

Infinite-order sudden approximation for rotational excitation of hydrogen molecules by electrons in the energy range 10–40 eV*

Donald G. Truhlar,[†] Ruth E. Poling,[‡] and Maynard A. Brandt

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455
(Received 10 October 1975)

Electron scattering by H₂ is treated using a noncentral interaction potential including short-range and long-range static contributions, exchange, and polarization effects. The molecule is treated as a rigid rotator and the scattering is treated in the infinite-order sudden approximation. The results show that the rotational excitation cross section exceeds the elastic scattering cross section at large scattering angles at intermediate energies but not at small angles at low energies.

I. INTRODUCTION

Recently, Srivastava *et al.*¹ measured the differential cross section $I_{13}(E, \theta)$ for pure rotational excitation ($j = 1 \rightarrow j' = 3$) of H₂ by electron impact at impact energies E of 3 to 100 eV and various scattering angles θ from 10° to 135°.

With one exception,² previous experimental^{3,4} and theoretical^{2,5} studies of rotational excitation differential cross sections were confined to low impact energies ($E < 12$ eV). Srivastava *et al.*¹ obtained the unexpected result at intermediate energies and large scattering angles that $I_{13}(E, \theta)$ exceeds the elastic scattering differential cross section $I_{e1}(E, \theta)$ at large scattering angles. Although the previous theoretical calculation² in this energy region had predicted the magnitude of the experimental differential cross section for rotational excitation within a factor of about 3, that calculation treated the scattering electron using the plane wave approximation which is certainly not valid at large scattering angles. In the present article we perform calculations which include the distortion of the scattering electron's wave function from a plane wave. The calculations also include the static potential of the molecular target and the effects of charge polarization of the molecule and of electron exchange. The results given below are in semiquantitative agreement with experiment and thus they show that these effects are sufficient to explain that $I_{13}(E, \theta)/I_{e1}(E, \theta)$ exceeds unity at large scattering angles at intermediate energies but not at small scattering angles or low energies.

II. THEORY

The calculation was carried out using the infinite-order sudden approximation for the scattering of an electron interacting with the molecular target through an effective potential.

A. Potential

The molecule was treated as a rigid rotator with internuclear distance R_e . The interaction energy between the electron and the molecule was written as

$$V(r, \chi) = V^{\text{static}}(r, \chi) + V^{\text{pol}}(r, \chi) + V^{\text{exch}}(r, \chi), \quad (1)$$

where r is the magnitude of the vector \mathbf{r} from the center-of-mass of the molecule to the electron and χ is the angle between the internuclear axis and \mathbf{r} . The

three terms in Eq. (1) are the static potential, the polarization potential, and the effective exchange potential, respectively. The first two terms were evaluated for $R_e = 1.4011 a_0$ using the procedure of Ref. 2 with the parameter set DSI (in Ref. 1 this parameter set was adjusted to make the static potential be in best agreement with the accurate *ab initio* static potential of Ardill and Davidson⁶ and to make the polarization potential agree with that calculated in the nonpenetrating (NP') approximation by Lane and Henry,⁷ and the quadrupole moment and polarizability components were obtained by linear interpolation from the calculations of Kolos and Wolniewicz^{8,9}). This yields¹⁰

$$V^{\text{static}}(r, \chi) = -(r_+^{-1} + 1.1692934) \exp(-2.3385869 r_+) - (r_-^{-1} + 1.1692934) \exp(-2.3385869 r_-) - 0.458035 r^{-3} f^{\text{B}'}(r) P_2(\cos \chi) \quad (2)$$

and

$$V^{\text{pol}}(r, \chi) = 2.591725 r^{-4} \{1 - \exp[-(r/2.1)^5]\} - 0.602205 r^{-4} \{1 - \exp[-(r/1.8)^5]\} P_2(\cos \chi), \quad (3)$$

where

$$r_{\pm} = (0.49077030 + r^2 \pm 1.4011 r \cos \chi)^{1/2}, \quad (4)$$

$$f^{\text{B}'}(r) = \begin{cases} (r/2.0)^4 & r < 2.0 \\ 1 & r \geq 2.0 \end{cases} \quad (5)$$

and $P_2(\cos \chi)$ is a Legendre polynomial of order 2.

