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PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

Theory of Small-Energy-Transfer Collisions in Dominant Long-Ranged Forces: H^+-H_2 and e^--H_2 Vibrational Excitation

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In the two-state approximation analytic formulas are derived for the inelastic cross section in the limit in which the particle velocity is large relative to the energy defect. These formulas involve a mixing parameter and two eigenphase shifts. For scattering in a $C(X)/R^n$ potential, where X is an internal coordinate of the target, the integral cross section is presented in closed form, with parameters given by the elastic-superelastic potential-difference strength, the coupling strength, the velocity, and a cutoff for the singular potential, taken to be the target radius. Results are given for H^+-H_2, e^--H_2, and e^--N_2 vibrational excitation. The theory appears to be correct for the high-energy tail of the cross sections.

I. INTRODUCTION

It is desirable to obtain an analytic representation of the multichannel theory wherever possible to avoid the heavy labor of the numerical solution of the close-coupling equations. In addition, an analytic representation facilitates the study of the scattering as a function of laboratory parameters and is more easily generalizable to classes of problems; thus, it may be of more direct use to the experimentalist than a numerical representation. Also, the inversion of scattering data to determine the potential parameters is greatly facilitated. Olson and Smith[1] have pursued this approach in cases where well-defined curve crossings allow the use of the Landau-Zener inelastic probability in conjunction with the quantum-mechanical addition of amplitudes to yield analytic results for the cross section in which a maximum use is made of experimental data. It is the purpose of this paper to derive analytic formulas for the multichannel problem (using the two-state approximation as a convenient example) in which the criterion of validity for the method of solution used is that the particle velocity be large relative to the energy defect. It is found that diagonalization of the close-coupling equations for two open channels yields a constant mixing parameter and two eigenphase shifts. The

eigenphase shifts are identical to the shifts in the Stueckelberg[2] theory if $k_1 = k_0$ and R_x (crossing point) replaces a large-R cutoff R_0 as the upper limit of integration. The validity of the theory does not require the existence of a crossing point in the potential curves. In addition, this representation appears to be easily generalized to include more than two states. The latter are inherent limitations of the Stueckelberg-Landau-Zener[3] (SLZ) theory, which in addition has an incorrect high-energy behavior.[4]

II. THEORY

We desire to diagonalize the close-coupling equations

$$(\underline{D}_D + \underline{V})\,\underline{\Phi} = 0\,, \tag{1a}$$

$$\underline{D}_D = \underline{I}D^2 = \underline{I}\left(\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2}\right) + k_i^2 \tag{1b}$$

by a unitary transformation,[5]

$$\underline{\Phi} = \underline{S}^\dagger \underline{F}\ . \tag{2}$$

We obtain

$$(\underline{D} + \underline{V}_D)\,\underline{F} = 0, \tag{3a}$$

$$\underline{V}_D = \underline{S}\,\underline{V}\,\underline{S}^\dagger\ , \tag{3b}$$

$$\underline{D} = \underline{I}D^2 + \underline{S}\,[D^2, \underline{S}^\dagger]\ . \tag{3c}$$

In general $\underline{S}$ is an R-dependent matrix, so the equations are still coupled in the kinetic energy matrix $\underline{D}$. For the moment let us adopt an "adiabatic" representation by setting the R-dependent $\underline{S}$ matrix equal to its value at some R_0. There the commutator in (3c) vanishes, and using the transformation matrix (at R_0)

$$\underline{S} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

$$= \begin{pmatrix} (1+\lambda_+^2)^{-1/2} & \lambda_+(1+\lambda_+^2)^{-1/2} \\ \lambda_-(1+\lambda_-^2)^{-1/2} & (1+\lambda_-^2)^{-1/2} \end{pmatrix}\ , \tag{4a}$$

$$\lambda_+ = -\lambda_- \tag{4b}$$

we derive the following parameters for the inelastic cross section[6] (in a.u.), where we have evaluated the eigenphase shifts in the JWKB approximation:

$$Q_{01} = (\pi/k_0^2)\textstyle\sum_l (2l+1)\,P_l(E)\ , \tag{5a}$$

$$P_l(E) = \frac{4\chi(R_0)^2}{[1+\chi(R_0)^2]^2}\sin^2(\eta_l^+ - \eta_l^-)\ , \tag{5b}$$

