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Dissociation of the hydrogen molecule by electron impact*

Sunggi Chung and Chun C. Lin
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

Edward T. P. Lee
Air Force Cambridge Research Laboratories, Bedford, Massachusetts 01730

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The electron-impact dissociation cross sections of the H_2 molecule have been calculated for the processes leading to $H(1s)+H(1s)$ and to $H(1s)+H(2s)$ by means of the Born-Rudge and Born-Ochkur methods. In addition to direct excitation to the repulsive $b\,^3\Sigma_u^+$ state for the first process, cross sections are also computed for excitation of the discrete levels of the $a\,^3\Sigma_g^+$, $c\,^3\Pi_u$, $d\,^3\Pi_u$, and $e\,^3\Sigma_u^+$ states in order to account for cascades. These two mechanisms are found to be of equal importance. The second process is found to proceed mainly through excitation of the $B'\,^1\Sigma_u^+$ state except near the threshold where $e\,^3\Sigma_u^+$ is an important contributor. The theoretical cross sections are in reasonably good agreement with experimental data for the first process. The cross sections of the second process account for nearly two-thirds of the measured cross sections of $H(2s)$-atom production by electron impact. The difference is attributed mainly to predissociation and dissociative excitation through the doubly excited states.

I. INTRODUCTION

Electron-impact dissociation of molecules is an important basic process for atmospheric physics[1] and laser work.[2] A molecule can be dissociated by electron impact when it is excited to the continuum "vibrational" levels of an electronic state. Such an excited electronic state may be a purely repulsive state or a bound state with discrete vibrational levels in addition to continuum levels. The atomic species of dissociation products are dictated by the dissociation limit to which the potential-energy curve is joined. In this paper we report theoretical studies of two electron-impact dissociation processes of the H_2 molecule,

$$H_2 \xrightarrow{e} H_2^* \rightarrow H(1s)+H(1s), \qquad (1)$$

$$H_2 \xrightarrow{e} H_2^* \rightarrow H(1s)+H(2s). \qquad (2)$$

The only excited state H_2^* in (1) is the $b\,^3\Sigma_u^+$ state. However, since the $b\,^3\Sigma_u^+$ state is also the lowest triplet state, excitation to the discrete levels of the higher triplet states will contribute to process (1) via cascade to $b\,^3\Sigma_u^+$ as well as direct excitation of the repulsive $b\,^3\Sigma_u^+$ state. The excited state H_2^* in (2) may be any one of the four states,[3] $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $a\,^3\Sigma_g^+$, all of which are bound states. Therefore, dissociation results from excitation only to the continuum levels of these states, i.e., excitation to these states above the dissociation limit. In Fig. 1, these two processes are illustrated.

Although the theory of electron-impact dissociation can be formulated under the same general framework as that of electron-molecule inelastic collisions, *ab initio* calculations of cross sections are complicated by the multicenter integrals in the transition amplitudes as well as the unbound (repulsive) nature of the dissociating states. How-

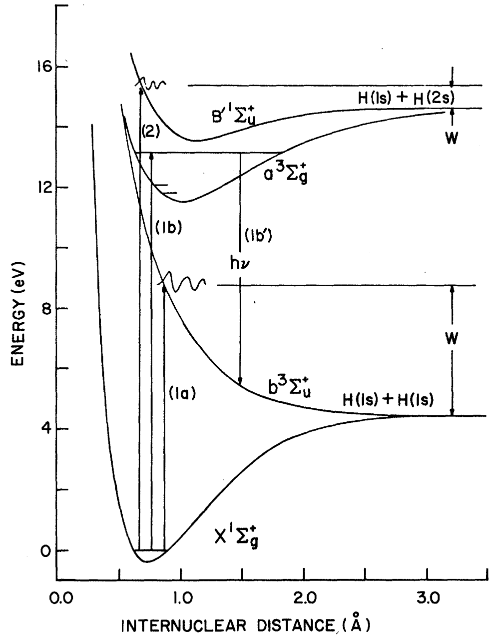

FIG. 1. Potential-energy curves of the H_2 molecule illustrating different mechanisms of dissociation by electron impact. Dissociation into $H(1s)+H(1s)$ results from direct excitation of the repulsive $b\,^3\Sigma_u^+$ state (1*a*), and also from excitation of higher triplet states such as $a\,^3\Sigma_g^+$ state (1*b*) followed by radiative cascade to the $b\,^3\Sigma_u^+$ state (1*b*′). Dissociation into $H(1s)+H(2s)$ results from excitation of the $B'\,^1\Sigma_u^+$ state (also $E\,^1\Sigma_g^+$, $e\,^3\Sigma_u^+$, and $a\,^3\Sigma_g^+$ states) above the dissociation limit (2).

ever, in the case of excitation to bound electronic states, the technique of Gaussian-type orbitals (GTO) has furnished a very efficient means of calculating cross sections.[4] We now extend the method of GTO to the case of dissociative collisions, and cross sections of electron-impact dissociation of H_2 are reported.

