REVIEWS OF MODERN PHYSICS VOLUME 41, NUMBER 1 JANUARY 1969

Survey of Vibrational Relaxation Data for Processes Important in the CO_2–N_2 Laser System*

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Vibrational relaxation data are surveyed in order to provide the rates of vibrational energy transfer for processes important in the CO_2–N_2 laser. A kinetic model is assumed for the vibrational energy transfer into and within the various vibrational modes of the molecules that make up a CO_2–N_2 laser, including the species H_2O, O_2, He, and H_2. Experimental data are assembled and interpreted for the rate constants and the probabilities per collision for the various kinetic processes of the assumed mechanism as a function of temperature. For certain processes, the experimental data are reinterpreted in terms of more recent knowledge of vibrational energy transfer. The data are compared with theoretical calculations and various anomalies in those comparisons are discussed. The significance of the various vibrational energy transfer processes for understanding the operation of the CO_2–N_2 laser are contrasted with the state of knowledge of the rate information.

I. INTRODUCTION

The CO_2–N_2 molecular system has shown considerable promise as a high-power gas laser. An understanding is available of the general mechanism which can produce the population inversion among the vibrational modes of the CO_2 molecules.[1–7] From this mechanism it is clear that a reasonable knowledge of the kinetic rates of energy exchange between the translational and vibrational modes as well as among the vibrational modes of the molecules is necessary for calculating laser power performance and limitations. It is the purpose of this review to survey the literature and compile the available data on the rate processes of interest. Since the electron collision processes and their function in the CO_2–N_2 laser have been discussed by others,[4–7] the emphasis in this paper will be on the heavy particle, vibrational energy exchange reactions. Also, there will be no discussion of the radiative processes in this laser system necessary for a complete detailed description of the laser output. Furthermore, there is no general attempt to evaluate the validity of the various experimental techniques or theories except by the over-all agreement or lack thereof of the data.

Considerable experimental information is available on the rates for the exchange of energy between the translational and vibrational (T–V) modes of a molecule, and a generally useful theory of T–V exchange has been developed.[8] Most of the experimental measurements of T–V rates have been made in pure gases, and less information is available on the efficiency of other collision partners.

For polyatomic molecules or for mixtures of gases exhibiting two or more vibrational modes, vibration–vibration (V–V) energy exchange becomes important. A V–V collisional exchange of energy can occur between the vibrational modes of two different molecules (intermolecular) or between two different vibrational modes of the same molecule (intramolecular). This process may be one of near or exact energy resonance depending upon the frequencies of the modes involved, with any difference in energy being exchanged with translation and/or rotation. Experimental information on the rates of V–V processes is limited in comparison to that available for T–V rates. For this reason, a theory for the V–V process is less developed and less reliable. Theoretical arguments indicate that, in general, a V–V rate is faster than the corresponding T–V process because of the smaller quantum of energy that must be exchanged with the translational mode. Furthermore, sound-dispersion experiments on many polyatomic molecules exhibit a single vibrational relaxation time,[9] indicating that the rate-controlling process for vibrational energy exchange in those molecules is a T–V exchange with one specific mode, and all the other modes of the molecule are equilibrated by rapid inter- and/or intramolecular V–V exchange.

While it is true that the T–V rate for the lower laser level is dominant in controlling gain and power of the CO_2–N_2 laser,[7] both T–V and V–V processes must be considered for a general understanding of the energy transfer within this system.

An important part of any over-all theory of laser operation is the mechanism for energy transfer to and within the states of the various molecules that make up an operating laser. The mechanism that is being assumed in the present paper is described in Sec. II. The status of the various kinetic rates that are needed for this mechanism is discussed in Sec. III. Section IV summarizes the results and provides some general conclusions concerning the status of knowledge of the rates and mechanism and the application of these results to the interpretation of laser performance.

II. MECHANISM

A necessary step in understanding any kinetic system is the formulation of a reasonable model or mechanism for the rate processes to be studied. Unfortunately, there is insufficient knowledge at present to specify with complete confidence the paths by which

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* This work was supported by the U.S. Air Force Avionics Laboratory, Systems Engineering Group, Research & Technology Division, Wright–Patterson Air Force Base, Ohio.

energy flows in as complicated a vibrational system as a gas composed of CO_2 and N_2 molecules. The model chosen here is based in large part on the mechanism proposed by Herzfeld[10,11] for vibrational energy exchange into and within the CO_2 molecule as modified by the inclusion of other species, i.e., N_2, O_2, He, H_2, and H_2O.

The model is illustrated schematically in the energy-level diagram, Fig. 1. Shown as the vertical scale are the energies in wavenumbers ω or temperature $\omega hc/K$ of the first or first few vibrational levels of the four fundamental modes of CO_2 (the symmetric stretching mode ν_1, the doubly degenerate bending mode ν_2, and the asymmetric stretching mode ν_3); the vibrational modes of N_2 and O_2; and the bending mode ν_2 of H_2O.[12] The two other fundamental modes of H_2O, the symmetric stretch ν_1 (3652 cm^{-1}), and the asymmetric stretch ν_3 (3756 cm^{-1}) are too high in energy to be significantly populated at temperatures of interest in this paper, and they are omitted from consideration in the mechanism. Although the temperature range of interest for the CO_2–N_2 laser is limited to a few hundred degrees around room temperature, in order to establish an effective temperature dependence for the kinetic process under discussion, it has been necessary in this survey to utilize as wide a range of data as possible. H_2O, H_2, and He have been included in the mechanism of Fig. 1 because these species have important laser application. O_2 has been included because it can be a constituent of a CO_2–N_2 laser due to the partial decomposition of CO_2 in the electrical discharge.[13] Also, by including O_2, the mechanism and rate data can be used for studies of energy transfer and propagation of 10.6-μ laser radiation in the atmosphere.

The arrows in Fig. 1 indicate the assumed paths for energy transfer into and among the modes. The various processes can be expressed as kinetic reactions as follows:

T–V processes

$$CO_2^*(\nu_2)+M \rightleftarrows CO_2+M+667\ cm^{-1}, \qquad (1)$$

$$N_2^*+M \rightleftarrows N_2+M+2331\ cm^{-1}, \qquad (2)$$

$$O_2^*+M \rightleftarrows O_2+M+1556\ cm^{-1}, \qquad (3)$$

$$H_2O^*(\nu_2)+M \rightleftarrows H_2O+M+1595\ cm^{-1}; \qquad (4)$$

V–V processes (intermolecular)

$$CO_2^*(\nu_3)+N_2 \rightleftarrows CO_2+N_2^*+18\ cm^{-1}, \qquad (5)$$

$$H_2O^*(\nu_2)+CO_2 \rightleftarrows H_2O+CO_2^*(\nu_2)+928\ cm^{-1}, \qquad (6)$$

$$CO_2^*(\nu_3)+H_2O \rightleftarrows CO_2+H_2O^*(\nu_2)+754\ cm^{-1}, \qquad (7)$$

$$N_2^*+H_2O \rightleftarrows N_2+H_2O^*(\nu_2)+736\ cm^{-1}, \qquad (8)$$

$$H_2O^*(\nu_2)+O_2 \rightleftarrows H_2O+O_2^*+39\ cm^{-1}, \qquad (9)$$

$$O_2^*+CO_2 \rightleftarrows O_2+CO_2^*(\nu_2)+889\ cm^{-1}, \qquad (10)$$

$$CO_2^*(\nu_3)+O_2 \rightleftarrows CO_2+O_2^*+793\ cm^{-1}, \qquad (11)$$

$$N_2^*+O_2 \rightleftarrows N_2+O_2^*+775\ cm^{-1}; \qquad (12)$$

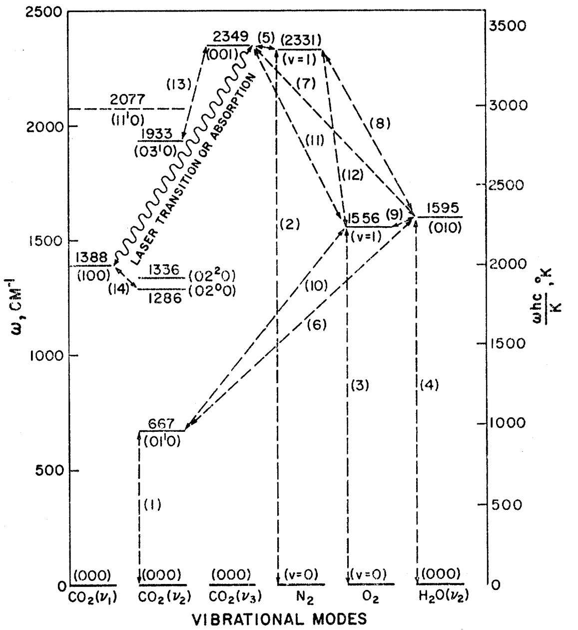

FIG. 1. Vibrational energy-level diagram for the CO_2–N_2–O_2–H_2O molecular system. Shown are the few lowest vibrational levels of the ν_1, ν_2, and ν_3 modes and the combination level $\nu_1+\nu_2$ of CO_2, levels of N_2, O_2, and of the ν_2 mode of H_2O. The arrows indicate the assumed paths for vibrational energy transfer within this system of molecules. The wavy arrow indicates the CO_2–N_2 laser transition at 10.6 μ.

V–V processes (intramolecular)

$$CO_2^*(\nu_3)+M \rightleftarrows CO_2^{***}(\nu_2)+M+416\ cm^{-1}, \qquad (13)$$

$$CO_2^*(\nu_1)+M \rightleftarrows CO_2^{**}(\nu_2)+M+102\ cm^{-1}. \qquad (14)$$

The equation numbers refer to the arrows indicated on Fig. 1; M is any collision partner in the gas—CO_2, N_2, O_2, H_2O, H_2, or He; and the asterisks indicate quanta of vibrational excitation in the given modes. Equations (1)–(14) have all been written in the exothermic direction; the amount of energy that must be absorbed into translational motion is indicated on the right-hand side of the equation. For the basic CO_2–N_2 mixture the mechanism obviously becomes considerably simpler. The laser radiative transition at 10.6 μ occurs between specific rotational levels of modes ν_3 and ν_1 of CO_2 and is indicated schematically as the wavy line on Fig. 1.

Some significant features of this mechanism are as follows:

(i) The T–V process by which energy is exchanged with the vibrational modes of the CO_2 molecule is considered to be Path (1) since the ν_2 mode is the lowest energetically.

(ii) Because of the known Fermi resonance between modes ν_1 and ν_2, Reaction (14) is believed to be very rapid.[10,11] If (14) is rapid enough, modes ν_1 and ν_2 can be considered to be in local equilibrium. Thus, whatever processes affect ν_2 also directly affect the lower laser level ν_1.

(iii) The exchange of vibrational energy between mode ν_2 (plus ν_1) and ν_3 is shown as the intramolecular V–V process (13). Reaction (13) would be closer to energy resonance if it connected ν_3 with the $v=4$ level of mode ν_2 or with the combination level $\nu_1+\nu_2$ (shown in Fig. 1 as the dashed horizontal line between ν_1 and ν_2). These alternative reactions may be expressed as

$$CO_2^*(\nu_3)+M\rightleftarrows CO_2^{****}(\nu_2)+M-204\ cm^{-1}, \quad (15)$$

$$CO_2^*(\nu_3)+M\rightleftarrows CO_2^*(\nu_1+\nu_2)+M+272\ cm^{-1}. \quad (16$$

It may be expected that since Reactions (15) or (16) are closer to energy resonance than (13), they would be faster. Unfortunately, the present experimental data do not allow a definite choice between these alternatives. Further comments concerning these processes will be made in Sec. III under the discussion of experimental data.

(iv) The CO_2 and N_2 molecules are coupled through the rapid near-resonant reaction (5) for which the energy difference of the modes is only 18 cm^{-1}.

(v) H_2O is universally effective as an efficient catalyst in speeding up vibrational relaxation of molecules. Also, H_2O is known to have an extremely fast T–V process (4) for self-excitation. The catalytic effect of H_2O can be due to V–V processes of the type (6)–(9) exchanging energy with the vibrational modes of the other species or due to the efficiency of H_2O as a T–V collision partner in Reactions (1)–(3) and as a collision partner in the V–V reaction (13). Some comparison of these two mechanisms can be made from the available data. There are alternate reactions similar to Process (13) by which H_2O could affect modes ν_1, ν_2, and ν_3 other than (6) or (7). For example, the nearly resonant process

$$CO_2^*(\nu_3)+H_2O\rightleftarrows CO_2^*(\nu_2)+H_2O^*(\nu_2)+87\ cm^{-1} \quad (17)$$

is an attractive alternate reaction for (7).[14] H_2O could also react directly with mode ν_1, i.e.,

$$H_2O^*(\nu_2)+CO_2\rightleftarrows H_2O+CO_2^*(\nu_1)+207\ cm^{-1}, \quad (18)$$

which becomes an alternate process to (6). It is to be noted that (18) is closer to energy resonance than the possible V–V exchange between mode ν_2 of H_2O and the $v=2$ level of ν_2 of CO_2.

It is evident that there are many possible mechanisms and a large number of rates that must be known for a complete specification of the vibrational energy transfer in this molecular system. Fortunately, not all of these Processes (1)–(14) are of equal importance, so that a smaller number of rates need actually be known for calculation of laser power in a particular application. Furthermore, the situation described in Fig. 1 and Reactions (1)–(14) has already been simplified, since many of the combination levels of the CO_2 molecule have been omitted.[11] In the present state of ignorance concerning the details of V–V energy exchange within and between molecules, some simplification is necessary, but it is believed that the mechanism described in Fig. 1 preserves most of the features of vibrational energy exchange important in this problem.

III. STATUS OF RATES OF VIBRATIONAL ENERGY TRANSFER

Experimental measurements of vibrational energy transfer are usually given as the vibrational relaxation time τ, where τ is defined as the exponential time constant for the vibrational mode under study to return to equilibrium conditions after a transient disturbance, e.g., after passage of a sound wave or shock wave through the gas. Data are generally presented as the vibrational relaxation time normalized to 1 atm pressure p, at the experimental temperature T.

The vibrational relaxation of a mixture of two gases A and B is composed of four types of T–V processes:

$$A^*+A\rightleftarrows A+A, \quad (19)$$

$$A^*+B\rightleftarrows A+B, \quad (20)$$

$$B^*+B\rightleftarrows B+B, \quad (21)$$

$$B^*+A\rightleftarrows B+A. \quad (22)$$

If one component, e.g., B, is present in small concentration, then Processes (21) and (22) can be neglected and the experimentally measured relaxation time τ_f is given by

$$\tau_f^{-1}=(\psi/\tau_{AA})+[(1-\psi)/\tau_{AB}], \quad (23)$$

where ψ is the mole fraction of component A. τ_{AA} is the relaxation time of pure A, Reaction (19), and τ_{AB} refers to the relaxation time of a molecule of A in a bath of B-type molecules, Reaction (20). Expression (23) is universally employed to obtain the efficiency of other collision partners for T–V reactions from data on gas mixtures.

For a polyatomic molecule in which the vibrational relaxation occurs by a slow T–V process into a particular mode i with a subsequent equilibration of the vibrational energy among the remaining modes by rapid V–V exchange, the experimentally measured time τ_f is related to the relaxation time τ_i for mode i by[15]

$$\tau_f=\tau_i\sum_j(c_j^{vib}/c_i^{vib}), \quad (24)$$

where c_j^{vib} is the vibrational heat capacity for mode j, and the summation is over all the vibrational modes of the molecule. For example, Relation (24) has been used in analyzing data on vibrational relaxation of CO_2 for Process (1).

When V–V exchange is important in gas mixtures, the vibrational relaxation becomes more complex. The relative rates of all four of the T–V processes are now important as well as the V–V process

$$A^*+B\rightleftarrows A+B^*, \quad (25)$$

In general, the importance of a V–V process for relaxing component A in a binary mixture will depend upon the rate of relaxation of B via T–V Processes (21) and (22) as well as the rate of Reaction (25).

