Low-energy rotational and vibrational-rotational excitation cross sections for H_2 by electron impact

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Results are presented for rotational and vibrational-rotational excitation of H_2 by electron impact in the static-exchange approximation. We use the T -matrix discrete basis set method introduced by Rescigno, McCurdy, and McKoy. Our approach for vibrational excitation involves solving the fixed-nuclei scattering problem at several internuclear separations. We compare our results with the experimental data of Linder and Schmidt and with other calculated results.

I. INTRODUCTION

Recent¹⁻³ applications of discrete-basis-set methods for nonspherical potential scattering have established their importance in *ab initio* calculations of electron-molecule processes. Discrete-basis-set techniques have an advantage in that they are particularly well suited for representing the bound-state nature of resonances. Compound states,⁴ or resonances, decay by the emission of the temporarily trapped incident electron into final states which are energetically accessible. In molecules there are various decay channels possible, among them are vibrational and rotational excitation.

The subject of this paper is the discrete-basis-function method, introduced by Rescigno, McCurdy, and McKoy,¹ applied to vibrational, rotational, and vibrational-rotational excitation of H_2 by low-energy electrons. Our approach involves solving the Lippmann-Schwinger equation for the transition operator in a Gaussian basis representation at different internuclear spacings R , positioned about the equilibrium point. We present the first *ab initio* static-exchange discrete-basis-set calculation for vibrational excitation in H_2 and compare these results with other theoretical results and experimental measurements.

Until now there has been some doubt as to whether one could reproduce the low-energy vibrational excitation cross section of molecules by including just the static-exchange interaction. Henry and Chang⁵ (HC) include a static field, effective polarization and exchange effects; however, they neglect the R dependence of their exchange term. Furthermore, to include the effects of polarization they use a cutoff parameter, whose functional form is related to an undetermined parameter. This adjustable parameter is chosen to give the best fit to the experimental results of Linder and Schmidt.⁶ Our results show that by treating the static-exchange potential correctly

one can account for the qualitative features of the vibrational excitation cross section.

Results are presented for the pure rotational excitation and simultaneous rotational-vibrational excitation cross sections in the adiabatic-nuclei approximation. In Sec. III we compare with theoretical results of Chang and Temkin,⁷ Henry and Chang,⁵ Henry and Lane,⁸ and experimental measurements of Linder and Schmidt.⁶ Variationally corrected results⁹ are presented for differential cross sections for rotational excitation.

II. THEORY

In a previous paper,³ hereafter referred to as I, we presented a method for calculating rotational excitation and momentum transfer cross sections analytically from the matrix solution of the Lippmann-Schwinger equation. We will review the highlights of the theory and extend it to include simultaneous vibrational-rotational effects.

Our starting point is the Lippmann-Schwinger equation for the transition matrix

$$T = U + U G_0^+ T, \quad (1)$$

where $U = 2V$ and G_0^+ is the free-particle Green's function with the outgoing wave boundary condition.¹⁰ To solve Eq. (1) we approximate the fixed-nuclei scattering potential by its projection onto a subspace of discrete-basis functions:

$$V^t(\vec{r}, \vec{r}') = \sum_{\alpha, \beta=1}^N |\alpha\rangle \langle \alpha| V |\beta\rangle \langle \beta|. \quad (2)$$

Inserting Eq. (2) into Eq. (1) we obtain an $N \times N$ matrix form of the Lippmann-Schwinger equation with solution

$$T^t = (1 - U^t G_0^+)^{-1} U^t. \quad (3)$$

The momentum representation of the on-shell T matrix is constructed by the transformation

$$\langle \vec{k}' | T | \vec{k} \rangle = \sum_{\alpha, \beta} \langle \vec{k}' | \alpha \rangle \langle \alpha | T | \beta \rangle \langle \beta | \vec{k} \rangle, \quad (4)$$

where $\vec{k}$ and $\vec{k}'$ denote plane-wave states of the form

$$\varphi_{\vec{k}}(\vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k} \cdot \vec{r}}, \quad (5a)$$

and α denotes a Cartesian Gaussian of the form

$$\mu_{lmn}^{\alpha, \vec{A}}(\vec{r}) = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha|\vec{r} - \vec{A}|^2}. \quad (5b)$$