Several theoretical studies[5-8] related to process (1) have been reported, but we have found no first-principles calculation published for process (2). Among the previously published theoretical treatments of electron-impact dissociation of the H_2 molecule [process (1)], the most recent and complete one to our knowledge is that of Cartwright and Kupperman,[5] based on the Born approximation, with Rudge[9] and Ochkur's[10] treatment for exchange. In their paper the molecular electronic wave functions were expressed in terms of the Slater-type orbitals (STO) and a considerable amount of numerical work was needed to evaluate a typical three-center integral. The "delta-function" approximation was adopted there,[5] resulting in a significant reduction of computation. However, the method of Gaussian orbitals makes the evaluation of the electronic transition moment (due to electron impact) a rather simple task and the Born integrals can be readily performed without invoking the δ-function approximation or the closely related Franck-Condon-factor (FC) approximation. In this work the continuum vibrational wave functions of the excited electronic state are determined at various energies (above dissociation limit), and the Born integrals are evaluated exactly with full allowance for variation of the electronic transition moment with respect to the internuclear distance. In order to account for the cascade contributions to process (1), we have also computed the excitation cross sections to the discrete levels of the $a\,^3\Sigma_g^+$, $c\,^3\Pi_u$, $d\,^3\Pi_u$, and $e\,^3\Sigma_u^+$ states.

Like the work of Cartwright and Kuppermann[5] and the earlier works,[6,7] the Born approximation with Rudge[9] and Ochkur's[10] modification for treating the exchange amplitude is adopted here. The incident electron energy is varied to as high as 1000 eV for excitation of the singlet states. Although we present the singlet excitation cross sections down to the threshold, the emphasis should be placed on the high-energy region because of the use of the Born approximation. In the high-energy region (say above 100 eV) the effect of the electron exchange is quite negligible. Nevertheless, the electron exchange in this case is taken into account by Ochkur's scheme. For the singlet-triplet excitation processes, cross sections have been computed from the threshold to 150 eV. Since the singlet-triplet cross sections decrease very rapidly with increasing energy, the interest lies mainly in the low-energy region. Although the plane-wave approximation inherent in the Born approximation is justified only at high-incident energies, the improvement resulted from the modifications introduced by Rudge and by Ochkur may make these modifications applicable to much lower energies than the original Born-Oppenheimer approximation. Indeed the excitation cross sections calculated by the Rudge scheme are in quite satisfactory agreement with the experimental data for the $C\,^3\Pi_u$ state of N_2.[4]

II. METHOD OF COMPUTATION

A. Formulation

The general theoretical formulation for dissociation of diatomic molecules via excitation to repulsive states is similar to that developed previously for excitation of discrete states.[4] Here we are mainly concerned with the calculation of excitation to a continuum vibrational state of an excited electronic state by means of the Born approximation with Rudge and Ochkur's modification. The rotational motion of the molecule will not be included explicitly in the formulation, but such an effect will be taken into account by averaging the cross sections over the orientation of the molecular axis in space.

Denoting the electronic coordinates of the H_2 molecule as $\vec{r}_1$, $\vec{r}_2$ and the internuclear separation as $\vec{R}$, we write the wave functions of the ground electronic-vibrational (00) state and of the final state (nW) as

$$\Psi_{00}(\vec{r}_1, \vec{r}_2, \vec{R}) = \psi_0(\vec{r}_1, \vec{r}_2, \vec{R})\,\chi_{00}(R), \tag{3}$$

$$\Psi_{nW}(\vec{r}_1, \vec{r}_2, \vec{R}) = \psi_n(\vec{r}_1, \vec{r}_2, \vec{R})\,\chi_{nW}(R), \tag{4}$$

where ψ_0 and ψ_n are the electronic wave functions of the ground (0) and excited (n) states, and χ_{00} is the discrete $(v=0)$ vibrational function of the ground state, whereas χ_{nW} is the unbound "vibrational" function of the upper state characterized by energy W above the dissociation limit (see Fig. 1). Since we do not consider the spin-orbit interactions, the spin functions can be factored out; we assume that this has been done in Eqs. (3) and (4). The spatial part of electronic functions ψ_0 and ψ_n is written as the products of one-electron orbitals, viz.,

$$\psi_0(\vec{r}_1, \vec{r}_2, \vec{R}) = \phi_{1\sigma_g}(\vec{r}_1, \vec{R})\phi_{1\sigma_g}(\vec{r}_2, \vec{R}), \tag{5}$$

$$\begin{aligned}\psi_n(\vec{r}_1, \vec{r}_2, \vec{R}) = \sqrt{\tfrac{1}{2}}\,[\phi_{1\sigma_g'}(\vec{r}_1, \vec{R})\phi_{\mathrm{ex}}(\vec{r}_2, \vec{R}) \\ \pm \phi_{1\sigma_g'}(\vec{r}_2, \vec{R})\phi_{\mathrm{ex}}(\vec{r}_1, \vec{R})],\end{aligned} \tag{6}$$

where the + and − signs refer to a singlet and triplet excited-state function, respectively, and distinction is made of the $1\sigma_g$ orbitals in Eqs. (5) and (6). The collision process is characterized by the wave vectors of the incident and scattered electron ($\vec{k}_{00}$ and $\vec{k}_{nW}$), their difference being designated by $\vec{K}$. It is convenient to introduce the electronic transition amplitude defined as

$$\mathcal{E}_{\text{on}}(K, R, \Theta, \Phi) = -\int \psi_n^*(\vec{r}_1, \vec{r}_2, \vec{R})(e^{i\vec{K}\cdot\vec{r}_1} + e^{i\vec{K}\cdot\vec{r}_2}) \times \psi_0(\vec{r}_1, \vec{r}_2, \vec{R})\, d\vec{r}_1\, d\vec{r}_2, \tag{7}$$

where Θ and Φ specify the relative orientation between $\vec{R}$ and $\vec{K}$. Analogous to the case of excitation to discrete vibrational levels, the differential cross sections for excitation to a unit energy range about W of a singlet and a triplet state (above the dissociation limit) are