$$\chi(R_0) = \text{damping function} = \tan\theta = \lambda_+$$

$$= -\,[2V_{01}(R_0)]^{-1}\,(\Delta V(R_0) + \epsilon - \{[\Delta V(R_0) + \epsilon]^2 + 4V_{01}(R_0)^2\}^{1/2})\ , \tag{5c}$$

$$\Delta V(R_0) = V_{00}(R_0) - V_{11}(R_0)\ , \tag{5d}$$

$$\eta_l^{(\pm)} = \tfrac{1}{2}\pi(l+\tfrac{1}{2}) - k_0 R_\pm + \int_{R_\pm}^{R_0} dR(\mu_\pm - k_0)\ , \tag{5e}$$

$$\mu_\pm = [k_0^2 - U_\pm(R) - (l+\tfrac{1}{2})^2/R^2]^{1/2}\,, \tag{5f}$$

$$U_\pm = \tfrac{1}{2}\{(U_{00}+U_{11}) - 2M\epsilon \pm [(U_{00} - U_{11} + 2M\epsilon)^2 + 4U_{01}^2]^{1/2}\}\ , \tag{5g}$$

$$U_{ij} = 2MV_{ij}\ , \tag{5h}$$

$$\epsilon = \text{energy defect} = k_0^2/2M - k_1^2/2M\ . \tag{5i}$$

The value of R_0 is arbitrary.

The theory may not be useful unless the following physical conditions are met: (a) For the damping function, Eq. (5c), $\Delta V \gg \epsilon$ over most of the range of R, and ΔV and V_{01} are the *same* function of R,

$$\Delta V = \alpha f(R),\quad V_{01} = \beta f(R)\ . \tag{6}$$

Then, neglecting ϵ relative to ΔV, $\chi = \chi_c$ is a constant and the transformation matrix in Eq. (2) is a constant matrix:

$$\chi_C = \text{damping constant} = -\,(1/2\beta)[\alpha - (\alpha^2 + 4\beta^2)^{1/2}]\ . \tag{7}$$

(b) For purposes of analysis we expand the eigenphase shifts in inverse powers of the energy; the phase difference in Eq. (5b) then becomes, to $O(E^{-1})$,

$$\Delta\eta_l = \eta_l^{(+)} - \eta_l^{(-)} = \int_0^\infty dt\,[(\Delta V + \epsilon)^2 + 4V_{01}^2]^{1/2}. \tag{8}$$

Asymptotically $\Delta\eta$ is of the order

$$\Delta\eta \approx \epsilon\tau_c = \epsilon a/\upsilon\ , \tag{9}$$

where a is the size of the potential and υ is the particle velocity. Thus to neglect ϵ at the infinity means that

$$\epsilon a/\upsilon \ll 1\ . \tag{10}$$

The Massey[7] adiabatic criterion for determining the velocity for maximum inelastic probability is

$$\epsilon a/\upsilon \approx 1\ , \tag{11}$$

so that this approximation will be valid in the high-energy tail of the cross section. Likewise, we have to meet the same condition encountered in condition (a) above for the damping function, that $\Delta V \gg \epsilon$ over most of the range of R; otherwise the error in the phase difference will be the same order as its magnitude. Both conditions (a) and (b) suggest that we choose a large R cutoff R_0 when ΔV is small relative to ϵ. The insensitivity of the

