\Delta E > 100$ cm^{-1}. Note also the substantial $\Delta v = 2$ cross sections.

Dillon and Stephenson found that in all cases calculated by them the probabilities for exchange of n quanta were much greater than the nth power of the corresponding probability for exchange of a single quantum. For exchange of 1, 2, and 3 vibrational quanta in near resonant processes, they obtained broad maxima for the exchange probability, whereas that for only the $\Delta v = 1$ process allowed by the Born approximation exhibits a continuing increase with n. They attributed this to the increased probability for larger Δj transitions for higher total excitation. Because of the substantial size of multiquantum transition probabilities, Dillon and Stephenson suggested that detailed kinetic modelling of gas lasers should be more appropriately carried out with many small rates rather than a few large ones.

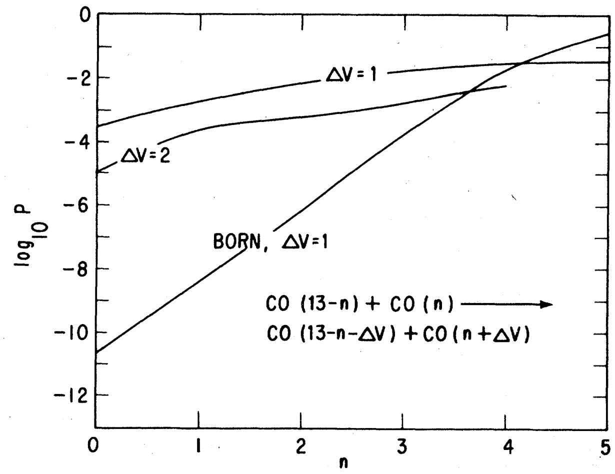

FIG. 35. Probability of vibrational energy exchange in CO. [from Dillon and Stephenson, 1973].

The importance of multiquantum transitions in V–V–T probabilities in collisions of vibrationally excited dissimilar diatomic molecules has been also emphasized by Kelley (1972). His approach parallels that of Dillon and Stephenson, and relies on an exact form of the unitary time evolution operator for an interaction potential containing terms linear, bilinear and quadratic in the oscillator coordinates. We refer the reader to his paper for a detailed discussion of several interesting model results.

In their second paper, Dillon and Stephenson modified the above formalism by using curved classical trajectories determined by a Lennard-Jones potential, exact vibrational wavefunctions obtained from spectroscopic data and, also, included the pure rotational interaction in the V–V transfer calculation. For the systems HF(DF), HCl–CO_2 they took the dipole–quadrupole interaction

$$V_R(t) = 3(\mu_0)_1(\Theta_0)_2 P_1(\cos\Theta_1) P_2(\cos\Theta_2) R^{-4}(t). \tag{196}$$

To calculate the R–R rates they make use of the discrepancy between the halide rotational constants (large) and CO_2 (small) to average over the CO_2 rotational states,obtaining for the transition probability

$$P_{j_i}{}^{j_f} = \sum_{l=1}^{j_i+j_f} \langle j_l(K_R)\rangle_{\mathrm{av}}{}^2 (2l+1)(2j_f+1)\begin{pmatrix} j_i & l & j_f \\ 0 & 0 & 0\end{pmatrix}^2, \tag{197}$$

