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Rotational-Vibrational Excitation of H_2 by Slow Electrons*

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The frame-transformation theory is applied to a calculation of electron scattering from H_2 in the energy range of 1–10 eV. Results are presented for differential as well as integrated cross sections for pure vibrational and rotational-vibrational excitation processes. Our calculations are in very satisfactory agreement with experiment and are subject to easy interpretation.

I. INTRODUCTION

The theory of frame transformation and its application to electron-molecule scattering have been discussed by Chang and Fano[1] (CF). In this paper, we adapt it to calculate rotational-vibrational cross sections in H_2 by electron impact, in the energy range 1–10 eV. We choose H_2 as the target molecule for a number of reasons besides its obvious simplicity. For example, from an experimental point of view, its unusually large rotational spacing permits electron beam measurements of both rotational and vibrational excitation cross sections. In fact, Linder[2] has measured differential cross sections for various excitation processes in H_2 at energies in the desired range. From the theoretical point of view, it is desirable to deal with homonuclear molecules, since the absence of coupling between electronic states of even and odd angular momentum l maximizes the effect of the centrifugal barrier. Consequently, for sufficiently low energies where the nonpenetrating states (d and higher partial waves) are unimportant ($\lesssim 10$ eV), the remaining penetrating states s and p are automatically uncoupled.[3] Thus l may be regarded as a good quantum number outside the core of H_2 (approximately given by the size of the molecule).

Another important consideration is the existence of a close-coupling calculation by Henry.[4] This allows direct comparison of results from the two theories which we will now review.

The close-coupling theory, used by Henry, utilizes a set of base functions, defined in the laboratory frame, and labeled by the observed channels corresponding to various rotational (j) and vibrational (v) states of the molecule. However, as an alternative approach, one may use a different set of base functions, defined in the molecular frame, and characterized by the projection Λ of l on the internuclear axis and by the parametrically fixed internuclear distance s (the Born-Oppenheimer approximation). These two sets are related by transformations described in CF. In principle, one may expand the wave function of the joint electron-molecule system in either set of base functions and obtain complete and equivalent solutions. However, in practice, one is forced to truncate the expansion to a very limited subset, and this is where choice of approach may dictate the validity of the results.

The cogent point is that when the electron is far away from the molecule, the electron-molecule interaction is weaker than the rotational and vibrational Hamiltonians, and the system is conveniently described by the quantum numbers j and v (laboratory frame). On the other hand, when the electron is close in, the opposite situation obtains, and the system is more appropriately described by the quantum numbers Λ and s. The regions, referred to as B and A, respectively,[5] can be determined by examination of the appropriate matrix elements. In general, region A is somewhat larger for the rotation problem than for the vibration. For example, for H_2 the region extends to approximately $10a_0$ and $5a_0$, respectively, where a_0 is the radius of the first Bohr orbit. However, for incident energies exceeding 1 eV, most of the phase-shift accumulation arises from within $5a_0$. Thus, the molecular frame is the appropriate one for calculation of phase shifts. Not only is truncation expected to have little effect, but also we may neglect coupling terms because they correspond to nondiagonal matrix elements of the rotational and vibrational Hamiltonians which are small in region A. The results of this calculation may then be transformed into the laboratory frame, yielding the appropriate rotational-vibrational cross sections.

This method, in the case of H_2, has the advantage of circumventing *coupled* equations, and also of effectively including all rotational and vibrational "intermediate" states. The adverse effect of neglecting intermediate states in the truncation of close coupling calculations in electron-atom scattering has been shown to result in a systematic overestimation of excitation cross sections.[6] Thus, comparison of our results with those of Henry[4] should reveal the significance of this effect in electron-molecule scattering.

Our calculation requires the electron-H_2 interaction potential and its variation with the internuclear distance. We include static field, an effective polarization potential, and electron exchange effects. These terms are essentially the same as used by Henry and are discussed further in Sec. II. A review of the frame transformation theory is given in Sec. III. In Sec. IV we present results for various rotational-vibrational differential and integrated cross sections, and discuss our results in relation to those of Henry and to experiment. Finally, we give our conclusions in Sec. V.

II. ELECTRON-H_2 POTENTIALS

We consider electron impact energies below the electronic excitation threshold of H_2. Thus, the Hamiltonian of the electron-molecule system may be represented by an effective one-electron Hamiltonian

$$H = -(\hbar^2/2m)\nabla^2 + H_R(\hat{s}) + H_V(s) + V(r, \hat{r};\, s, \hat{s}), \tag{2.1}$$

where m is the reduced mass of the electron-H_2 system, the first term is the kinetic energy of the electron, H_R and H_V are the rotational and vibrational Hamiltonians of the molecule, respectively, and V is the interaction potential with the molecule in the ${}^1\Sigma_g^+$ ground state ϕ_0. As in electron-atom scattering, V contains short-range direct and exchange potentials and a long-range polarization potential. In addition, we now have potentials due to the molecule's permanent electric multipoles. In general, these potentials have spherically symmetric components as well as anisotropic ones. We use rydberg units for the remainder of the paper.