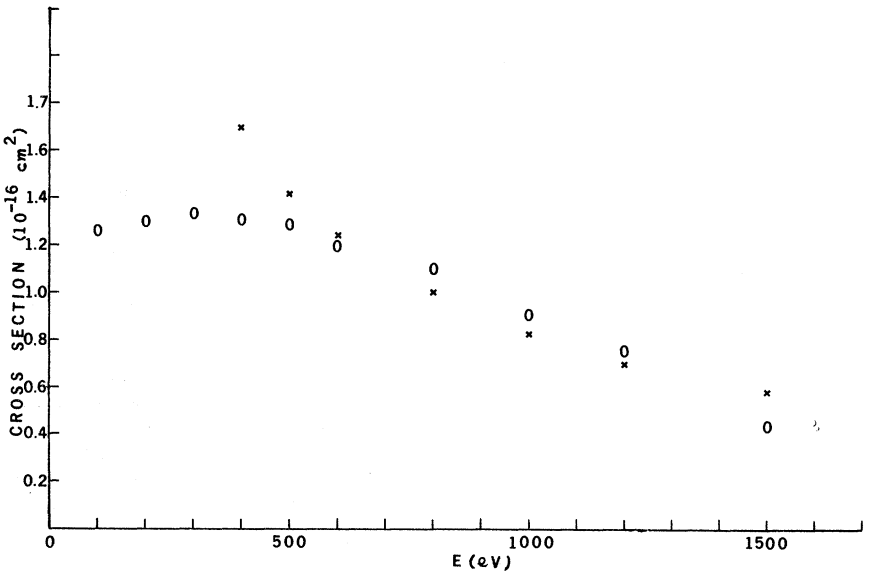

FIG. 1. Cross section vs incident energy for H^+-H_2 $0 \rightarrow 1$ vibrational excitation. Open circles: experimental results of Herrero and Doering (Ref. 13); crosses: present theory.

cross section to such a cutoff (R_0 large enough to represent infinity for a given potential) is then a measure of the usefulness of the theory. In the calculations considered in Sec. III, conditions (a) and (b) are satisfied, and calculations for R_0 chosen when $\Delta V \ll \epsilon$ indicates that R_0 represents infinity for the potential used.

III. CALCULATIONS

In this section we perform calculations for vibrational excitation of H_2 and N_2 by a structureless charged particle. We assume the dominant potential is the isotropic part of the polarization potential, $-\alpha_0(X)/2R^4$, where α_0 is the polarizability as a function of vibrational coordinate X. Extensive calculation[8] on H^+-H_2 vibrational excitation in which the quadrupole and polarization potentials as well as the short-range part of the Hartree potential are included show this to be the case above 200-eV incident energy. If we use Eq. (8) for the phase difference, the integrations over time and impact parameter [using $l+\frac{1}{2}=k_0 b$ and $\sum = k_0 \int db$ in (5a)] can be performed, and we obtain [see the Appendix for general $C(X)/R^n$]

$$Q_{01} = 2\pi p_c \left(\frac{\pi e^2 \alpha_0 \mathfrak{L}}{4\hbar v}\right)^2 \left[\frac{1}{4\sigma^4} - \frac{2}{3!}\left(\frac{\pi e^2 \alpha_0 \mathfrak{L}}{\hbar v}\right)^2 \frac{1}{10\sigma^{10}} + \left(\frac{\pi e^2 \alpha_0 \mathfrak{L}}{\hbar v}\right)^4 \left(\frac{2}{5!}+\frac{1}{3!^2}\right) \frac{1}{16\sigma^{16}} + O(\sigma^{-22} v^{-6})\right] , \quad (12a)$$

$$p_c = 4\chi_c^2/(1+\chi_c^2)^2 , \quad (12b)$$

$$\alpha_0 \mathfrak{L} = (\alpha^2 + 4\beta^2)^{1/2} \quad (12c)$$

[see Eqs. (6) and (7)]. For the $0 \rightarrow 1$ transition in H_2, we have[9]

$$\alpha = -\tfrac{1}{2}(5.414 - 5.885) , \quad (13a)$$

$$\beta = -\tfrac{1}{2}(0.739) , \quad (13b)$$

$$\alpha_0 = \alpha_0(X_{eq}) = 5.178\,62 . \quad (13c)$$

The condition $\Delta V \gg \epsilon$ can now be verified for most of R. For $R=1$, $\Delta V \approx 0.25$ and $\epsilon \approx 0.02$ a.u. $\Delta V \ll \epsilon$ when R is equal to about 3, but most of the scattering has occurred in this region; thus the cutoff R_0 was chosen to be infinity when the integrations to produce (12a) were performed. The parameter σ is a short-range cutoff in the singular potential; in these calculations it is taken to be the internuclear distance, $\sigma = X_{eq}$. This choice is problematic, but so are methods[10] of deriving smooth cutoff functions which allow the polarization potential to be taken into the origin. These cutoffs reduce the potential in the vicinity of the target radius; this may produce a good behavior for electrons which accelerate in this region producing less polarization, but a bad behavior (not enough attraction[11]) for protons or positrons which decelerate to produce more polarization.