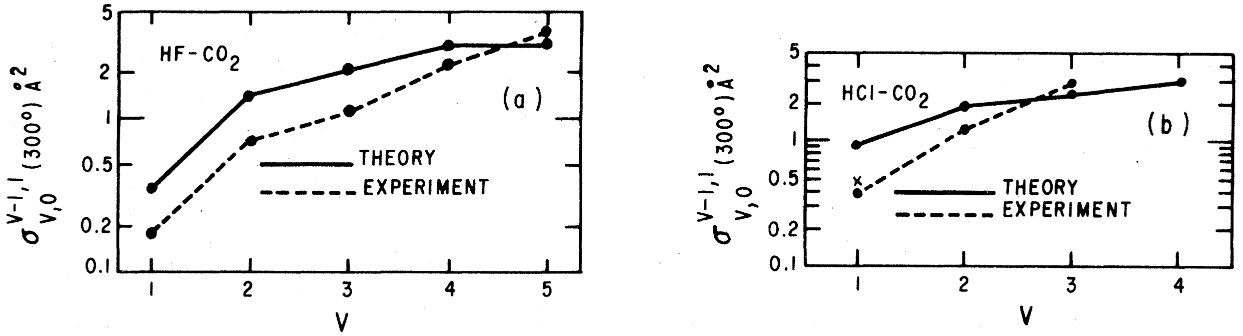

FIG. 36. (a) Comparison of theoretical and experimental cross sections for the transfer of a vibrational quantum from HF in the vth vibrational state to the asymmetric stretching vibration of a CO$_2$ molecule initially in the ground vibrational state. The temperature is 300°K and the cross sections $\sigma_{v,0}^{v-1,1}$ are expressed in units of square angstroms. Experimental values are from Airey and Smith (1972) (from Dillon and Stephenson, 1973). (b) Comparison of theoretical and experimental cross sections for the transfer of a vibrational quantum from HCl in the vth vibrational level to the asymmetric stretch mode of a CO$_2$ molecule initially in its ground vibrational state. The temperature is 300°K and the cross sections $\sigma_{v,0}^{v-1,1}$ are expressed in units of Å. The experimental value denoted by x is from Stephenson *et al.* (1972) and the values connected by a dashed line are from Ridley and Smith (1972) [from Dillon and Stephenson, 1973].

where the phase integral K_R is given by

$$K_R(b, v, \omega) = K_R{}^0 I_R(\beta, G, x). \tag{198a}$$

$$I_R(\beta, G, x) = \frac{\beta}{G}\int_0^\infty \cos(xy) Z^4(y)\, dy, \tag{198b}$$

$$\beta \equiv b/d, \qquad x \equiv \omega b/v, \qquad Z \equiv d/r(t),$$

$$y \equiv vt/b, \qquad G \equiv (mv^2/8\epsilon_0)^{1/2}, \qquad t_0 \equiv (md^2/8\epsilon_0)^{1/2},$$

$$K_R{}^0 = \frac{6(\mu_0)_1(\Theta_0)_2(m/8\epsilon_0)^{1/2}}{(\hbar d^3)}, \tag{198c}$$

where b is the impact parameter, v the relative velocity, and m the collision reduced mass; the permanent dipole and quadrupole moments are μ_0 and Θ_0, and ϵ_0 and d are the Lennard-Jones parameters. The energy defect $\bar{\omega}_{if}$ is, for this case, given by $\bar{\omega}_{if} = B_e(j_i + j_f + 1)$. For tables of pure rotational transition probabilities in the HCl, HF, and DF-CO$_2$ systems we refer the reader to their paper.

As noted by Dillon and Stephenson, the diagonalization transformation cannot be used for rotational operators because these cannot be represented by finite-dimensional matrices. However, in their calculations of V-V transfer in HX-CO$_2$, they observe that the pure rotational and pure vibrational operators commute, so that

$$\langle \alpha' jm' \mid S_R S \mid \alpha jm \rangle$$

$$= \sum_{n=j}^{j} \Delta_{m',n}{}^{i}\Delta_{m,n}{}^{j}\langle \alpha' \mid S_R S(n) - S_R \mid \alpha \rangle. \tag{199}$$

The form of this expression is used for the prescription for including pure rotational effects whereby the substitution

$$j_l(nK) \rightarrow j_l(nK_v + K_R) - j_l(K_R) \tag{200}$$

is made, followed by the transformation

$$\mid V_{RKR} \rangle = \sum_{V_{HO}} \langle V_{HO} \mid V_{RKR} \rangle \mid V_{HO} \rangle \tag{201}$$

to allow for the fact that Eq. (194) is obtained in a basis of harmonic oscillator states and not the RKR states used in this case. The phase integral for the transition dipole-transition dipole interaction is now

$$nK_V(b, \omega, v) = nK_V{}^0 I_V(\beta, G, x), \tag{202a}$$

$$K_V{}^0 = 8(\partial\mu/\partial q)_1(\partial\mu/\partial q)_2\gamma_1\gamma_2(m/8\epsilon_0)^{1/2}(\hbar d^2)^{-1}, \tag{202b}$$

and

$$I_V(\beta, G, x) = \frac{\beta}{G}\int_0^\infty Z^3(y) P_2[\cos\theta(y)] \cos(xy)\, dy. \tag{202c}$$