For the short-range potential, we use the wave function given by Wang[7] to represent the ground state ϕ_0 of H_2. If we ignore the cross terms in $|\phi_0|^2$ in calculating the electron-molecule interaction potential, we may write

$$v_\lambda(r,s)=\begin{cases}(2\lambda+1)\int_{-1}^{1}U(y)P_\lambda(t)dt & (\lambda \text{ even})\\ 0 & (\lambda \text{ odd})\end{cases}, \tag{2.2}$$

where r is the distance of the electron from the center of the molecule, s is the internuclear separation,

$$y=(r^2+s^2/4+rs)^{1/2}, \tag{2.3}$$

$$U(y)=[y^{-1}+z(s)]\,e^{-2z(s)y}, \tag{2.4}$$

and P_λ is a Legendre polynomial of order λ. The effective nuclear charge $z(s)$ has been calculated by Rosen[8] for various internuclear separations. A fit to Rosen's results yields

$$z(s)=1+(0.863-0.319s)\,e^{-0.641s}. \tag{2.5}$$

Asymptotically our choice of molecular wave function results in exponential behavior for the static potential contributions to v_0 and v_2. In order to have the correct asymptotic behavior for the interaction potential we add long-range electron-quadrupole and polarization interactions to the short-range portions. These long-range potentials have been calculated by Lane and Geltman[9] and Lane and Henry,[10] respectively, at the equilibrium internuclear separation. Following Henry,[4] we assume that the long-range interactions are of the form

$$v_\lambda^L(r,s)=\begin{cases}G_\lambda(s)g_\lambda(r) & \text{for } r\geq R_c(s)\\ 0 & \text{for } r<R_c(s)\end{cases}, \tag{2.6}$$

where $g_\lambda(r)$ is calculated at the equilibrium internuclear separation and factors $G_\lambda(s)$ for the quadrupole moment and polarizabilities have been calculated by Kolos and Wolniewicz[11,12] and are given in Table I. We note that only even values of λ are nonvanishing owing to symmetry under permutation of the nuclei.

We have introduced here a cutoff radius R_c for the long-range potentials, a procedure analogous to that used in electron-atom scattering. Parameter R_c is determined by the size of the molecule which in turn is dependent on the internuclear separation s. The reason for its introduction is that for $r\leq R_c$ the incident electron is moving at speeds comparable to those of the bound electrons, thus causing the adiabatic picture to break down. Further, since the perturbing effect of the nearby electron on the molecule is large, the present treatment becomes inadequate. However, these potentials are not expected to be important in this region since exchange effects tend to exclude the incident electron and, if it should enter, it moves through very rapidly.

In Henry's calculation R_c is chosen to be zero for all values of s. Consequently, the maximum absolute value of his attractive potential occurs at the same r for any value of s. However, the value of r at which maximum attraction occurs should increase as s is increased. To account for this we choose $R_c(s)$ so that

$$\int_0^{R_c(s)}|\phi_0(\vec{r}_i,s)|^2 d\vec{r}_i=x, \tag{2.7}$$

with x nonzero. Thus, the cutoff radius is a measure of the "percentage size" of the molecule for a given internuclear separation. In the last column of Table I we give $R_c(s)$ for $x=0.25$.

Electron exchange effects are included in the manner given by Henry and Lane,[13] who used a five-term single-center function to describe the H_2 molecule. We neglect the dependence of the molecular function on s and so the exchange term reduces to that given in Ref. 10, Eq. (24).

III. BODY-FRAME TREATMENT AND FRAME TRANSFORMATION

We review the essentials of the laboratory-frame and body-frame approaches as discussed in CF. Since the total wave function is always a doublet spin state and the target remains in a singlet state, we may completely disregard spin. In other words, we may describe the eigenfunctions of H in Eq. (2.1) as if for a "spinless" electron, provided we properly account for exchange as part of the potential. Hence, in the laboratory-frame treatment we may represent the total wave function for e^--H_2 by the expansion

$$\Psi_{JM}(\vec{r},\vec{s})=\sum_{ljv}r^{-1}F_{ljv}^{J}(r)\Phi_{JM}^{lj}(\hat{r},\hat{s})Z_v(s), \tag{3.1}$$

where F is a radial function. The vibrational wave function Z_v is an eigenfunction of H_v, and Φ is obtained by coupling an eigenfunction of H_R to the electron's orbital angular momentum l, conserving total angular momentum J and its projection M. Substituting (3.1) into the Schrödinger equation with H given by (2.1) and integrating over s, we obtain the infinite set of coupled equations given by Eq. (10) of Henry.[4] The close-coupling approximation results from truncating the set to a manageable number of equations, and solving for the appropriate scattering matrices which can then be related to cross sections.

