

## Inelastic Scattering of Electrons by the Hydrogen Molecule Ion\*

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The inelastic scattering of electrons by  $H_2^+$  is investigated by means of the first Born approximation. Using the exact electronic wave functions, the integral that must be evaluated to find the differential cross section for fixed internuclear separation is studied for an electronic excitation from the ground state to any discrete excited state. Values related to this integral are tabulated for the processes  $1s\sigma_g-2p\sigma_u$ ,  $1s\sigma_g-2p\pi_u$ ,  $1s\sigma_g-2s\sigma_g$  at the equilibrium internuclear distance, while the first case is studied at two additional internuclear separations. The corresponding total cross sections are calculated for incident energies up to 400 eV. Assuming that rotational and vibrational levels of the final electronic state cannot be resolved, it is known that an observed cross section necessarily depends on the initial vibrational state of the molecular ion. The effect of two different initial vibrational states ( $\nu=0,3$ ) is investigated for the  $1s\sigma_g-2p\sigma_u$  case and it is observed that the vibrational state has a marked influence on the total cross section.

### INTRODUCTION

THE problem of inelastic electron scattering by molecules has a complication in addition to those found when considering scattering by atomic systems in that the internal degrees of freedom of the molecule must be taken into consideration. However, in the range of incident energies where the first Born approximation can be expected to be valid, experimentally determined cross sections which resolve rotational effects on electronic transitions have yet to be published, and it appears that the resolution of vibrational structure is just now becoming an experimental possibility. This being the case, it seems highly plausible to treat the internal degrees of freedom so that specific vibrational and rotational excitations are ignored while considering a given electronic process. A detailed analysis of the first Born approximation to scattering by molecules, where the above treatment of the internal modes was employed, has been given by Lassettre<sup>1</sup> and by Craggs and Massey.<sup>2</sup> Following their treatment, the differential cross section, where the excitation is  $n \rightarrow n'$  for the electronic system,  $L, M \rightarrow L', M'$  for rotation and  $\nu \rightarrow \nu'$  for vibration, can be written

$$I(nLM\nu, n'L'M'\nu'; \theta) = (4k_{n'}/k_n K^4) \left| \int_0^\infty \int_0^{2\pi} \int_0^\pi \epsilon(K, \delta, \xi, R) \cdot \Theta_{LM}(\delta, \xi) \Theta_{L'M'}^*(\delta, \xi) X_\nu(R) X_{\nu'}^*(R) R^2 \times \sin\delta d\delta d\xi dR \right|^2. \quad (1)$$

$\Theta, X$  are rotation and vibration functions, respectively, where it has been assumed that these functions do not mutually interact in addition to the usual assumption that the nuclear and electronic coordinates are separable. This expression and all remaining equations are given in atomic units unless stated otherwise. The quantity  $\epsilon$  is defined for a molecule with  $j$  electrons as (neglecting spin variables)

$$\epsilon(K, \delta, \xi, R) = \int \Psi_{n'}^*(\mathbf{r}_1 \cdots \mathbf{r}_j; R) \left[ \sum_{i=1}^j \exp(i\mathbf{K} \cdot \mathbf{r}_i) \right] \times \Psi_n(\mathbf{r}_1 \cdots \mathbf{r}_j; R) d\mathbf{r}_1 \cdots d\mathbf{r}_j, \quad (2)$$

where the states  $n, n'$  cannot be the same. The quantities  $K, \delta, \xi, R$  refer to the parameters that must be fixed during the integration over the electronic coordinates. The symbol  $K$ , the magnitude of  $\mathbf{K}$ , defines the momentum change of an incident electron scattered through an angle  $\theta$ ;  $K^2 = k_n^2 + k_{n'}^2 - 2k_n k_{n'} \cos\theta$ , where  $k_n, k_{n'}$  are the magnitudes of the momentum for the incident electron before and after scattering. The angles  $\delta, \xi$  fix the orientation of the molecule in space and  $R$  is the internuclear distance. Lassettre<sup>1</sup> has shown that the differential cross section becomes

$$I(n\nu, n'\nu'; \theta) = (4k_{n'}/k_n K^4) \left\{ (1/4\pi) \times \int_0^{2\pi} \int_0^\pi \left| \int_0^\infty \epsilon(K, \delta, \xi, R) X_\nu(R) X_{\nu'}^*(R) R^2 dR \right|^2 \times \sin\delta d\delta d\xi \right\} \quad (3)$$

when one sums over all final rotational states and averages over the degenerate levels of the initial state. Equation (3) will be true if the rotation of the molecule can be described by a symmetrical top and if the dependence of  $k_{n'}, K$  on  $L'M'$  is ignored.<sup>1</sup> It has been

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<sup>1</sup> E. N. Lassettre, Ohio State University Research Foundation, Columbus, Ohio, 1957, R. F. Project 464, Report No. 1 (unpublished).