The exchange potential is calculated using the semiclassical exchange approximation¹¹ as

$$V^{\text{exch}}(r, \chi) = \frac{1}{2} [E - V^{\text{static}}(r, \chi)] - \frac{1}{2} \{ [E - V^{\text{static}}(r, \chi)]^2 + [\alpha(r, \chi)]^2 \}^{1/2}, \quad (6)$$

where

$$[\alpha(r, \chi)]^2 = 4\pi \rho(r, \chi) \quad (7)$$

and $\rho(r, \chi)$ is the electronic density of the molecular target. Consistent with the treatment² of the target which we used, we approximated this as a linear combination of scaled atomic densities¹² to obtain

$$\rho(r, \chi) = \rho^{\text{at}}(r_+) + \rho^{\text{at}}(r_-) \quad (8)$$

where²

$$\rho^{\text{at}}(r_{\pm}) = 0.50888619 \exp(-2.3385869 r_{\pm}). \quad (9)$$

TABLE I. Integral cross sections (10^{-20} m^2).

E (eV)	IOS approximation			Experiment ^a
	Q_{11}	Q_{13}	$Q_{11} + Q_{13}$	
10	8.58	1.29	9.88	7.68
15	5.99	0.908	6.90	5.54
20	4.56	0.709	5.27	3.73
30	3.04	0.492	3.54	2.24
40	2.65	0.379	3.03	1.66

^aSrivastava *et al.* (Ref. 19).

Also we did not include the quadrupole term in V^{static} in Eq. (6).

B. Infinite-order sudden approximation

Rather than solve the close-coupling equations¹³ for scattering of a particle by a rigid rotator, we use the infinite-order sudden (IOS) approximation which has been described elsewhere.¹⁴⁻¹⁷ One advantage of this method is that it is not necessary to expand the interaction potential in Legendre polynomials of $\cos\chi$. In the IOS approximation the differential cross section $I_{jmj'm'}(\theta)$ and scattering amplitude $f_{jmj'm'}(\theta)$ for the excitation $jm \rightarrow j'm'$ (where $j\hbar$ is the rotational angular momentum and $m\hbar$ is its projection on a space-fixed axis) with scattering angle θ is given by

$$I_{jmj'm'}(E, \theta) = |f_{jmj'm'}(E, \theta)|^2$$

and

$$f_{jmj'm'}(E, \theta) = \int d\Omega_{\chi} Y_{j'm'}^*(\chi, \phi_{\chi}) f(E, \chi, \theta) Y_{jm}(\chi, \phi_{\chi}), \quad (10)$$

i. e.,¹⁸

$$f_{jmj'm'}(E, \theta) = \delta_{m'm} \sum_L [(2j+1)/(2j'+1)]^{1/2} \times f_L(E, \theta) \langle jL00 | jLj'0 \rangle \langle jLm0 | jLj'm \rangle, \quad (11)$$

where $\langle j_1 j_2 m_1 m_2 | j_3 j_4 m_3 m_4 \rangle$ is a Clebsch-Gordan coefficient and $f_L(E, \theta)$ is obtained by the expansion

$$f(E, \chi, \theta) = \sum_{L=0}^{L_{\max}} f_L(E, \theta) P_L(\cos \chi) \quad (12)$$

of the scattering amplitude $f(E, \chi, \theta)$ for the potential $V(r, \chi)$ considered as a function of r which depends parametrically on χ . We are interested in the cross

TABLE II. Momentum transfer cross sections (10^{-20} m^2).

E (eV)	IOS approximation	Experiment
10	4.79	5.31, ^a 9.2 ^b
15	2.54	3.04 ^a
20	1.55	1.92 ^a
30	0.747	1.00 ^a
40	0.441	0.59 ^a

^aSrivastava *et al.* (Ref. 19).^bEngelhardt and Phelps (Ref. 20).TABLE III. Integral cross sections (10^{-20} m^2) neglecting exchange.