From experimental measurements on binary gas mixtures, it is observed[16] that after an initial time defined by the excitation of B via T–V Process (21) plus (22), the two modes A and B couple and subsequently relax with the same relaxation time τ_f. Two parameters are important for specifying the vibrational relaxation behavior of the gas mixture: α, the fraction of final equilibrium energy in component B when the V–V process couples the two species; and τ_f, the experimentally observed relaxation time for both components after they are coupled.

Using these experimentally derived parameters and the vibrational energy relaxation equations, in principle, the rate for the V–V process can be obtained. For a situation in which the relaxation time of A is controlled by the V–V coupling to B, i.e., $\tau_f \ll \tau_{AA}+\tau_{AB}$, the final result becomes[16]

$$\tau_{AB}{}^e = (1-\psi)\left(\frac{[1-\exp(-\Theta_A)]}{[1-\exp(-\Theta_B)]}-(1-\alpha)\right)\tau_f; \quad (26)$$

$\tau_{AB}{}^e$ is the relaxation time for A via the V–V process (25), and $\Theta = hc\omega/KT$.

Expression (26) can be used with the necessary data on α and τ_f to obtain the rate of the V–V process, $\tau_{AB}{}^e$. In this section, analysis of data via a V–V transfer mechanism is attempted, although measurements of α are not always available. To obtain some bounds on the rate in these situations, it can be assumed that either $\alpha=1$ (weak coupling) or $\alpha=0$ (strong coupling.)

Although the experimental measurements of τ usually relate to the relaxation of a set of vibrational levels (i.e., a mode of the molecule), the data can be analyzed for the rate of the specific transition between the lowest involved levels by assuming that (i) the modes can be approximated as harmonic oscillators, (ii) the transitions between levels are given by the Landau–Teller selection rules[17] [a consequence of (i)], and (iii) throughout the relaxation the levels maintain a Boltzmann distribution.[18] The fundamental kinetic quantity frequently derived from the relaxation time is P, the probability per collision of a T–V or V–V exchange process. Under the assumptions (i)–(iii) above, the probabilities become

for a T–V process

$$P(\mathrm{A}i(1\rightarrow 0),\mathrm{B}) = \{\tau_{AB}Z_{AB}[1-\exp(-\Theta_{Ai})]\}^{-1}, \quad (27)$$

for a V–V process

$$P(\mathrm{A}i(1\rightarrow 0),\mathrm{B}j(0\rightarrow 1)) = (\tau_{AB}{}^e Z_{AB})^{-1}, \quad (28)$$

where $P(\mathrm{A}i(1\rightarrow 0),\mathrm{B})$ is the probability that in a collision between A and B, mode i of A loses one quantum of vibrational energy from the first vibrational level (1→0) to the translational mode.* For the V–V probability $P(\mathrm{A}i(1\rightarrow 0),\mathrm{B}j(0\rightarrow 1))$, the energy lost by the ith mode of A(1→0) is transferred to the jth mode of B(0→1) and to translation, if necessary for energy conservation. For more complex reactions such as (13) or (14), more than one quanta per mode may be exchanged in a collision. Also, for intramolecular processes, both modes i and j are in the same molecule, and the specification of an additional inert collision partner B is necessary. In quoting probabilities of energy transfer per collision, it is customary to define P for the exothermic reaction. The collision number Z_{AB} is the number of gas kinetic collisions per second for an A molecule in a gas of B molecules at 1 atm pressure and temperature T and is given by

$$Z_{AB} = (8\pi KT/\mu_{AB})^{1/2}\sigma_{AB}{}^2 N_B, \quad (29)$$

where μ_{AB} is the reduced mass of the collision pair, σ_{AB} is the average collision diameter for the molecules given by $\sigma_{AB}=\frac{1}{2}(\sigma_A+\sigma_B)$ (where the individual collision diameters are taken from the Lennard-Jones potential),[19] and N_B is the number density of B molecules at 1 atm pressure at temperature T given by $L(273/T)$, where L is Loschmidt's number.

In this paper we have decided to present the experimental data in terms of kinetic rate constant k, in cubic centimeters per particle per second where

$$k(\mathrm{A}i(1\rightarrow 0),\mathrm{B}) = (\tau_{AB}N_B)^{-1}$$
$$= P(\mathrm{A}i(1\rightarrow 0),\mathrm{B})[1-\exp(-\Theta_{Ai})]Z_{AB}/N_B, \quad (30)$$
$$k(\mathrm{A}i(1\rightarrow 0),\mathrm{B}j(0\rightarrow 1)) = (\tau_{AB}{}^e N_B)^{-1}$$
$$= P(\mathrm{A}i(1\rightarrow 0),\mathrm{B}j(0\rightarrow 1))Z_{AB}/N_B. \quad (31)$$

It can be seen that k and P are related by

$$k_{TV} \propto PT^{1/2}[1-\exp(-\Theta/T)] \quad (32)$$

or

$$k_{VV} \propto PT^{1/2}. \quad (33)$$

Therefore, in the subsequent graphs of experimental data, additional scales as shown above in Eqs. (32) and (33) and a scale of $T^{1/2}$ have been included to allow for an easy conversion between rate constant k and probability per collision P.

In most of the following compilations of data for the various kinetic processes, graphs of k (and P) are shown as a function of temperature as $\bar{T}^{-1/3}$. This temperature scale is used because theoretical considerations indicate that log P, hence k, is proportional to $\bar{T}^{-1/3}$ for many processes. $\bar{T}$ is the experimental translational temperature in degrees Kelvin for isothermal studies where the temperature perturbation is small, e.g., in sound dispersion and absorption. In noniso-

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* The above notation has been used throughout the text for convenience. However, in the figures the more standard notation

$$P(\overset{10}{\mathrm{A}i}, \underset{01}{\mathrm{B}j})$$

has been retained.

TABLE I. Molecular parameters used in data analysis and theoretical calculations.

Molecule	Molecular weight	σ (Å)	ϵ/k (°K)	α_N (cm$^3\times10^{25}$)	μ_P (D)
CO_2	44	3.947	202	26.5	···
N_2	28	3.714	85.7	17.6	···
He	4	2.576	10.22	···	···
H_2O	18	2.824	230.9	···	1.831
H_2	2	2.928	37.0	7.9	···
O_2	32	3.608	92.6	16.0	···

thermal shock-tube experiments, $\bar{T}$ is the arithmetic average of the gas temperature before and after vibrational relaxation.

The usual analysis of shock-tube experiments assumes that τ is constant throughout the nonisothermal relaxation region, and an average temperature and density ρ are used to normalize τ. Johannesen and his co-workers[20] have criticized these analyses and derived an exact procedure which determines τ at the local conditions of T and ρ throughout the relaxation region behind the shock. Blythe[21] has compared this exact method with the approximate analyses and, for the gases and the temperature range of interest in this study, the differences between the two methods are of the order of 10%–20%. In this paper no attempt will be made to resolve such discrepancies since the general scatter of shock-tube data is generally much larger than 20%. For a more complete discussion of this problem, the reader is referred to the papers by Johannesen and Blythe.

In a few cases, authors have been vague as to the definition of the temperature or density normalization used to present their data, so that there is some unavoidable ambiguity in these compilations. The following additional notations are used: $C\equiv CO_2$, $N\equiv N_2$, $O\equiv O_2$, $H\equiv H_2O$, $H_2\equiv H_2$, and $He\equiv He$, and the vibrational modes are designated by numbers, e.g., $C2\equiv$ mode ν_2 of CO_2.

Comparison of the experimental data with a theoretical calculation is usually made in order to provide some criteria for accessing the validity of the data or its temperature dependence or, where limited data are available, to provide a temperature dependence. The theory generally used for this purpose is based on the work of Schwartz, Slawsky, and Herzfeld. Since this theory is adequately described in detail elsewhere,[8,22,23] no further description will be presented here. The necessary molecular potential parameters needed for these calculations are obtained from the constants of the Lennard-Jones 6–12 potential[19] and are listed in Table I for the molecules of interest in this survey.

1. $CO_2^*(\nu_2)+M\rightleftarrows CO_2+M+667$ cm^{-1}

(a) Of all the processes (1) through (14), the most extensively studied experimentally is the vibrational relaxation of mode ν_2 of CO_2 by CO_2–CO_2 collisions [Reaction (1a)]. Figure 2 shows the experimental data for this process for 36 separate experiments. The measurements at and around room temperature are predominately those using sound absorption and/or dispersion, although a few measurements made with the impact tube and spectrophone technique are included. There is one sound absorption experiment which spans the range 300°–1300°K. The high-temperature data come primarily from shock-tube experiments utilizing a variety of diagnostic techniques: schlieren, interferometer, electron beam, and infrared emission.

Although there are considerable data for Reaction (1) on Fig. 2, there is obviously a large scatter. Cottrell and McCoubrey[24] have reviewed the lower-temperature experiments and conclude that the most probable value of τ at room temperature is 6–7 μsec·atm

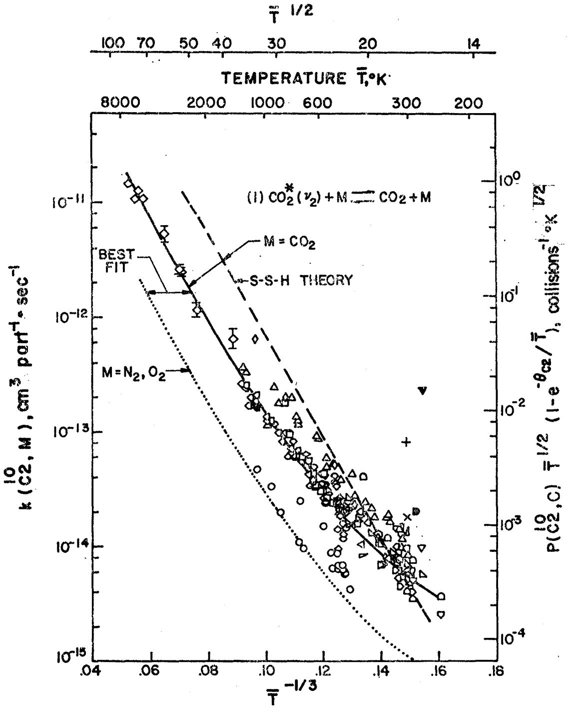

FIG. 2. Experimentally derived rate constants $k(C2(1\rightarrow0),\ C)$ and $k(C2(1\rightarrow0),\ N)$ for vibrational relaxation of mode ν_2 of CO_2 by CO_2–CO_2 collisions and collisions with other partners, as functions of temperature $\bar{T}$. The solid line is the best fit to the CO_2 data. The dotted line is the suggested fit to the N_2 and O_2 data. The dashed line is a calculation of $k(C2(1\rightarrow0),\ C)$ by means of the Schwartz–Slawsky–Herzfeld (S–S–H) theory of vibrational energy transfer. The sources of the data are as follows. (1a) sound absorption and dispersion: ◁ Ref. 40, ⌂ Ref. 46, ▽ Ref. 48, ⬭ Ref. 53, ⬡ Ref. 55, ◺ Ref. 99, ∩ Ref. 100, ◿ Ref. 101, ◿ Ref. 102, ◿ Ref. 104, ▽ Ref. 105, ◇ Ref. 106, ▷ Ref. 107, ◻ Ref. 108, ◺ Ref. 109, ▽ Ref. 110, ⬠ Ref. 111, ▷ Ref. 112, ⬯ Ref. 113, △ Ref. 114, ◁ Ref. 117, ▽ Ref. 118, ▱ Ref. 119; (1a) impact tube: ▽ Ref. 103, × Ref. 115, ▽ Ref. 116; (1a) spectrophone: + Ref. 38, ⬯ Ref. 39; (1a) laser fluorescence: ◁ 90; (1a) shock tube: ◇ Ref. 25, △ Ref. 26, ○ Ref. 30, □ Ref. 32, — Ref. 33, ◇ Ref. 34, ⬠ (ν_2) ⬠ (ν_3) Ref. 35; (1b) sound dispersion: ▼ Ref. 118, ● Ref. 41.

$[k(C2(1\rightarrow 0),\ C)=5-6\times 10^{-15}\ \mathrm{cm^3\ part^{-1}\cdot sec^{-1}}]$. To establish a reasonable temperature dependence from the data, the higher-temperature shock-tube results must be considered. The experiments around room temperature directly measure the relaxation of mode ν_2 since this is the only mode appreciably populated. At higher temperatures the other modes of CO_2 become excited and the interpretation of the measurement is more difficult. There is considerable disagreement among the shock-tube experiments concerning which mode or modes are involved in the vibrational relaxation. Some investigators claim to measure the relaxation of ν_2, $\nu_2+\nu_1$, ν_3, or the sum of all the modes. In order to present a consistent set of data on Fig. 2, some reinterpretation of the shock-tube experiments has been necessary.

Smiley and Winkler[25] made the first shock-tube measurement of the vibrational relaxation of CO_2 from 370°–1050°K using an optical interferometer to measure the density change behind the shock. In the interpretation of their data, they did not distinguish between the various modes of CO_2. More recent work (to be discussed) indicates that the various modes of CO_2 apparently relax together. Hence the Smiley and Winkler data are interpreted as yielding the relaxation of the sum of all the modes, and the rate for Process (1) has been determined from their data using Relation (24). Smiley and Winkler also admit that their experiment may have had impurity problems, hence the fact that their data are generally high (fast rate) on Fig. 2 is understandable.

The next investigation of CO_2 relaxation was by Griffith, Brickl, and Blackman[26] over the temperature range of 300°–1270°K, also using an interferometer. This paper invoked a great deal of controversy, since the final "equilibrium" density measured did not correspond to full equilibrium but only to the excitation of the bending modes. The data were interpreted as yielding the relaxation times for the bending mode only. To the present authors' knowledge, this result has never been repeated. Later experiments by Johannesen, Zienkiewicz, Blythe, and Gerrard[27] gave a final density which agreed with that based on equilibration of all the modes. Further critical examination and comparison[28] of the two sets of data have not resolved this discrepancy. Since the Griffith *et al.* result has not been repeatable, it must be considered to be in error. The relaxation times obtained by Griffith *et al.*, if they are to be considered valid at all, must refer to the sum of all the modes, and their data have been converted to a rate for Process (1) by means of Relation (24).

In a later communication, Greenspan and Blackman[29] claimed to have observed three separate relaxation times corresponding to the three modes of CO_2. However, the details of this study were never published, and, in view of the more recent work, these data are believed to be in error and are not considered further.

Daen and deBoer[30] measured the relaxation of CO_2 from 460°–1100°K using an integrated-schlieren technique which also monitors the density change behind the shock. The procedure for the reduction of their data to relaxation times is sketchy but indicates that no correction was made to account for the temperature change occurring in the relaxation zone behind the shock. Since the other shock-tube data shown on Fig. 2 do use some correction procedure, albeit approximate, it was decided to apply the Blackman constant-enthalpy correction[21,31] to the Daen and deBoer data as well as to adjust the times for Process (1). The data shown on Fig. 2 have been corrected accordingly, and these data are consistently low compared to the other results.

Witteman[32] has also measured the vibrational relaxation of CO_2 using the integrated-schlieren technique from 440°–816°K. He has used the initial slope of the density change behind the shock to determine the rate for Process (1). The initial slope is with sufficient accuracy a direct measure of Process (1) at the local conditions of T and ρ existing just behind the shock. However, there is a shock-front curvature effect that must be accounted for. Whether Witteman has suitably corrected for this is difficult to judge, but his data have been plotted directly on Fig. 2 as a measure of Process (1).

Johannesen and co-workers[27] have used an interferometer to measure the relaxation of CO_2 from 370°–1200°K. They use an exact method to analyze their data which results in the relaxation time being determined continuously throughout the relaxation region behind the shock. They observe only one relaxation time, indicating that all modes relax together. In a later paper, Zienkiewicz and Johannesen[33] have interpreted their data in terms of Process (1), and these are the results plotted on Fig. 2. These data are shown as line segments on Fig. 2 because the analytic method gives τ as a function of T for each run. In principle, these line segments should fall on a single curve if τ has a unique temperature dependence. The fact that they do not quite line up has been discussed extensively by Johannesen and his colleagues in a series of papers.[20,21,27,28,33] Whether this result is an experimental artifact or suggests that the relaxation time depends upon the departure from equilibrium is at present not resolved.