Figures 1–3 show results for H^+-H_2, e^--H_2, and e^--N_2, respectively. The e^--N_2 results are very crude since the H_2 matrix elements[9] were used, scaled to account for the different polarizability of N_2 at X_{eq}. Also, only the high-energy tail of the experimental[12] cross section is nonresonant, so that the smooth curve shown is drawn through the middle of the resonance oscillations. Figure 1 shows excellent agreement with the results of Herrero and Doering[13] above 500 eV. At 10^3 eV, $\epsilon/v \approx \frac{1}{10}$, but below 500 eV, $\epsilon/v \approx \frac{1}{5}$, so that the approximation begins to become poor. In addition, the curve may be rising too rapidly in this region,

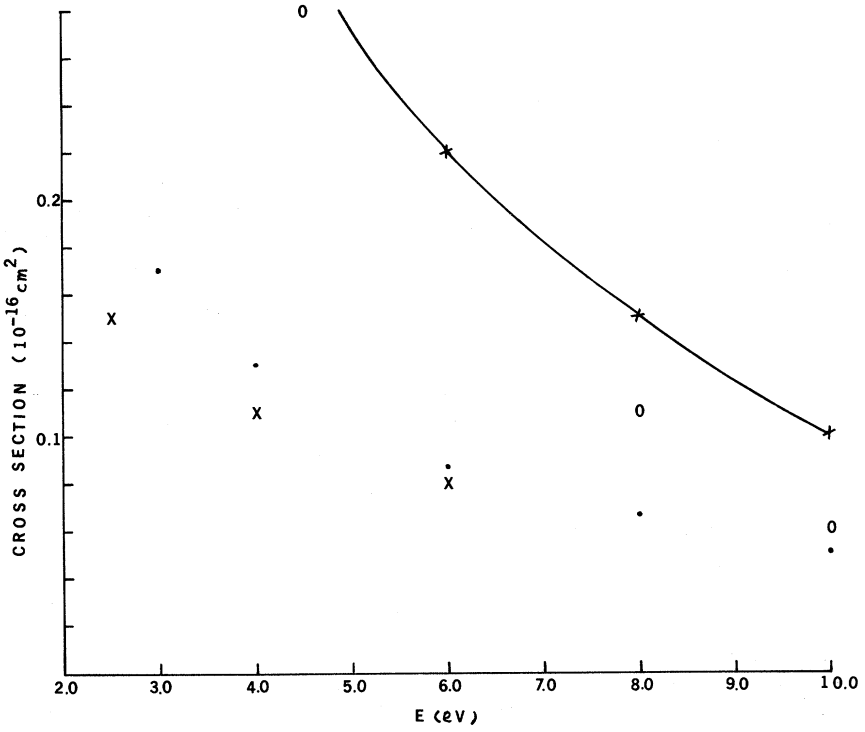

FIG. 2. Cross section vs energy for e^--H_2 $0 \rightarrow 1$ vibrational excitation. Open circles: measurements by Linder (Ref. 16); solid curve: close-coupling calculation by Henry (Ref. 9) including a short-range potential and all long-range potentials modified at small R by smooth cutoff functions; crosses: close-coupling calculation of Henry (Ref. 9) without the short-range potential; data points: present theory.

not as a result of the growth of ϵ/v, but as a result of the nonconvergence of the $\sigma^{-n}v^{-n}$ expansion [Eq. (12a)] in this region (the expansion converges to within $\frac{1}{10}$ at 700, $\frac{1}{6}$ at 500, and $\frac{1}{4}$ at 400 eV). The good agreement may be fortuitous: A more careful treatment of the full second-order potential (analog of the Dalgarno-Lynn[14] potential for H^+-H), which is known to give too much attraction in the monopole contribution but a more reasonable attraction in the R^{-6} quadrupole polarization potential, needs to be considered. However, if the agreement is not fortuitous, then the calculation illustrates the importance of polarization forces in energy regions where most of the scattering is in the forward direction. Below 200 eV, small-impact-parameter wide-angle scattering will become increasingly important and so too will competing electron capture, whose cross section[15] is comparable to the excitation cross section in this region. Figure 2 shows reasonable agreement at 10-eV electron energies, where $\epsilon/v \approx \frac{1}{40}$, but this theory underestimates the cross section at lower energies. Henry's calculation[9] (see his Fig. 3) demonstrates the importance of nonpolarization potential coupling in this region, expected for electrons scattering in an *attractive* short-range potential. Also shown are Henry's results without V_{sr}; these are in much better agreement with our results, which are larger because of the absence of a reducing cutoff function. We believe that the agreement of the no-V_{sr} curves could be quantitative if the calculations contained the same long-range potential, cut off in the same way. However, the agreement with the no-V_{sr} numerical