In the body-frame approach we may expand the total wave function as follows:

$$\Psi_{JM}(\vec{r}',\vec{s})=\sum_{l\Lambda}r^{-1}\,G_{l\Lambda}^{J\pm}(r,s)X_{JM}^{l\Lambda\pm}(\hat{r},\hat{s}), \tag{3.2}$$

where G is a radial function parametric in s. The body-frame function X is characterized by Λ, the projection of l (or J) on the molecular axis, and the sign ± indicates the eigenvalue of reflection in a plane containing this axis. The prime on r indicates electron coordinates in the molecular frame. As explained in CF, the base functions in Eqs. (3.1) and (3.2) are related through the following successive unitary transformations. Rotation transforms eigenfunctions of j to those of Λ by

$$X_{JM}^{l\Lambda\pm}=\sum_j \Phi_{JM}^{lj}\; U_{j\Lambda}^{lJ\pm} \tag{3.3a}$$

and its inverse is

$$\Phi_{JM}^{lj}=\sum_\Lambda X_{JM}^{l\Lambda\pm}\;\tilde{U}_{\Lambda j}^{lJ\pm}\,, \tag{3.3b}$$

while vibration transforms eigenfunctions depending on v to functions parametric in s by

$$G_{l\Lambda}^{J\pm}(r,s)=\sum_{vj} F_{ljv}^{J}(r)\,Z_v(s)\,U_{j\Lambda}^{lJ\pm} \tag{3.4a}$$

and its inverse is

$$F_{ljv}^{J}(r)=\sum_\Lambda \int ds\, G_{l\Lambda}^{J\pm}(r,s)\,Z_v(s)\,\tilde{U}_{\Lambda j}^{lJ\pm}\,. \tag{3.4b}$$

We observe that Eq. (3.1) transforms into Eq. (3.2) after using Eqs. (3.3b) and (3.4b) and the following closure relations:

$$\sum_j \tilde{U}_{\Lambda j}^{lJ\pm}\; U_{j\Lambda'}^{lJ\pm}=\delta_{\Lambda\Lambda'}\;, \tag{3.5a}$$

$$\sum_v Z_v(s)Z_v(s_1)=\delta(s-s_1)\;. \tag{3.5b}$$

The same transformation reduces the laboratory-frame equations of Henry[4] to the following molecular-frame equations:

$$\begin{aligned}\left(-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-E\right)G_{l\Lambda}^{J}(r,s)&\\ +\sum_{l'}(X_{JM}^{l\Lambda}\,|\,V_d\,|\,X_{JM}^{l'\Lambda})G_{l'\Lambda}^{J}(r,s)&\\ +\sum_{\Lambda'}(X_{JM}^{l\Lambda}\,|\,H_R\,|\,X_{JM}^{l\Lambda'})\,G_{l\Lambda'}^{J}(r,s)&\\ +\sum_v H_V(s)\,Z_v(s)\int_0^\infty ds_1\;G_{l\Lambda}^{J}(r,s_1)\,Z_v(s_1)&\\ =\sum_{l'\Lambda'}\int d\vec{r}_1\,K(l\Lambda,\;l'\Lambda';\;JM\,|\,r_1,\,r;\;s)G_{l'\Lambda'}^{J}(r_1,s)\;,&\end{aligned} \tag{3.6}$$

where the direct potential is given by

$$V_d(r,s)=\sum_{\lambda=\text{even}}[V_\lambda(r,s)+V_\lambda^L(r,s)]P_\lambda(\cos\hat{r}\cdot\hat{s}) \tag{3.7}$$

and K is an exchange kernel given by

$$\begin{aligned}K(l\Lambda,\;l'\Lambda';\;JM\,|\,r_1,r;\;s)&\\ =\int d\hat{r}\int d\vec{r}_2\,X_{JM}^{l\Lambda *}(\hat{r},\hat{s})\;\phi_0(\vec{r}_1,\,\vec{r}_2,\,s)&\\ \times(1/|\vec{r}-\vec{r}_2|)\,\phi_0(\vec{r},\vec{r}_2,\,s)\,X_{JM}^{l'\Lambda'}(\hat{r}_1,\hat{s})\;.&\end{aligned} \tag{3.8}$$

In Eq. (3.6) we have suppressed the sign ± with the understanding that only functions of the same sign will couple. Note that the term involving H_R couples non-Σ states of one parity to the Σ state, while similar states of the opposite parity are not coupled to a Σ state, thus giving rise to Λ-doubling. In the next term involving H_V, closure given by (3.5b) can no longer be carried out; thus, both the summation over v and integration over s_1 remain. This term represents the coupling of Born-Oppenheimer states with different internuclear separations or vibronic coupling.