Two shock-tube experiments that provide information on the coupling of the modes of CO_2 are those due to Camac[34] and Weaner, Roach, and Smith.[35] In both experiments, simultaneous measurements are made of the total density change behind the shock, using either an electron-beam technique (Camac) or an optical interferometer (Weaner *et al.*), and the infrared emission from mode ν_3 at 4.3 μ. Over the temperature range of these experiments, 450°–6000°K, most of the vibrational heat capacity is due to modes $\nu_1+\nu_2$, and the density measurements determine the relaxation times of these modes. The infrared emission yields a direct measurement of the ν_3 relaxation time. Both experiments show that within the scatter of the data the relaxation times for modes $\nu_1+\nu_2$ and ν_3 are identical, indicating no substantial de-coupling of the modes of CO_2 from 450°–6000°K. The data of Weaner *et al.* for both $\nu_1+\nu_2$ and ν_3 are shown on Fig. 2.

Hurle and Gaydon[36] have measured the vibrational relaxation of CO_2 behind shock waves using the sodium-line-reversal technique. They interpret their data as exhibiting vibrational relaxation and dissociation of CO_2. Only three data points of vibrational relaxation times are given in their note; these indicate a k of $6.6-11\times10^{-15}$ cm^3 part$^{-1}\cdot$sec^{-1} around 2500°K. This result is obviously not in agreement with the general trend of the data on Fig. 2. Hurle and Gaydon recognize this fact and suggest that their longer times indicate a separate and slower relaxation time for mode ν_3. However, in view of the results of Camac and Weaner *et al.* which indicate that the modes of CO_2 relax together in the temperature range of Hurle and Gaydon's experiment, it is felt that the latter results are not a measurement of ν_3 vibrational relaxation. The interpretation of the sodium-line-reversal temperature as a vibrational temperature is dependent upon the excitation rate of sodium by the vibrational degree of freedom. Perhaps in CO_2 this excitation rate is not as fast as in other gases, such as N_2, where the technique seems to measure the vibrational temperature.

One further comment can be made concerning the vibrational relaxation of the various modes of CO_2. The spectrophone[37] is potentially a powerful technique to measure the vibrational relaxation time of individual modes of polyatomic molecules. However, the data are difficult to interpret, and the results of the technique are still somewhat controversial. Slobodskaya[38] has recently used the spectrophone to measure the relaxation times of modes ν_2 and ν_3 in pure CO_2 at room temperature. Her results yield $k(C2(1\rightarrow0),C)=7.9\times10^{-14}$ cm^3 part$^{-1}\cdot$sec^{-1}. As is seen, this result is not in agreement with the sound dispersion data of Fig. 2. On the other hand, Cottrell, Macfarlane, and Read[39] have also investigated the relaxation of CO_2 with the spectrophone and conclude that their data are consistent with a $k(C2(1\rightarrow0),C)$ of 6.0×10^{-15} cm^3 part$^{-1}\cdot$sec^{-1}, in excellent agreement with the sound-dispersion data.

Although the question is not completely closed, the sum total of all the experimental evidence indicates that from 300°–6000°K the vibration relaxation of modes ν_1 plus ν_2 and ν_3 of CO_2 are the same to within a factor of 2.

The solid curve on Fig. 2 has been freely drawn through the data to indicate the present authors "best fit" for the vibrational relaxation time of mode ν_2 of CO_2 for CO_2–CO_2 collisions. This curve was passed through the highest concentration of data points in the temperature range of 300°–700°K consistent with the high temperature data of Camac. At 300°K the curve gives a value of $k=5.5\times10^{-15}$ cm^3 part$^{-1}\cdot$sec^{-1} which is in close agreement with the result proposed by Cottrell and McCoubrey[24] as the most probable value. Also the recent ultrasonic data of Carnevale, Carey, and Larson[40] spanning the temperature range of 300°–1300°K are in good agreement with this fit.

Also shown as the dashed line is a calculation of $k(C2(1\rightarrow0),C)$ based on the Schwartz–Slawsky–Herzfeld (S–S–H) theory of vibrational energy transfer.[11] This theoretical result exhibits the temperature dependence of the data but predicts a larger rate constant by a factor of about 2 to 5.

(b) There is considerably less information on the effect of other collision partners on Process (1). For CO_2–N_2 laser calculations, an important collision partner is N_2 [Reaction (1b)]. Two old sound-dispersion experiments of limited extent indicate that N_2 is more efficient than CO_2 in deactivating mode ν_2. The more accurate of these two measurements[41] yields a value of 2.0×10^{-14} cm^3 part$^{-1}\cdot$sec^{-1} for $k(C2(1\rightarrow0),N)$, at $T=291$°K. This value is about three times larger than the corresponding value for $k(C2(1\rightarrow0),C)$ as is seen from Fig. 2.[42] Unpublished sound-dispersion measurements of Henderson and Shelley[43] indicate that at $T=323$°K, N_2 is about as efficient or slightly less efficient than CO_2 for Process (1). From the S–S–H theory, one calculates that $k(C2(1\rightarrow0),N)\cong 3k(C2(1\rightarrow0),C)$.

However, more recent results obtained from operating parameters of the CO_2–N_2 laser[44] suggest that N_2 may be less efficient than CO_2, perhaps by a factor of 10 to 20. These results are also consistent with the fact that Ar is known to be about 3–10 times less efficient than CO_2 in Process (1), and that Ar and N_2 are about equally efficient in deactivating mode ν_3 of CO_2.[7,45] Based on these more recent experimental data, the suggested rate for Process (1) is revised to make $k(C2(1\rightarrow0),N)\sim 0.2k(C2(1\rightarrow0),C)$ where $k(C2(1\rightarrow0),C)$ is obtained from the curve fit of Fig. 2. Since there are no experimental data on the temperature dependence of $k(C2(1\rightarrow0),N)$, the temperature dependence of $k(C2(1\rightarrow0),C)$ is used. It should be emphasized that the rate for Process (1) with $M\equiv N_2$ is not well known and further experimental measurements of this rate and its temperature dependence are desirable.

(c) There is only one experimental measurement of the efficiency of O_2 in Process (1). This sound-absorption experiment of Van Itterbeek, deBruyn, and Mariëns[46] was interpreted as showing that O_2 had essentially zero efficiency in exciting mode ν_2 of CO_2 at $T=300$°K. This result is hard to believe; one would expect that N_2 and O_2 would be similar in their behavior. However, for most CO_2–N_2 laser applications, as long as O_2 is not considerably more efficient than N_2, the rate of Process (1) for N_2 will dominate that for O_2. Because of a lack of more definitive information, it is suggested that $k(C2(1\rightarrow0),O)=k(C2(1\rightarrow0),N)$ both in magnitude and temperature dependence.

Further comments concerning other possible $CO_2(\nu_2)$–O_2 processes will be made in Reactions (3) and (10).

(d) H_2O is known to significantly reduce the vibrational relaxation time of mode ν_2 of CO_2 [Reaction (1d)]. Shown on Fig. 3 are the rate data for CO_2–H_2O from 12 experiments covering the temperature range 291°–673°K. All these data were obtained with sound dispersion and/or absorption except one measurement using a pulsed-laser amplifier technique. These rates are quite large, e.g., values greater than 10^{-11} cm^3 $part^{-1}\cdot sec^{-1}$ were obtained at room temperature. Also, unlike the previous data for CO_2–CO_2, the rate constants for CO_2–H_2O decrease with increasing temperature.

This temperature dependence is not explained on the basis of the S–S–H theory. Widom and Bauer[47] have qualitatively explained this phenomenon as due to the "chemical affinity" between CO_2 and H_2O. The compound H_2CO_3, carbonic acid, is known to exist in solution. The result of the Widom and Bauer calculation is shown as the dashed line on Fig. 3. This calculation has already been adjusted slightly in magnitude by Widom and Bauer to agree with the data of Eucken and Nümann.[48] This calculation does not give a rate constant decreasing with increasing temperature as shown by the data.

Marriot[49] has also calculated the vibrational relaxation of CO_2 by H_2O as a T–V process including the coupling between the various modes of CO_2. No chemical affinity effects have been included in this calculation, but some effects arising from the dipole moment of the H_2O molecule have been included in the interaction potential. However, his final results are not directly compared to the experimental τp data, although reasonable agreement is claimed.

Also, since H_2O is a hydridelike molecule, vibration–rotation (V–R) energy exchange could be important for the CO_2–H_2O interaction. It has been pointed out by Cottrell, Dobbie, McLain, and Read[50] and Moore[51] that for collisions involving molecules containing hydrogen atoms, vibration–rotation energy exchange may be important. Due to the high rotational velocity of molecules containing light atoms, collisions involving the rotational motion of one molecule and the vibrational motion of the other molecule can be non-adiabatic and lead to V–R energy exchange. It is an experimental fact that the vibrational relaxation times of polyatomic molecules containing many hydrogen atoms are abnormally fast compared to like molecules without hydrogen, although the vibrational frequencies of the hydridelike molecules are generally larger.

Moore[51] has presented a simple theory of V–R exchange. The major effect of the V–R collisions is exhibited through a decrease in the effective reduced mass of the collision pair. This change in reduced mass tends to increase the rate and to decrease the temperature dependence. Moore's theory has had success in correlating the vibrational relaxation times of a wide variety of hydridelike, polyatomic molecules. However, Moore has pointed out that his theory is more applicable for collisions involving an asymmetric rotor, e.g., diatomics involving one hydrogen.

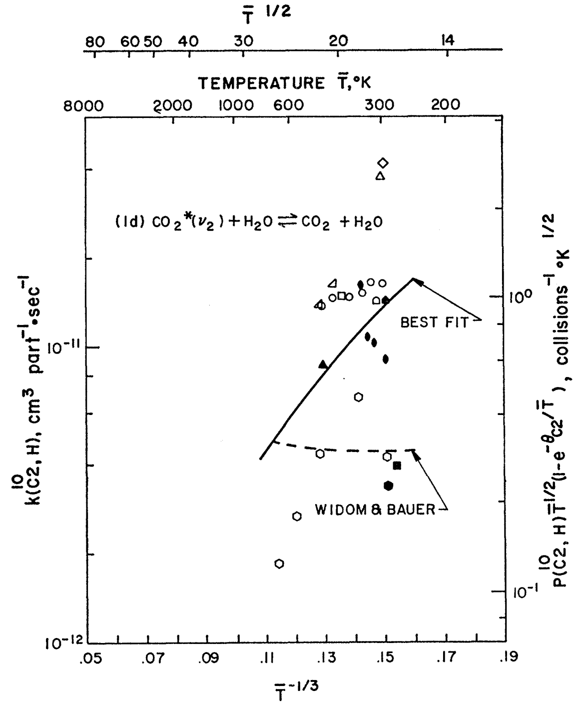

FIG. 3. Experimentally derived $k(C2(1\rightarrow0), H)$ as a function of T. The solid line is the best fit to the data. The dashed line is a theoretical calculation of $k(C2(1\rightarrow0), H)$ by Widom and Bauer.[47] Sources of data—sound absorption and dispersion: ⬢ Ref. 46, ⬡ Ref. 48, ○ Ref. 52, ■ Ref. 118, ☗ Ref. 100, ⬮ Ref. 112, ◺ Ref. 119, ⌓ Ref. 120, ◇ Ref. 121, □ Ref. 122; laser fluorescence: △ Ref. 90; shock tube: ▲ Ref. 25.

A calculation of the V–R probability for Reaction (1d) using Moore's formulation leads to values that are not in agreement with the data of Fig. 3 and to a temperature dependence similar to the S–S–H calculation. Therefore, no direct comparison of the V–R theory with the data is shown, but the influence of V–R exchange in collisions between CO_2 and H_2O should be recognized.

The correct calculation of the vibrational relaxation of mode ν_2 of CO_2 by H_2O would appear to be very complex. The solid line on Fig. 3 is suggested as the best fit to these data. This fit attempts to average the experimental results of Eucken and Nümann and Lewis and Lee.[52]

The effect of H_2O on $CO_2(\nu_2)$ as a V–V exchange process will be discussed under Reaction (6).

(e) Data for Process (1) for CO_2–He collisions [Reaction 1(e)] are shown on Fig. 4. There are data from six experiments utilizing the technique of sound absorption and/or dispersion and one experiment from the pulsed laser amplifier covering the temperature range of 291°–685°K. The solid line on Fig. 4 is, again,

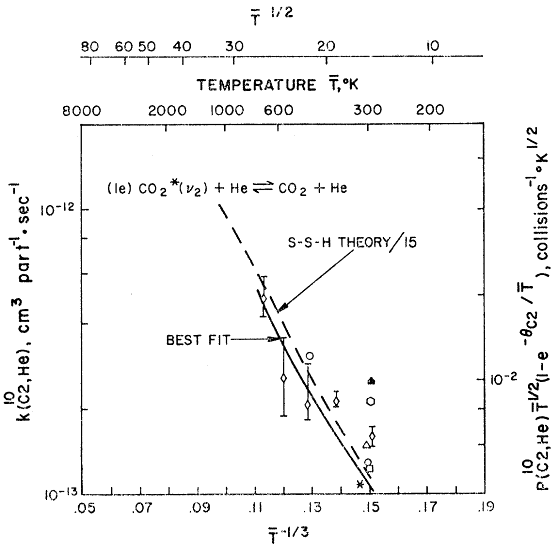

Fig. 4. Experimentally derived $k(C2(1\rightarrow0), He)$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation adjusted to the data by dividing by 15. Sources of data—sound absorption and dispersion: ⬡ Ref. 48, ✳ Ref. 53, ⬟ Ref. 100, ◊ Ref. 106, □ Ref. 123, ○ Ref. 124; laser fluorescence: △ Ref. 90.

the best fit to these data. In constructing this line, more weight has been given to the smallest value of k. In vibrational relaxation experiments, a major source of systematic error is the presence of impurities in the gas which shorten the measured times. Therefore, the smallest rate constants are usually considered more reliable.

Two features of Fig. 4 are to be noted. First, it can be seen by comparing Figs. 2 and 4 that He is a much more efficient collision partner than CO_2 or N_2 for deactivating mode ν_2. This result is in accordance with theory and is known as the mass effect, i.e., the smaller reduced mass of the CO_2–He pair results in more nonadiabatic collisions. The use of He to increase power in the CO_2–N_2 laser arises partly from the high efficiency of He in deactivating the lower laser level via Process (1). Second, it can be seen that the data of Fig. 4 exhibit much less temperature dependence than Fig. 2. This result is also due to the mass effect; the nonadiabatic collisions are less temperature dependent.

A theoretical calculation results in values of $k(C2(1\rightarrow0), He)$ much larger than the data of Fig. 4.[53] The dashed line on Fig. 4 is a calculation by means of the S–S–H theory which has been matched in magnitude to the data by dividing by a factor of 15. It is observed that the theoretical temperature dependence closely matches the best fit to the data. Therefore, the adjusted theory is considered an equally good fit to the data.

(f) Data for Process (1) for CO_2–H_2 collisions [Reaction 1(f)] are shown on Fig. 5. Five experiments involve the technique of sound absorption and/or dispersion and one involves the pulsed-laser amplifier, and these data cover the temperature range 291°–682°K. As can be seen, H_2 is also an efficient collision partner for deactivating the lower laser level; indeed, more efficient per collision than He by about a factor of 10. This result is in qualitative agreement with the mass effect predicted by the S–S–H theory. However, Fig. 5 indicates very little, if any, temperature dependence for $k(C2(1\rightarrow0), H_2)$. The theoretical temperature dependence based on the S–S–H theory is indicated by the dashed line on Fig. 5. This calculation has been divided by a factor of 2.5 to adjust the magnitude to the experimental data.

Marriot[54] has also calculated the probability for Reaction (1f) considering only T–V processes but including the coupling between all the vibrational states of CO_2. This calculation yields relaxation times that have a temperature dependence which is more in agreement with the data but smaller by an order of magnitude. It is obvious that a completely satisfactory theory of the vibrational relaxation of $CO_2(\nu_2)$ by H_2 is still lacking.

To obtain a best fit to the probability data of Fig. 5, the most recent result due to Winter[55] has been given most weight. This assumption leads to the solid line shown on Fig. 5.