$$I_{nW}^{S}(\theta\phi) = \frac{\omega_n k_{nW}}{4\pi k_{00}} \int |\chi_{nW}^*(R)\chi_{00}(R)(2K^{-2} - T^{-2}) \times \mathcal{E}_{\text{on}}(K, R, \Theta, \Phi)|^2 R^2\, dR \sin\Theta\, d\Theta\, d\Phi, \tag{8}$$

$$I_{nW}^{T}(\theta\phi) = \frac{3\omega_n k_{nW}}{4\pi k_{00}} \int |\chi_{nW}^*(R)\chi_{00}(R) T^{-2} \mathcal{E}_{\text{on}}(K, R, \Theta, \Phi)|^2 \times R^2\, dR \sin\Theta\, d\Theta\, d\Phi, \tag{9}$$

respectively, where ω_n is the degeneracy of the excited state and T^2 is equal to k_{00}^2 and $[k_{nW} - i(2\epsilon)^{1/2}]^2$ for the Ochkur and Rudge modification, respectively, with ϵ being the ionization energy in a.u. of the initial state.

Integration of Eqs. (8) and (9) over the scattered angle θ and ϕ gives the cross section $Q(n, W)$ of exciting to a unit energy range about W of the upper state,

$$Q(nW) = \int I_{nW}(\theta\phi) \sin\theta\, d\theta\, d\phi. \tag{10}$$

Then the total dissociation cross section through excitation of an electronic state is

$$Q(n) = \int_0^\infty Q(nW)\, dW. \tag{11}$$

Equation (9) [or (8)] may be simplified if the FC approximation is invoked to suppress the R dependence of $\mathcal{E}_{\text{on}}$, viz.,

$$I_{nW}^{T} \simeq \frac{3\omega_n k_{nW} q_{nW}}{4\pi k_{00}} \int |T^{-2}\mathcal{E}_{\text{on}}(K, R_0, \Theta, \Phi)|^2 \sin\Theta\, d\Theta\, d\Phi, \tag{12}$$

where R_0 is usually taken as the equilibrium bond length of the ground state, and q_{nW} is

$$q_{nW} = \left| \int \chi_{nW}^*(R)\chi_{00}(R) R^2\, dR \right|^2. \tag{13}$$

Although our calculations are not based on the FC approximation, this concept serves a useful purpose, as the cross sections are now simply proportional to q_{nW}. For the purpose of later discussion we define the sum of the FCs of the discrete levels (S_d) and of the continuum levels (S_c) as

$$S_d(n) = \sum_{v\,(\text{discrete})} q_{nv} = \sum_{v\,(\text{discrete})} \left| \int \chi_{nv}^*(R)\chi_{00}(R) R^2\, dR \right|^2, \tag{14}$$

$$S_c(n) = \int_{(\text{continuum})} dW\, q_{nW} = \int dW \left| \int \chi_{nW}^*(R)\chi_{00}(R) R^2\, dR \right|^2, \tag{15}$$

where in Eq. (14) χ_{nv} is the vth discrete vibrational function of an excited electronic state (n). The quantities $S_d(n)$ and $S_c(n)$ provide us with an estimate of relative excitation cross sections to discrete levels and to continuum levels of a given electronic state (n). Finally, it is noted that S_d and S_c would add up to unity.

B. Details of computation

The electronic wave functions of the H_2 molecule are determined by the self-consistent-field (SCF) method with a basis set consisting of six s-type and four p-type GTO's for seven different values of internuclear distances, $R = 0.5$, 0.6, 0.7, 0.74, 0.8, 0.9, and 1.0 Å. With these wave functions we have computed $\mathcal{E}_{\text{on}}(K, R, \Theta, \Phi)$ for 32 values of K. The vibrational wave functions χ_{00} and χ_{nW} are computed in a tabular form by the procedure described in the Appendix. The potential-energy curves used are due to Kolos and Wolniewicz[11, 12] for the $X\,^1\Sigma_g^+$, $b\,^3\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $a\,^3\Sigma_g^+$ states; due to Spindler[13] for the $B'\,^1\Sigma_u^+$ state; and due to Sharp[3] for the $e\,^3\Sigma_u^+$ state. Numerical integration of Eqs. (8) and (9) then gives the differential cross sections. The cross sections $Q(nW)$ of Eq. (10) are computed for continuum energy W from 2 to 10 eV for the $b\,^3\Sigma_u^+$ state, and from 0 to 4 eV for the other states. In addition, the cross sections to the discrete vibrational levels of the $a\,^3\Sigma_g^+$, $c\,^3\Pi_u$, $d\,^3\Pi_u$, and $e\,^3\Sigma_u^+$ states are also computed by the procedure described previously.[4]

III. $H_2 \xrightarrow{e} H(1s)+H(1s)$

As described in Sec. I, the H_2 molecule may dissociate into two H(1s) atoms through direct excitation to the $b\,^3\Sigma_u^+$ state or excitation to higher triplet states followed by radiative cascades to the $b\,^3\Sigma_u^+$ state. Calculations for excitation via these two different mechanisms are described separately in Secs. III A–III B.

A. Excitation to $b\,{}^3\Sigma_u^+$ state

The cross sections of the $b\,{}^3\Sigma_u^+$ state are calculated by using Rudge's treatment of exchange amplitude and presented in Table I and Fig. 2. In obtaining the total cross sections we have taken the limits of integration for Eq. (11) as 2 to 10 eV. This is seen to be quite sufficient as we find $S_c(b\,{}^3\Sigma_u^+)$ of Eq. (15) to be 0.998 using the same limits of integration. A similar calculation with Ochkur's exchange gives considerably larger cross sections than those shown in Table I, especially at energies below 40 eV. It has been suggested[4] that Rudge's scheme is preferable to Ochkur's for the singlet-triplet excitation; hence only cross sections by Rudge's scheme are presented for the triplet states.