Several interesting results were obtained in these calculations. The very good agreement of the calculated cross sections for the transfer of a vibrational quantum from the vth vibrational state of HF(HCl) to CO$_2$(00^{0}1) with those measured by Airey and Smith (1972) and Ridley and Smith (1972) is shown in Fig. 36. The calculated exchange rate for HCl(1)-CO$_2$, although about 50% too high in absolute value, showed a temperature dependence also in excellent agreement with experiment. These calculations established the result of the earlier paper that large V-V cross sections could result from Δj changes large enough to absorb as rotational excitation large energy defects. In the case of HF, for example, for an initial state $j_i = 2$, a final state $j_f = 9$ was most probable. The apparent qualitative experimental evidence supporting such results has already been mentioned in Sec. III (e.g., Ahl and Cool, 1973). The calculations also showed that the cross sections for simultaneous transfer of two vibrational quanta from HF and HCl to CO$_2$ were small, but those for DF-CO$_2$ quite large and only about 2-6 times smaller than the calculated single quantum transfer cross section from the same initial state. Finally, Dillon and Stephenson evaluated foreign gas broadening half-widths for pure rotational transitions in the ground vibrational states of HF, HCl, and DF. They obtained very good agreement with experiment for HCl and HF (there is no data for DF).

Dillon and Stephenson also indicated a procedure for assessing the sensitivity of their prescription to, for example, changes of molecular moments or the Lennard–Jones parameters. They generated several plots (cf. their Fig. 6) showing variations in a given $HX(v = 1) - CO_2(00^01)$ cross section when one interaction, e.g., rotational K_R^0, was held fixed at its *a priori* value, Eq. (198c), while the other was varied. From such plots one can infer (for example) that changing the strength of the rotational interaction by a factor of 2, changes the vibrational excitation cross section by more than an order of magnitude for HF, but only by about a factor of 2 for DF.

For more recent developments of quantal methods we refer the reader to the papers in the bibliography we have not had the space to discuss (e.g., Alexander, 1973, 1974; Zarur and Rabitz, 1973, 1974).

VIII. SUMMARY AND CONCLUSIONS

A summary of the material reviewed requires a few preliminary comments to define a framework for the concluding remarks.

Two startling and rather saddening observations can be inferred from this review. First, the extremely fast low temperature relaxation processes in hydrogen fluoride *have not* been predicted by *any* theory and today, nearly five years after their initial observation, there is still no consistent and satisfactory theoretical explanation of either the magnitudes or the temperature dependence of the rates for these and numerous related relaxation phenomena. Second, only very few real molecular systems of practical interest have been described by means of models endowed with the degree of sophistication indicated as being necessary by numerous experiments. The few examples cited, and the few that will undoubtedly be reported by the time this review appears, are only a very minute beginning in a host of problems that must be solved to provide some answers to several perplexing questions posed by the data.

As has been noted by Gordon in his description of possible approaches to molecular collision problems (1973), the overwhelming variety of available methods is primarily due to the complexity of these problems and their rich content, which permit the use of different approximations in different situations, rather than to the conceit of the many theoreticians each developing his own point of view. One might add that the choice of a given approximation is frequently, and unfortunately, dictated by institutional and therefore, to a large extent, individual bias, rather than by an objective evaluation of the problem, so that the results stemming from such choices can be hard to assess or meaningfully discuss.