2. $N_2^* + M \rightleftarrows N_2 + M + 2331\ cm^{-1}$

(a) The vibrational relaxation data for pure N_2 are shown on Fig. 6. This process has been primarily

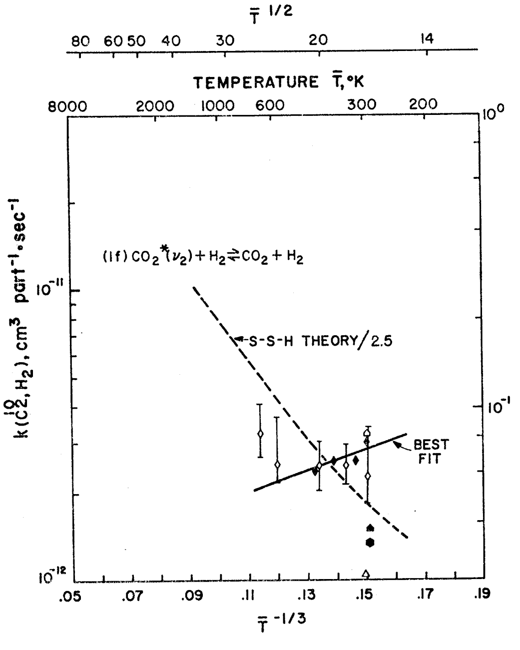

Fig. 5. Experimentally derived $k(C2(1\rightarrow0), H_2)$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation adjusted to the data by dividing by 2.5. Sources of data—sound absorption and dispersion: ⬢ Ref. 46, ◆ Ref. 55, ⬟ Ref. 100, ◊ Ref. 106, ⌂ Ref. 121; laser fluorescence: △ Ref. 90.

studied at high temperatures, and except for one impact tube and two sound-velocity experiments, all the data are from shock tubes. The best-fit line on Fig. 6 is the solid line normalized to the high temperature (greater than 1200°K) data proposed by Millikan and White,[56] who have made a comparison similar to Fig. 6. This fit ignores the low-temperature results. There is no theoretical reason for expecting a significant change in slope of k at the lower temperatures. Furthermore, if the high-temperature fit is extrapolated into the low-temperature regime, a very slow rate constant is predicted which is several orders of magnitude smaller than the low-temperature data shown on Fig. 6. For such long relaxation times, the low-temperature experiments would be very susceptible to unavoidable impurity effects. In fact, Huber and Kantrowitz[57] state that their N_2 could contain as much as 0.05% H_2O and 0.25% CO_2. Such a concentration of polyatomics can lead to the experimental results shown on Fig. 6 for their data.[16]

The sound-velocity measurement of Shilling and Partington[58] at 1270°K is to be considered just an estimate[59,60] and hence little significance should be attached to that result. Of all the low-temperature experiments, the result of Lukasik and Young,[60] using an acoustical resonant cavity, would appear to be the most reliable. Why these data do not agree with an extrapolation of the higher-temperature results is not readily apparent, but perhaps the impurity concentration stated by Lukasik and Young ($\leq 0.005\%$) is too optimistic.

The shock-tube results appear to be reliable and, as can be seen from Fig. 6, the agreement between the various investigations is excellent. Hurle[61] has stated that the earlier measurements of Gaydon and Hurle[62] were analyzed incorrectly and that the corrected results are in better agreement with the trend of the other shock-tube results. Appleton[63] has recently presented the results of a shock-tube study of the vibrational relaxation of N_2 using ultraviolet absorption over the temperature range 3000°–9000°K. From 3000° to 5500°K his results are in close agreement with other shock-tube investigations. Above 5500°K, Appleton observes that the relaxation time decreases during the approach to equilibrium behind the shock. He presents his data as line segments showing the variation of τ for each run. Because of the difficulty of reproducing Appleton's data on the k plot of Fig. 6 with its compressed scale, we have chosen to plot average values obtained from his results. Since the variation of τ during each run is within $\pm 15\%$ this approximation appears justified for the present survey. As can be seen from Fig. 6, Appleton's data presented in this manner do not deviate appreciably from the straight-line fit. The significance of Appleton's more detailed observations at high temperature needs further study. The dashed line on Fig. 6 is a calculation of $k(N(1\rightarrow 0), N)$ based on the S–S–H theory.

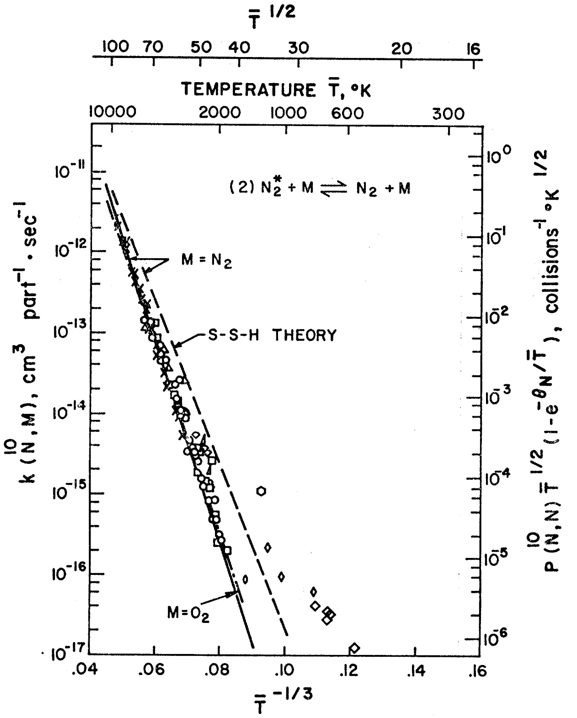

FIG. 6. Experimentally derived $k(N(1\rightarrow 0), N)$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dash-dot line is the Millikan and White[65] correlation for $k(N(1\rightarrow 0), O)$. The dashed line is a theoretical calculation of $k(N(1\rightarrow 0), N)$. Sources of data—sound absorption and dispersion: ⬡ Ref. 58, ◊ Ref. 60; impact tube: ◇ Ref. 57; shock tube: △ Ref. 31, ○ Ref. 56, □ Ref. 61, ⬠ Ref. 62, × Ref. 63, ◺ Ref. 83, ⏢ Ref. 125, 0 Ref. 126.

(b) There appear to be limited experimental data on the efficiency of CO_2 [Reaction (2b)] as a catalyst for Process (2). Henderson[64] has reported a sound-absorption measurement that shows the CO_2 molecule as several hundred times more efficient than N_2 in relaxing N_2 at 476°K. This result is surprising since CO_2 and N_2 show similar efficiencies for other processes, and since theoretically one expects that $k(N(1\rightarrow 0), N) \approx 7k(N(1\rightarrow 0), C)$ at 1000°K. However, Henderson does not obtain the correct relaxation time for "pure" N_2 and recognizes the possible effect of impurities in his experiments. If his measurement of this high efficiency of CO_2 is reliable, it may indicate that the process responsible involves V–V transfer and not the T–V process (2b). However, unless CO_2 is an abnormally efficient catalyst, the energy transfer by Process (2) for CO_2 as a partner will be generally unimportant for present laser applications.

(c) There are no direct experimental measurements on the efficiency of O_2 for Process (2). However, based on the correlation of Millikan and White[65] for diatomic molecules, one expects that O_2 is similar to N_2. Using the Millikan and White correlation scheme, which provides a scaling law similar to the S–S–H theory, the value of $k(N(1\rightarrow 0), O)$ has been determined from

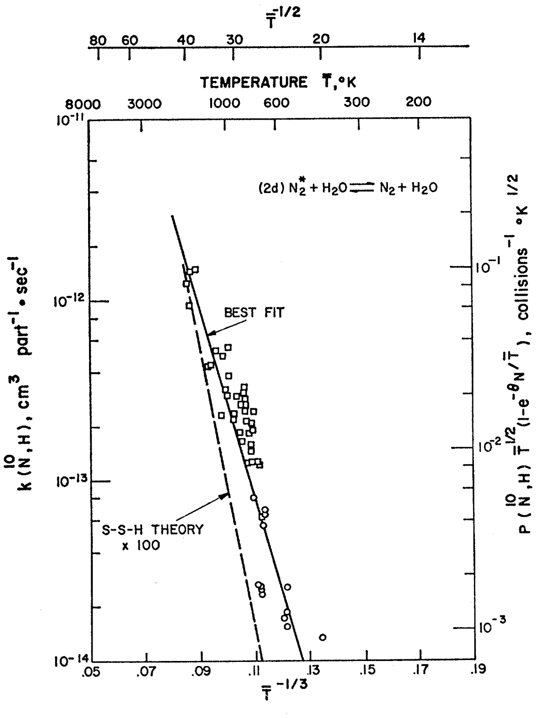

Fig. 7. Experimentally derived $k(N(1\rightarrow0), H)$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation multiplied by 100. Sources of data—impact tube: ○ Ref. 57; shock tube: □ Ref. 66.

the pure-N_2 data and is shown in Fig. 6 as the dot-dashed line.

(d) Analogous to the results for $CO_2(\nu_2)$, H_2O is known to reduce the relaxation time of N_2 [Reaction (2d)]. However, only two experiments have measured this rate. The rate data from the impact-tube experiment of Huber and Kantrowitz[57] are shown on Fig. 7. The total temperature range of the data is 413° to 761°K. Also shown on Fig. 7 are unpublished data by the present authors on shock heated CO_2–N_2–H_2O mixtures.[66] These data have been analyzed for the rate of the T–V process (2d) and cover the temperature range 700°–1600°K. As is evident, the two sets of data show agreement in their region of overlap.

The dashed line is a calculation of $k(N(1\rightarrow0), H)$ multiplied by a factor of 100. This calculation matches the temperature dependence of the data fairly well but not the magnitude. In view of possible V–R energy exchange in this interaction, further comparison is not deemed meaningful. The best fit to the experimental data is the solid curve on Fig. 7. The interpretation of the data in terms of the V–V process (8) will be discussed subsequently.

(e), (f) Quite recently, White[67,68] has presented some shock-tube data on the effect of H_2 [Reaction (2e)] and He [Reaction (2f)] on the vibrational relaxation of N_2. These rate data are shown in Fig. 8. Also shown are theoretical calculations of $k(N(1\rightarrow0), He)$ and $k(N(1\rightarrow0), H_2)$ based on the S–S–H theory which have been divided by a factor of 80 to adjust the magnitude of the calculations to the data. As is evident, the limited data match the theoretical temperature dependence fairly well, and it is suggested that these adjusted theoretical curves be used as the best fits to these data.[69]

3. $O_2^*+M\rightleftharpoons O_2+M+1556$ cm^{-1}

(a) Process (3) has been extensively studied in pure O_2. The experimental data have been summarized by White and Millikan[70] and are repeated in Fig. 9 with the addition of a few recent experiments. The data cover a wide temperature range, 300°–10 000°K, and are in excellent agreement with the correlation proposed by Millikan and White[65] (solid line, $M=O_2$). The fact that the experimental relaxation times at $T=300$°K are shorter than the proposed correlation is indicative of possible residual impurity effects in these low-temperature data similar to the results for N_2 shown in Fig. 6. A theoretical calculation of $k(O(1\rightarrow0), O)$ is shown as the dashed line on Fig. 9.

(b) There are no direct experimental measurements of the efficiency of N_2 in Process (3). Based on the Millikan and White correlation scheme, N_2 should be slightly more efficient than O_2 because of the smaller

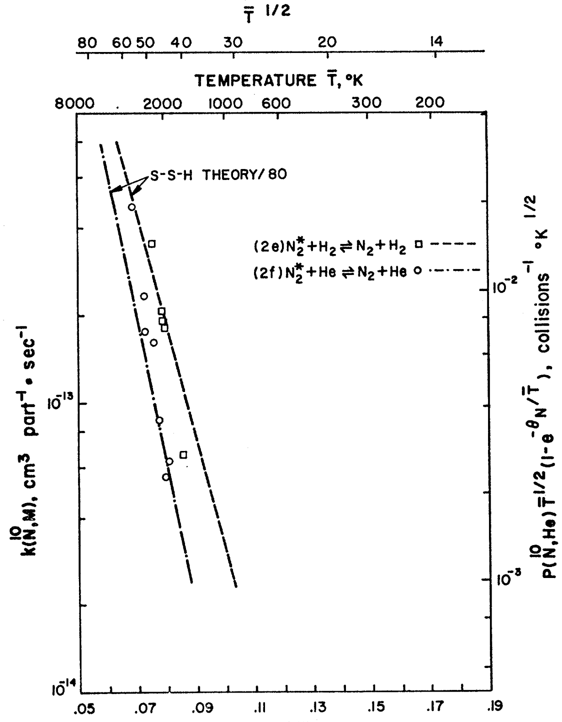

Fig. 8. Experimentally derived $k(N(1\rightarrow0), H_2)$ □, and $k(N(1\rightarrow0), He)$ ○, as a function of $\bar{T}$. The dashed lines are theoretical calculations which have been divided by 80. These adjusted theoretical curves are suggested as the best fits for these data. Sources of data—shock tube: □ Ref. 67, ○ Ref. 68.

reduced mass of the collision pair. The dot–dashed line on Fig. 9 is an estimate of the efficiency of N_2 based on this correlation scheme.

Bauer and Roesler[71] have carried out a series of sound absorption measurements on O_2–N_2 mixtures. By analyzing their data with the full set of four T–V and one V–V energy exchange process, they obtain $k(O(1\rightarrow0),N)=1.7\times10^{-18}$ cm^3 part^{-1}·sec^{-1}. This result is in very good agreement with the correlation curve on Fig. 9. However, in the same experiment they measured $k(O(1\rightarrow0),\ O)=2.1\times10^{-18}$ cm^3 part^{-1}·sec^{-1} which would indicate that O_2 is slightly more efficient than N_2. In any event the correlation proposed for $k(O,N)$ is not in severe disagreement with this one measurement.

(c) Henderson and Queen[72] in a sound absorption experiment report that CO_2 is about 600 times more efficient than O_2 in relaxing O_2 at room temperature. This result is surprising and not expected on the basis of a simple S–S–H theoretical calculation for this T–V process. This result is similar to the high efficiency of CO_2 in relaxing N_2 also observed by Henderson[64] and discussed under Process (2b). Henderson and Queen's result is best explained as a possible measurement of the V–V reaction (10) and will be discussed under that process.

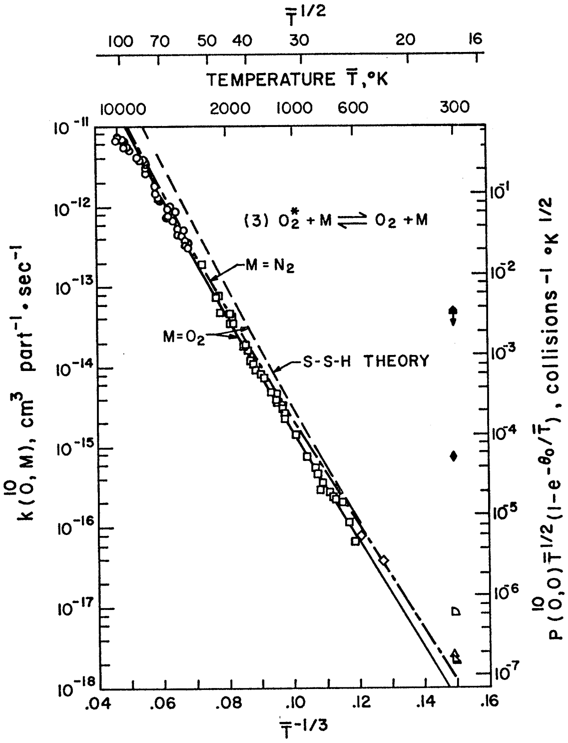

FIG. 9. Experimentally derived $k(O(1\rightarrow0),\ O)$ and $k(O(1\rightarrow0),\ H)$ as a function of $\bar{T}$. The solid line is the best fit to the data for O_2 as suggested by Millikan and White.[65] The dash-dot line is the Millikan and White correlation for N_2. The dashed line is a theoretical calculation for $k(O(1\rightarrow0),\ O)$. The arrow on the H_2O data point indicates an upper bound for the $k(O(1\rightarrow0),\ H)$ rate. Sources of data—(3a) sound dispersion and absorption: ◗ Ref. 71, △ Ref. 127, ◇ Ref. 128, ◺ Ref. 129; (3a) impact tube: ○ Ref. 130; (3a) shock tube: □ Ref. 70; (3d) sound absorption and dispersion: ☗ Ref. 74; (3d) theoretical: ◆ Ref. 73.