The on-shell T matrix is related to the scattering amplitude by

$$f_{\vec{k}}(\hat{r}) = -2\pi^2 \langle \vec{k}' | T | \vec{k} \rangle, \quad (6)$$

where

$$\hat{r} = \hat{k}'.$$

Equations (4) and (6) for the on-shell T matrix and the scattering amplitude couple the dynamical and geometrical factors of the scattering problem. Using a single-center expansion for the scattering amplitude

$$f_{\vec{k}}(\hat{r}) = 4\pi \sum_{ll'm} f_{ll'm}(k) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{k}), \quad (7)$$

We can treat the target orientation dependence analytically. We need to relate the partial-wave matrix elements of the scattering amplitude, $f_{ll'm}$, to the basis-set representation of the T matrix, $T_{\alpha\beta}$. This allows us to solve the dynamical problem in the body-fixed frame and then transform to the laboratory frame using the rotational properties of spherical harmonics. The single-center expansion of the on-shell T matrix is of the form

$$\langle \vec{k}' | T | \vec{k} \rangle = \frac{1}{k} \sum_{ll'm} i^{l'-l} T_{ll'm} Y_{lm}(\hat{k}') Y_{lm}^*(\hat{k}). \quad (8)$$

Equating the right-hand sides of Eqs. (4) and (8) and using the spherical expansion of a plane wave

$$e^{i\vec{k} \cdot \vec{r}} = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{k}), \quad (9)$$

we obtain the body-frame single-center expansion coefficients for T^i :

$$T_{ll'm}^i = \frac{2k}{\pi} \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | T | \beta \rangle \langle \beta | j_l Y_{lm} \rangle. \quad (10)$$

By substituting Eq. (10) into Eq. (8) and equating coefficients of spherical harmonics in Eqs. (7) and (6) we get

$$f_{ll'm}(k) = -i^{l'-l} \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \times \langle \alpha | T | \beta \rangle \langle \beta | j_l Y_{lm} \rangle. \quad (11)$$

In I we discuss the analytical evaluation of the matrix element $\langle j_l(kr) Y_{lm}(r) | \alpha(\vec{r}) \rangle$. The laboratory-frame scattering amplitude is related to $f_{ll'm}(k)$ according to

$$f_k(\vec{R}, \hat{r}) = 4\pi \sum_{ll'mm'} \left(\frac{2l'+1}{4\pi} \right)^{1/2} f_{ll'm}(k) D_{m'm}^{(l)}(\hat{R}) \times D_{0m}^{(l')*}(\hat{R}) Y_{lm'}(\hat{r}), \quad (12)$$

where $\vec{R}$ denotes the internuclear separation of the homonuclear diatomic and its orientation in the laboratory frame. Using the expressions given by Temkin *et al.*¹¹ for the scattering amplitude we obtain a prescription for their fixed-nuclei dynamical coefficients:

$$a_{ll'm}(kR) = -[4\pi(2l'+1)]^{1/2} i^{l'-l} \sum_{\alpha\beta} \langle j_l Y_{lm} | \alpha \rangle \langle \alpha | T | \beta \rangle \times \langle \beta | j_{l'} Y_{l'm'} \rangle. \quad (13)$$

In terms of the dynamical coefficients, the laboratory-frame scattering amplitude is given by

$$f_k(\vec{R}, \hat{r}) = \sum_{ll'mm'} a_{ll'm}(kR) D_{m'm}^{(l)}(\hat{R}) \times D_{0m}^{(l')*}(\hat{R}) Y_{lm'}(\hat{r}). \quad (14)$$