To avoid misunderstanding of some of the statements made below, it may be also appropriate, though likely to provoke a storm, to define this author's personal interpretation of a few frequently encountered words. We do not consider

(a) a daily adjustable algebraic prescription to be a "theory";

(b) the consequence of a calculation that approximates an experimental result to be a "prediction" if the calculation is performed *after* the experiment:

(c) "agreement" between theoretical and experimental curves, or between several theoretical curves, as being "excellent" (or even "good") when illustrated by nearly orthogonal curves on semilogarithmic plots (especially if error bars are not shown for the data and estimates of the errors due to various approximations made in calculations are not made); and lastly

(d) the mere estimation of the values and relationship between some parameters as being synonymous with, or implying an "understanding" or an "explanation" of the physics responsible for the parameters having the estimated values.[15]

Our main conclusions, taken roughly in the order of the subjects treated, are now stated. First, there ought by now to be general agreement that one dimensional models are "passé". Their value is historical, to some extent pedagogical, and their use should be confined to providing test material for selected aspects of new theories and, when possible, for new computational algorithms. While it is true that three dimensional problems can be very difficult to formulate and handle and that their solution can be expensive, we prefer to argue that, (a) the former should be regarded as a challenge to be met and not an excuse for stretching out our imaginations in one dimension, and (b) progress cannot and must not be determined mainly by cost effectiveness criteria. Similarly to be deemphasized are simple analytical procedures. Rather than elaborate, we quote Bernstein (1971) "neither the old Landau–Teller relation, nor the Lambert–Salter 'law' nor any 'resonance defect' empiricism is good enough" to determine detailed microscopic relaxation rate constants. We also concur with Rapp and Kassal in their dismissal of models involving extensive fitting to experimental parameters because "such models can be used to explain everything and predict nothing."

The preceeding suggests the need for greater emphasis on more complex models in future. The selection of these today is not simple, and is probably best made on a case by case basis. There is no doubt that the full potential of Monte Carlo methods remains to be explored. However, a distinction must be strongly made between strictly classical Monte Carlo trajectory calculations and the more recent developments based on the classical S matrix ideas.

The limitations of strictly classical methods are apparent. They can be expected to, and made to, work when strictly classical effects determine a process, or if one is not interested in quantal details or their possible cummulative effects. However, as more refined measurements become available and more detailed selected state by state analyses become necessary, the limitations of even classical Monte Carlo methods will be quickly reached. It would be unrealistic to impose on these methods the condition that they correctly simulate strictly quantal effects or attempt to stretch their use to prove that they can do so. Their systematic use as approximations could be justified only after the limits of validity have been established by tests against more comprehensive models (as is being done in the development of the classical S matrix methods), but it would be unrealistic to use the approximations themselves to define these limits. Further, in three dimensional models, such methods will also involve extensive parameter fitting to experimental data and the results obtained could be as suspect as those of their one dimensional counterparts, because all the uncertainties of the latter with the attendant confusion could be simply enhanced. The dangers of inferring too much from potential energy calculations have been indicated by Parr and Truhlar (1971).

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[15] However, in the body of the review, the various authors' terminology has been usually adhered to.

The situation with classical S-matrix (semiquantal) theories, and with more recent perturbation approaches, is different. These have only just been developed to the point where systematic calculations on realistic systems can be contemplated. As pointed out by Secrest (1973) it is not clear yet whether they will prove as good as fully quantal methods (cf., LaBudde and Berstein 1973) but there are indications that for some cases at least, this will be so. The argument (see Zarur and Rabitz, 1973) for the use of the effective Hamiltonian approach to reduce the dimensionality of the problem by eliminating experimentally redundant information, while still attempting to obtain experimentally relevant data, is especially appealing in this context.

As to fully quantal methods the situation is rather clear. Their increasing use in molecular collisions is slowly (with results) leading to a situation similar to that which has evolved in the considerably simpler electron-atom scattering field over the last twelve years. There, the shift away from analytic and simplistic methods, *within the framework of sound theoretical prescriptions*, has led to numerous predictions and a substantially improved understanding of several collision processes. It should be stressed that the size of calculations need not be a deterrent. Some of the first ten channel close coupling calculations by the author (1926/63) required six tape drives and 26 hours (!) of CDC 1604 time for each value of k^2, L, S and Π. Needless to say, they never ran more than three hours because of parity errors and other factors (such as the weather). Today's (informal) debates are about what problems are best handled with 13 or 17 channel codes and which codes and techniques are best for 25 channel problems. Note the use of "what" and "which", and not "whether".