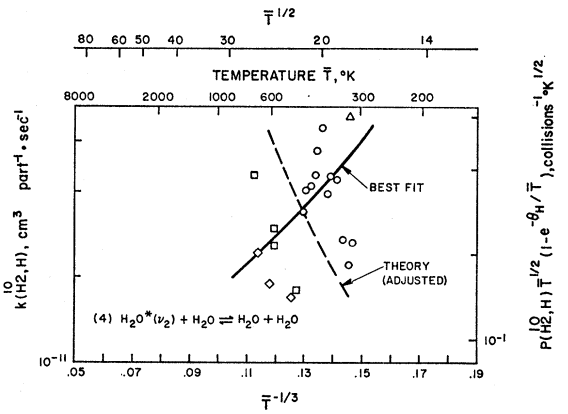

FIG. 10. Experimentally derived $k(H2(1\rightarrow0),\ H)$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation which has been adjusted in magnitude to fit the data. Sources of data—sound absorption and dispersion: ◇ Ref. 131, ○ Ref. 132, △ Ref. 133; impact tube: □ Ref. 57.

(d) The efficiency of H_2O in Process (3) is not known with any certainty. A calculation by Jones, Lambert, and Stretton[73] based on the S–S–H theory yields $k(O(1\rightarrow0),H)=7.2\times10^{-16}$ cm^3 part^{-1}·sec^{-1}. The analysis of sound-dispersion data on O_2-H_2O mixtures by Henderson, Clark, and Lintz[74] yields a value of $k(O(1\rightarrow0),H)\leq4.8\times10^{-14}$ cm^3 part^{-1}·sec^{-1}. These values have been plotted in Fig. 9. If these experimental and theoretical estimates are reliable, then the efficiency of H_2O is at least three orders of magnitude larger than that for O_2 and N_2 indicating that H_2O is an important collision partner for this process. However, the total rate for Process (3) is sufficiently slow so that it is generally not an important energy transfer reaction in the mechanism.

(e), (f) Since the inclusion of O_2 into this survey was primarily motivated by atmospheric transmission studies, the effect of He and H_2 on O_2 vibrational relaxation will not be discussed. Some data on these collision partners have been presented and correlated by Millikan and White.[65]

4. $H_2O^*(\nu_2)+M\rightleftharpoons H_2O+M+1595$ cm^{-1}

(a) H_2O is considered an abnormal molecule because its vibrational relaxation time is extremely fast compared to other simple triatomics, as shown by the data of Fig. 10. The data shown are from one impact-tube and three sound-dispersion experiments and cover a range of temperatures from 315° to 700°K. The measurements apply to mode ν_2 of H_2O, since the other two modes would not be significantly populated at these temperatures. As is evident from Fig. 10, the rate of Process (4) is very large, 10^{-11}–10^{-10} cm^3 part^{-1}·sec^{-1}, compared to 6×10^{-15} for Process (1) for CO_2–CO_2 collisions.

The total data of Fig. 10 indicate a decreasing $k(H2(1\rightarrow0), H)$ with rising temperature. However, examination of the data for each individual experiment indicates the opposite trend; the former conclusion is due to the large systematic difference in the data from the various experiments. It is difficult to establish a best fit to this data. The dashed curve on Fig. 10 has been constructed to average the experimental data but make use of the theoretically expected T–V temperature dependence. The solid curve has been constructed as best fit to the data as shown. It is obvious that the two interpretations lead to opposite slopes!

No quantitative comparison of the experimental probabilities of Fig. 10 and theory has been shown, since a calculation of $k(H2(1\rightarrow0), H)$ by means of the S–S–H formalism would yield values many orders of magnitude smaller than the data. As with CO_2–H_2O and N_2–H_2O interactions, vibration–rotation energy transfer may be an important path for relaxing the vibrational mode in the H_2O–H_2O collisions. Chemical interaction through hydrogen bonding is very important in the condensed phases of H_2O. Therefore, analogous to the situation for CO_2–H_2O, chemical affinity effects could also be important for the H_2O–H_2O interaction. If V–R or chemical affinity interactions are important, then the S–S–H theory is not applicable and the temperature dependence used in constructing the dashed curve on Fig. 10 is incorrect.

(b)–(f) No direct data are available on the efficiency of other collision partners for Process (4). Since H_2O will be a component in small concentration in laser systems, the efficiency of CO_2 and N_2 in Reaction (4) is very important. There are a number of sound-dispersion experiments on O_2–H_2O mixtures[74] which indicate that the relaxation time of O_2 in such mixtures is quadratic in the H_2O concentration. This observation shows that the rate controlling reaction in O_2–H_2O mixtures is Process (4) with $M\equiv H_2O$, and therefore O_2 must be considerably less efficient than H_2O. These data on O_2–H_2O mixtures have been analyzed by Henderson *et al.*[74] Under the assumption that the rate of the V–V process between $H_2O(\nu_2)$ and O_2 [Reaction (4)] is very fast, Henderson *et al.* obtain $k(H2(1\rightarrow0), O)\leq4.8\times10^{-14}$ cm^3 $part^{-1}\cdot sec^{-1}$ for $T=300°K$. Theoretical calculations by Jones *et al.*[73] using the S–S–H theory yield $k(H2(1\rightarrow0), O)\sim 1.1\times10^{-14}$. For the lack of better information it can be assumed that $k(H2(1\rightarrow0), O)\cong k(H2(1\rightarrow0), N)$ and that the temperature dependence of these rates are similar to that for $k(H2(1\rightarrow0), H)$.

There are no experimental data on the efficiencies of CO_2, He, or H_2 for Process (4). The latter two species would be expected to be fairly efficient due to the mass effect. Since H_2O is extremely efficient in relaxing mode ν_2 of CO_2 [Process (1d)], it might be guessed that this same interaction, whatever its origin, might work for the inverse process. As a lower bound on the rate, a value similar to that for O_2 or N_2 might be chosen. See also Sec. III.6.

5. $CO_2^*(\nu_3)+N_2\rightleftarrows CO_2+N_2^*+18\ cm^{-1}$

Of all the V–V energy-exchange reactions in the mechanism of Fig. 1, Process (5) is the closest to energy resonance. The difference in energy between the $v=1$ level of mode ν_3 and the $v=1$ level of N_2 is only 18 cm^{-1}. Because of this near energy resonance, Reaction (5) is expected to be rapid and to couple the N_2 and $CO_2(\nu_3)$ modes. It is known that the rapid process (5) is necessary to invert the upper level population in the CO_2–N_2 laser.

There are several recent experimental investigations of this rate. Taylor, Camac, and Feinberg[16] were the first to directly measure the rate of this process by employing infrared emission to follow the vibrational temperature of mode ν_3 behind shocks into CO_2–N_2 mixtures. Moore, Wood, Hu, and Yardley[7] used a Q-switched CO_2–N_2 laser to overpopulate mode ν_3 of CO_2 and subsequently studied the collisional deactivation by N_2 at room temperature by following the fluorescence radiation from ν_3. This is the same technique used by Rosser, Wood, and Gerry,[75] except that these investigators used a heated cell to cover the temperature range 300°–1000°K. Lastly, Taylor and Bitterman[76] have repeated the shock-tube experiment over a wider range of temperature and compared the various experiments and theory.[77]

The situation is described by Fig. 11. Although the data show considerable scatter, particularly the shock-

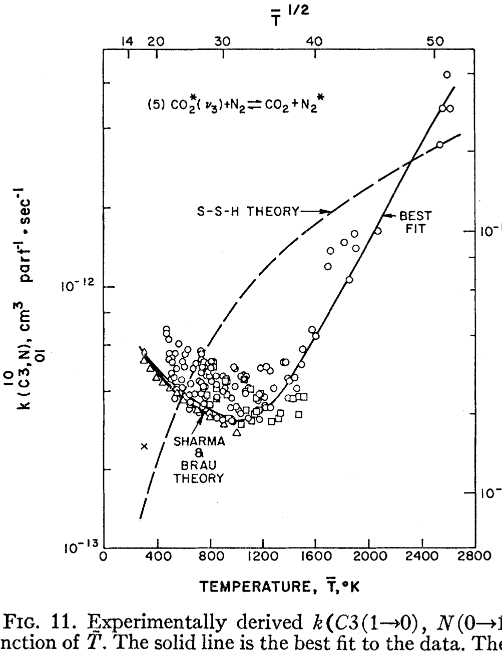

Fig. 11. Experimentally derived $k(C3(1\rightarrow0), N(0\rightarrow1))$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a calculation of $k(C3(1\rightarrow0), N(0\rightarrow1))$ based on the S–S–H theory. The heavy solid line is a calculation based on the Sharma and Brau theory.[78] Sources of data—laser fluorescence: ◇ Ref. 7, △ Ref. 75; shock tube: □ Ref. 16, ○ Ref. 76. Also included on the plot is a laser fluorescence experiment of Moore[92] ×, for the rate $k(C3(1\rightarrow0), CO(0\rightarrow1))$.

tube results, there is a definite indication of a minimum in the rate constant at about 1000°K. The data are plotted against $\bar{T}$ instead of $\bar{T}^{-1/3}$ on Fig. 11, since for a resonant V–V process the probability of energy exchange is calculated from the S–S–H theory to be proportional to temperature. The dashed line is a calculation of the rate of Reaction (5) by Herzfeld.[11] It is clear that the S–S–H theory cannot explain the low-temperature behavior of $k(C3(1\rightarrow0), N(0\rightarrow1))$.

Sharma and Brau[75] have suggested that for this process the important interaction is due to the long-range force between the dipole moment of $CO_2(\nu_3)$ and the quadrupole moment of N_2. Such an interaction is more important at low temperatures and for processes of near energy resonance. In their theory, rotational transitions in both CO_2 and N_2 can account for some of the 18 cm^{-1} of energy necessary for closer energy resonance of Process (5). The heavy, solid line on Fig. 11 is a calculation of $k(C3(1\rightarrow0), N(0\rightarrow1))$ by Sharma and Brau.[75] This calculation shows excellent agreement with the data of Rosser *et al.* both in terms of magnitude and temperature dependence.

As is evident from Fig. 11, the data for Process (5) appear to consist of two separate interactions. At low temperatures, long-range forces are important and the rate is proportional to $T^{-1/2}$. At high temperatures the interaction is dominated by short-range (nonadiabatic) forces, and the rate is approximately proportional to $T^{3/2}$. The crossover point for these two regimes appears to be about 1000–1200°K. It is also evident that the S–S–H calculation shown on Fig. 11 needs to be revised both in terms of magnitude and temperature dependence in order to have better agreement with the high-temperature data of Fig. 11. The best fit to these data is shown as the solid line which reflects the two regimes of interaction described above.

6. $H_2O^*(\nu_2)+CO_2\rightleftarrows H_2O+CO_2^*(\nu_2)+928\ cm^{-1}$

The effect of H_2O on mode ν_2 of CO_2 can be considered as either V–V Process (6) or (18), or T–V Process (1d). The rates for the latter reaction have been discussed in Sec. III.1(d) and shown on Fig. 3. In order to interpret the experimental data on CO_2–H_2O mixtures as V–V Process (6), it is necessary to use Relation (26) to calculate $\tau_{HC}{}^e$. Information concerning the state of excitation of $H_2O(\nu_2)$ in the experiments when the modes couple is not available. However, assumptions of the value of α can be made to calculate $\tau_{HC}{}^e$. However, the concentration of H_2O is also not available for many of the investigations.[79]

Nevertheless, using the approximate concentrations of H_2O given by the authors and the assumptions of $\alpha=1$ and 0.5, $\tau_{HC}{}^e$ and the rate constants $k(H2(1\rightarrow0), C2(0\rightarrow1))$ were calculated. For both assumptions these results lead to large rates, even larger than for the T–V process $k(C2(1\rightarrow0), H)$ shown in Fig. 3. However, in view of the large number of assumptions and uncertainties inherent in these calculations, the results will not be presented.

No clear choice is possible from the data between a T–V or V–V process for relaxation of mode ν_2 of CO_2 in collisions with H_2O. Since the available experimental data do not admit of a very meaningful V–V interpretation and since the large efficiency of H_2O as a T–V collision partner seems explainable on the basis of a chemical affinity[47] or V–R effect, it is concluded that the effect of H_2O on mode ν_2 of CO_2 be considered as T–V Process (1) and not as V–V Reaction (6). However, more experimental work is needed to establish this conclusion with certainty.

7. $CO_2^*(\nu_3)+H_2O\rightleftarrows CO_2+H_2O^*(\nu_2)+754\ cm^{-1}$

Although H_2O vapor is used frequently in the CO_2–N_2 laser to increase power, it has been observed experimentally that under some conditions H_2O decreased laser power.[80,81] Presumably this is due to H_2O deactivating the upper laser level ν_3. Several alternate processes can be assumed to account for this effect: (i) the direct deactivation of mode ν_3 by H_2O in V–V Reaction (7) and/or (17); (ii) the series path composed of the rapid transfer from ν_3 to N_2 by (5) followed by deactivation of N_2 by H_2O via (2) and/or (8), and (iii) the intramolecular V–V deactivation of ν_3 by Reaction (13) with H_2O acting as an efficient collision partner. Because of the lack of information on the mechanism, the effect of H_2O in deactivating mode ν_3 of CO_2 will be considered as a simple collision partner in the V–V process (13), choice (iii) above. The experimental data for H_2O interpreted in this manner are discussed in Sec. III.13.

8. $N_2^*+H_2O\rightleftarrows N_2+H_2O^*(\nu_2)+736\ cm^{-1}$

As previously discussed, the effect of H_2O on the vibrational relaxation of N_2 can be assumed to occur through the V–V process (8) or via the T–V reaction (2). The latter reaction was discussed in Sec. III. 2(d) and the data were shown on Fig. 7.

In order to interpret the data on N_2–H_2O mixtures for the probability of V–V energy exchange via Process (8), it is necessary to utilize Relation (26). The experimental values of τ can be identified as τ_f, however no values of α are available, i.e., the state of excitation of H_2O when the two modes couple is not known. Two limiting assumptions were made: (i) $\alpha\approx1$, i.e., the T–V process (4) for H_2O–H_2O and H_2O–N_2 collisions is fast enough to vibrationally relax mode ν_2 of H_2O before Reaction (8) couples ν_2 to N_2; or (ii) $\alpha\approx0$, i.e., the V–V process (8) is faster than T–V Process (4) so that the two modes are coupled throughout the relaxation.

Based on the rates for T–V excitation of H_2O, Process (4), and the experimental conditions, Assumption (i) appears to be the most reasonable. Accordingly, the rate constants $k(N(1\rightarrow0), H2(0\rightarrow1))$ have been calculated and are shown in Fig. 12. The dashed line is a calculation of $k(N(1\rightarrow0), H2(0\rightarrow1))$ by means of

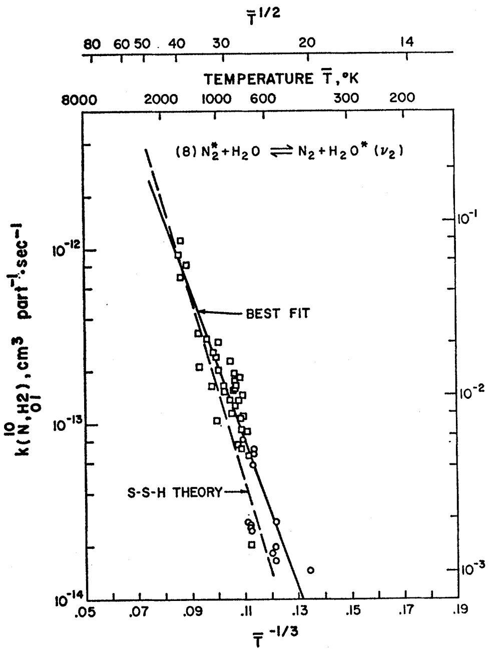

Fig. 12. Experimentally derived $k(N(1\rightarrow0), H2(0\rightarrow1))$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation of $k(N(1\rightarrow0), H2(0\rightarrow1))$. Sources of data—impact tube: ○ Ref. 57; shock tube: □ Ref. 66.

the V–V form of the S–S–H theory. The solid line is the best fit to the data.