To calculate rotational, vibrational, or rotational-vibrational excitation cross sections we use the adiabatic nuclei approximation¹²

$$f_{\Gamma\Gamma'}(\hat{r}) = \langle \psi_{\Gamma'}(\vec{R}) | f_k(\vec{R}, \hat{r}) | \psi_{\Gamma}(\vec{R}) \rangle + \epsilon, \quad (15)$$

where ψ_{Γ} , $\psi_{\Gamma'}$ are target wave functions with initial (final) vibrational-rotational quantum states $\Gamma(\Gamma')$. The error term ϵ is small for rotational excitation when the speed of the incident electron is large compared to the motion of the target nuclei. For vibrational excitation the error is small when the delay time for scattering is $\ll \hbar / \Delta E_{v'v}$. We will see that the Σ_u resonance in H_2 is broad enough to satisfy the above conditions. To incorporate vibrational excitation into our formalism we perform the analytical angular integrations and then numerically integrate over R . Thus for vibrational-rotational excitation the dynamical coefficients become

$$a_{ll'm}(v', v) = \int_0^\infty \chi_{v'}(R) a_{ll'm}(R) \chi_v(R) R^2 dR, \quad (16)$$

where χ_v and $\chi_{v'}$ are the initial and final vibrational wave functions for the target molecule.

In the adiabatic-nuclei approximation the total electronically elastic cross section is given by

$$\sigma_{v'v} = \frac{k_{v'}}{k_v} \sum_{u'm} \frac{|a_{u'm}(v, v')|^2}{2l'+1} \quad (17)$$

Also, the differential-rotational and differential-rotational-vibrational cross sections are, respectively,

$$\frac{d\sigma_{j' \leftarrow j}}{d(\cos\theta)} = \frac{k_{j'}}{k_j} \sum_L A_L(j', j) P_L(\cos\theta), \quad (18a)$$

$$\frac{d\sigma_{j'v' \leftarrow jv}}{d(\cos\theta)} = \frac{k_{j'v'}}{k_{jv}} \sum_L A_L(j'v'; j, v) P_L(\cos\theta), \quad (18b)$$

where the fixed-nuclei expansion coefficients are given by

$$A_L(j', j) = \frac{1}{2} \sum_{\lambda\lambda'\eta} a_{l'l'm}(R) a_{\lambda\lambda'\eta}^*(R) (-1)^{m+\eta+j+l'+\lambda'} \times [(2l+1)(2\lambda+1)]^{1/2} (l'm-m|J0) \times (\lambda\lambda'\eta-\eta|J0)(l\lambda 00|L0)(l'\lambda'00|L0) \times (jJ00|j'0)^2 \begin{Bmatrix} l & \lambda & L \\ l' & \lambda' & J \end{Bmatrix}. \quad (19)$$

The $A_L(j'v'; jv)$ coefficients are calculated by replacing the fixed-nuclei dynamical coefficients $a_{l'l'm}(R)$ by $a_{l'l'm}(v', v)$. For 0-1 vibrational excitation the only significant term in the sum is $l, l', \lambda, \lambda' = 1; m, \eta = 0$. Then

$$A_L(j', v' = 1; j, v = 0) \cong |a_{110}(1, 0)|^2 (-1)^J (1100|J0)^2 \begin{Bmatrix} 1 & 1 & L \\ 1 & 1 & J \end{Bmatrix} \times (1100|L0)^2 (jJ00|j'0)^2. \quad (20)$$

As we discuss in Sec. III, Eq. (20) is a good approximation in H_2 because only the p_σ phase shift varies significantly with internuclear separation. The total rotational excitation cross section is given by

$$\sigma_{j' \leftarrow j} = \frac{k_{j'}}{k_j} \sum_{l'l'm\mu} \frac{(-1)^{m+\mu}}{(2l'+1)} a_{l'l'm}(R) a_{l'l'm}^*(R) \times \sum_J (l'l'm-m|J0)(l'l'm-\mu|J0) \times (jJ00|j'0)^2, \quad (21)$$

Analogously with Eq. (20) we get

$$\sigma_{j'1 \leftarrow j0} = \frac{k_{j'1}}{k_{j0}} \frac{|a_{110}|^2}{3} \sum_J (1100|J0)^2 (jJ00|j'0)^2. \quad (22)$$