In order to see how the computed cross sections depend on the accuracy of the wave functions, we have repeated the calculation by using the wave function of Phillipson and Mulliken[14] (PM) for the $b\,{}^3\Sigma_u^+$ state and that of McLean, Weiss, and Yoshimine[15] (MWY) for the ground state. The latter wave function is made of five different electronic configurations so that a good deal of electron correlation is believed to be accounted for. To facilitate the numerical procedure, the STO basis functions of the above wave functions are curve-fitted into the GTO form. The substitution of the PM function for our Gaussian-basis SCF wave function of the $b\,{}^3\Sigma_u^+$ state produces virtually no change in the cross sections, whereas the use of the MWY function for the ground state gives results which are about 7% smaller than those in Table I.

TABLE I. Dissociation cross sections for production of H(1s) + H(1s) via excitation of the $b\,{}^3\Sigma_u^+$ state (repulsive) and the $a\,{}^3\Sigma_g^+$, $e\,{}^3\Sigma_u^+$, $c\,{}^3\Pi_u$, and $d\,{}^3\Pi_u$ states (bound) in units of 10^{-17} cm^2.

Energy (eV)	Cross sections $b\,{}^3\Sigma_u^+$	$a\,{}^3\Sigma_g^+$	$c\,{}^3\Pi_u$	$e\,{}^3\Sigma_u^+$ [a]	$d\,{}^3\Pi_u$
10	1.76				
13	4.47	1.07	1.96		
15	4.18	1.22	1.98	0.334	0.408
20	2.69	0.854	1.19	0.286	0.311
30	1.10	0.342	0.433	0.122	0.120
40	0.525	0.160	0.196	0.0574	0.0532
50	0.287	0.0857	0.104	0.0309	0.0278
70	0.112	0.0328	0.0396	0.118	0.0103
100	0.0401	0.0116	0.0140	0.0041	0.0036
150	0.0123	0.0035	0.0042	0.0012	0.0011

[a] Excitation to discrete vibrational levels only.

B. Excitation to discrete vibrational levels of $a\,{}^3\Sigma_g^+$, $c\,{}^3\Pi_u$, $d\,{}^3\Pi_u$, and $e\,{}^3\Sigma_u^+$ states

In order to account for the cascade contributions to dissociation into two H(1s) atoms, we have computed the cross sections for excitation to the discrete levels of the $a\,{}^3\Sigma_g^+$, $c\,{}^3\Pi_u$, $d\,{}^3\Pi_u$, and $e\,{}^3\Sigma_u^+$ states, and the results are included in Table I. There is very little overlap between the ground electronic-vibrational state and continuum level of these excited states except the $e\,{}^3\Sigma_u^+$ state, for which S_d and S_c of Eqs. (14) and (15) are, respectively, 0.80 and 0.20. The cross sections of the $e\,{}^3\Sigma_u^+$ state in Table I refer to excitation of *discrete levels only*.

As shown in Table I, about one-half of the dissociation cross sections comes from excitation of the higher triplet states and subsequent cascades. We see that the major part of such contribution comes from the two lowest triplet states, i.e., $c\,{}^3\Pi_u$ (20%) and $a\,{}^3\Sigma_g^+$ (16%), and much smaller amount from the $e\,{}^3\Sigma_u^+$ (6%) and $d\,{}^3\Pi_u$ (5%) states. In view of the trend of diminishing cross sections, the cascade contributions from still higher states are expected to be small and will not be considered here.

C. Comparison with other theoretical calculations

Cartwright and Kuppermann[5] have calculated the excitation cross sections of the $b\,{}^3\Sigma_u^+$ state by means of the Born approximation with the "δ-function approximation" for treating the continuum vibrational functions. Their results obtained by means of the Rudge modification of the Born ap-

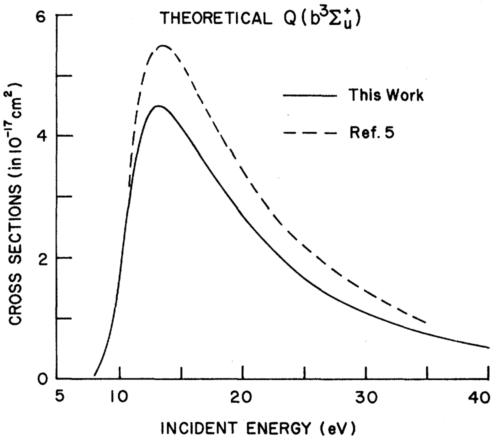

FIG. 2. Excitation cross sections of the $b\,{}^3\Sigma_u^+$ state calculated by the Born-Rudge scheme. The results of this work are represented by the solid curve, and those of Ref. 5 by the dashed curve.