The general utilization of frame transformation theory is discussed in CF but here we need only observe that in (3.6) for $r \lesssim 5a_0$, the matrix elements of H_R and H_V are generally small in comparison with other terms. We have also found that most phase accumulation occurs inside this region in the energy range considered, or, in other words, the important interaction region is $r \lesssim 5a_0$. Hence we can make a reliable approximation by deleting these small terms, thus simplifying Eq. (3.6). In fact, considering only the penetrating s and p orbitals and recalling that λ takes on only even values, Eq. (3.6) reduces to three uncoupled equations for s, p_σ, and p_π electrons, respectively:

$$\begin{aligned}&\left(\frac{d^2}{dr^2}+k^2-v_0(r;\,s)\right)G_{00}(r;\,s)=\text{exchange terms}\;,\\ &\left(\frac{d^2}{dr^2}-\frac{2}{r^2}+k^2-v_0(r;\,s)-\tfrac{1}{5}(3\Lambda^2-2)\,v_2(r;\,s)\right)\\ &\quad\times G_{1\Lambda}(r;\,s)\\ &\quad=\text{exchange terms}\quad\text{for }\Lambda=0,1\;.\end{aligned} \tag{3.9}$$

The exchange terms have been discussed in Sec. II. The equations depend parametrically on the internuclear separation s, but are not dependent on either the total angular momentum J, or on the sign ±. In fact these equations become essentially the fixed-nuclei approximation equations.[3]

In principle, we should integrate Eqs. (3.9) to $r \simeq 5a_0$, transform to the close-coupling equations of Henry[4] by (3.4a), and then integrate to infinity. However, almost all phase accumulation occurs inside $5a_0$ for the energy region considered, and so integrating further has little effect on the eigenphases. Thus, we only solve Eqs. (3.9) subject to the boundary conditions

$$\begin{aligned}&G_{l\Lambda}(0;\,s)=0\;,\\ &G_{l\Lambda}(r;\,s)\underset{r\to\infty}{\sim}\sin(kr-\tfrac{1}{2}l\pi)+R_{l\Lambda}(s)\cos(kr-\tfrac{1}{2}l\pi)\;,\end{aligned} \tag{3.10}$$

where the R matrix is simply $\tan\delta_{l\Lambda}(s)$, and is related to a t matrix through

$$\begin{aligned}t_{l\Lambda}(s)&=R_{l\Lambda}(s)\,[1-iR_{l\Lambda}(s)]^{-1}\\ &=\sin\delta_{l\Lambda}(s)\,e^{i\delta_{l\Lambda}(s)}.\end{aligned} \tag{3.11}$$

In Eqs. (3.9) we have oversimplified the problem by misrepresenting the potential inside the core. In particular, at the position of the nuclei, a single-center expansion about the molecular center is inadequate. The only saving feature is that for s waves, the exchange force tends to keep the incident electron out of the core by requiring its wave function to have a node at the molecular mean radius, and for p and higher partial waves, the centrifugal barrier also tends to keep the incident electron outside the core. We may attempt to amend this oversimplification in a single center expansion by taking many terms in the summation over l in Eq. (3.1). Such a calculation was performed for an energy of 4.5 eV at the internuclear separation $s = 1.4 a_0$, with $l = 1, 3, \ldots, 9$. The result showed that the p_σ phase shift changes by about 5% over that obtained from Eqs. (3.9). This indicates that errors introduced by using Eqs. (3.9) are not serious, and that these simple equations will yield meaningful semiquantitative results.

The t matrix in the body frame, as given in Eq. (3.11), is related to that in the laboratory frame by the transformation equations (3.3) and (3.4). Specifically, we have

$$T_l^J(v'j', vj) = \sum_\Lambda U_{j\Lambda}^{lJ} \int Z_v(s)\, t_{l\Lambda}(s)\, Z_{v'}(s)\, ds\, \tilde{U}_{\Lambda j'}^{lJ}, \tag{3.12}$$

where Λ takes on values from $-l$ to l. This procedure is equivalent to summing over + and − states of reflection in the body frame. Finally, the differential cross section may be obtained from Eq. (3.12) by the normal procedure, e.g., as discussed by Henry.[4] Further, a more transparent result follows when we recouple angular momenta to the angular momentum transfer j_t and apply sum rules which involve total angular momenta, as is outlined in CF. Thus, we obtain[14]

$$\frac{d\sigma}{d\Omega}(j'v', jv) = \frac{k_{j'}}{k_j^3} \sum_{j_t L l l'} b_l^{vv'} b_{l'}^{vv'*}\, W(ll'\,ll'; j_t L)$$

$$\times C(ll'L; 000)^2\, C(jj_tj'; 000)^2 P_L(\cos\theta), \tag{3.13}$$

with

$$b_l^{vv'} = \sum_\Lambda (2l+1)\, i^l\, (-1)^{l+\Lambda}\, C(llj_t; \Lambda -\Lambda 0)$$

$$\times \int Z_v(s)\, t_{l\Lambda}(s)\, Z_{v'}(s)\, ds. \tag{3.14}$$

Note that for H_2, l assumes the values 0 and 1, L the values 0, 1, and 2, and for j_t, the values 0 and 2.

IV. RESULTS AND DISCUSSION

We calculate cross sections for simultaneous rotational and vibrational excitation of molecular hydrogen by electron impact by solving the set of uncoupled equations (3.9) subject to the boundary conditions (3.10). The numerical solution is obtained by using Numerov's method to integrate the equations outwards and inwards, with subsequent matching to obtain a final solution. The asymptotic method of Burke and Schey[15] is used to determine the R matrix from the radial function $G_{l\Lambda}$. Equations (3.9) are solved for internuclear separations $s = 0.8$, 1.2, 1.4, 1.6, 2.0, and $2.4 a_0$, and then the cross sections are obtained from Eq. (3.14).