Similar progress can be expected, and is beginning to appear, in molecular collision dynamics. However, the requisite technology may not be yet sufficiently developed. Gordon's algorithm,[16] currently the fastest, has not been fully exploited. By the time it is, should it become too slow, others will hopefully be found. The potential of next generation computers has hardly been contemplated. Nonetheless, one can readily envisage very sophisticated a priori scattering calculations, carried out with a priori potential surfaces, in combination with intricate measurements, resulting in significant revisions of our current concepts of energy transfer mechanisms.

To undertake and carry out sophisticated modelling one must have confidence in the model, and for this there is need for sound theoretical prescriptions which, as we have seen, are in rather short supply. Hence, we conclude this summary as we did the review with some comments on the Dillon–Stephenson theory.

The order of magnitude estimates of multiquantum transition probabilities and their quantum number dependence, obtained by these authors within the framework of a physically sound prescription, can probably be considered the single most important recent theoretical contribution to the calculation of vibrational relaxation rates. The foundation of their method on a rigorous physical theory has already been noted. As we have seen, a large number of calculations for independent processes (V–V, R–R, line broadening, temperature dependence), for different molecules, with the same intermolecular potential and the same set of a priori values for molecular parameters for each molecule have, without variation of molecular parameters, led to very good results. We also note that with this theory, the entire weight of group theoretical methods and the derived techniques is brought to bear for the first time (to our knowledge) directly, and in a quantitatively tractable general manner, on the problems outlined in this review. It is logical and pleasing that this should be so, and in keeping with Weyl's prescription that quantum kinematics forms a group. We suggest that substantial progress in our understanding of vibrational relaxation in molecules (and numerous applications) can be looked forth to in future as a result of using this theory, either alone or in combination with some of the others we have indicated.

Note added in proof: Some recent developments

The purpose of this note is to draw attention to several recent developments. The new papers cited, as well as others related to our topics but not discussed, are indicated by "S" and refer to the Supplementary References.

The results of several Monte Carlo quasiclassical trajectory studies indicate that fast halide relaxation rates may in some cases be attributed, in part at least, to reactive rather than nonreactive collisions. An exhaustive and systematic examination of such partitioning and of the effects of initial reactant vibration and rotation energies on reaction rates and energy transfers, has been described for the H(Br) + HBr system by White and Thompson (S-1974) and for the Cl + Cl_2 and I + I_2 systems by Thompson (S-1974). White and Thompson established that atom exchange provided an important path for vibrational relaxation of HBr and that both initial vibration and rotation of the reactant molecule enhanced the deactivation rates. In the case of the H + HBr system, the contribution to the total relaxation rate of the reactive paths, relative to the nonreactive, were shown to increase with increasing energy of the transition, but the converse behavior was found for the Br + HBr process. For example, in the case of vibrational relaxation of HBr ($v = 2$) by Br at 1000°K, the contributions of the reactive paths were 35% for $\Delta v = 2$, and 48% for $\Delta v = 1$. Also for the H + HBr reaction, contributions of both reactive and nonreactive orbiting collisions were found to be significant. These authors found predominantly forward peaking in the angular distributions of the product molecule for Br + HBr and backward peaking for H + HBr.

For the halogen systems, Thompson found the angular distribution of product molecules to be peaked in the backward direction with a slight shift to forward scattering for high initial vibrational states. For I + I_2, nonreactive processes were shown to contribute more to the relaxation at the lower (1100°K) temperature, whereas at the higher (1500°K) temperature, reactive processes were more important. No definite temperature dependence for the relative contribution of these processes was established for the Cl + Cl_2 system for which the rates of reactive and nonreactive relaxation were, in general, comparable.