E (eV)	IOS approximation		
	Q_{11}	Q_{13}	$Q_{11} + Q_{13}$
10	4.85	0.908	5.75
40	1.66	0.318	1.98

sections $I_{jj'}(E, \theta)$ for $j \rightarrow j'$ transitions summed over m' and averaged over m , i. e.,

$$I_{jj'}(E, \theta) = (2j+1)^{-1} \sum_m \sum_{m'} I_{jmj'm'}(E, \theta). \quad (13)$$

Specializing this to $j=1$ for a homonuclear target yields

$$I_{1j'}(E, \theta) = \left(\frac{1}{3}\right) |f_{j'010}(E, \theta)|^2 + \left(\frac{2}{3}\right) |f_{j'111}(E, \theta)|^2. \quad (14)$$

Substituting (11) into (14) gives

$$I_{11}(E, \theta) = |f_0(E, \theta)|^2 + \left(\frac{2}{25}\right) |f_2(E, \theta)|^2 \quad (15)$$

and

$$I_{13}(E, \theta) = \left(\frac{3}{25}\right) |f_2(E, \theta)|^2 + \left(\frac{4}{81}\right) |f_4(E, \theta)|^2. \quad (16)$$

C. Scattering calculations

We calculated $f(E, \chi, \theta)$ at N_{χ} values χ_i of χ given by

$$\chi_i = (i-1)\pi/L_{\max}(N_{\chi}) \quad i=1, 2, \dots, N_{\chi}, \quad (17)$$

where

$$L_{\max}(N_{\chi}) = 2(N_{\chi} - 1). \quad (18)$$

Each $f(E, \chi, \theta)$ involved 77-151 partial waves. Then we solved the N_{χ} simultaneous linear equations

$$f(E, \chi_i, \theta) = \sum_{L=0}^{L_{\max}(N_{\chi})} f_L(N_{\chi}, E, \theta) P_L(\cos \chi_i) \quad i=1, 2, \dots, N_{\chi} \quad (19)$$

for the $f_L(N_{\chi}, E, \theta)$. Note that we need to obtain

$$f_L(E, \theta) = \lim_{N_{\chi} \rightarrow \infty} f_L(N_{\chi}, E, \theta). \quad (20)$$

In practice we found that $f_L(17, E, \theta)$ provided an adequate approximation to $f_L(E, \theta)$ for $L=0, 2$, and 4. Then we used (15) and (16) to calculate the differential cross sections. We also calculated the integral cross sections using

$$Q_{jj'}(E) = 2\pi \int d\theta \sin\theta I_{jj'}(E, \theta) \quad (21)$$

and we approximated the momentum transfer cross section as

TABLE IV. Momentum transfer cross sections (10^{-20} m^2) neglecting exchange.

E (eV)	IOS approximation
10	2.58
40	0.314

TABLE V. Differential cross sections (10^{-20} m²/sr) at $E = 10$ eV.

θ (deg)	IOS approximation			Experiment		
	I_{11}	I_{13}	I_{13}/I_{11}	I_{11}	I_{13}	I_{13}/I_{11}
0	5.07	0.395	0.078	a	a	a
10	4.10	0.173	0.042	a	a	a
20	3.18	0.164	0.052	1.69 ^b	0.047 ^b	0.028 ^b
				2.61 ^c	0.073 ^c	0.027 ^c
30	2.39	0.160	0.067	1.99 ^c	0.076 ^c	0.038 ^c
40	1.73	0.152	0.088	1.44 ^c	0.070 ^c	0.049 ^c
50	1.23	0.139	0.113	1.11 ^c	0.070 ^c	0.063 ^c
60	0.853	0.122	0.143	0.80 ^c	0.064 ^c	0.080 ^c
70	0.585	0.102	0.175	0.61 ^c	0.065 ^c	0.11 ^c
80	0.400	0.0829	0.21	0.45 ^c	0.061 ^c	0.14 ^c
90	0.275	0.0665	0.24	0.35 ^c	0.056 ^c	0.16 ^c
100	0.194	0.0564	0.29	0.28 ^c	0.051 ^c	0.18 ^c
110	0.146	0.0554	0.38	0.25 ^c	0.054 ^c	0.22 ^c
120	0.121	0.0646	0.53	0.23 ^c	0.055 ^c	0.24 ^c
135	0.117	0.0958	0.82	a	a	a
150	0.134	0.137	1.02	a	a	a
180	0.163	0.186	1.14	a	a	a