Phase shifts obtained from a solution of the uncoupled fixed-nuclei equations (3.9) with $x = 0.25$ are given in Fig. 1 as a function of internuclear separation s for energies $E = 1.0$ and 4.5 eV. The vertical bar denotes the equilibrium separation position $s_0 = 1.4 a_0$. On the plot of the p_σ phase shift versus s, we have also given the product of vibrational wave functions for $v = 0$ and $v = 1$. These functions are closely approximated by harmonic oscillator functions and are confined essentially to $1.0 a_0 < s < 2.0 a_0$. Our results can be easily understood if we expand $t_{l\Lambda}(s)$ about s_0 for any values of l and Λ, i.e.,

$$2it(s) = \{i \sin 2\delta(s_0) - [1 - \cos 2\delta(s_0)]\}$$

$$+ \left\{ (s - s_0)\, [i \cos 2\delta(s_0) \right.$$

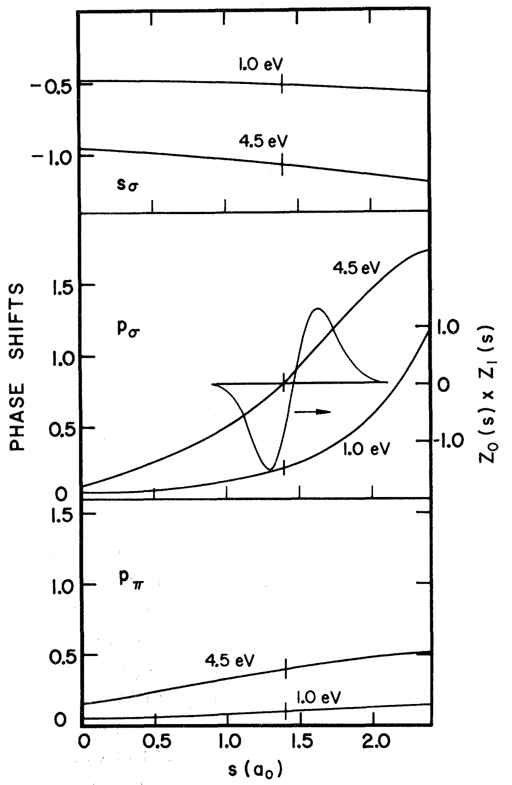

FIG. 1. Phase shifts s_σ, p_σ, and p_π as a function of internuclear separation s for energies $E = 1.0$ and 4.5 eV. Also, product of vibrational wavefunctions for $v = 0$ and $v = 1$ vs s.

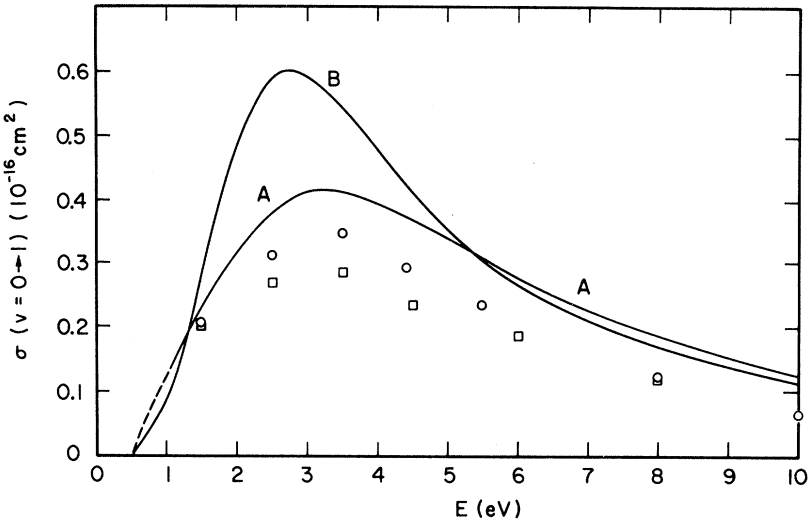

FIG. 2. Pure vibrational cross section $\sigma(v=0\rightarrow1)$ vs energy. Curve A: body-frame approximation; curve B: laboratory-frame approximation (Ref. 4); ○, Linder (Ref. 2); □, Linder (Ref. 17).

$$-\sin2\delta(s_0)\,]\frac{d\delta}{ds}\bigg|_{s=s_0}\bigg\}+\cdots\,.$$

Now, because of orthogonality of the vibrational wave functions, only the first curly bracket {} contributes to b_l^{00} while only the second {} contributes to b_l^{01}. Hence, Fig. 1 shows that all three orbitals contribute significantly to the elastic processes since their mean phase shifts $\delta_{l\Lambda}(s_0)$ are far from zero (or multiples of π). On the other hand, excitation processes of the type $v=0\rightarrow1$ are dominated by the p_σ orbital, since it is the only one with a large derivative $(d\delta/ds)_{s=s_0}$. The physical interpretation is that excitation of a vibrational quantum occurs via a resonant $(1s\sigma_g^2\ 2p\sigma_u)\,{}^2\Sigma_u^+$ H_2^- state,[16] where the incoming electron is trapped in a p_σ orbital by a combination of polarization, exchange, static-field, and centrifugal-barrier effects.