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The participation of reactive and nonreactive processes in the deactivation of HF and DF, and their temperature dependence, has also been investigated by Wilkins. He uses a very efficient technique which makes feasible the calculation of numerous trajectories but which, unfortunately, has never been published (cf. the papers cited). His results for the characteristics of nonreactive collision processes and for the relative importance of multiquantum transitions are in general agreement with those of Thompson, outlined in Sec. VI. According to Wilkins, reactive paths could provide an efficient energy transfer mechanism for the deexcitation of HF by H (S-1973b) because the rate of the atom exchange reaction was found to be nearly four times that for the deactivation by nonreactive collisions. He also showed that reactive paths could contribute to the deactivation of HF by F from high ($v \geq 3$) excited states but states (S-1974d) that vibrationally excited HF cannot be efficiently relaxed by F. In a comparative study of HF and DF relaxation by H and D, Wilkins (S-1974c) reports rates for HF deactivation by H an order of magnitude greater than those for DF by D for temperatures below 200°K, and presents several other results of interest. He stresses, however, that the absolute values of the rate coefficients are subject to the uncertainties discussed by Truhlar (S-1972), Muckerman and Newton (S-1972) (see also Thompson, 1974).

In a recent examination of the HCl/H, Cl system, Wilkins (S-1974d) finds that the atom exchange paths for vibrational relaxation of HCl by both Cl and H are quite important (cf., Ridley and Smith (1971) and Sec. III). He confirms Thompson's findings that V–T and V–R transfers are, respectively, the more important mechanisms for deexcitation of HCl by H and Cl, and finds that the reactive contributions are approximately twice as efficient as the nonreactive ones in the case of de-excitation by H. For deactivation by Cl the two contributions are about equal. His results indicate an enhancement in the deactivation rates of HCl by H with increased vibrational energy in the reagent. The reported angular distributions are, however, surprising (in contrast with those for the H–HBr system) since they apparently indicate predominently backward scattering for product molecules in *both* the H + ClH and Cl + HCl reactions. The v dependence of the reactive contributions to HCl deactivation by H decreases with increasing initial vibrational excitation (20% for $v = 1$ and 10% for $v = 6$).

Wilkins also finds that the effect of increasing the vibrational energy in the reagent results in small (large) enhancement of the deactivation rate according as the potential energy well of the surface used is large (3.8 kcal/mole) or small (0.77 kcal/mole). Lastly, according to his results, the rapid deactivation of HCl by both H and Cl can also be explained by postulating the formation of bound complexes. Note, by the way, a possible method of modelling this effect in nonreactive calculations via orbiting collisions, as discussed by Dillon and Stephenson (S-1974). They showed that allowance for such collisions within the framework of their model resulted in a steeper temperature dependence, at low temperatures, for the HF(DF)–CO_2 transfer rates and thus improved the agreement with experiments.

In summary, the various results brought forth by the quasiclassical Monte Carlo calculations, while promising, should not be considered final, and the general trends on which there is agreement are probably more reliable than the absolute rate values quoted in the literature. The reason for this stems from the uncertainties surrounding the choices of potential energy surfaces used in these models, as well as the problems involved in the interpretation of the results due to ambiguities caused by assignments of classical continuous states to quantized states. It might be worthwhile emphasizing here that the critical test of any theoretical model is provided by angular distribution calculations and measurements rather than by absolute total cross section values. These problems are recognized and thoroughly discussed in the literature (see for example, Thompson (S-1974), White (S-1973), Wilkins (S-1974a) and references therein), and serve to stress the need for very accurate ab initio potential energy surfaces.

The possibility that some conclusions based on results of Monte Carlo methods may ultimately have to be revised was raised by Schatz *et al.* (S-1973). In a detailed comparison of accurate quantum mechanical and quasiclassical trajectory calculations for the $F + H_2 \rightarrow FH + H$ reaction, they found the very low energy (0.025–0.075 eV) quasiclassical reaction probabilities significantly in excess of those of quantal calculations. This contrasted with their earlier results for H + H_2 where the two methods agreed with each other. These authors stressed that their results were based on a collinear model and that the consequences of neglecting quantal effects had to be ultimately tested with three dimensional calculations.

As we have seen, fully quantal three dimensional models are still in their infancy. However, several rather encouraging results have been recently obtained by Rabitz and co-workers by means of the effective Hamiltonian method (Rabitz, 1972, 1973). An important aspect of this formalism is that it permits investigations of various dynamic approximations. When used with the close coupling technique, it leads to a drastic reduction in the number of equations that have to be solved for either the atom-diatom (Zarur and Rabitz, 1973b), or the diatom–diatom (Zarur and Rabitz, 1974) problems. Another formalism that also aims at a reduction of the size of the computational problems has been proposed by Csanak *et al.* (S-1974) but remains to be tested.