<sup>2</sup> J. D. Craggs and H. S. W. Massey, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, Part 1, p. 332.

assumed that the final vibrational levels cannot be resolved, so a sum over all  $\nu'$  can be made, which gives

$$I(n\nu, n'; \theta) = (4k_{n'}/k_n K^4) \left\{ (1/4\pi) \times \int_0^\infty \int_0^{2\pi} \int_0^\pi |\epsilon(K, \delta, \xi)|^2 |X_\nu(R)|^2 R^2 \sin\delta \times d\delta d\xi dR \right\} \quad (4)$$

if the dependence of  $k_{n'}$ ,  $K$  on  $\nu'$  is neglected. This is then the first Born approximation for a given electronic excitation of a molecule when the final rotational and vibrational states of the system are unresolved.

The simplest molecular system available for study is the hydrogen molecule ion. Previous calculations on electron scattering by this system have been reported by Ivash<sup>3</sup> and Kerner.<sup>4</sup> Ivash treats the electronic excitation  $1s\sigma_g-2p\sigma_u$  (in the notation of Bates, Ledsham and Stewart<sup>5</sup>), where he approximates to the ground vibrational state by fixing  $R=R_e$ , the equilibrium internuclear distance, and then evaluates Eq. (4) by ignoring the integration over  $R$ . In evaluating Eq. (2), he also treats the possibility of electron exchange. Kerner does not use Eq. (4), but evaluates Eq. (1) by considering an excitation to a specific rotational and vibrational state while treating the  $1s\sigma_g-2p\sigma_u$  electronic transition. In each of these studies, the electronic wave functions that appear in Eq. (2) were replaced by linear combinations of  $1s$  atomic orbitals. Since the exact wave functions for  $H_2^+$  (assuming fixed nuclei) are available<sup>6</sup> and the use of exact wave functions for the scatterer is assumed in the derivation of the first Born approximation, it would seem that electron scattering by  $H_2^+$  should be reexamined using these wave functions. This will make it possible to give a quantitative estimate of the error introduced into the first Born approximation when approximate electronic wave functions are used to evaluate Eq. (2), at least for this relatively simple case. In addition, there are a number of electronic processes which can be expected to contribute to the inelastic scattering by  $H_2^+$  and it would be interesting to obtain quantitative information about some of these electronic transitions.

The integral defined in Eq. (2) is studied for transitions from the ground state to any discrete excited electronic state. It is found that this integral can be evaluated analytically with respect to all coordinates except one. The behavior of this integral as a function of  $K$  and the orientation parameters is explored and a quantitative example is given for one transition. A

table of this integral, after the appropriate integration over nuclear orientation has been performed, is given for the transitions  $1s\sigma_g-2p\sigma_u$ ,  $1s\sigma_g-2p\pi_u$ ,  $1s\sigma_g-2s\sigma_g$ . All transitions are studied at the equilibrium internuclear distance while the  $1s\sigma_g-2p\sigma_u$  case is evaluated at two additional internuclear separations. The total cross section for incident energies up to 400 eV and fixed  $R$  is then calculated for these various cases. The effect of two different vibrational states for the ground state,  $\nu=0, 3$ , is also studied for the  $1s\sigma_g-2p\sigma_u$  transition and the corresponding total cross sections are given.

### GENERAL CONSIDERATIONS

The total cross section corresponding to Eq. (4) is

$$Q_\nu = \int I(n\nu, n'; \theta) d\Omega = (8\pi/k_n^2)(1/4\pi) \times \int_{k_n-k_{n'}}^{k_n+k_{n'}} \int_0^\infty \int_0^{2\pi} \int_0^\pi \left\{ \frac{|\epsilon(K, \delta, \xi, R)|^2}{K^3} \right\} |X_\nu(R)|^2 \times R^2 \sin\delta d\delta d\xi dR dK, \quad (5)$$

where  $d\Omega$  is the solid-angle volume element. Carrying out the integration over the orientation angles,<sup>1</sup>

$$|\epsilon(K, R)|^2 = (1/4\pi) \int_0^{2\pi} \int_0^\pi |\epsilon(K, \delta, \xi, R)|^2 \sin\delta d\delta d\xi \quad (6)$$

is found. Defining

$$Q(R) = (8\pi/k_n^2) \int_{k_n-k_{n'}}^{k_n+k_{n'}} [|\epsilon(K, R)|^2/K^3] dK \quad (7)$$

and interchanging the order of integration, the total cross section becomes

$$Q_\nu = \int_0^\infty Q(R) |X_\nu(R)|^2 R^2 dR. \quad (8)$$

In order to obtain  $Q(R)$  the integrations defined by Eqs. (2), (6), (7) must be carried out for a fixed  $R$ . Then  $Q(R)$  must be found as a function of  $R$  to effect the evaluation of Eq. (8).