^aNot available.^bSrivastava *et al.* (Refs. 1 and 19).^cLinder and Schmidt (Ref. 3).

$$Q_m(E) \approx 2\pi \int d\theta \sin\theta (1 - \cos\theta) [I_{11}(E, \theta) + I_{13}(E, \theta)]. \quad (22)$$

III. RESULTS AND DISCUSSION

A. Integral and momentum transfer cross sections

Table I gives the values calculated for $Q_{11}(E)$ and $Q_{13}(E)$ and Table II gives the values calculated for $Q_m(E)$. In the experiments of Srivastava and co-workers,^{1,19} 66% of the molecules are initially in the $j = 1$ state. Further they found¹ that rotational excitation was dominated by the $1 - 3$ transition. Thus they interpreted¹ their measurements¹⁹ of

$$I_{01} + I_{\text{rot}} \equiv \sum_j P_j \sum_{j'} I_{jj'}, \quad (23)$$

TABLE VI. Differential cross sections (10^{-20} m²/sr) at $E = 40$ eV.

θ (deg)	IOS approximation			Experiment ^a		
	I_{11}	I_{13}	I_{13}/I_{11}	I_{11}	I_{13}	I_{13}/I_{11}
0	5.37	0.971	0.181	b	b	b
10	3.03	0.293	0.097	1.34	0.0160	0.012
20	1.61	0.185	0.115	0.75	0.0105	0.014
30	0.791	0.120	0.151	b	b	b
35	0.544	0.0960	0.176	0.38	0.00680	0.018
40	0.371	0.0768	0.21	b	b	b
50	0.173	0.0486	0.28	b	b	b
60	0.0829	0.0302	0.36	0.18	0.00713	0.039
70	0.0410	0.0184	0.45	0.062	0.016	0.26
80	0.0204	0.0110	0.54	b	b	b
90	0.0100	0.00659	0.66	0.028	0.0123	0.44
100	0.00485	0.00408	0.84	b	b	b
105	0.00340	0.00329	0.97	b	0.0137	b
110	0.00244	0.00272	1.12	b	b	b
115	0.00181	0.00233	1.29	0.0098	0.0142	1.45
120	0.00142	0.00210	1.47	b	b	b
135	0.00109	0.00211	1.93	0.0074	0.0146	1.97
150	0.00139	0.00300	2.16	b	b	b
180	0.00199	0.00456	2.30	b	b	b

^aSrivastava *et al.* (Refs. 1 and 19).^bNot available.TABLE VII. Differential cross sections (10^{-20} m²/sr) at $\theta = 20^\circ$.

E (eV)	IOS approximation					Experiment		
	$I_{11} + I_{13}$	I_{11}	I_{13}	I_{13}/I_{11}	$I_{11} + I_{13}$	I_{11}	I_{13}	I_{13}/I_{11}
10	3.35	3.18	0.164	0.052	2.68 ^a	2.61 ^a	0.073 ^a	0.028
					1.74 ^b	1.69 ^b	0.047 ^b	0.028
15	2.96	2.79	0.175	0.063	1.66 ^b	c	c	c
20	2.66	2.47	0.192	0.078	1.19 ^b	c	c	c
30	2.16	1.96	0.197	0.100	0.85 ^b	c	c	c
40	1.79	1.61	0.185	0.115	0.76 ^b	0.75 ^b	0.0105 ^b	0.014

^aLinder and Schmidt (Ref. 3).^cNot available.^bSrivastava *et al.* (Refs. 1 and 19).