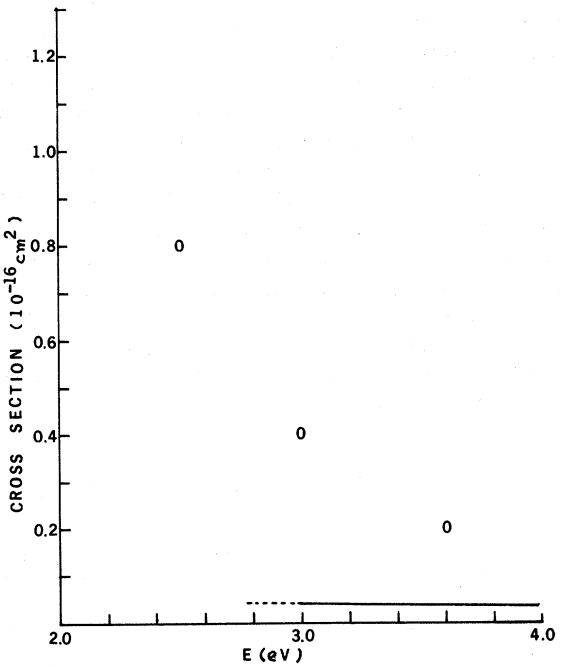

FIG. 3. Cross section vs energy for e^--N_2 $0 \rightarrow 1$ vibrational excitation. Open circles: experimental results of Schulz (Ref. 12) smoothed over resonance oscillations; solid curve: present theory.

close-coupling results is still quite remarkable and is a test of the accuracy of the present theory in this region of energy.

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APPENDIX

The cross section for arbitrary R^{-n} is given by

$$Q_{01} = 2\pi p_c \left(\frac{\pi e^2\lambda}{4\hbar v}\right)^2 \left[(2n-4)^{-1}\sigma^{-(2n-4)} - 2\left(\frac{\pi e^2\lambda}{4\hbar v}\right)^2 \times (4n-6)^{-1}\sigma^{-(4n-6)} + O(\sigma^{-(6n-8)}v^{-4})\right].$$

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Multiquantum Vibrational-Energy Exchange*

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A theory for exchange of vibrational quanta between molecules is formulated which does not rely on the Born expansion of the S matrix. A transformation is derived which diagonalizes the vibrational operators responsible for exchange. The scattering operator is then expanded in a series of rotational tensor operators which permits evaluation of S-matrix elements to all orders. This formulation shows that multiquantum processes, both rotational and vibrational, play an important role when transition moments are large. Numerical calculations for vibrational exchange rates of carbon monoxide are compared with results of the first Born approximation from which they differ significantly. The dependence of the cross section on vibrational-energy defect is much less drastic than that of the Born approximation. The present calculations indicate that cross sections for the exchange of more than one vibrational quantum are substantial, in marked contrast to the Born approximation where they are forbidden. The size of these multiquantum cross sections indicates that they can play an important role in the detailed kinetic modeling of CO lasers.

I. INTRODUCTION

The exchange of quanta of vibrational energy from one molecule to another during a collision (V-V) frequently plays a crucial role in the mechanism of infrared gas lasers. Since the total energy change (defect) associated with such a process is fairly small, the rates for exchange are considerably larger than the rates for thermalization (V-T) processes where a vibrational quantum is given up to the thermal bath. Treanor *et al.*[1] has shown that a nonthermal vibrational population distribution evolves in anharmonic oscillators if the (V-V) exchange rates are sufficiently faster than the (V-T) thermalization rates. The resulting population inversion (partial or complete) gives rise to gain and laser action for the higher vibrational levels. This mechanism has been proposed for several diatomic molecules (e.g., CO, NO) which show laser action in their higher vibrational