As can be seen the theory and data show close agreement both in magnitude and temperature dependence. This agreement must be considered fortuitous in view of the assumptions used in analyzing the data and the uncertainty in the theory due to possible V–R effects. However, analyzing the data using Assumption (ii) leads to difficulties in interpretation of the experiments and much poorer agreement of the experimental rates with theory. It can also be noted that the use of Assumption (i) to analyze the data leads to a consistent result, since the values of $k(N(1\rightarrow0), H2(0\rightarrow1))$ obtained on Fig. 12 are sufficiently small compared to $k(H2(1\rightarrow0), H)$ or $k(H2(1\rightarrow0), N)$ that the assumption of $\alpha = 1$ appears reasonable.

The choice between T–V Process (2d) shown on Fig. 7 and V–V Process (8) shown in Fig. 12 for the vibrational relaxation of N_2 by H_2O is not possible from the present experimental data above. Since the V–V process shows better agreement with present theory, it is preferred, although a more definitive check of the mechanism is needed. Since the rate constants shown in Figs. 7 and 12 are derived from the same experimental data, use of either mechanism with its associated rates will lead to consistent results.

9. $H_2O^*(\nu_2) + O_2 \rightleftharpoons H_2O + O_2^* + 39$ cm^{-1}

Process (9) is a nearly resonant V–V transfer reaction similar to (5). Unfortunately, very little is known about the rate of this process. The experimental data on O_2–H_2O mixtures[74] mentioned earlier in the discussion of Processes (3) and (4) indicate that the rate of (9) is fast, i.e., it is not the rate-controlling step in that system. Therefore, no quantitative estimates are available from an analysis of those data. A theoretical calculation by Jones *et al.*[73] yields $k(H2(1\rightarrow0), O(0\rightarrow1)) = 3.1\times10^{-13}$ cm³ part⁻¹·sec⁻¹. However, it is doubtful if the S–S–H theory is valid for these nearly resonant V–V processes at low temperatures.[78]

Yardley and Moore[82] have recently measured the resonant V–V transfer rate between mode ν_2 of CH_4 and O_2 ($\Delta E = 30$ cm^{-1}) and obtain a rate of 6.9×10^{-13} cm³ part⁻¹·sec⁻¹. Since CH_4 and H_2O are hydridelike molecules, their vibrational relaxation behavior may be expected to be similar.

Based on this very limited information, $k(H2(1\rightarrow0), O(0\rightarrow1)) \sim 3\times10^{-12}$–$3\times10^{-13}$ cm³ part⁻¹·sec⁻¹ seems a reasonable guess. Based on the success of the long-range-interaction theory of Sharma and Brau,[78] for Process (5), we have chosen to suggest the temperature dependence predicted by that theory, $k \propto T^{-1/2}$, for the regime of interest, although there are no specific calculations by the SB theory for Process (9).

10. $O_2^* + CO_2 \rightleftharpoons O_2 + CO_2^*(\nu_2) + 889$ cm^{-1}

The effect of O_2 on the vibrational relaxation of mode ν_2 of CO_2 was mentioned in the discussion of T–V process (1). As was stated, one experiment indicates that O_2 is very inefficient in relaxing mode ν_2. This limited result suggests that the V–V process (10) is not an important mechanism for ν_2 relaxation. Note that a more nearly resonant V–V reaction is possible between the $v = 2$ level of mode ν_2 and O_2: $\Delta E = 270$ cm^{-1}. However, the result of Henderson and Queen[72] [see Sec. III. 3(c)] indicating a large efficiency for CO_2 in relaxing O_2 at room temperature can be explained by V–V process (10). If Henderson and Queen's result is interpreted as reaction (10), a rate $k(O(1\rightarrow0), C2(0\rightarrow1)) \cong 10^{-13}$ cm³ part⁻¹·sec⁻¹ is obtained for weak coupling. The corresponding rate for the inverse endothermic reaction, the V–V deactivation of ν_2, is then $k(C2(1\rightarrow0), O(0\rightarrow1)) \cong 10^{-15}$ at $T = 300$°K. As can be seen from comparison of this latter rate with the data of Fig. 2, the V–V deactivation of mode ν_2 of CO_2 by O_2 is sufficiently slow compared to the direct T–V process (1c) to be unimportant at low temperatures.

11. $CO_2^*(\nu_3) + O_2 \rightleftharpoons CO_2 + O_2^* + 793$ cm^{-1}

The effect of O_2 on mode ν_3 of CO_2 will be included in the consideration of V–V Process (13), and the discussion of the relative importance of Reaction (11) will be postponed until the data for the former process are shown.

12. $N_2^* + O_2 \rightleftharpoons N_2 + O_2^* + 775$ cm^{-1}

There are considerable experimental data on the rate of the V–V process (12) between N_2 and O_2 obtained from analysis of vibrational relaxation of N_2–O_2 mixtures. The analysis of the relaxation behavior of binary mixtures of diatomic molecules has been discussed by Taylor *et al.*[16] These authors showed that the vibrational relaxation time of the mixture may often be controlled by the V–V coupling reaction, e.g., Process (12) for N_2–O_2. Using the energy relaxation equations derived for this situation, Taylor *et al.* analyzed shock tube relaxation measurements by White and Millikan[83] in air for the rate of (12)–$k(N(1\rightarrow0), O(0\rightarrow1))$. This analysis was of necessity approximate because not all the relevant parameters were measured in the experiment. Nevertheless, these results for $k(N(1\rightarrow0), O(0\rightarrow1))$ are given on Fig. 13.[84]

Recently Breshears and Bird[85] have used the analysis of Taylor *et al.* to determine the rate of (12) in various O_2–N_2 mixtures. The purpose of their shock tube experiment was to determine the efficiency of O atoms on the vibrational relaxation of N_2. However, the determination of $k(N(1\rightarrow0), O(0\rightarrow1))$ was a necessary prerequisite in the complete analysis of their data. Also, White[86] has analyzed shock-tube relaxation data in various N_2–O_2 mixtures for the rate of Process (12).

Bauer and Roesler[71] have carried out a series of sound dispersion measurements on N_2–O_2 mixtures at room temperature and obtain a value for $k(N(1\rightarrow0), O(0\rightarrow1))$. This result is shown on Fig. 13 and is the only low temperature, experimental measurement of the rate of Process (12).

A calculation of $k(N(1\rightarrow0), O(0\rightarrow1)$ by means of the S–S–H theory is shown on Fig. 13 as the dashed curve. As can be seen, the combined experimental data are in good agreement and exhibit the theoretical temperature dependence but lie uniformly lower by factors of 5–10. These experimental data reasonably well define the rate of Process (12). The best fit to the data is shown as the solid line on Fig. 13.

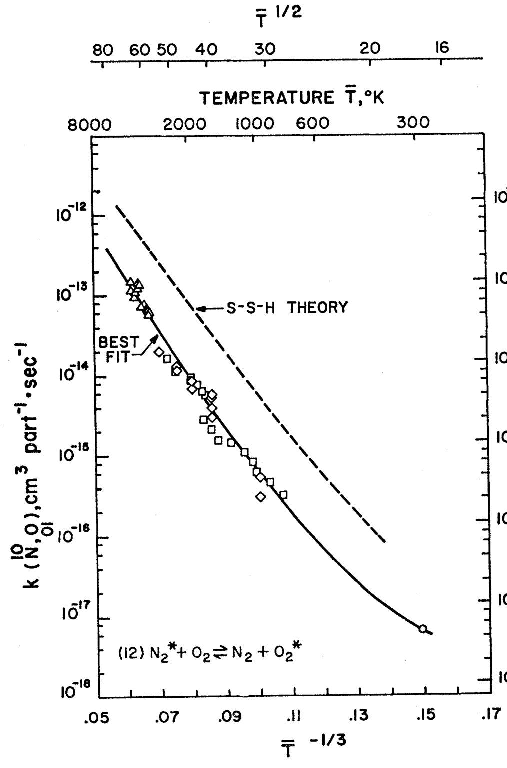

FIG. 13. Experimentally derived $k(N(1\rightarrow0), O(0\rightarrow1))$ as a function of $\bar{T}$. The solid line is the best fit to the data. The dashed line is a theoretical calculation of $k(N(1\rightarrow0), O(0\rightarrow1))$. Sources of data—sound absorption and dispersion: ○ Ref. 71; shock tube: □ Ref. 83, △ Ref. 85, ◇ Ref. 86.

13. $CO_2^*(\nu_3)+M\rightleftharpoons CO_2^{***}(\nu_2)+M+416\ cm^{-1}$

A very important reaction in the CO_2–N_2 laser is the process that collisionally couples the upper and lower laser levels.[87] Yardley and Moore[45] have carried out a laser fluorescence experiment on mode ν_3 of CO_2 using the rare gases as collision partners. From an analysis of their data they conclude that the most favorable collisions for the deactivation of ν_3 occur when less than about 300 cm^{-1} of energy is exchanged with the translational mode. In terms of the energy levels on Fig. 1, this would indicate that Reactions (15) and/or (16) are more probable than Reaction (13). In analogy to this result for the rare gases, Moore concludes that the same processes are probably the dominant paths for N_2 and CO_2 as collision partners.

However, in the present survey the mechanism that is assumed for the V–V coupling between modes ν_3 and ν_2 (or ν_1) is Process (13), because the bulk of the experimental data have already been analyzed for this process. Furthermore, calculations indicate that the rate constants do not change appreciably whether Reactions (13), (15), or (16) are used to analyze the data. It should be re-emphasized that the rate constants discussed in this section apply to the specific reaction (13), and, if converted to a corresponding relaxation time, should not be confused with the experimentally measured relaxation time or rate for mode ν_3 deactivation. The experimental τ_f for ν_3 would be determined from a relation similar to (26), but derived for the specific V–V process (13).[16]

(a) There are several experimental measurements of the relaxation of mode ν_3 in pure CO_2 [Process (13a)]. Laser fluorescence experiments have been carried out by Hocker, Kovacs, Rhodes, Flynn, and Javan,[88] and Moore *et al.*[7] Houghton[89] has also performed a fluorescence experiment, but used a modulated standard light source instead of a laser. Cheo[90] has measured the rate of (13) using a pulsed-laser amplifier and gain-measurement technique. These measurements were all performed at $T=300°K$, and as can be seen on Fig. 14, the agreement between the various investigations is excellent.

Slobodskaya and co-workers[38] and Cottrell *et al.*[39] have used the spectrophone technique to measure the

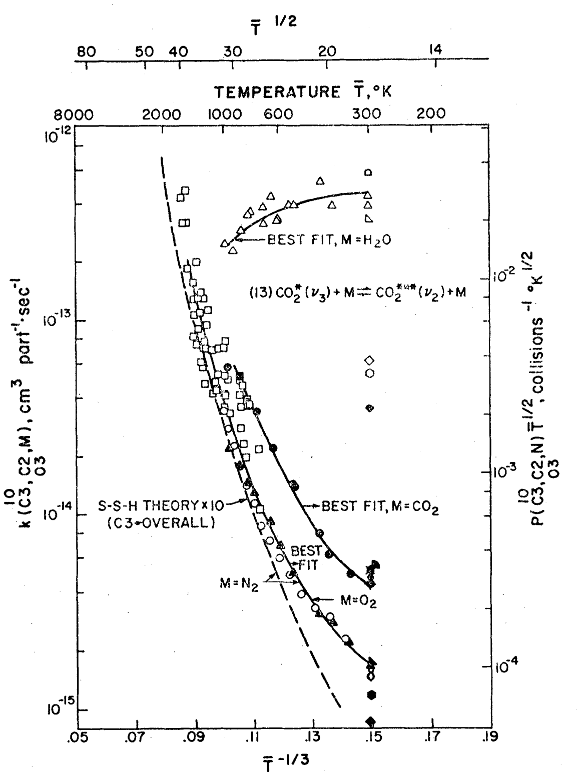

FIG. 14. Experimentally derived $k(C3(1\rightarrow 0), C2(0\rightarrow 3), M)$ as a function of $\bar{T}$ for various collision partners M: CO_2, N_2, O_2, H_2O, He, H_2. Each solid line is the best fit to the indicated collision partner. The dashed line is a theoretical calculation by Herzfeld[11] of the over-all rate out of mode ν_3 of CO_2, in a N_2–CO_2 mixture, multiplied by 10. Collision partner and sources of data are as follows. M = CO_2, spectrophone: + Ref. 38, ◆ Ref. 39; M = CO_2, fluorescence: ⧫ Ref. 7, ● Ref. 75, ☗ Ref. 88, ◗ Ref. 89, X Ref. 90; M = N_2, laser fluorescence: ◇ Ref. 7, ○ Ref. 75, ⬯ Ref. 90; M = N_2, shock tube: □ Ref. 91; M = O_2, laser fluorescence: ◣ Ref. 92, ▲ Ref. 75; M = H_2O, laser fluorescence: ◺ Ref. 7, △ Ref. 75, ⌂ Ref. 90; M = He, laser fluorescence: ⬢ Ref. 7, ◆ Ref. 90; M = H_2, laser fluorescence: ⬡ Ref. 7, ◇ Ref. 90.

relaxation of mode ν_3 in pure CO_2. Cottrell *et al.* have analyzed their data by assuming that the vibrational energy in mode ν_3 is transferred to mode ν_2 via some unspecified V–V process with the subsequent T–V de-excitation of ν_2. The value of the relaxation rate for the V–V process for CO_2–CO_2 collisions that they obtain from their data is 3.4×10^{-14} cm³ part⁻¹·sec⁻¹. This result is plotted on Fig. 14 and is about a factor of 7 larger than the other room-temperature data.

The most extensive data on Process (13a) are provided by the laser fluorescence experiments of Rosser *et al.*[75] Measurements have been made from 300° to 1000°K for a number of collision partners. The results are shown on Fig. 14. At room temperature, agreement is excellent with the other measurements.

An interesting aspect of the data for (13a) shown on Fig. 14 is the change in slope of the rate constant in the vicinity of 400°K. This is more dramatic when the data are plotted as probabilities per collision and may indicate a change in the mechanism of the V–V coupling between modes ν_3 and ν_2 as the temperature increases. For example, V–V processes not so close to energy resonance as Reaction (13) would be expected to become more important at elevated temperatures.[11]

(b) Data for Process (13) with N_2 as a collision partner [Process (13b)] have been obtained by Moore *et al.*, Cheo, and Rosser *et al.*, and are shown on Fig. 14. Also shown are some recent shock-tube data in CO_2–N_2 mixtures by Taylor and Bitterman,[91] which exhibit good agreement with the fluorescence data of Rosser *et al.* in their region of overlap and which extend the measurements to 1575°K. The rate constant for Process (13b) also shows a change in slope around 500°K and a steeper dependence upon temperature than (13a). Except at the highest temperatures, the efficiency of CO_2 as a collision partner in Reaction (13) is seen to be 2–3 times that of N_2.

(c) The efficiency of O_2 in Reaction (13) has been measured only by Moore[92] at room temperature and by Rosser *et al.* up to 1000°K. These results, as shown on Fig. 14, are in excellent agreement at $T=300$°K. Also, it can be seen that the rates for N_2 and O_2 in Reaction (13) are essentially identical.

(d) As previously indicated, H_2O [Reaction (13d)] can reduce CO_2–N_2 laser performance under some conditions. The rate for H_2O deactivating mode ν_3 of CO_2 has been measured at room temperature by Moore *et al.* and Cheo and up to 1000°K by Rosser *et al.*, and the rate constants have been plotted on Fig. 14. At $T=300$°K, the rate for (13d) with H_2O as a collision partner is two orders of magnitude larger than for CO_2, N_2, or O_2. Also, the rate for $k(C3(1\rightarrow 0), C2(0\rightarrow 3), H)$ shows a slightly negative temperature dependence in sharp contrast to that for the other species. This behavior is similar to the relaxation of mode ν_2 of CO_2 by H_2O and suggests that Reaction (13d) may not be the correct mechanism for this rate. Direct V–V exchange with H_2O, V–R exchange, or chemical-affinity effects, either alone or in combination, could play a role in the CO_2–H_2O interaction.