For the hydrogen molecule ion, Eq. (2) becomes

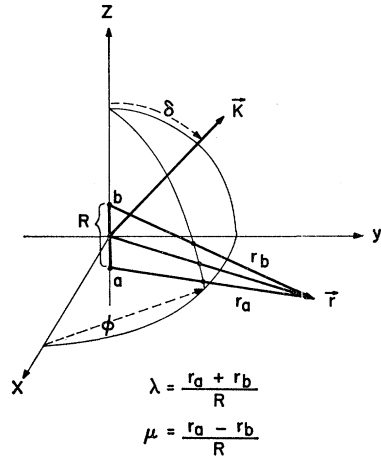
$$\epsilon(K, \delta, R) = \int_1^\infty \int_0^{2\pi} \int_{-1}^1 \exp\{iKR/2\} [\lambda\mu \cos\delta + [(\lambda^2-1)(1-\mu^2)]^{1/2} \sin\phi \sin\delta] \times \Psi_n \Psi_{n'}^*(R/2)^3 (\lambda^2-\mu^2) d\mu d\phi d\lambda, \quad (9)$$

where the coordinate system is shown in Fig. 1. It should be noted that for any linear scattering system  $\xi$  can be suppressed. The wave functions to be used in evaluating Eq. (9) are given by Bates, Ledsham, and

<sup>3</sup> E. V. Ivash, Phys. Rev. **112**, 155 (1958).

<sup>4</sup> E. H. Kerner, Phys. Rev. **92**, 1441 (1953).

<sup>5</sup> D. R. Bates, Kathleen Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London **A246**, 215 (1953).

FIG. 1. The coordinate system for  $H_2^+$  and its orientation with respect to  $\vec{K}$ .


Stewart<sup>5</sup> and are of the form

$$\Psi_n = \left[ (\lambda+1)^\sigma (\lambda^2-1)^{m/2} e^{-p\lambda} \sum_i q_i \left( \frac{\lambda-1}{\lambda+1} \right)^i \right] \times \left[ \sum'_t f_t P_{t+m}^m(\mu) \right] e^{\pm im\phi}. \quad (10)$$

The primed sum means that only even or odd values of  $t$  are to be used. The quantities  $\sigma$ ,  $p$ ,  $m$  are eigenparameters for the  $n$ th state and  $P_{t+m}^m$  is an associated Legendre polynomial of the first kind. The product  $\Psi_n \Psi_{n'}^*$  appearing in Eq. (9) can be written in the form

$$\begin{aligned} \mu^2 \Psi_n \Psi_{n'}^* &= \mu^2 f(\lambda) \exp(im\phi) \sum'_t a_t P_{t+m}^m(\mu) \\ &= f(\lambda) \exp(im\phi) \sum'_t b_t P_{t+m}^m(\mu), \quad (11) \end{aligned}$$

since the product of any two Legendre polynomials can be written as a sum of Legendre polynomials. [See Ref. 6 for a general formula applicable to the case  $m=0$ .] The ground state involves only terms of the type  $P_{2k}$ ; hence, the sum in Eq. (11) will have values of  $m$  and  $t+m$  identical to those representing the excited state.

In this notation Eq. (9) becomes

$$\begin{aligned} \epsilon(K, \delta, R) &= 4\pi(R/2)^3 \left\{ \sum'_n i^n a_n \right. \\ &\times \int_1^\infty \lambda^2 f(\lambda) j_{n+m}(y) P_{n+m}^m(\cos\psi) d\lambda \\ &\left. - \sum'_n i^n b_n \int_1^\infty f(\lambda) j_{n+m}(y) P_{n+m}^m(\cos\psi) d\lambda \right\}, \quad (12) \end{aligned}$$

where

$$y = (KR/2)(\lambda^2 - \sin^2\delta)^{1/2}, \quad (13)$$

$$\cos\psi = \lambda \cos\delta / (\lambda^2 - \sin^2\delta)^{1/2}, \quad (14)$$

and  $j$  is a spherical Bessel function. The details of this derivation are sketched in the Appendix.

### NUCLEAR ORIENTATION

The qualitative behavior of  $\epsilon(K, \delta, R)$  as a function of  $\delta$  for various final states can easily be determined from Eq. (9) or Eqs. (12)–(14). Expanding the exponential of Eq. (9) in a power series of the exponent and then noticing the symmetry of the integral with respect to  $\mu$  or  $\phi$ , a large number of terms will be found to vanish. In addition, each nonvanishing term in this series will have a very restricted dependence on  $\delta$ . Listing the results for the cases studied here, it is found all nonvanishing terms involve  $\cos(2k+1)\delta$  for final  $n\rho\sigma_u$  states,  $\sin(2k+1)\delta$  for final  $n\rho\pi_u$  states, and  $\cos 2k\delta$  for final  $n\sigma_g$  states, where  $n$ ,  $k$  are positive integers. These same conclusions can be reached by using Eqs. (12)–(14). It is also known that  $\epsilon(K, \delta, R)$  must be either symmetric or antisymmetric about  $\delta=0, \pi/2, \pi$ , since  $|\epsilon(K, \delta, R)|^2$  must be symmetric about these points. This follows immediately from the symmetry of  $H_2^+$  and implies that we need  $\epsilon(K, \delta, R)$  only over the range  $0 \leq \delta \leq \pi/2$ .