Recently, we presented a method for including a variational correction⁹ in the discrete-basis-set results. This is necessary because in certain cases the accuracy of our results may be limited by the lack of variational stability with respect to errors due to the approximation of the scattering potential by an $N \times N$ matrix, i.e., the difference $U - U^t$. The approach follows Kohn's¹³ prescription for the variationally corrected scattering amplitude in three dimensions. Assuming axial symmetry for the target molecule one obtains an equation for the variationally stable partial-wave K matrix:

$$K_{ll'm}^s = K_{ll'm}^t + \langle \psi_{out}^t | (U - U^t) | \psi_{in}^t \rangle_{ll'm}. \quad (23)$$

The trial wave functions ψ_{in}^t , ψ_{out}^t and the approximate K -matrix element $K_{ll'm}^t$ are constructed from the discrete-basis-set solution of the Lippmann-Schwinger equation

$$K = U + U G_0^P K, \quad (24)$$

where G_0^P is the principal value part of the free-particle Green's function. Application of the method to e^-H_2 scattering in the static-exchange approximation showed that higher partial-wave K -matrix elements and nondiagonal matrix elements were most improved by the variational correction. This suggests that the variational correction will be important in differential-rotational excitation cross sections where off-diagonal terms become important. For a process which is dominated by a single partial-wave we expect the uncorrected results of Eq. (3) to be valid.

III. CALCULATIONS AND RESULTS

The procedure used in calculating the truncated static-exchange (SE) potential V^t has been described in I. For the self-consistent field (SCF) calculation of the target σ_g occupied orbital we used a (10s5p_g) set of primitive Gaussians contracted to [7s5p_g] on each nucleus. The exponents and contraction coefficients for these bases are those of Huzinaga¹⁴ and are given in Table I. To construct a basis set which defines the matrix elements of the static-exchange potential we augment the target basis set with diffuse Gaussian functions that span the asymptotic region. For a homonuclear diatomic molecule the scattering potential is block diagonal in the symmetries $^2\Sigma_g, ^2\Sigma_u, ^2\Pi_g, ^2\Pi_u, \dots$, thus allowing us to solve the Lippmann-Schwinger equation separately for each symmetry. In Table II we list the scattering basis sets used for each symmetry.

For vibrational excitation we need to calculate $V_{SE}^t(R)$ and $E_{HF}(R)$, the H_2 ground-state potential

TABLE I. Valence Σ basis set.

Type	Center	Exponent	Contraction coefficient
(000)	(0,0 $\pm$ 0.7003) ^a	1685.517	0.004 2273
(000)	(0,0 $\pm$ 0.7003)	249.9384	0.035 026
(000)	(0,0 $\pm$ 0.7003)	55.658 34	0.192 0389
(000)	(0,0 $\pm$ 0.7003)	15.2743	0.833 3764
(000)	(0,0 $\pm$ 0.7003)	4.8628	
(000)	(0,0 $\pm$ 0.7003)	1.7316	
(000)	(0,0 $\pm$ 0.7003)	0.668 05	
(000)	(0,0 $\pm$ 0.7003)	0.274 37	
(000)	(0,0 $\pm$ 0.7003)	0.116 98	
(000)	(0,0 $\pm$ 0.7003)	0.041 133	
(001)	(0,0 $\pm$ 0.7003)	4.8	
(001)	(0,0 $\pm$ 0.7003)	2.53	
(001)	(0,0 $\pm$ 0.7003)	1.33	
(001)	(0,0 $\pm$ 0.7003)	0.701	
(001)	(0,0 $\pm$ 0.7003)	0.369	

^a For the three additional internuclear spacings the centers are for $R=1.0$, 1.7 , and 2.0 a.u.: $(0,0 \pm 0.5)$, $(0,0 \pm 0.85)$, and $(0,0 \pm 1.0)$ respectively. The exponents are the same for all four internuclear spacings.