Rabitz and Zarur (S-1974a) extended their earlier calculations of rotational excitation in the He–H_2 system to 1.5 eV, thereby allowing for vibration–rotation excitation. The focus of their study was a comparison of coupling and energetic resonance effects, comparison of effective Hamiltonian and breathing sphere models, and investigation of the energy dependence of the cross sections. They found that the total de-excitation cross sections ($\sigma(0J - 1J')$) at 1.5 eV were dominated by transitions with $\Delta J \geq 2$ and showed that this was due to resonance effects which were enhanced with increasing J. In comparing their cross sections with those of the breathing sphere model they found corresponding total cross sections to be comparable and the differential cross sections (at 1.5 eV) exhibiting similar features. However, they also found that numerous $0J - 1J'$ ($J \neq J'$) cross sections were of the same order of magnitude as the breathing sphere cross sections.

In another paper (S-1974b), these authors made explicit use of this latter result to investigate the vibration rotational excitation of He–H$_2$ over the range 200–700°K. Their relaxation times are in excellent agreement with experimental data, while those obtained with the breathing sphere cross sections are too low by one or two orders of magnitude. In particular, they were able to reproduce the curvature at low temperatures in the experimental relaxation rate. These results imply that further applications of the effective Hamiltonian method could probably lead to feasible tests of the three dimensional classical trajectory models in the very near future. It should be noted that the failure of the breathing sphere model demonstrated in this work is not surprising because only open channels were included. In application of the breathing sphere model to the He–HF system, also restricted to only the open channel cases, Smith *et al.* (S-1974) found that they could not reproduce the low temperature rates without empirical modifications in the potential (cf. Bott, 1971 and Sec. III). It remains to be verified whether resonance effects that are to be expected from coupling in of the closed channels from the higher lying vibrational levels, could lead to improved results for the low temperature rates in both the He–H$_2$ and the He–HF systems.

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Additional note added in proof

A few still more recent results are noted below.

A possible partial explanation of the spread in the room temperature self-relaxation rates of HF and DF reported in the literature (cf. Table VIII) has been discussed by Bott (1974) in terms of gas dynamic corrections to laser-induced fluorescence measurements made in mixed-in-flow (as opposed to pre-mixed) mixtures. However, most of the dilution effect reported by Hancock and Green, and the large values of Blair *et al.* (cf. Sec. III) are still a problem. New results on V–R coupling effects illustrating the inadequacy of simpler theories in hydrogen-helium mixtures below 450°K have been reported by Audibert *et al.* (1974a, b), and for fluorine-helium mixtures in the range 500–1050°K, by Diebold *et al.* (1975). Isotope effects in vibrational relaxation of CO, in line with the trends outlined in Sec. III for other systems, have been reported by Hancock *et al.* (1974).

On the theoretical side, a semiempirical correlation scheme for determining final state energy partitioning in reactive and nonreactive collisions has been developed in the framework of information theoretic concepts with some very stimulating results (e.g., Bernstein and Levine, 1974; Procaccia and Levine, 1975a, b; see also Wilson and Levine, 1974). The range of final vibrational states, i.e., the entire array of detailed rate constants for vibrational energy transfer can, under certain conditions, be characterized by a single parameter. A semiclassical three-dimensional model of nonreactive atom–diatom collisions which does not involve the use of complex trajectories has been discussed by Sorensen (1974); while an extension of the semiclassical S-matrix theory for diatom–diatom problems which examines intermediate state formation has been discussed by Cohen and Alexander (1974). New numerical techniques for handling some problems in S-matrix formalism have also been developed (Kreek and Marcus, 1974; Kreek *et al.*, 1974), and applications of the Gordon algorithm to other systems are being studied (Verter, 1975).

All these and other results, while encouraging, do not alter the central conclusion of this review that the current understanding of vibrational relaxation mechanisms, in the halides in particular, is far from complete, and much, much more work is needed before it will become better. However, because gaseous lasers continue to be an important element of many technologies, rapid progress in this field can be expected.

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