From the above analysis or directly from Eqs. (12)–(14), it can be shown that for certain transitions  $\epsilon(K, \delta, R)$  will vanish identically for a specific orientation. It is apparent that  $\epsilon(K, \delta, R)$  is zero when  $\delta = \pi/2$  for  $n\rho\sigma_u$  final states and when  $\delta = 0$  for  $n\rho\pi_u$  final states.  $\epsilon(K, \delta, R)$  is never identically zero for final states of the type  $n\sigma_g$ . This type of orientation selection rule has been noticed by other authors and the results here are consistent with the conclusions of Dunn<sup>7</sup> for the homonuclear diatomic molecule.

The quantitative behavior of  $\epsilon(K, \delta, R)$  as a function of  $K$  and  $\delta$  is shown in Fig. 2 for the case  $1s\sigma_g-2\rho\sigma_u$ ,  $R=2.0$ . In the limit of small  $K$ ,  $\epsilon(K, \delta, R)$  approaches

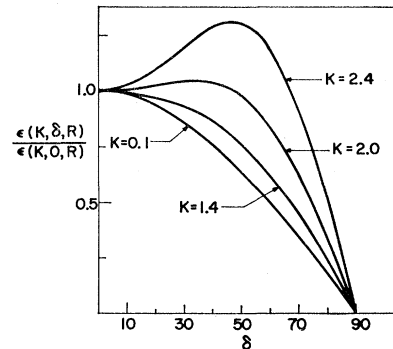


FIG. 2. The behavior of  $\epsilon(K, \delta, R)$  shown as a function of  $\delta$  for the  $1s\sigma_g-2\rho\sigma_u$  ( $R=2.0$ ) case and several values of  $K$ .

<sup>6</sup> E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, Cambridge, 1958), p. 331.

<sup>7</sup> G. H. Dunn, *Phys. Rev. Letters* 8, 62 (1962).

TABLE I. Values of  $|\epsilon(K,R)|^2/K^2$  [see Eq. (6)] for the electronic transitions  $1s\sigma_g-2p\sigma_u$  ( $R=1.4, 2.0, 3.2$ ),  $1s\sigma_g-2p\pi_u$  ( $R=2.0$ ),  $1s\sigma_g-2s\sigma_g$  ( $R=2.0$ ) as a function of  $K$ .

$K$	$ \epsilon(K,R) ^2/K^2$				
	$1s\sigma_g-2p\sigma_u$ ( $R=2.0$ ) ( $\Delta E=0.43509$ )	$1s\sigma_g-2p\sigma_u$ ( $R=1.4$ ) ( $\Delta E=0.67219$ )	$1s\sigma_g-2p\sigma_u$ ( $R=3.2$ ) ( $\Delta E=0.18102$ )	$1s\sigma_g-2p\pi_u$ ( $R=2.0$ ) ( $\Delta E=0.67385$ )	$1s\sigma_g-2s\sigma_g$ ( $R=2.0$ ) ( $\Delta E=0.74176$ )
0.0	0.3676	0.2296	0.7656	0.3414	0.0
0.05	0.3666	0.2291	0.7632	0.3403	
0.1	0.3641	0.2277	0.7559	0.3369	0.001091
0.2	0.3539	0.2221	0.7275	0.3237	0.004143
0.3	0.3378	0.2130	0.6826	0.3031	0.008633
0.4	0.3166	0.2011	0.6247	0.2765	0.01382
0.5	0.2915	0.1869	0.5579	0.2461	0.01890
0.6	0.2638	0.1711	0.4867	0.2140	0.02320
0.7	0.2349	0.1543	0.4145	0.1818	0.02622
0.8	0.2058	0.1373	0.3453	0.1513	0.02777
0.9	0.1777	0.1205	0.2816	0.1233	0.02785
1.0	0.1512	0.1045	0.2250	0.0987	0.02667
1.1	0.1270	0.0896	0.1762	0.0777	0.02456
1.2	0.1053	0.0760	0.1355	0.0602	0.02185
1.3	0.0863	0.0639	0.1024	0.0460	0.01886
1.4	0.0700	0.0532	0.0762	0.0347	0.01585
1.5	0.0562	0.0439	0.0558	0.0259	0.01301
1.6	0.0447	0.0360	0.0404	0.0191	0.01047
1.7	0.0353	0.0293	0.0289	0.0140	0.00827
1.8	0.0277	0.0237	0.0205	0.0102	0.00643
1.9	0.0215	0.0191	0.0145	0.0073	0.00493
2.0	0.0166	0.0153		0.0053	0.00374
2.1					0.00281
2.2	0.0098				

cosine behavior; hence, the differential cross section will have a cosine-squared dependence on  $\delta$ . As  $K$  increases, the behavior changes from a cosine curve to one quite eccentric, although still possessing cosine symmetry. Note that the maximum in  $\epsilon(K,\delta,R)$  moves away from  $\delta=0$  and approaches  $\delta=\pi/2$ . From the form of Eq. (9), when the exponential is expanded in a power series, it is possible to say something about the behavior of this eccentricity as the internuclear separation is altered. As  $R \rightarrow 0$ ,  $\epsilon(K,\delta,R)$  becomes much less dependent on  $K$  while, as  $R$  is allowed to become large, its behavior becomes much more dependent on  $K$  and quite complex in general. This behavior is observed in the case where several internuclear separations are studied. These general arguments apply to other transitions but both the symmetry and quantitative behavior can be expected to be different.