TABLE II. Scattering basis sets.

$^2\Sigma_g^c$					
$\vec{A}^a = (0,0, \pm 0.7003)$ $(l,m,n)^b = (0,0,0)$	$(0,0, \pm 0.7003)$ $(0,0,1)$	$(0,0,0)$ $(0,0,0)$	$\vec{A} = (0,0, \pm 0.7003)$ $(l,m,n) = (0,0,0)$	$(0,0, \pm 0.7003)$ $(0,0,1)$	$(0,0,0)$ $(0,0,1)$
1685.517	4.8	0.025	1685.517	4.8	0.1
249.9584	2.53	0.15	249.9584	2.53	0.05
55.658 34	1.33	0.009	55.658 34	1.33	0.025
15.2743	0.701	0.0054	15.2743	0.701	0.0125
4.8628	0.369	0.003 24	4.8628	0.369	0.006 25
1.7316		0.001 944	1.7316		0.003 125
0.668 05		0.001 166	0.668 05		
0.274 37		0.0006	0.274 37		
0.116 98			0.116 98		
0.041 133			0.041 133		
		$^2\Pi_u^e$		$^2\Pi_g^f$	
	$\vec{A} = (0,0, \pm 0.7003)$ $(l,m,n) = (1,0,0)$	$(0,0,0)$ $(1,0,0)$	$\vec{A} = (0,0, \pm 0.7003)$ $(l,m,n) = (1,0,0)$		
	17.3	0.221	17.3	0.132	
	9.12	0.132	9.12	0.0792	
	4.8	0.0792	4.8	0.0474	
	2.53	0.0474	2.53	0.0284	
	1.33	0.0284	1.33	0.017	
	0.701	0.017	0.701	0.01	
	0.369	0.01	0.369	0.006	
		0.006	0.221	0.003	
		0.003		0.0015	
		0.0015			

^a $\vec{A}$ denotes the coordinates of the center of the basis function $\mu_{lmn}^{\vec{A}}(\vec{r})$.

^b (l,m,n) denotes the symmetry type of $\mu_{lmn}^{\vec{A}}(\vec{r})$.

^c See the footnote for Table I. The Σ_g contribution to the total cross section was computed for additional internuclear spacings equal to 1.0 and 2.0 a.u.

^d See the footnote at the bottom of Table I. The Σ_u contribution to the total cross section was computed for additional internuclear spacings equal to 1.0, 1.7, and 2.0 a.u.

^e See the footnote for Table I. The Π_u contribution to the total cross section was computed for additional internuclear spacings equal to 1.0 and 2.0 a.u.

^f See the footnote of Table I.

curve. The Hartree-Fock approximation to the energy of the ground state of H_2 is valid for small displacements about the internuclear equilibrium position (R_e). To obtain $E_{HF}(R)$ we repeat the SCF calculation of the target occupied orbital for $R=1.0, 1.7$, and 2.0 a.u. (see Table III). Using a cubic spline fit to these values we get a vibrational frequency, $\omega_e=0.0218$ a.u. and $R_e=1.41$ a.u. McLean¹⁵ has extracted spectroscopic constants from HF potential curves and reports an $\omega_e=0.0208$ a.u. for $R_e=1.4$ a.u.

Since we are interested in low-lying vibrational states we use harmonic-oscillator functions (defined by our spectroscopic parameters), as our vibrational wave functions. We find that the sum

TABLE III. Ground-state potential curve of H_2 .

R (a.u.)	$E_{HF}(R)$ (a.u.)
1.0	-1.085 090 6
1.4006	-1.133 543 9
1.7	-1.119 230 6
2.0	-1.091 448 7

in Eq. (17) can be truncated after 4 partial waves.