where P_j is the thermal probability of finding state j , as approximations to $I_{11} + I_{13}$. Thus in Table I we compare our values of $Q_{11} + Q_{13}$ to their experimental results for the sum of elastic scattering and rotational excitation and in Table II we compare our momentum transfer cross section to their experimental determination of the contribution of elastic scattering and rotational excitation to the momentum transfer cross section. We also compare our momentum transfer cross section to that obtained from swarm experiments at 10 eV by Englehardt and Phelps.²⁰ Their value is the one recommended in a critical review by Itikawa.²¹ Their value is much larger. Henry and Lane²² used the close-coupling method (including the static, polarization, and exchange effects in the potential) to calculate a momentum transfer cross section at 10 eV of 6.3×10^{-20} m², in reasonable agreement with the present calculations. The sums of the present integral cross sections agree with the experimental results of Srivastava *et al.*¹ within 29%, 25%, 41%, 58%, and 83%, respectively, at the five energies from 10 to 40 eV and the present momentum transfer cross sections agree with their values within 10%–25% in this energy range. Their estimated experimental errors are 18% in the integral cross sections and 20% in the momentum-transfer cross sections. This comparison shows that the magnitudes of the integral cross sections and the momentum transfer cross sections and the energy dependencies of these cross sections are in qualitative agreement with experiment.

The only measurements of the rotational excitation integral cross sections $Q_{13}(E)$ with which we can make comparison are those of Ehrhardt and Linder and Linder and Schmidt³ at 10 eV. These workers obtained 0.51×10^{-20} and 0.71×10^{-20} m², respectively. The present calculation is 82% higher than the more recent of these measurements.

Additional calculations were performed at 10 and 40 eV in which the effect of exchange was neglected, since this is a commonly used approximation. The results are given in Tables III and IV. Neglecting exchange reduces the cross sections considerably, improving agreement with experiment for the integral cross sections and making the agreement worse for the momentum transfer cross sections. Since we have previously shown that the semiclassical exchange approximation is a good one in this energy range, any improvement in the results due to neglecting exchange should be attributed to cancellation of errors. The most important aspect of the results in Tables III and IV is that they

TABLE VIII. Differential cross sections (10^{-20} m²/sr) at $\theta=115^\circ$.

E (eV)	IOS approximation				Experiment			
	$I_{11}+I_{13}$	I_{11}	I_{13}	I_{13}/I_{11}	$I_{11}+I_{13}$	I_{11}	I_{13}	I_{13}/I_{11}
10	0.190	0.131	0.0587	0.45	0.29 ^a 0.29 ^b	0.24 ^a	0.055 ^a	0.23
15	0.0804	0.0524	0.0280	0.53	0.15 ^b	0.11 ^b	0.0432 ^b	0.40
20	0.0390	0.0237	0.0153	0.65	0.092 ^b	0.061 ^b	0.0314 ^b	0.52
30	0.0108	0.00563	0.00520	0.92	0.042 ^b	0.021 ^b	0.0214 ^b	1.0
40	0.00414	0.00181	0.00233	1.29	0.024 ^b	0.0098 ^b	0.0142 ^b	1.4

^aLinder and Schmidt (Ref. 3).^bSrivastava *et al.* (Refs. 1 and 19).

show that the effect of exchange is large (neglecting it causes errors of 13% to 43%) and therefore it must be included for a quantitative explanation of the scattering in this energy region.

B. Differential cross sections

It is possible to make four comparisons of the differential cross sections with experiment: these are at $E=10$ eV (Table V) and 40 eV (Table VI) as functions of θ and at $\theta=20^\circ$ (Table VII) and $\theta=115^\circ$ (Table VIII) as functions of E . Tables V and VII illustrate that the normalizations of Linder and Schmidt³ and of Srivastava *et al.*¹⁹ differ but their cross section ratios are in good agreement. Since errors tend to cancel in measuring a ratio of cross sections, the experimental cross section ratios are more reliable. We will therefore discuss the comparison of theory and experiment for these ratios. The theoretical values of $I_{13}(E, \theta)/I_{11}(E, \theta)$ are increasing functions of θ , just like the experimental ones. At 10 eV, the angular dependence of this ratio is in good agreement with experiment (the theoretical ratio is greater than the experimental one by about a factor of 1.7 roughly independent of θ for $\theta \leq 110^\circ$). At 40 eV, however, the theoretical ratio is in good agreement with experiment for $\theta > 70^\circ$ but is much too small for small θ . Thus the theoretical ratio also has about the right dependence on E for large θ but increases too rapidly with E for small θ . At $\theta=115^\circ$, the calculations correctly indicate how rotational excitation exceeds elastic scattering at 40 eV but not at energies below 30 eV. This new experimental result can therefore be explained using a realistic effective potential and should no longer be considered surprising.