In order to compare directly calculations performed in the body-frame representation with those in the laboratory frame, we choose $x=0$ for all s in Eq. (2.7). Both computations are made with the same e-H_2 interaction potential. Pure vibrational cross sections as a function of energy are given in Fig. 2 for $E\leqslant10$ eV. Circles and squares denote the experimental results of Linder,[2,17] with the squares representing the more accurate measurements. Cross sections obtained in the fixed-nuclei approximation, where we have retained contributions from s_σ, p_σ, and p_π phase shifts, are given by curve A, while curve B represents cross sections obtained by Henry[4] in the close-coupling approximation, i.e., laboratory-frame representation. The fact that both theoretical curves lie above the experimental results indicates that omission of a cutoff in the polarization potential results in excessive attraction. Moreover, the energy range where curves A and B differ significantly coincides with the ${}^2\Sigma_u^+$ resonance at approximately 2–4 eV. This discrepancy reflects the effect of truncation of higher vibrational states in the close-coupling calculations (curve B). As discussed in the analogous situation of electron-atom scattering,[6] the effect of disallowing the system to occupy the truncated states tends to pile up flux in the neighboring allowed states, resulting in overestimation of excitation cross sections. Similarly, we see in Fig. 2 that curve B is substantially higher than curve A or experiment. The manifestation of the truncated effect in only the resonance energy region can be explained by reexamining Fig. 1. Again, both the s_σ and p_π orbitals are very flat and have essentially no second or higher derivatives at all energies. However, the p_σ orbitals possess large second and higher derivatives, particularly in the resonance energy range (not explicitly shown), corresponding to transitions to $v=2$ or higher intermediate states. These effects are implicitly included in the present method (curve A).

The assumption that the long-range portion of the potential can be separated into terms depending on r and s is probably too severe a constraint on the potential, so we relax this assumption by introducing nonzero x. Total vibrational cross sections $\sigma(v=0\rightarrow1)$ are compared with experiment in Fig. 3 as a function of energy for $E\leqslant10$ eV. The solid curve represents the sum of pure vibrational and simultaneous rotational-vibrational cross sections obtained in the present calculation. We have chosen the adjustable parameter x in Eq. (2.7) so as to give the best fit to experimental results of Linder,[17] which are given by squares. The value we have adopted is $x=25\%$, which is used throughout the rest of this section. Linder used a crossed-beam technique to measure the energy dependence in the range $1.5<E<10.8$ eV and the angular dependence (20°–

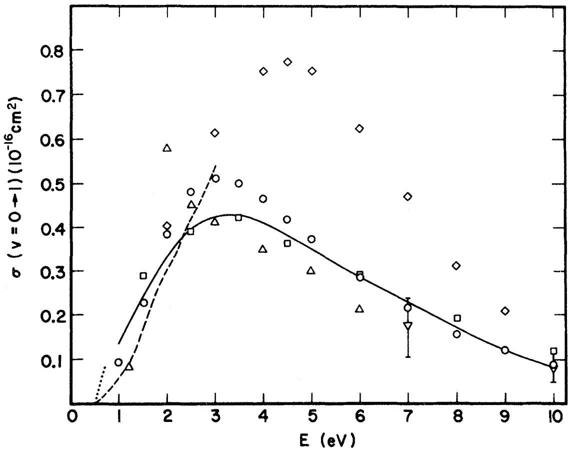

FIG. 3. Total vibrational cross section $\sigma(v=0\rightarrow 1)$ vs energy. Solid curve: present results in uncoupled adiabatic approximation with $x=0.25$. Experimental results are given by □, Linder (Ref. 17); ○, Ehrhardt *et al.* (Ref. 19); ▽, Trajmar *et al.* (Ref. 20); △, Schulz (Ref. 21); ◇, Engelhardt and Phelps (Ref. 22); dashed line, Crompton *et al.* (Ref. 23); dotted line, Burrow and Schulz (Ref. 24).

120°) of the differential cross sections. By extrapolating measurements and integrating over the angular range, Linder obtained relative total cross sections which are normalized to absolute total cross sections of Golden *et al.*[18] Circles denote results of Ehrhardt *et al.*,[19] who also used a crossed-beam technique to obtain relative cross sections which are subsequently normalized in the same manner as that used by Linder.[2,17] Cross sections from another scattering experiment by Trajmar *et al.*[20] are given by inverted triangles. Electrostatic-energy-analyzer studies of Schulz[21] are presented as triangles, and diamonds denote cross sections deduced by Engelhardt and Phelps[22] from analysis of transport data. More accurate swarm experiment measurements have been taken by Crompton, Gibson, and Robertson[23] and their deduced vibrational cross sections are given by a dashed curve. The dotted curve near threshold energies represents the results of Burrow and Schulz,[24] who used a trapped-electron method to measure a slope of 4.3×10^{-17} cm^{2}eV^{-1} for the vibrational $\sigma(v=0\rightarrow 1)$ cross section. The present theoretical calculation is not designed to clarify the conflicting experimental results near threshold. However at higher energies the experiments of Schulz,[21] Ehrhardt *et al.*,[22] Trajmar *et al.*,[20] Crompton *et al.*,[23] and Linder[16] are in agreement to within 25%.