(e), (f) Moore *et al.* and Cheo have measured the rates of He and H_2 as collision partners in Reaction (13). These results at $T=300$°K are shown on Fig. 14. Surprisingly, it is seen that He is not as efficient a collision partner as the other species and even H_2 is not as efficient as H_2O.

The solid lines on Fig. 14 are the suggested fits to the data. These curves have been freely drawn through the data. Since no high-temperature data exist for He and H_2, it is suggested that curves similar in slope to those for N_2 or O_2 be used adjusted in magnitude to give the measured rate at $T=300$°K.

Herzfeld[11] has calculated the rates for the collisional deactivation of mode ν_3 for a large number of possible V–V mechanisms. If the kinetic contribution from these large number of processes are added, the over-all rate given by the dashed line on Fig. 14 is obtained, and it is to be noted that this curve has been multiplied by a factor of 10. It can be seen that the over-all rate of collisional deactivation of mode ν_3 is one to two orders of magnitude less than the experimental data, although the temperature dependence is moderately well represented.

14. $CO_2^*(\nu_1)+M \rightleftarrows CO_2(\nu_2)^{**}+M+102\ cm^{-1}$

It is known that there is a strong interaction between the ν_1 and ν_2 modes of CO_2 due to the accidental degeneracy of the $v=2$ level (02^00) of mode ν_2 and the $v=1$ level of ν_1.[93] This Fermi resonance leads to a strong perturbation of the degenerate levels. Because of this strong interaction, it has been suggested that V–V transfer process of the type indicated by Reaction (14) will be rapid.[10] Theoretical calculations of the rate of Process (14) by Herzfeld[11] indicate that the energy transfer between the Fermi coupled levels is rapid.

Recent experimental data by Rhodes, Kelley, and Javan[94] using the laser fluorescence technique indicate that the collisional coupling between modes ν_1 and ν_2 is indeed very rapid in pure CO_2. This experiment has been reviewed by Sharma[95] who suggests on the basis of theoretical calculations that the rate-limiting step is the rapid resonant intramode V–V transfer between the $v=1$ level of ν_2 and the non-Fermi-coupled level (02^20):

$$(01^10)+(01^10) \rightleftarrows (02^20)+(000)+1\ cm^{-1} \qquad (34)$$

with the subsequent rapid equilibration between the (100), (02^20) and (02^00) levels. Both theory and experiment yield a rate constant for Reaction (34) of about 1.5×10^{-11} cm^3 part$^{-1}\cdot$sec^{-1} at $T=300$°K with the subsequent equilibration of the energy between the (100), (02^00) and (02^20) levels being at least a factor of 2 faster.

IV. SUMMARY

Based on the preceding data compilations, the following general comments are made about the rates for the various vibrational transfer processes in the CO_2–N_2 system.

(1) Because of the large amount of experimental data available, the rate of Reaction (1) for CO_2–CO_2 collisions is reasonably well established. As can be seen from Fig. 2, there is good agreement between theory and experiment, both for the magnitude and temperature dependence of the rate constant. However, some reservations are necessary. Reaction (1) is very important for specifying laser performance, since it provides the deactivation of the lower laser level via the strong coupling to mode ν_1. The available data, particularly the shock-tube results, show considerable scatter and also wide disagreement concerning the coupling of the various vibrational modes of CO_2. To settle these questions, a careful high-temperature (>500°K) experiment is needed.

For other collision partners, the rate of Reaction (1) is less certain. The only documented experimental measurements of the efficiency of N_2 differ by more than an order of magnitude. If N_2 is more efficient than CO_2, then N_2 collisions probably control the rate of (1) in the CO_2–N_2 laser. However, other possibilities can be suggested.[96] The rate for N_2 as the collision partner in Reaction (1) is considered one of the more important numbers that needs to be measured for CO_2–N_2 laser applications.

Appreciable data are available for He and H_2 as a catalyst in Reaction (1). Unfortunately, the measurements extend only to 685°K. For calculations at higher temperatures, it is suggested that the adjusted theoretical curve shown on Fig. 4 be used for $CO_2(\nu_2)$–He collisions and the curve fit weighted by the most recent data as shown on Fig. 5 be used for $CO_2(\nu_2)$–H_2 collisions. Higher-temperature data are needed for both Reactions (1e) and (1f) to establish better fits.

The effect of H_2O on mode ν_2 of CO_2 can be considered either as a T–V process (1) or the V–V process (6) or (18). The present experimental data appear to support the former interpretation. However, Process (1d) needs further experimental investigation. The available data show (i) considerable scatter and (ii) the opposite temperature dependence expected for T–V processes. The latter effect is particularly intriguing since it indicates that H_2O is a less efficient catalyst at higher temperatures. Comparing the best-fit curves of Figs. 2 and 3, H_2O is seen to be a less efficient collision partner than either CO_2 or N_2 for temperatures above 1500°K. Of course, the chemical-affinity effect which explains this inverted temperature dependence may go over to another mechanism, e.g., the nonadiabatic process, for higher-energy collisions. Such a change in collision mechanism with temperature is known[97] in previous studies of T–V energy transfer and has been more recently observed for the resonant V–V process (5) as discussed in Sec. III.5.

(2) Because of its slow rate, Reaction (2) for N_2–N_2 collisions is relatively unimportant for CO_2–N_2 laser applications. The only experimental measurement of the rate of (2) suggesting CO_2 as an efficient collision partner, disagrees with theoretical expectations. However, for the concentrations of this molecule generally used in lasers and because of the slow rate for N_2–N_2 collisions, CO_2 cannot increase the rate of Reaction (2) to an important extent. The recent data obtained on the efficiency of H_2 and He for vibrationally relaxing N_2 also indicate that, in moderate amounts, these species will not affect N_2 relaxation through Reaction (2).

Analogous to the situation for $CO_2(\nu_2)$, H_2O can affect N_2 vibrational relaxation either as a T–V catalyst in Reaction (2) or via the V–V process (8). The available data appear to be interpretable as either mechanism. Further experimental work on this reaction is necessary to settle this question and also to provide additional data on the rate and its temperature dependence. For laser calculations, either mechanism can be used.

(3) The rate of Reaction (3), the T–V process for O_2 relaxation, has been studied over a wide range of temperature, 300°–10000°K. As shown in Fig. 9, the data for O_2–O_2 collisions are internally consistent and excellent agreement with theory is obtained. For other collision partners only limited data are available. The high efficiency of CO_2 can be explained on the basis of a V–V mechanism, Reaction (10). H_2O appears to be a more efficient collision partner than O_2 by several orders of magnitude, a result which is not unexpected. This T–V efficiency of H_2O on O_2 relaxation is in addition to a very rapid, near-resonant V–V process, Reaction (9).

(4) The rate for the direct T–V excitation of mode ν_2 of H_2O by collisions with H_2O is sufficiently fast to allow H_2O to participate in V–V exchange processes with CO_2, N_2 and O_2. Whether this statement also applies to dilute H_2O mixtures where H_2O–M($M \neq H_2O$) collisions dominate is an open question. Because of the very fast rate of (4) for H_2O–H_2O collisions, it is believed that V–R energy exchange must be the dominant process. Analogous to other hydridelike molecules, V–R exchange would also be expected to be important for H_2O–CO_2 and H_2O–N_2 collisions. Also, the chemical-affinity effect speculated to be important for CO_2 and H_2O might reasonably be expected to increase the rate of H_2O relaxation. Considering all of these facts and trends, it is believed that the T–V relaxation of H_2O will be rapid for the other important collision partners in the CO_2–N_2 laser system, and hence, H_2O may be able to participate in V–V reactions even if present in small concentrations.

Since the present data on Reaction (4) for H_2O–H_2O collisions cover a limited temperature range and show considerable scatter, it is very difficult to decide on a proper fit for calculational purposes. One suggestion on Fig. 10 has been established by adjusting a theoretical calculation to the data. This provides a curve which matches the magnitude of the data over the temperature range 315°–700°K and provides the theoretical dependence for extrapolation to other temperatures. It should be recognized that this temperature dependence is based on the assumption of a T–V mechanism which is most probably not the dominant mechanism for this process.

(5) The situation with regard to Reaction (5) is very interesting. Until recently a significant discrepancy existed between the two sets of data obtained in different temperature regimes.[76] By extending both experiments to a wider temperature range this discrepancy is resolved. At low temperatures the process appears to be controlled by long range forces and at higher temperatures by short range interactions, and the best fit suggested on Fig. 11 is based on the entire set of data and this interpretation.

It is interesting to speculate that the explanation of the low-temperature result for Process (5) may be generally valid for other near-resonant V–V processes such as (17) and (18). In fact, the inverted temperature dependence for the deactivation of mode ν_2 of CO_2 by H_2O, seen in Fig. 3, could conceivably be explained by such a mechanism applied to Reaction (18).[98]

(6) As discussed in Sec. III, the mechanism for H_2O interacting with mode ν_2 of CO_2 is more reasonably interpreted as the T–V reaction (1d) and not the V–V process (6) or (18). However, the experimental data do not rule out the possibility of a V–V mechanism, e.g., see the discussion in Sec. IV. 4 above. The importance of H_2O for increasing laser power makes it imperative that further experimental studies be carried out to test various mechanisms and measure rates for the processes by which H_2O interacts with the various vibrational modes of the CO_2 molecule.

(7) Experimentally, it is observed that H_2O has a large effect on the deactivation of mode ν_3 of CO_2 (see Fig. 14). However, it has been assumed that the mechanism responsible is Reaction (13) with H_2O acting as an efficient collision partner in the transfer of energy from mode ν_3 into ν_2 (and/or ν_1). Other interpretations of the data are possible however. The unique temperature dependence of the data shown on Fig. 14 will hopefully provide a test of the proper mechanism as various theories of V–V energy exchange are developed.

(8) The V–V process (8) provides an alternate mechanism for the effect of H_2O on N_2 vibrational relaxation. The experimental data seem to support the V–V mechanism, especially if the rate of T–V excitation of H_2O by collisions with N_2 is fast enough to relax H_2O before the modes couple.

(9) The near-resonant V–V process (9) provides a rapid path for exchange of vibrational energy between O_2 and H_2O. Although no direct measurements of the rate of this process have been made, indirect evidence suggests a fast rate, $\sim 10^{-12}$ cm^3 part$^{-1}\cdot$sec^{-1} at $T = 300$°K, similar to that for the near-resonant reaction (5). Thus, in any system involving O_2 and H_2O, the O_2 relaxation will probably be controlled by this rapid V–V process. The experimental determination of the temperature dependence of Reaction (9) may provide a further basis for a test of the Sharma–Brau concept of the importance of long-range forces in near-resonant V–V processes.

(10) The high efficiency of CO_2 relaxing O_2 observed by Henderson and Queen seem explainable only on the basis of a V–V mechanism such as Reaction (10). Using that assumption, the rate of (10) obtained from the data are consistent with such a V–V process and also consistent with the observed fact that O_2 is inefficient in relaxing $CO_2(\nu_2)$.

(11) The effect of O_2 on $CO_2(\nu_3)$ has been included in the V–V process (13). As is seen on Fig. 14, both N_2 and O_2 exhibit identical rates for relaxing ν_3 via Path (13). This comparison is reasonable and expected if both N_2 and O_2 were acting as collision partners in a

similar reaction such as (13). Furthermore the V–V process (5), which is analogous to Reaction (11) for O_2, is very fast and is easily separated from the slower process (13) in the experiments. Since no similar fast process is observed in the $CO_2(\nu_3)$–O_2 experiments, it must be concluded that Reaction (11) is not important relative to Process (13).

(12) There appears to be a resonable amount of consistent data on the V–V process between N_2 and O_2, as is seen from Fig. 13. Although the data yield a rate smaller than the theoretical calculation, similar comparisons have been noted by Taylor *et al.* for other simple V–V processes such as between CO–NO and N_2–NO.[16]

(13) Based on the most recent data shown on Fig. 14, the rate for the intramolecular V–V process coupling modes ν_2 and ν_3 of CO_2 for a number of collision partners is available. The specific process(es) by which this transfer takes place are not known, but near resonant reactions of the type (13), (15), or (16) appear to be most likely candidates.

CO_2 is measured to be more efficient than N_2 for Reaction (13), but not to the extent predicted by the Herzfeld.[10] In fact, present calculations based on the S–S–H theory do not appear adequate for predicting the magnitude of the rate constants shown on Fig. 14, even when other states of the CO_2 molecule are included in the interaction.[45,11] This may indicate that the detailed mechanism for intramolecular V–V energy transfer in polyatomic molecules is very complex. The change in temperature dependence shown by the rate data is additional proof that the mechanism is not a simple process. However, for the present purposes, the mechanism for coupling modes ν_2 and ν_3 of CO_2 is assumed to be Reaction (13).

(14) In view of the recent experiment of Rhodes *et al.*,[94] the assumption that the coupling of modes ν_1 and ν_2 of CO_2 is very strong, leading to local equilibrium of these modes, appears reasonable. Therefore, all reactions affecting ν_2, such as (1) or (6), will also affect ν_1 and the lower laser level.

Because of the low dissociation energy of CO_2, some CO is expected in electrical discharge CO_2–N_2 or CO_2 lasers.[2,4] Hence, the effect of CO in the vibrational energy transfer mechanism, Fig. 1, is of interest. However, CO is not found to strongly effect laser efficiency; hence, the details of its vibrational transfer rates are not included in this paper. Some brief comments will be made.

First, CO is expected to be similar to N_2 in most of its vibrational transfer behavior. The known T–V rates for CO–CO, CO–He, and CO–H_2 collisions are close to the similar processes for N_2.[65] Second, CO is known to couple very strongly to N_2 by a V–V transfer process,[56] since the energy difference between the modes is only 188 cm^{-1}. Third, the only major uncertainty appears to be the rate of coupling of CO with mode ν_3 of CO_2, since the reaction

$$CO_2^*(\nu_3)+CO\rightleftarrows CO_2+CO^*+206\ \text{cm}^{-1} \tag{35}$$

is not nearly as close to energy resonance as Reaction (5) for N_2.

Moore[92] has recently measured this rate and gives a tentative value of $k(C3(1\rightarrow0),\ CO(0\rightarrow1))\approx2.45\times10^{-13}$ cm^3 part$^{-1}\cdot$sec^{-1} at $T=300°$K. This value has been plotted on Fig. 11 and is about a factor of 2 or 3 less than the probability for Reaction (13). Moore further concludes that the rate of the sum of reactions of the type

$$CO_2^*(\nu_3)+CO\rightleftarrows CO_2^*(\nu_1+\nu_2)+CO+272\ \text{cm}^{-1} \tag{36}$$

and

$$CO^*+CO_2\rightleftarrows CO+CO_2^*(\nu_1+\nu_2)+66\ \text{cm}^{-1} \tag{37}$$

is at least one order of magnitude smaller than the rate of Reaction (35).

Hence, in any CO_2–N_2–CO mixture, it would appear that the role of CO is similar to that of N_2. Since the over-all rates of vibrational transfer for CO are close to those for N_2, no substantial change in laser behavior is expected for small concentrations of CO.

In conclusion, the most important reactions for calculating laser performance are the set of reactions (1), (5), and (13) with the importance of H_2O occurring through its effect on the ν_2 and ν_3 levels of CO_2. The present mechanism proposed for the vibrational energy exchange in the CO_2–N_2 system is complex, and evidence is available that the exact, physical mechanism may be even more detailed. More experimental and theoretical studies are necessary to unravel this important and interesting kinetic system.

ACKNOWLEDGMENTS

It would be impossible to acknowledge all the people who have helped us in the preparation of this survey. Particular thanks should go to our scientific colleagues at the Avco Everett Research Laboratory for many helpful discussions and criticisms. We particularly acknowledge the encouragement and advice of Professor C. Bradley Moore at the University of California at Berkeley, and Professor A. Javan of the Massachusetts Institute of Technology. Our appreciation is also extended to Miss Irene Barbanti who typed and retyped this paper, often under considerable pressure.

REFERENCES

[1] C. K. N. Patel, Phys. Rev. Letters **13**, No. 21, 617 (1967).

[2] F. Legay and N. Legay-Sommaire, Compt. Rend. **259**, 99 (1964).