*Supported in part by the National Science Foundation and the University of Minnesota Computer Center.

[†]Author to whom correspondence should be addressed; Alfred P. Sloan Research Fellow, 1973–present; Joint Institute for Laboratory Astrophysics Visiting Fellow, 1975–1976.

[‡]Lando Summer Research Fellow, 1975. Present address: Department of Chemistry, Indiana University, Bloomington, IN 47401.

¹S. K. Srivastava, R. I. Hall, S. Trajmar, and A. Chutjian, Phys. Rev. A 12, 1399 (1975).

²D. G. Truhlar and J. K. Rice, J. Chem. Phys. 52, 4480

(1970); erratum 55, 2005 (1971); see Ref. 1 for comparison of some of these results to experiment for rotational excitation. For comparison of this treatment to experiment for elastic scattering see S. Trajmar, D. G. Truhlar, and J. K. Rice, J. Chem. Phys. 52, 4502 (1970); erratum 55, 2004 (1971); D. G. Truhlar and J. K. Rice, Phys. Lett. A 47, 372 (1974).

³H. Ehrhardt and F. Linder, Phys. Rev. Lett. 21, 419 (1968); F. Linder and H. Schmidt, Z. Naturforsch. A 26, 1603 (1969).

⁴G. Joyez, F. Comer, and F. H. Read, J. Phys. B 6, 2427 (1973).

⁵For reviews of the theoretical work, see K. Takayanagi and Y. Itikawa, Adv. At. Molec. Phys. 6, 105 (1970); D. E. Golden, N. F. Lane, A. Temkin, and E. Gerjuoy, Rev. Mod. Phys. 43, 642 (1971); K. Takayanagi, Comm. At. Molec. Phys. 3, 95 (1972).

⁶R. W. B. Ardill and W. D. Davidson, Proc. R. Soc. A 304, 465 (1968).

⁷N. F. Lane and R. J. W. Henry, Phys. Rev. 173, 183 (1968).

⁸W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

⁹W. Kolos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).

¹⁰Hartree atomic units ($e=\hbar=m_e=a_0=1$) are used throughout the theory section. Thus energies are in hartrees (1 hartree = 27.21 eV = 4.360×10^{-18} J), distances are in bohrs (1 a_0 = 0.5292×10^{-10} m), and cross sections are in square bohrs (1 a_0^2 = 0.2800×10^{-20} m²).

¹¹M. E. Riley and D. G. Truhlar, J. Chem. Phys. 63, 2182 (1975).

¹²D. G. Truhlar, Chem. Phys. Lett. 15, 486 (1972).

¹³A. M. Arthurs and A. Dalgarno, Proc. R. Soc. London, Ser. A 256, 540 (1960).

¹⁴T. P. Tsien and R. T. Pack, Chem. Phys. Lett. 6, 54 (1970); T. P. Tsien and R. T. Pack, Chem. Phys. Lett. 6, 400 (1970); T. P. Tsien and R. T. Pack, *ibid.* 8, 579 (1971); R. T. Pack, *ibid.* 14, 393 (1972); T. P. Tsien, G. A. Parker, and R. T. Pack, J. Chem. Phys. 59, 5373 (1973); R. T. Pack, *ibid.* 60, 633 (1974).

¹⁵M. A. Brandt and D. G. Truhlar, Chem. Phys. Lett. 23, 48 (1973).

¹⁶D. Secrest, J. Chem. Phys. 62, 710 (1975).

¹⁷L. W. Hunter, J. Chem. Phys. 62, 2855 (1975).

¹⁸E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970), 2nd ed., pp. 389–396.

¹⁹S. K. Srivastava, A. Chutjian, and S. Trajmar, J. Chem. Phys. 63, 2659 (1975).

²⁰A. G. Englehardt and A. V. Phelps, Phys. Rev. 131, 2115 (1963).

²¹Y. Itikawa, At. Data Nucl. Data Tables 14, 1 (1974).

²²R. J. W. Henry and N. F. Lane, Phys. Rev. 183, 221 (1969).