These observations about the dependence of  $\epsilon(K,\delta,R)$  are useful when the integration of Eq. (6) is performed.  $\epsilon(K,\delta,R)$  need be evaluated only over the range  $0 \leq \delta \leq \pi/2$ , as pointed out above. Since this must be done numerically, a considerable saving in labor ensues. In addition, since the form of the trigonometric behavior is well specified, this gives a strong hint as to the method of numerical integration that should be used. If one evaluates  $\epsilon(K,\delta,R)$  at a series of equally spaced values of  $\delta$  for a given  $K$  and then fits these points with a trigonometric interpolation formula,<sup>8</sup> a simple series results which contains only terms like  $\cos(2n+1)\delta$  for

the  $1s\sigma_g-2p\sigma_u$  case. Similar behavior results for the other cases. It is a simple matter to then square this series and carry out the indicated integration. In practice,  $\epsilon(K,\delta,R)$  was evaluated for increments of 10 deg in  $\delta$ ; hence, the series consists of nine terms. This procedure is exact if the expansion of the exponential in Eq. (9) can be truncated to the first nine nonvanishing terms. Obviously, as  $K$  and  $R$  increase, this expansion becomes less valid. However, for the cases studied, a sufficient range of  $K$  could be covered so that all significant contributions to the total cross section were obtained. The resulting values of  $|\epsilon(K,R)|^2/K^2$  for the various cases are given in Table I. An accurate error analysis seems out of the question but it is estimated that any error should be confined to the last figure quoted.

One check of the values given in Table I can be made through the relationship

$$\lim_{K \rightarrow 0} f(K,R) \rightarrow f(R) \quad (15)$$

where

$$f(K,R) = 2\Delta E \frac{|\epsilon(K,R)|^2}{K^2}. \quad (16)$$

$f(R)$  is the optical oscillator strength and  $f(K,R)$  is the generalized optical oscillator strength as defined by Bethe.<sup>9</sup> Values of  $f(R)$  for the  $1s\sigma_g-2p\sigma_u$  case are

<sup>8</sup> C. Lanczos, *Applied Analysis* (Prentice Hall, Inc., Englewood Cliffs, N. J., 1956), p. 229.

<sup>9</sup> N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1952), p. 248.

available<sup>10</sup> and are 0.309 ( $R=1.4$ ), 0.319 ( $R=2.0$ ), 0.281 ( $R=3.2$ ) which are to be compared with 0.3087, 0.3198, 0.2772, the values of  $f(R)$  obtained from Eq. (15). The optical oscillator strength for the  $1s\sigma_g-2p\pi_u$  transition<sup>11</sup> is 0.460 which is to be compared to 0.4601. Obviously,  $f(R)$  vanishes for the forbidden  $1s\sigma_g-2s\sigma_g$  transition, as does the limit of Eq. (15) for this case. [Nonvanishing limits were found directly from Eq. (9) rather than using Eq. (12).] Agreement is quite good for all cases except  $1s\sigma_g-2p\sigma_u$  ( $R=3.2$ ) and the value obtained here is within the limits of accuracy (3%) claimed by Bates.<sup>10</sup>

### TOTAL CROSS SECTIONS

The total cross sections  $Q(R)$ , defined by Eq. (7), were found from the values listed in Table I in the following way: For small values of  $K$  ( $K \leq 0.4$ ) Table I was interpolated graphically to intervals in  $K$  of 0.01. Then the integrand of Eq. (7) was evaluated for available values of  $|\epsilon(K,R)|^2/K^2$  and the integration was

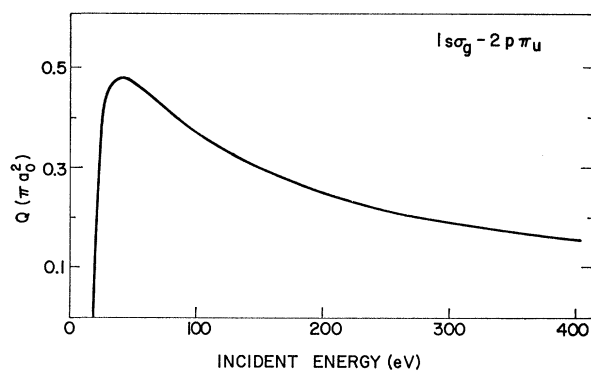


FIG. 3. The total cross section  $Q(R)$  for the  $1s\sigma_g-2p\pi_u$  ( $R=2.0$ ) case.

carried out using Simpson's rule. In general, Table I does not contain values of  $|\epsilon(K,R)|^2/K^2$  for  $K$  large enough to include the upper limit of the integral in Eq. (7). However, the contributions to the total cross section from this range are quite small and in practice this remainder was estimated by fitting the integrand with a function depending on  $K^{-5}$ .