For the $0 \rightarrow 1$ vibrational excitation we expect the sum in Eq. (17) to be dominated by the partial waves that vary most with internuclear separation, about R_e . The excitation cross section can be approximated by

$$\sigma_{01} \propto \sum_{l'l'm} \delta_{l'l'm} \frac{\langle 0 | (R - R_e) | 1 \rangle^2}{2l' + 1} \left[\frac{1}{4} \left(\frac{\partial}{\partial R} \sin \frac{\delta_{lm}}{2} \right)_{R_e}^2 + \left(\frac{\partial}{\partial R} \sin^2 \delta_{lm} \right)_{R_e}^2 \right] \quad (25a)$$

$$= \frac{1}{2\alpha^2} \sum_{lm} \frac{1}{2l+1} \left[\frac{1}{4} \left(\frac{\partial}{\partial R} \sin \frac{\delta_{lm}}{2} \right)_{R_e}^2 + \left(\frac{\partial}{\partial R} \sin^2 \delta_{lm} \right)_{R_e}^2 \right], \quad (25b)$$

where $\alpha = (\mu\omega)^{1/2}$ and μ is the reduced mass. Faisal and Temkin¹⁶ applied a similar analysis to prove the validity of adiabatic nuclei theory for $e-H_2$ scattering. In Fig. 1 we plot the s_o , p_o , and p_π phase shifts derived from the T^t matrix, Eq. (3), and those of HC, as a function of internuclear separation. Since the dependence of the phase shift upon internuclear separation will also vary with energy, a more meaningful comparison is possible if we choose energies that are the same relative distance from the location of the near-resonance peak. For this reason the T -matrix results are given at 5.32 eV, whereas the results of Henry and Chang are extrapolated from their paper at 4.5 eV. From Fig. 1 and Eq. (24b) we see that one need only consider the $l=1$, $m=0$ contribution. This resonance wave is well represented by a discrete basis set so that the variational correction is small. All T matrix $0 \rightarrow 1$ vibrational-excitation cross sections are calculated in the above approximation. The R dependence of HC's p_o phase shift differs significantly from ours. Their larger slope at R_e is partly due to the effect of polarization which increases with increase in internuclear separation.¹⁷ However, their treatment of both polarization and exchange is approximate.

In Fig. 2 we present our $0 \rightarrow 1$ vibrational cross section as well as the frame transformation calculation of HC and the experimental data of Linder

and Schmidt.⁶ Our smaller cross sections are consistent with our analysis of the p_o phase shift. Our cross-section peaks at a higher energy than experiment because we have neglected polarization. Using Eq. (23) we calculate simultaneous rotational-vibrational ($0 \rightarrow 1$) cross sections and in Fig. 3 compare with Henry and Chang and the experimental results of Linder and Schmidt.⁶ In Figs. 4 and 5 we present differential rotational-vibrational ($0 \rightarrow 1$) cross sections at one set of energies in the resonance region (T -matrix results at 5.32 eV and HC at 1.5 eV) and the second set at lower energies (T -matrix results at 2.32 eV, HC at 1.5 eV). The magnitude of our cross sections are consistent with our total vibrational results. The static-exchange results exhibit the correct qualitative behavior.

Differential cross sections for rotation excitation contain information about higher partial-wave K -matrix elements since pure s -wave scattering does not contribute. Unlike cross sections for vibrational excitation of H_2 , which are dominated by p -wave scattering, pure rotational excitation cross sections include significant contributions from off-diagonal K -matrix elements. The variationally corrected Σ and Π symmetry fixed-nuclei K -matrix elements used to calculate the rotational-excitation cross sections at 3.40- and 6.67 eV incident energy presented here are given in Ref. 9. Similar calculations were carried out at 4.42-

FIG. 1. Comparison of static-exchange and uncoupled adiabatic approximation of Henry and Chang's phase shifts for different internuclear spacings. The T -matrix results (solid line) are given for 5.32 eV whereas the results of Henry and Chang (broken line) are given for 4.5 eV. See text for explanation.

FIG. 2. Vibrational-excitation cross section. —, T -matrix results; ---, Henry and Chang (adjustable parameter); □, Linder and Schmidt (experimental).

FIG. 3. Rotational-vibrational ($0 \rightarrow 1$) cross section. Curves defined as in Fig. 2.