proximation are included in Fig. 2 and are seen to be about 20% larger than ours. In order to better understand this difference, we repeated our calculation with the δ-function approximation (also known as the "reflection approximation"). The error in the total cross sections [Eq. (11)] introduced by the use of this approximation is only about 3%, although the distribution of cross sections $Q(nW)$ [Eq. (10)] with respect to W is shifted by about 0.2 eV toward high W. Therefore we believe that a large part of the difference must be attributed to the difference in the electronic wave functions used in their and our calculations, and to the different means of evaluating the electronic transition moment. Their ground-state function was taken to be the two-parameter wave function of Weinbaum which may give cross sections appreciably different from those resulted from our SCF wave functions. Khare and Moiseiwitsch[6] have reported calculation of excitation cross sections of the $b\,^3\Sigma_u^+$ state using the Ochkur exchange. These authors introduced a separate-atoms approximation to simplify the computational work. The vibrational wave functions were not taken into account in their work and the $b\,^3\Sigma_u^+$ excited electronic state was regarded as a single level at 11 eV above the ground state. Nevertheless, their peak cross section of 1.2 πa_0^2 is in reasonable agreement with our peak value of 1.01 πa_0^2 when the Ochkur exchange is used. Khare[7] has subsequently recalculated the $b\,^3\Sigma_u^+$ cross sections using one-center wave functions so that the separate-atoms approximation could be discarded and the excitation energy of the $b\,^3\Sigma_u^+$ state was taken as 10.6 eV with the vibrational part of the wave function neglected. The peak cross section[16] for $b\,^3\Sigma_u^+$ of Khare's calculation with Ochkur's exchange as presented in Fig. 7 of the paper of Cartwright and Kuppermann is only a few percent below our value of 1.01 πa_0^2. This agreement, however, should be regarded as fortuitous in view of the difference between Khare's approach and ours. We have performed some test calculations and found that the FC approximation gives a reasonably good estimate of cross sections (typically within 10%), which may be explained by the fact that the R dependence of the transition moment in Eqs. (8) and (9) is nearly linear so that the value of the transition moment at the equilibrium separation (R_0) is close to the averaged value over R.

Edelstein[8] used a variational method to calculate the dissociation cross sections. In his work the molecular vibration is not explicitly included. His cross sections show a special feature of peaking at two different incident energies which is not found in the results of Cartwright and Kuppermann or of ours. We are not able to find enough details of the computational procedure in Ref. 8 to analyze the reasons for this discrepancy.

Cartwright and Kuppermann[5] have also computed excitation cross sections of the bound $a\,^3\Sigma_g^+$ state by using Rudge's exchange. Their cross sections are about 20% larger than our results. We believe this difference is mainly due to the different wave functions used in the calculations as in the case of the $b\,^3\Sigma_u^+$ state. Theoretical cross sections of the $c\,^3\Pi_u$ and $a\,^3\Sigma_g^+$ states computed by using Ochkur's exchange have been given in Ref. 7. Because of the difference in approach between Khare's work and ours, no comparison between the two sets of results will be made.

D. Comparison with experiments

Corrigan[17] investigated the electron-impact dissociation of the H_2 molecule by monitoring the rate of pressure decrease in a closed system as the dissociation products are removed. Because of the nature of his experiment, the measured cross sections (Q_m) include contributions not only from excitation to electronic states (Q_{ex}), but also from ionization of molecular hydrogen (Q_{ion}). By subtracting the latter contribution (Q_{ion}),[18] he obtained the dissociation cross sections via the excited states of the neutral H_2 molecule. Corrigan put the experimental uncertainty for Q_m as ±20% due to scatter of data and ±10% due to other systematic sources of error. Since the cross sections for production of H(1s)+H(1s) are obtained by $Q_{ex} = Q_m - Q_{ion}$, the percentage uncertainty becomes progressively greater as the incident energy is increased (see Fig. 2 of Ref. 17). However, since no error estimate was given for the Q_{ion} data[18] used by Corrigan, the uncertainty limit for Q_{ex} is not clearly defined.

These reported cross sections (Q_{ex}) still cover the cross sections for producing excited-state $H(nl)$ atoms as no distinction is made of the atomic species. In order to make Corrigan's experimental data compatible with the present theoretical cross sections for producing ground-state H(1s) atoms only, it is necessary to subtract from Corrigan's data the experimental cross sections for the production of the excited-state atoms. Mumma and Zipf[19] measured the Lyman-α radiation of atomic hydrogen resulting from electron-impact dissociation of molecular hydrogen from the threshold to 350 eV. We have used these cross sections to correct for H(2p). Although we have computed the cross sections for electron-impact dissociation into H(1s)+H(2s), because of competing mechanisms such as predissociation (see Sec. IV) which we have not dealt with here, we decided to use the published experimental cross sections to account for the production of H(2s). The experimental data of Vroom and de Heer[20] show that the ratio of emission cross section for formation of H(2s) to the cross section for H(2p) by electron impact is 0.485 and constant in the entire impact-energy range (0.05–6 keV) of their experiment. Assuming that this ratio (0.485) remains substantially unchanged below 50 eV, we have also corrected for H(2s). It should be pointed out that these H(2p) and H(2s) cross sections include cascades from higher excited states as well as direct formation of H(2p) and H(2s) from dissociation. Vroom and de Heer[20] further found that the cross sections for formation of H(np) atoms for $n \geq 3$ are quite small. Therefore, we believe that the correction for H(2p) and H(2s) as outlined above should account for nearly all of H(nl) production ($nl \neq 1s$). The "experimental" cross sections for dissociation into two H(1s) atoms obtained by this method of correction are shown in Fig. 3. Taking into account the stated error limits in Refs. 19 and 20, this procedure of correcting for production of H(2s) and H(2p) atoms introduces additional uncertainties of 3 and 11% at 20 and 30 eV, respectively, which are quite small compared with the uncertainties in the data of Q_{ex} discussed above. Thus the error bars for the "experimental" cross sections in Fig. 3 should be about the same as those of Q_{ex} of Corrigan's work.