The cross section  $Q(2.0)$  for the  $1s\sigma_g-2p\pi_u$  case is shown in Fig. 3. (The equilibrium internuclear distance of  $H_2^+$  is  $R_e=2.0 a_0$ .) It is apparent that this transition contributes quite heavily to scattering by  $H_2^+$  and must be taken into account when considering processes where this final state is possible. The  $1s\sigma_g-2s\sigma_g$ ,  $R=2.0$  case is shown in Fig. 4. This corresponds to an optically forbidden transition and the total cross section is

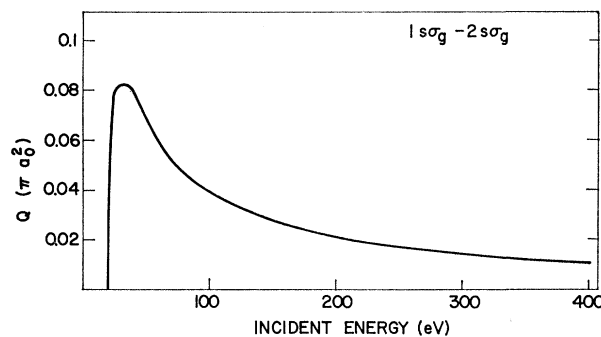


FIG. 4. The total cross section  $Q(R)$  for the  $1s\sigma_g-2s\sigma_g$  ( $R=2.0$ ) case.

relatively small, as expected. The  $1s\sigma_g-2p\sigma_u$  case is shown in Fig. 5 for three internuclear separations. The curve for  $R=2.0$  corresponds to the equilibrium internuclear separation and is, therefore, an approximation to the Born cross section when the effects of the integration in Eq. (8) are ignored. This is, of course, most accurate when  $H_2^+$  is in the  $\nu=0$  vibrational state. The other two curves are for internuclear separations that correspond roughly to the turning points of the vibrational state  $\nu=3$ . It is apparent that the cross section for this case is strongly dependent on internuclear distance for intermediate incident energies. In the limit of infinite incident energies, these cross sections approach constant ratios of each other; specifically,  $Q(3.2)/Q(2.0)=2.1$  and  $Q(2.0)/Q(1.4)=1.6$ . The effect of this strong dependence of  $Q(R)$  on  $R$  is investigated below where Eq. (8) is evaluated for two different vibrational states.

The curve for  $1s\sigma_g-2p\sigma_u$  ( $R=2.0$ ) can be compared with the results, ignoring exchange, given by Ivash<sup>8</sup>

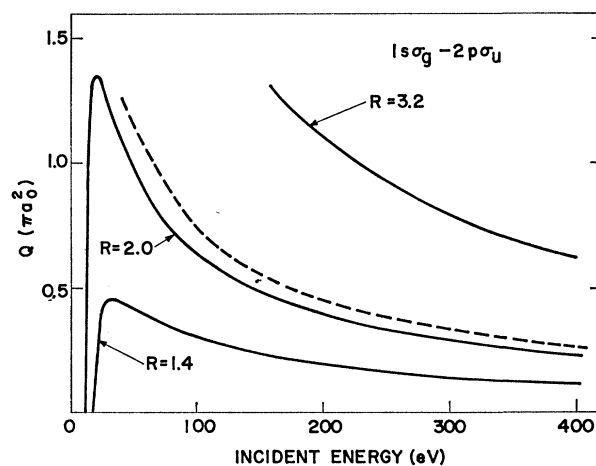


FIG. 5. The total cross section  $Q(R)$  for the  $1s\sigma_g-2p\sigma_u$  ( $R=1.4, 2.0, 3.2$ ) case. The dashed line is from a calculation by Ivash (Refs. 3, 12).

<sup>10</sup> D. R. Bates, J. Chem. Phys. **19**, 1122 (1951).

<sup>11</sup> D. R. Bates, R. T. S. Darling, S. C. Hawe, and A. L. Stewart, Proc. Phys. Soc. (London) **A66**, 1124 (1953).

which are shown as the dashed curve<sup>12</sup> in Fig. 5. To obtain this curve, he used wave functions of the form  $\Psi = u_a + u_b$ , where  $u$  is a  $1s$  screened hydrogen wave function. His results are uniformly above the present calculation of  $Q(2.0)$  by 20% or more in this energy range and in the high-energy limit will be greater by 17%. The difference between the two calculations is not large but the present treatment has the advantage that all aspects of the derivation of the first Born approximation remain valid as a result of using the exact  $H_2^+$  wave functions. A direct comparison with Kerner's calculation does not seem justified since he treats a specific rotational and vibrational excitation in conjunction with the  $1s\sigma_g-2p\sigma_u$  electronic transition. However, it is interesting to note that his cross section is roughly an order of magnitude less than  $Q(2.0)$ .