[3] N. Legay-Sommaire. L. Henry, and F. Legay, Compt. Rend. **260**, 3339 (1965).

[4] N. N. Sobolev and V. V. Sokovikov, ZhETF Pis. Red. **4**, 303 (1966) [JEPT Lett. **4**, 204 (1966)].

[5] N. N. Sobolev and V. V. Sokovikov, ZhETF Pis. Red. **5**, 122 (1967) [JEPT Lett. **5**, 99 (1967)].

[6] N. N. Sobolev and V. V. Sokovikov, *The Physics of Electronic and Atomic Collisions: Invited Papers from the Fifth International Conference*, Leningrad, 17–23 July, 1967, L. M. Branscomb, Ed. (Univ. Colorado Press, Boulder, Colorado, 1968), pp. 40–69.

[7] C. B. Moore, R. E. Wood, B. Hu, and J. T. Yardley, J. Chem. Phys. **46**, 4222 (1967).

[8] K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, Inc., New York, 1959), pp. 260–348.

[9] J. L. Stretton, Trans. Faraday Soc. **61**, 35 (1965).

[10] K. Herzfeld, Disc. Faraday Soc. **33**, 22 (1962).

[11] K. Herzfeld, J. Chem. Phys. **47**, 748 (1967).

[12] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Co. Inc., New York, 1950) also *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* 2nd. ed. (D. Van Nostrand Co. Inc., New York, 1945).

[13] CO is also a significant constituent in many electrical discharge CO_2 and CO_2–N_2 lasers. However, the vibrational relaxation of CO will not be included in the main portion of this paper. Some brief comments on the effect of CO will be made in Sec. IV.

[14] Yardley and Moore call processes of this type (17), "intramolecular V–V energy sharing" because the vibrational energy exchanged is shared between the molecules.

[15] T. L. Cottrell and J. C. McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths Scientific Publications Ltd., London, 1961), pp. 26–29.

[16] R. L. Taylor, M. Camac, and R. M. Feinberg, "Measurements of Vibration-Vibration Coupling in Gas Mixtures," *Proceedings of the Eleventh Symposium (International) on Combustion*, 14–20 August, 1966 (Combustion Institute, Pittsburg, Pa., 1967), pp. 49–65.

[17] L. Landau and E. Teller, Physik. Z. Sowjetunion **10**, 34 (1936).

[18] Reference 8, pp. 83–90.

[19] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, New York, 1954), pp. 1110–1111.

[20] N. H. Johannesen, J. Fluid Mech. **10**, 25 (1961).

[21] P. A. Blythe, J. Fluid Mech. **10**, 33 (1961).

[22] R. N. Schwartz, Z. I. Slawsky, and K. Herzfeld, J. Chem. Phys. **20**, 1591 (1952).

[23] F. I. Tancoz, J. Chem. Phys. **25**, 439 (1956).

[24] Reference 15, pp. 88–91.

[25] E. F. Smiley and E. H. Winkler, J. Chem. Phys. **22**, 2018 (1954).

[26] W. Griffith, D. Brickl, and V. Blackman, Phys. Rev. **102**, 1209 (1956).

[27] N. H. Johannesen, H. K. Zienkiewicz, P. A. Blythe, and J. H. Gerrard, J. Fluid Mech. **13**, 213 (1962).

[28] H. K. Zienkiewicz, N. H. Johannesen, and J. H. Gerrard, J. Fluid Mech. **17**, 267 (1963).

[29] W. D. Greenspan and V. H. Blackman, Bull. Amer. Phys. Soc. **2**, 217 (1957).

[30] J. Daen and P. C. T. deBoer, J. Chem. Phys. **36**, 1222 (1962).

[31] V. Blackman, J. Fluid Mech. **1**, 61 (1956).

[32] W. J. Witteman, J. Chem. Phys. **37**, 655 (1962).

[33] H. K. Zienkiewicz and N. H. Johannesen, J. Fluid Mech. **14**, 499 (1963).

[34] M. Camac, "CO_2 Relaxation Processes in Shock Waves," Avco Everett Research Laboratory Research Report 194, 1964 (unpublished).

[35] D. Weaner, J. F. Roach, and W. R. Smith, J. Chem. Phys. **47**, 3096 (1967).

[36] I. R. Hurle and A. G. Gaydon, Nature **184**, 1858 (1959).

[37] P. V. Slobodskaya and E. S. Gasilevich, Opt. Spectry. **7**, 58 (1959).

[38] P. V. Slobodskaya, Opt. Spectr. **22**, 14 (1967).

[39] T. L. Cottrell, I. M. Macfarlane, and A. W. Read, Trans. Faraday Soc. **63**, 2093 (1967).

[40] E. H. Carnevale, C. Carey, and G. Larson, J. Chem. Phys. **47**, 2829 (1967).

[41] M. H. Wallman, Ann. Phys. (Leipzig) **20**, 671 (1934).

[42] The other measurement by I. M. Metter [Phys. Zeit. Sowjetunion **12**, 233 (1937)] yields a much larger rate constant $k(C2(1\to0), N)=2.2\times10^{-13}$ cm^3·part^{-1}·sec^{-1} at $T=273$°K and is also shown on Fig. 2. However, the details of this experiment are not available.

[43] D. Shelley, Ph.D. thesis, Catholic University of America, Washington, D.C., private communication from M. C. Henderson.

[44] P. K. Cheo, J. Appl. Phys. **38**, 3563 (1967); confirmed by unpublished data of J. Wilson at Avco Everett Research Laboratory.

[45] J. T. Yardley and C. B. Moore, J. Chem. Phys. **46**, 4491 (1967).

[46] A. Van Itterbeek, P. DeBruyn, and P. Mariens, Physica **6**, 511 (1939).

[47] B. Widom and S. H. Bauer, J. Chem. Phys. **21**, 1670 (1953).

[48] A. Eucken and E. Nümann, Z. Phys. Chem. **36B**, 163 (1937).

[49] R. Marriott, Proc. Phys. Soc. (London) **88**, 83 (1966).

[50] T. L. Cottrell, R. C. Dobbie, J. McLain and A. W. Read, Trans. Faraday Soc. **60**, 251 (1964).

[51] C. B. Moore, J. Chem. Phys. **43**, 2979 (1965).

[52] J. W. L. Lewis and K. P. Lee, J. Acoust. Soc. Am. **38**, 813 (1965).

[53] T. L. Cottrell and M. A. Day, *Molecular Relaxation Processes* (Academic Press Inc., New York, 1966), pp. 253–256.

[54] R. Marriott, Proc. Phys. Soc. (London) **86**, 1041 (1965).

[55] T. G. Winter, J. Chem. Phys. **38**, 2761 (1963).

[56] R. C. Millikan and D. R. White, J. Chem. Phys. **39**, 98 (1963).

[57] P. W. Huber and A. Kantrowitz, J. Chem. Phys. **15**, 275 (1947).

[58] W. G. Shilling and J. R. Partington, Phil. Mag. **6**, 920 (1928); **9**, 1020 (1930).

[59] P. S. H. Henry, Nature **129**, 200 (1932).

[60] S. J. Lukasik and J. E. Young, J. Chem. Phys. **27**, 1149 (1957).

[61] I. R. Hurle, J. Chem. Phys. **41**, 3911 (1964).

[62] A. G. Gaydon and I. R. Hurle, *Proceedings of the Eighth Symposium on Combustion*, 1961 (Academic Press Inc., New York, 1962), pp. 309–318.

[63] J. P. Appleton, J. Chem. Phys. **47**, 3231 (1967).

[64] M. C. Henderson, "Thermal Relaxation in N_2, O_2, and CO with Admixtures," *Fourth International Congress on Acoustics, Copenhagen*, 21–28 August, 1962 (The Organization Committee of the Fourth International Congress on Acoustics, Copenhagen, 1962).

[65] R. C. Millikan and D. R. White, J. Chem. Phys. **39**, 3209 (1963).

[66] R. L. Taylor and S. Bitterman, Bull. Am. Phys. Soc. **13**, 1591 (1968).

[67] D. R. White, J. Chem. Phys. **46**, 2016 (1967).

[68] D. R. White, J. Chem. Phys. **48**, 525 (1968).

[69] These adjusted theoretical calculations are essentially the same curves suggested by White to fit his data. White used empirical correlations developed by Millikan and White[65] on the basis of a study of relaxation data for many diatomic molecules.

[70] D. R. White and R. C. Millikan, J. Chem. Phys. **39**, 1803 (1963).

[71] H. J. Bauer and N. Roesler, *Molecular Relaxation Processes* (Chemical Society Special Publication No. 20, The Chemical Society, Burlington House, London, 1966), pp. 245–252.

[72] M. C. Henderson and E. J. Queen, J. Acoust. Soc. Am. **34**, 714 (1962).

[73] D. G. Jones, J. D. Lambert, and J. L. Stretton, Proc. Phys. Soc. (London) **86**, 857 (1963).

[74] M. C. Henderson, A. V. Clark, and P. R. Lintz, J. Acoust. Soc. Am. **37**, 457 (1965).

[75] W. A. Rosser, Jr., A. D. Wood, and E. T. Gerry (to be published).

[76] R. L. Taylor and S. Bitterman (to be published).

[77] There has been some referencing of an experimental measurement by J. E. Morgan and H. I. Schiff [Canadian J. Chem. **41**, 903 (1963)] as the probability of Process (5). However, as stated in their paper, Morgan and Schiff's measurement refers to the deactivation of mode ν_2 of CO_2, i.e., Process (1). The rate value obtained by Morgan and Schiff at $T=300$°K is not in agreement with the present data for Process (5) but is in excellent agreement with the experimental data for Process (1), Fig. 2. Also, W. L. Starr and T. M. Shaw [J. Chem. Phys. **44**, 4181 (1966)] have measured the deactivation of vibrationally excited N_2 by CO_2 in a flow system. Their rate of $(8.0\pm0.9)\times10^{-14}$ cm^3·part^{-1}·sec^{-1} at $T=300$°K is also in disagreement with the more direct measurements shown on Fig. 11.

[78] R. D. Sharma and C. A. Brau, Phys. Rev. Letters **19**, 1273

(1967). A more complete version of the Sharma–Brau theory is found in J. Chem. Phys. **50**, 924 (1969).

[79] The concentration of H_2O is needed to analyze the relaxation data for the T–V Process (1). Fortunately, the investigators had already analyzed their data for a T–V process, so that even if ψ was not given, τ_{CH} or $P(C2(1\rightarrow0), H)$ was directly available in the papers.

[80] W. J. Witteman, Phys. Letters **18**, 125 (1965).

[81] W. J. Witteman, IEEE J. Quantum Electronics, 375 (1966).

[82] J. T. Yardley and C. B. Moore, J. Chem. Phys. **48**, 14 (1968).

[83] D. R. White and R. C. Millikan, AIAA J. **2**, 1844 (1964).

[84] These results on Fig. 13 have been corrected for an error which makes the results shown in Fig. 12 of Ref. 16 too high by a factor of about 2.6. The authors are indebted to Dr. White for pointing out this error.

[85] W. D. Breshears and P. F. Bird, J. Chem. Phys. **48**, 4768 (1968).

[86] D. R. White, J. Chem. Phys. **49**, 5472 (1968).

[87] Remember that ν_2 and ν_1 are assumed to be in local equilibrium through Reaction (14).

[88] L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, Phys. Rev. Letters **17**, 233 (1966).

[89] J. T. Houghton, Proc. Phys. Soc. (London) **91**, 439 (1967).

[90] P. K. Cheo, Bull. Am. Phys. Soc., **13**, 207 (1968).

[91] R. L. Taylor and S. Bitterman (further details to be published, see Ref. 66).

[92] C. B. Moore, *Fluorescence*, G. G. Guilbault, Ed. (Marcel Dekker, New York, 1967), Chap. 3, pp. 133–199.

[93] G. Herzberg, Ref. 12, Part II, pp. 215–218.

[94] C. K. Rhodes, M. J. Kelley, and A. Javan, J. Chem. Phys. **48**, 5730 (1968).

[95] R. Sharma, J. Chem. Phys. (to be published).

[96] C. B. Moore (private communication) has suggested that since N_2 and Ar are about equally efficient in deactivating mode ν_3 (Refs. 7 and 45), this same comparison may hold for mode ν_2. This suggestion leads to

$$k(C2(1\rightarrow0), N) \sim (0.1\text{–}0.3)\, k(C2(1\rightarrow0), C)$$

in moderate agreement with the CO_2–N_2 laser result of Cheo.[44]

[97] K. L. Wray, J. Chem. Phys. **36**, 2597 (1962).

[98] R. D. Sharma and C. A. Brau (private communication, 1968).

[99] F. A. Angona, J. Acoust. Soc. Am. **25**, 1116 (1953).

[100] A. Eucken and R. Becker, Z. Phys. Chem. **27B**, 235 (1934).

[101] R. H. Frick, Ph.D. dissertation, University of California, 1942.

[102] E. F. Fricke, J. Acoust. Soc. Am. **12**, 245 (1940).

[103] W. Griffith, J. Appl. Phys. **21**, 1319 (1950).

[104] M. C. Henderson and L. Peselnick, J. Acoust. Soc. Am. **29**, 1074 (1957).

[105] H. O. Kneser and H. Roesler, Acoustica **9**, 224 (1959).

[106] L. Küchler, Z. Phys. Chem. **41B**, 199 (1938).

[107] R. W. Leonard, J. Acoust. Soc. Am. **12**, 241 (1940).

[108] W. T. Richards and J. A. Reid, J. Chem. Phys. **2**, 193 (1934).

[109] F. D. Shields, J. Acoust. Soc. Am. **29**, 450 (1957).

[110] F. D. Shields, J. Acoust. Soc. Am. **31**, 248 (1959).

[111] A. Van Itterbeek and P. Mariens, Physica **5**, 153 (1938).

[112] A. Van Itterbeek and P. Mariens, Physica **7**, 125 (1940).

[113] K. F. Buschmann and K. Schäfer, Z. Phys. Chem. **50B**, 73 (1941).

[114] W. H. Pielemeier, H. L. Saxton and D. Telfair, J. Chem. Phys. **8**, 106 (1940).

[115] M. Gustavson, Ph.D. dissertation, Cornell University, 1952.

[116] A. Kantrowitz, J. Chem. Phys. **14**, 150 (1946).

[117] M. C. Henderson and J. Z. Klose, J. Acoust. Soc. Am. **31**, 29 (1959).

[118] I. M. Metter, Phys. Z. Sowjetunion **12**, 233 (1937).

[119] R. W. Higgs and R. N. Torborg, J. Acoust. Soc. Am. **42**, 1038 (1967).

[120] F. A. Gutowski, J. Acoust. Soc. Am. **28**, 478 (1956).

[121] V. O. Knudsen and E. Fricke, J. Acoust. Soc. Am. **12**, 255 (1940).

[122] W. H. Pielemeier, J. Acoust. Soc. Am. **15**, 22 (1943).

[123] H. J. Bauer and E. Liska, Z. Phys. **181**, 356 (1964).

[124] J. W. L. Lewis and F. D. Shields, Bull. Am. Phys. Soc. **2**, 532 (1966).

[125] J. G. Clouston, A. G. Gaydon and I. I. Glass, Proc. Roy. Soc. (London) **248**, 429 (1958).

[126] V. H. Blackman, Tech. Report II-20, NR 061-020, Phys. Dept. Princeton Univ., 1955.

[127] R. Holmes, F. A. Smith and W. Tempest, Proc. Phys. Soc. (London) **81**, 311 (1963).

[128] F. D. Shields and Kun Pal Lee, J. Acoust. Soc. Am. **35**, 251 (1963).

[129] J. G. Parker, J. Chem. Phys. **34**, 1763 (1960).

[130] S. A. Losev and N. A. Generalov, Sov. Phys.-Dokl. **6**, 1081 (1962).

[131] D. D. Eden, R. B. Lindsay and H. Zink, J. Eng. Power **83**, 137 (1961).

[132] Y. Fujii, R. B. Lindsay and K. Urushihara, J. Acoust. Soc. Am. **35**, 961 (1963).

[133] H. Roesler and K. F. Sahm, J. Acoust. Soc. Am. **37**, 386 (1965).