Included in Fig. 3 are also our theoretical dissociation cross sections (sum of the contributions from the b, a, c, e, d states as listed in Table I). The over-all agreement with the corrected experimental data is seen to be quite good. As mentioned in Sec. III B, population of the $b\,^3\Sigma_u^+$ state by means of excitation to the very high triplet states (such as those above $d\,^3\Pi_u$) with subsequent cascade has been neglected in our calculations and inclusion of these contributions may somewhat increase the theoretical cross sections. Also at the high-energy end the cross sections reported by Corrigan are subject to larger percentage uncertainties because of his subtraction of the effects of ionization (Q_{ion}) as discussed above.

Cross sections obtained from energy-loss experiment have been reported by Ramien[21] in 1931. His cross sections, however, are smaller than Corrigan's by about a factor 2. Comparison between Corrigan's data with the cross sections of Ramien[21] and of Engelhardt and Phelps[22] has been discussed in Ref. 17.

IV. $H_2 \xrightarrow{e} H(1s)+H(2s)$

Dissociation of H_2 into H(1s)+H(2s) is complicated by the possibility of predissociation. Formation of H(1s) and H(2s) by electron impact may result from (i) direct excitation to the continuum portion of the $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $a\,^3\Sigma_g^+$ states whose adiabatic dissociation limits correspond to H(1s)+H(2s)[3,12,23,24]; (ii) excitation to some other excited electronic states which cross (or nearly cross) with the B', a, E, and e states in such a manner as to produce predissociation[25]; (iii) excitation to the higher excited states followed by dissociative cascade to the four states leading to H(1s)+H(2s). An *ab initio* calculation of electron-impact predissociation requires very accurate knowledge of the potential curves of numerous excited states which is beyond the scope of this work. Also, the lack of detailed information concerning the branching ratios among many available cascade channels from any given higher excited state makes it difficult to obtain a quantitative estimate of process (iii). Thus in the present work we will confine ourselves to process (i). Since the potential-energy curves of the four states listed above merge at large R with those of the molecular states (e.g., $B\,^1\Sigma_u^+$, $C\,^1\Pi_u$) which dissociate to H(1s)+H(2p), there exists the possibility of transitions between the two sets of states as the two hydrogen atoms move away from each other. However, we expect the probability of such a nonadiabatic transition to be small in the present case, since the speed of

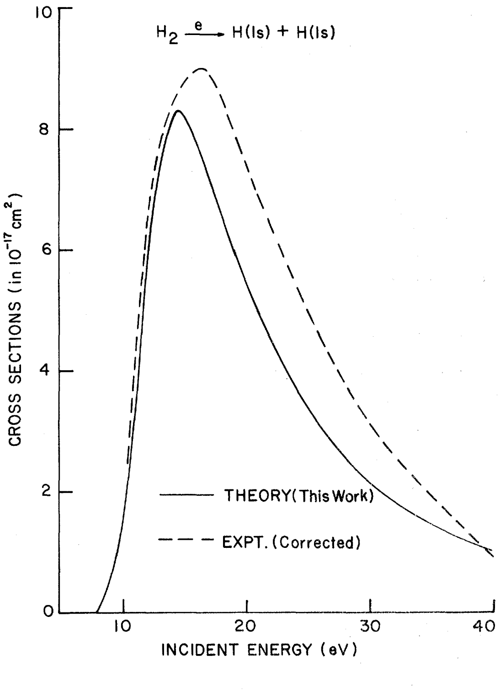

FIG. 3. Theoretical cross sections of this work (solid curve) for the dissociation process $H_2 \xrightarrow{e} H(1s)+H(1s)$ as compared with the experimental values of Ref. 17 corrected to represent the production of H(1s) atoms only as described in Sec. III D (dashed curve).

relative motion of the two atoms is small (kinetic energy of less than ~2 eV) and the merging of the potential curves occur at relatively large distance where the two atoms are well separated. This indeed is shown to be the case by Menthall and Gentieu[26] in their photodissociation experiment of the H_2 molecule. Their experiment indicated that the fraction of H(2*p*) is at most 15% of the total H($n=2$) produced, when the major mechanism of dissociation is photoexcitation of the $D\,^1\Pi_u$ state followed by predissociation[23] via the $B'\,^1\Sigma_u^+$ state which connects adiabatically to H(1*s*) + H(2*s*). Moreover, the fraction (15%) also includes contribution from excitation to the continua of $C\,^1\Pi_u$ and $B\,^1\Sigma_u^+$. Therefore, we shall assume in this paper that excitation of the $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, $E\,^3\Sigma_g^+$, and $a\,^3\Sigma_g^+$ states leads exclusively to production H(1*s*) + H(2*s*) in the dissociation process.

A. Dissociation via $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, and $E\,^1\Sigma_g^+$

The dissociative excitation cross sections of the $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, and $E\,^1\Sigma_g^+$ states are presented in Table II and the sum of cross sections (of B', e, and E states) is shown in Fig. 4. Because the potential-energy curve of the $a\,^3\Sigma_g^+$ state is so unfavorable for dissociative excitation [$S_c(a\,^3\Sigma_g^+)$ of Eq. (15) is only 0.0026], we omit this state from consideration. However, one can estimate the dissociative excitation cross sections of the $a\,^3\Sigma_g^+$ state by using the FC approximation along with $S_c = 0.0026$ and the cross sections of the $a\,^3\Sigma_g^+$ state (discrete levels) in Table I. It is seen that they are indeed much smaller than the contributions from the other three states.

From Table II we see that the $B'\,^1\Sigma_u^+$ state account for more than 95% of this dissociation process above 60 eV. Near the threshold excitation of the $e\,^3\Sigma_u^+$ state is shown to be an important contributor. It should be pointed out that due to the variation of the transition moment with R, the ratio of cross sections ($e\,^3\Sigma_u^+$) of discrete levels to those of continuum levels[27] differ from the corresponding ratio $S_d(e\,^3\Sigma_u^+)/S_c(e\,^3\Sigma_u^+)$, which is 0.8/0.2.