To study the effect of vibration on the total cross section, it is necessary to evaluate Eq. (8). If a diatomic molecule is in its lowest vibrational state ( $\nu=0$ ) and it is assumed that  $Q(R)$  varies slowly with  $R$ , it is a good approximation<sup>2</sup> to replace  $Q_0$  with  $Q(R_e)$ , since  $|X_0(R)|^2$  will be strongly peaked at the equilibrium internuclear distance  $R_e$ . For the transition under consideration,  $Q(R)$  is seen to be rather strongly dependent on  $R$ , so it appears that  $Q_0$  must be evaluated without using the above approximation. In addition, it is known that  $H_2^+$  is often observed in excited vibrational states which have a rather long lifetime. Hence,  $Q_\nu$  will be evaluated using Eq. (8) for the vibrational state  $\nu=3$ . This state is chosen because it is a highly probable vibrational state for  $H_2^+$  if this ion results from the ionization of  $H_2$  in its ground electronic and vibrational state.

The integral defined by Eq. (8) was estimated in the following way:  $Q(R)$  for a given incident energy was fit by a polynomial in  $R$ . Since  $Q(R)$  is known for only three points this polynomial was necessarily a quadratic. Then, using the vibrational functions given by Cohen, Hiskes, and Riddell,<sup>13</sup>  $Q_\nu$  was evaluated by Simpson's rule.

The results for  $Q_0$ ,  $Q_3$  are shown in Table II along

TABLE II. The total cross sections  $Q(R)$  and  $Q_\nu$  (in units of  $\pi a_0^2$ ) for the  $1s\sigma_g-2p\sigma_u$  transition tabulated as a function of the incident energy.

$E(\text{eV})$	$Q(1.4)$	$Q(2.0)$	$Q(3.2)$	$Q_0$	$Q_3$
50	0.426	0.977	3.25	1.09	1.92
100	0.304	0.635	1.92	0.698	1.17
200	0.197	0.396	1.11	0.431	0.691
300	0.148	0.295	0.795	0.320	0.502
400	0.120	0.230	0.612	0.248	0.383

<sup>12</sup> Ivash's calculation has been extended to include the energy range of interest in this investigation.

<sup>13</sup> S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., University of California Radiation Laboratory Report No. UCRL-8871, 1959 (unpublished); S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., Phys. Rev. **119**, 1025 (1960).

with  $Q(1.4)$ ,  $Q(2.0)$ ,  $Q(3.2)$ . It is interesting to note that  $Q_0$  is about 10% higher than  $Q(2.0)$  and that  $Q_3$  is almost 70% higher at 400 eV with the deviation increasing as the incident energy decreases. Hence, to predict the inelastic electron scattering into the  $2p\sigma_u$  state, it is necessary to know precisely what vibrational levels are populated, and to what degree. It does not follow that scattering into other final electronic states will show such marked dependence on  $\nu$ , but points out the necessity for caution before neglecting the initial vibrational state. Relationships equivalent to Eq. (8) can easily be derived for the differential cross section and the generalized oscillator strength. The effects of  $\nu$  on the differential and total cross sections can be expected to be quite similar. However, using the information in Table I, it can be seen that  $f(K,R)$  has a maximum near  $R_e$  for the  $1s\sigma_g-2p\sigma_u$  case; hence, the generalized oscillator strength will be much less dependent on  $\nu$ .

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#### APPENDIX

Substituting Eq. (11) into Eq. (9), integrals of the type

$$I_k^m = \int_1^\infty \int_{-1}^1 \int_0^{2\pi} f(\lambda) \exp\{i(KR/2) \times [\lambda\mu \cos\delta + (\lambda^2-1)^{1/2}(1-\mu)^{1/2} \sin\phi \sin\delta] - im\phi\} P_{k+m}^m(\mu) d\phi d\mu d\lambda \quad (\text{A1})$$

are obtained. Utilizing the integral<sup>14</sup>

$$\int_\alpha^{2\pi+\alpha} e^{i(n\phi-Z \sin\phi)} d\phi = 2\pi J_n(Z), \quad (\text{A2})$$

where  $J_n$  is a Bessel function of the first kind,

$$I_k^m = 2\pi \int_1^\infty \int_{-1}^1 f(\lambda) \exp\{i(KR/2)\lambda\mu \cos\delta\} \times J_m[\frac{1}{2}KR(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2} \sin\delta] \times P_{k+m}^m(\mu) d\mu d\lambda \quad (\text{A3})$$

is found. Gegenbauer's finite integral<sup>15</sup> can be rewritten

<sup>14</sup> G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1958), p. 20.