Figure 4 depicts pure vibrational and simultaneous rotational-vibrational cross sections versus energy for $E\leq 7$ eV. Experimental results of Linder[17] are given by circles and squares, respectively, for $\sigma(v=0\rightarrow 1,\ \Delta j=0)$ and $\sigma(v=0\rightarrow 1,\ j=1\rightarrow 3)$.

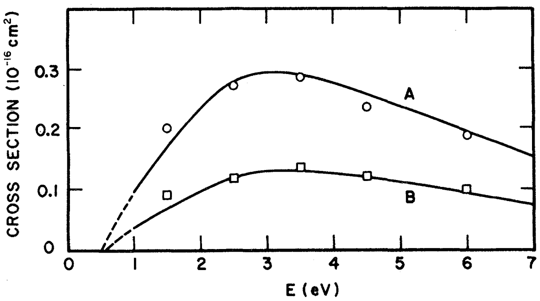

FIG. 4. Pure vibrational cross section and rotational-vibrational cross section vs energy. Solid curves: uncoupled adiabatic approximation with $x=0.25$; circles and squares denote experimental results of Linder (Ref. 17). $\sigma(v=0\rightarrow 1,\ \Delta j=0)$, curve A and ○; $\sigma(v=0\rightarrow 1,\ j=1\rightarrow 3)$, curve B and □.

Curves A and B are the corresponding results in the present method with $x=0.25$. For $E<1.0$ eV, this approximation is invalid because phase accumulation occurs for $r>10a_0$, where neglected terms in (3.6) are comparable to those which have been retained in Eqs. (3.9).

Differential cross sections for $v=0\rightarrow 1$, $\Delta j=0$ vibrational excitation and $v=0\rightarrow 1$, $j=1\rightarrow 3$ rotational-vibrational excitation of molecular hydrogen by electron impact are given as a function of angle at $E=1.5$ and 4.5 eV in Fig. 5. Theoretical curves A and B are calculated by our method and represent cross sections $\sigma(v=0\rightarrow 1,\ \Delta j=0)$ and $\sigma(v=0\rightarrow 1,$

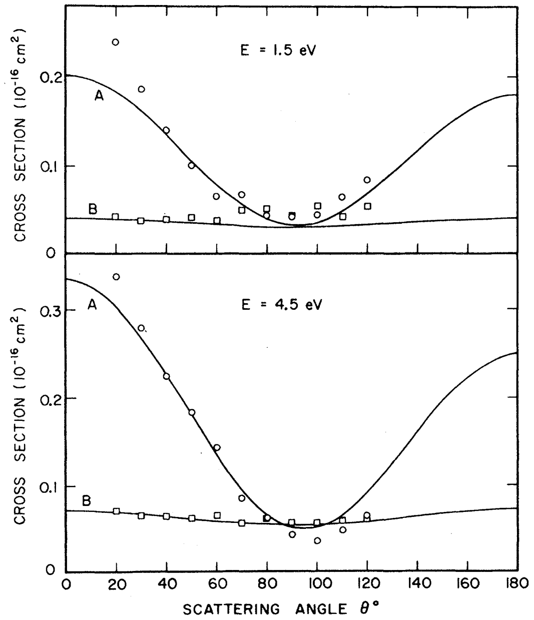

FIG. 5. Differential cross sections for $v=0\rightarrow 1$, $\Delta j=0$ and $v=0\rightarrow 1$, $j=1\rightarrow 3$ vs scattering angle θ for $E=1.5$ and 4.5 eV. Curves A and B and □ and ○ as in Fig. 4.

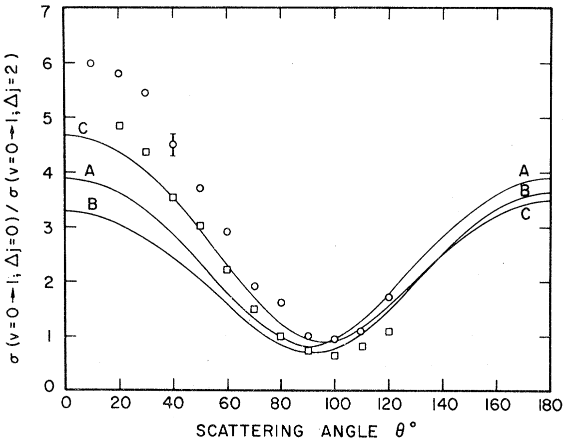

FIG. 6. Ratio $\sigma(v=0\rightarrow 1,\ \Delta j=0)/\sigma(v=0\rightarrow 1,\ j=1\rightarrow 3)$ vs scattering angle for $E=4.5$ eV. Curve A: Abram and Herzenberg (Ref. 26); curve B: Henry (Ref. 4); curve C: present results. Experimental results are given by ○, Ehrhardt and Linder (Ref. 25); □, Linder (Ref. 17).