TABLE II. Dissociation cross sections for production of H(1*s*) + H(2*s*) via excitation[a] of the $B'\,^1\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $e\,^3\Sigma_u^+$ states in units of 10^{-18} cm^2.

Energy (eV)	Cross sections $B'\,^1\Sigma_u^+$	$E\,^1\Sigma_g^+$	$e\,^3\Sigma_u^+$
15	0.0623	0.0290	0.151
18	1.33	0.113	0.860
20	1.98	0.141	0.800
40	3.91	0.166	0.163
60	3.75	0.133	0.0509
80	3.41	0.108	0.0217
100	3.09	0.0910	0.0112
150	2.50	0.0645	0.0033
200	2.10	0.0498	
500	1.13	0.0219	
1000	0.674	0.0108	

[a] Excitation to these states above the dissociation limit only.

B. Comparison with experiment

Vroom and de Heer[20] measured the cross sections for the electron-impact production of H(2*s*) atoms in the energy range 50–6000 eV. More recently, the standard[28] used for normalization of experimental cross sections was reexamined, and as a result Mumma and Zipf[19] suggested a factor of 0.8 by which the previously reported experimental cross sections should be multiplied. Therefore, the cross sections of Vroom and de Heer have been corrected accordingly and are shown in Fig. 4. It appears that the present theoretical cross sections account for (61–67)% of the experimental values. The difference [(33–39)% of experimental data] may well be due to other competing processes leading to formation of H(2*s*) atoms. First, predissociation into H(1*s*) + H(2*s*) through excitation to the states of Π_u symmetry is shown to be an important process by experiments.[29] Second, consideration should be given to the possibility of excitation of the higher excited states with subsequent cascades to the dissociating states. However, not all of the highly excited H_2 molecule will decay to the dissociating states ($B'\,^1\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $e\,^3\Sigma_u^+$) since there are lower states (such as

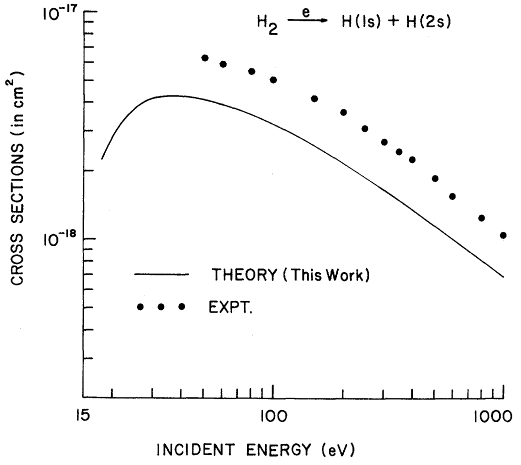

FIG. 4. Theoretical cross sections of this work (solid curve) for the dissociation process $H_2 \xrightarrow{e} H(1s) + H(2s)$ via excitation of the $B'\,^1\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $e\,^3\Sigma_u^+$ states. The experimental cross sections of Ref. 20 are multiplied by a factor of 0.8 as suggested by Ref. 19. The experimental cross sections are for the rate of production of H(2*s*) atoms, thus they also include other modes of dissociation (see Sec. IV B).

$B\,^1\Sigma_u^+$, $X\,^1\Sigma_g^+$, and $b\,^3\Sigma_u^+$) which offer competing cascade paths. Moreover, the $B'\,^1\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $e\,^3\Sigma_u^+$ are bound states, unlike the $b\,^3\Sigma_u^+$ state, so that only the fraction of cascades to the continuum portion of these states will contribute to the formation of H(2*s*) atoms. Because of these competitions we believe that the cascade contribution to formation of H(2*s*) atoms is not likely to be very substantial. Finally the experimental data of Vroom and de Heer may contain, in addition to process (2), contribution from excitation through doubly excited states, i.e.,

$$H_2 \xrightarrow{e} H(2s) + H(nl), \quad nl \neq 1s$$

(at energies above the appropriate threshold), which have been excluded in our theoretical consideration. In the experiment of electron-impact dissociation of H_2 described in Ref. 29, some of the H(2*s*) atoms produced exhibit a threshold of incident electron energy in the neighborhood of 29 eV, indeed suggesting a possible dissociative mechanism such as

$$H_2 \xrightarrow{e} H(2s) + H(2p),$$

although no determination of the absolute cross sections for this process was reported. In the experimental condition of Ref. 20, the measured cross sections represent the sum of contributions from the processes discussed above. Therefore one would expect our theoretical cross sections to be smaller than the experimental values.

The energy dependence of the experimental cross sections[20] shows that the dissociating state is an optically allowed one. Our results are in agreement with the experiment in this regard as the major contributor is found to be the $B'\,^1\Sigma_u^+$ state. This characteristic energy dependence will remain unchanged when predissociation of the $^{1,3}\Pi_u$ states is considered. We may note here that the optical oscillator strength 0.0588 at $R = 1.4\ a_0$ of this work agrees well with the corresponding values of 0.058, 0.057, and 0.048 computed by three different versions reported by Rothenberg and Davidson.[30]

To summarize, our calculation indicates that the dissociative excitation of the $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, and $E\,^1\Sigma_g^+$ states accounts for as much as two-thirds of measured cross sections for production of H(2*s*) atoms. The remainder is very likely due to predissociation of $^{1,3}\Pi_u$ states and to the excitation of doubly excited states.