<sup>15</sup> Ref. 14, p. 378.

in the form

$$\int_{-1}^1 \exp(iy\mu \cos\psi) J_m[y(1-\mu^2)^{1/2} \sin\psi] P_{k+m}^m(\mu) d\mu \\ = 2i^k P_{k+m}^m(\cos\psi) j_{k+m}(y), \quad (\text{A4})$$

where  $j_n(x)$  is a spherical Bessel function defined by

$$j_n(x) = (\pi/2x)^{1/2} J_{n+1/2}(x). \quad (\text{A5})$$

Let

$$y = (KR/2)(\lambda^2 - \sin^2\delta)^{1/2} \quad (\text{A6})$$

$$\cos\psi = \lambda \cos\delta / (\lambda^2 - \sin^2\delta)^{1/2}; \quad (\text{A7})$$

then

$$\sin\psi = (\lambda^2 - 1)^{1/2} \sin\delta / [\lambda^2 - \sin^2\delta]^{1/2}. \quad (\text{A8})$$

Substituting Eqs. (A6)–(A8) into Eq. (A4), we find an integral of the same form that appears in Eq. (A3),

and it follows that

$$I_k^m = 4\pi i^k \int_1^\infty f(\lambda) j_{k+m}(y) P_{k+m}^m(\cos\psi) d\lambda. \quad (\text{A9})$$

Using these results, Eqs. (12)–(14) are easily verified.

Assuming that Eq. (A9) cannot be evaluated analytically, the following numerical scheme was used for this purpose. A program for a digital computer, the Control Data Corporation's 1604, was written which carried out the integration of Eq. (A9) for a given choice of  $K$ ,  $\delta$ ,  $R$  by means of Weddle's quadrature formula. With these values it is then possible to evaluate Eq. (12). The sum in Eq. (12) was usually truncated to three terms, although four terms were used in some cases. The same program was used to evaluate  $\epsilon(K, \delta, R)$  and carry out the integration of Eq. (6).

## $\Delta S = \pm 1$ Magnetic Multipole Radiative Transitions\*

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The magnetic multipole transition probability is calculated in terms of the matrix elements of the magnetic multipole. The magnetic  $jm$  moment  $Q_{jm}^{(m\theta)}$  is defined as

$$(e/\mu) [4\pi / (2j+1)]^{1/2} \sum_i (\nabla r_i^j Y_{jm}) [(j+1)^{-1} \mathbf{i}_i + \mathbf{s}_i],$$

where  $e$  and  $\mu$  are electron charge and electron mass,  $r_i$ ,  $\mathbf{i}_i$ , and  $\mathbf{s}_i$  are the coordinate, orbital angular momentum, and spin-angular momentum of the  $i$ th electron and  $Y_{jm}$  is the spherical harmonic. Magnetic quadrupole and octupole moments are explicitly given. It is shown that for the  ${}^3\Sigma_u^+ \leftrightarrow {}^1\Sigma_g^+$  transition of the hydrogen molecule, the magnetic quadrupole transition is more important than the conventional spin-orbit electric dipole transition. The magnetic octupole transition has the same order of magnitude as the spin-orbit magnetic dipole transition.

### INTRODUCTION

THE transition between states with different multiplicity is a very weak one. The corresponding emission line of some ions were first found in the spectra of some nebulas<sup>1</sup> and the theory has been given by Condon and other people.<sup>2</sup> This type of transition has been investigated for many ions since then, a brief review can be found in Garstang's article.<sup>3</sup> In all these theories the mixing of different multiplicity states through the spin-orbit interaction was assumed to be important. The  ${}^1D_2$  state of O III, for example, has

0.0074 of  ${}^3P_2$  wave function mixed through the spin-orbit interaction, and the transition to a triplet state can occur through this small part of the wave function. Most of the phosphorescences of molecules are interpreted as due to the singlet-triplet transition.<sup>4</sup> McClure first suggested the transition through the spin-orbit interaction for these molecules.<sup>5</sup> The present author and Koide formed a theory starting with the Dirac equation of electron and calculated the singlet-triplet transition probability of the benzene molecule.<sup>6</sup> The result with some approximation gave about 1 sec for the lifetime of the lowest  ${}^3B_{2u}$  state of this molecule. Hameka and Oosterhoff<sup>7</sup> refined the calculation and showed the lifetime of the same state to be 190 sec. Calculations for

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<sup>1</sup> I. S. Bowen, *Astrophys. J.* **67**, 1 (1928).

<sup>2</sup> See C. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), pp. 282–283.

<sup>3</sup> R. H. Garstang, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Part 1.

<sup>4</sup> M. Kascha, *Chem. Rev.* **41**, 401 (1947).

<sup>5</sup> D. C. McClure, *J. Chem. Phys.* **17**, 665 (1949).

<sup>6</sup> M. Mizushima and S. Koide, *J. Chem. Phys.* **20**, 765 (1952).

<sup>7</sup> H. F. Hameka and L. J. Oosterhoff, *Mol. Phys.* **1**, 358 (1958).