$j=1\rightarrow 3$), respectively. Circles and squares denote absolute cross sections obtained experimentally by Linder[17] for the respective processes. Agreement between theory and experiment is very satisfactory.

Figure 6 gives the ratio of the pure vibrational $\sigma(v=0\rightarrow 1,\ \Delta j=0)$ to the rotational-vibrational $\sigma(v=0\rightarrow 1,\ j=1\rightarrow 3)$ cross section for H_2 as a function of scattering angle for $E=4.5$ eV. Circles and squares represent measurements of Ehrhardt and Linder[25] and Linder,[17] respectively. Curve A denotes the result of Abram and Herzenberg,[26] which may be derived from Eq. (3.13) by retaining only the resonant p_σ orbital. Then it can be shown that coefficients b_1^{01} cancel in the ratio of the indicated cross section, and we obtain their result based purely on angular momenta considerations. Curve B depicts the close-coupling result of Henry,[4] and curve C gives the present result. Since curve A contains only p waves, it is necessarily symmetric about 90°. Our present calculation includes s waves which, although not important for vibrational excitation processes, produce a noticeable effect in the angular distribution as shown in Fig. 6. It should be noted that $\sigma(v=0\rightarrow 1,\ \Delta j=2)$ is unaffected by s waves. However, the interference of s waves with p waves produces a rise in the forward directions (and an equal drop in the backward directions) which accounts for the difference between curves C and A. Clearly, the agreement of the present result, curve C, with the more reliable data of Linder[17] (squares), is very satisfactory.

V. CONCLUSION

The present calculation of electron-H_2 scattering illustrates the power and usefulness of the frame transformation theory. Under favorable circumstances, which are fulfilled in the present problem in the specified energy range, the calculation is particularly simple, requiring only the solutions of uncoupled differential equations in the body frame. Not only is the calculation simpler than that performed in the laboratory frame, but also the result for vibrational excitation is superior, as shown in Fig. 2. The reason is that the complete set is truncated so that vibrational states $v \geq 2$ are excluded in the laboratory-frame approach, whereas all states are implicitly included in the body frame.

The primary result of our calculation is given in Fig. 1, which shows s and p phase shifts as functions of the internuclear distance s at different energies. The main point of note is that the $^2\Sigma_u^+$ resonance is associated with a rapid rise in the p_σ phase shift around the equilibrium distance $s_0=1.4a_0$. Together with Eqs. (3.13) and (3.14), these curves enable us to calculate any differential or integrated cross section from the initial state (j, v) to the final state (j', v'). The subsequent graphs represent only a few selected results. Results not shown are also in good agreement with experiment in the energy range 1.0–10 eV.

At lower energies, the corresponding longer wavelengths would increase the range where the electron-molecule interaction is important. In particular this range would extend well into region B, invalidating the approximations made in reducing Eq. (3.6) to Eqs. (3.9). In fact, for extremely low energies, for example the threshold behavior of pure rotational excitations, the range of important interaction has shifted almost entirely into region B. Hence the alternative approach utilizing the laboratory frame becomes appropriate.[27]

At energies above 10 eV, d and higher partial waves become important. In principle, each orbital can be calculated by the "coupled wave approximation."[28,29] However, the deep penetration of the electron into the core would probably invalidate the single-center representation of the molecule, and a two-center approach[30] would then be necessary.

Finally, the simplicity of this calculation and the accuracy of our results encourage calculations on more complex molecules using the frame trans-

TABLE I. Long-range-potential parameters as a function of internuclear separation s.

s	$Q_2(s)^a$ $(e^2a_0^3)$	$\alpha_0(s)^b$ (a_0^3)	$\alpha_2(s)^b$ (a_0^3)	$R_c(s)$, $x=0.25$ (a_0)
0.8	0.1714	2.9231	0.2812	1.06
1.2	0.3536	4.3448	0.8017	1.19
1.4	0.4574	5.1786	1.2019	1.29
1.6	0.5646	6.0786	1.7021	1.38
2.0	0.7705	7.9954	2.9690	1.55
2.4	0.9330	9.8568	4.4000	1.72

[a] Reference 11. [b] Reference 12.

formation theory. However, practical simplifications as used in our calculation should be made with caution. For example, the fixed internuclear distance assumption is poor in electron-O_2 scattering since the process is dominated by long-lived O_2^- intermediate states.[31]

Note added in proof. F. H. M. Faisal and A. Temkin, Phys. Rev. Letters (to be published) have made an independent adiabatic-nuclei calculation based on a Taylor series expansion of $t(s)$, with results qualitatively similar to our own.

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