V. CONCLUSION

The mechanism of electron-impact dissociation of molecules may be subdivided into (i) direct excitation of repulsive states (including excitation of bound state above the dissociation limits), (ii) excitation of discrete levels of bound states followed by cascades to a dissociating state, and (iii) excitation of bound states which are predissociative (i.e., mixed with dissociating states). The method of GTO has been proven to be a very efficient means of dealing with excitation of discrete levels of molecules. As the computation of continuum functions poses no difficulty, the method of GTO can be readily extended to *ab initio* calculations of processes (i) and (ii). In order to make reliable calculation of predissociation [process (iii)], accurate electronic wave functions and detailed knowledge of potential-curve crossing are required. Once this information is available, the Gaussian technique can be applied to treat the problem of excitation to the predissociative states.

In this paper we have presented the results of the electron-impact dissociation of the H_2 molecule into H(1*s*) + H(1*s*), and into H(1*s*) + H(2*s*) computed within the framework of the Born approximation. In the former case we find that the total dissociation cross sections receive about equal contributions from the direct excitation of the repulsive $b\,^3\Sigma_u^+$ state and from the excitation of higher triplet states with subsequent cascade to $b\,^3\Sigma_u^+$. The present theoretical cross sections are in a reasonably good agreement with the experimental values of Corrigan when the latter are made compatible so as to represent the process leading to H(1*s*) + H(1*s*) only.

As to the process of H(1*s*) + H(2*s*), the excitation of the $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, and $E\,^1\Sigma_g^+$ states (above the dissociation limit) may account for almost two-thirds of the measured cross sections of Vroom and de Heer. Among these dissociating states the $B'\,^1\Sigma_u^+$ state is by far (95% or more) the most important contributor at incident energies above 60 eV. At lower energies the $e\,^3\Sigma_u^+$ becomes important, particularly near the threshold. The balance (about one-third) is expected (but not independently verified) to come from excitation of the $^{1,3}\Pi_u$ states which are predissociated by the $B'\,^1\Sigma_u^+$ and $e\,^3\Sigma_u^+$ states. It is also likely that some contribution comes from excitation of some doubly excited states. Although our results are consistent with the experimental data, further studies concerning predissociation and the nature of some of the doubly excited states are necessary in order to have a more complete understanding of dissociation of H_2 into H(1*s*) + H(2*s*).

APPENDIX

The differential equation for the nuclear motion is (omitting the angular momentum term)

$$\left(\frac{d^2}{dR^2} + 2\mu[W - V_n(R)]\right) P_{nW}(R) = 0, \tag{A1}$$

where $P_{nW}(R)$ is related to the vibrational function as

$$P_{nW}(R) = R\chi_{nW}(R), \tag{A2}$$

and μ is the reduced mass of two atoms, W is the energy, and $V_n(R)$ is the potential energy of the electronic state n. In the case of discrete vibrational states the numerical method is well known.[31] For the continuum states the boundary conditions are $P_{nW}(0) = 0$, and for large R where $V_n(R) \cong 0$,

$$\begin{aligned} P_{nW}(R) &\cong a\sin(\kappa R) + b\cos(\kappa R) \\ &= A\sin(\kappa R + \eta), \end{aligned} \tag{A3}$$

$$\kappa^2 = 2\mu W. \tag{A4}$$

We may choose A such that the density of states per unit energy range (in a.u.) is unity,[32] i.e.,

$$A = (2\mu/W\pi^2)^{1/4}. \tag{A5}$$

The phase η, however, depends on V and W.

For the presentation of the numerical procedure, we first define

$$\begin{aligned} &R_i = i\Delta R, \quad i = 1, 2, \ldots, \\ &F_i = F_{nW}(R_i), \\ &U_i = 2\mu[W - V_n(R_i)], \end{aligned} \tag{A6}$$

where ΔR is the step size. The recurrence formula based on Numrov's method is

$$\begin{aligned} F_{i+2} = \{ &[2 + \tfrac{5}{6}(\Delta R)^2 U_{i+1}]F_{i+1} \\ &- [1 - \tfrac{1}{12}(\Delta R)^2 U_i]F_i\}/[1 - \tfrac{1}{12}(\Delta R)^2 U_{i+2}]. \end{aligned} \tag{A7}$$

If F_i and F_{i+1} are known, then Eq. (A7) may be used to obtain all succeeding F_i's. In practice, we choose $F_i = 0$ and F_{i+1} equal to a small arbitrary value in the region of R where F decays exponentially. Because of this arbitrary choice of the starting values, the Numrov-developed solution F will differ from the properly normalized function P by a constant factor N, i.e.,

$$P_i = NF_i. \tag{A8}$$

By equating the Eqs. (A8) and (A3) at two different points R_A and $R_B = R_A + \Delta R$ of large R, we have

$$A\sin(\kappa R_A)\cos\eta + A\cos(\kappa R_A)\sin\eta = NF(R_A), \tag{A9}$$

$$A\sin(\kappa R_B)\cos\eta + A\cos(\kappa R_B)\sin\eta = NF(R_B), \tag{A10}$$

From Eqs. (A9) and (A10), it is simple to determine η and N. This matching procedure may be repeated to see that N and η are well converged.

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crete and continuum excitation to allow for this fact, no significant changes are expected. For example, the fraction of cross sections ($B'\,{}^1\Sigma_u^+$) due to the highest three vibrational levels (summed over all rotational states) does not exceed 1.5% of the total cross section for either discrete excitation or continuum dissociation at incident energy greater than 2 eV above the dissociation limit.

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