FIG. 4. Differential-vibrational ($0 \rightarrow 1$)-rotational cross section (nonresonant-energy region). Curves defined as in Fig. 2. T -matrix calculation given at 2.32-eV HC and experiment are multiplied by 0.5 for $\Delta j = 0$ and given at 1.5 eV.

FIG. 5. Differential-vibrational ($0 \rightarrow 1$)-rotational cross section (resonant-energy region). Curves defined as in Fig. 2. T -matrix calculation given at 5.32-eV HC and experiment are given at 4.5 eV and multiplied by 0.5 for $\Delta j = 0$.

eV incident energy. In addition we have included diagonal d_{Δ} phase shifts in the Born approximation.

Differential cross sections for $j=1 \rightarrow j=3$ rotational excitation are shown in Fig. 6 for 3.40-, 4.42-, and 6.67-eV incident energy. The solid lines denote our results. The circles indicate the experimental data of Linder and Schmidt⁶ at ap-

FIG. 6. Differential cross sections for rotational excitation ($j=1 \rightarrow j=3$) at collision energies indicated.

FIG. 7. Differential cross section for rotational excitation ($j=1 \rightarrow j=3$) at 4.42-eV collision energy. Solid line, full K -matrix SE result; dashed line, diagonal phase-shift approximation SE result; dotted line, semiempirical diagonal phase-shift approximation result from Ref. 7 normalized to present theory.

proximately the same incident energies: 3.5, 4.5, and 6.0 eV. The dashed line shows theoretical results of Henry and Lane⁸ at 4.42-eV collision energy. Their calculation includes exchange and approximate polarization. The theoretical and experimental results shown in Fig. 6 are in good qualitative agreement except in the region of 6.0-eV collision energy where the experimental result is significantly larger at small scattering angles. This is the region of the Σ_u symmetry resonance enhancement. As in the case of vibrational excitation, we attribute the discrepancy between theory and experiment in this energy region to polarization effects. This has recently been verified by Kaldor and Klonover¹⁸ using the T -matrix method. They account for polarization effects by including second-order contributions to the optical potential. Their static-exchange results for $j=1 \rightarrow j=3$ rotational excitation, which are not variationally corrected, are in good agreement with ours, and their results including polarization are in much better agreement with experiment.

To show the effect of off-diagonal K -matrix elements, Fig. 7 compares our diagonal K -matrix approximation result (dashed line) with our complete K -matrix result (solid line) at 4.42-eV collision energy. Figure 7 also shows the semi empirical adiabatic-nuclei results of Chang and Temkin⁷ (dotted line) normalized to our results. Their results were obtained by assuming the diagonal phase-shift approximation and it is interesting to note the excellent qualitative agreement between their results and our diagonal phase-shift approximation results.

IV. DISCUSSION AND CONCLUSIONS

Our results indicate that the static-exchange model is a useful quantitative first step in the calculation of vibrational and rotational cross

sections. There are limitations in the predictions of this model. For example, the maximum in the vibrational-excitation cross sections occurs 1.5 eV higher than is experimentally observed. However, there are no significant qualitative changes in these inelastic cross sections in going from the static-exchange potential to the static-exchange plus polarization potentials. This is confirmed by the recent results of Klonover and Kaldor¹⁹ who introduced polarization effects into the present L -2 T -matrix approach. This consideration is not often fully appreciated when semi empirical polarization potentials are introduced into calculations.

The results for the e -H₂ system have encouraged us to study the more difficult problem of resonant vibrational excitation of N₂. Preliminary results again indicate that considerable structure in these vibrational-excitation cross sections already occur in the static-exchange approximation. Methods for including polarization at different internuclear spacings are currently being investigated with results on both questions forthcoming.

Rotational-excitation cross sections contain information about the anisotropic components of the molecular target potential. Our results show that the sd off-diagonal K -matrix element contributes significantly to pure rotational excitation of H₂. Since this effect should increase for scattering by other molecules, experimental results for rotational excitation of other molecules would be of considerable interest.

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