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Dissociative cross sections of H_2 by electron impact

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In the reflection approximation, the dissociative cross sections of H_2 by electron impact for production of H(1*s*) and H(2*s*) are accurately computed in the Bethe approximation using highly correlated electronic wave functions. It is found that the calculated Bethe cross sections, expected to be valid only for high-incident electron energies, agree surprisingly well with other theoretical values for low impact energies, where electron exchange must surely be included. The discrepancy between theory and experiment reported for total production of H(2*s*) at incident energies above 500 eV may be attributed to lack of inclusion in the theoretical model of double excitations, particularly those corresponding to optically forbidden transitions.

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I. INTRODUCTION

Electron-impact dissociation of molecules is one of the most fundamental processes for atmospheric physic and laser physics. In the Bethe approximation [1], theoretical study [2] of the electron-impact dissociation of H_2^+ with production of H and H^+ has shown that theory and experiment are in good agreement for incident energies as low as 50 eV. As part of the ongoing theoretical study of the electron-impact spectra of H_2, Liu and Hagstrom [3] recently developed an accurate method for computing molecular wave functions and generalized oscillator strengths (GOS's) for some of the low-lying excited states. Here we report the Bethe cross section for the electron-impact dissociation of H_2 leading to production of H(1*s*) and H(2*s*).

Despite the apparent simplicity of this dissociative process, to date very few theoretical studied have been reported [4,5]. The early theoretical calculations [4,5] were mainly concerned with dissociative processes of low incident energies, which contrasts with our interest here in collision processes at high incident electron energies, where the Bethe theory is known to be valid. Nevertheless, it is interesting to compare our values with these low-energy results [4,5], especially for the results [4] obtained using the Born-Bonham-Ochkur-Rudge method [6] and simple Hartree-Fock molecular wave functions. In this connection, we note that the theoretical values calculated in the Born-Bonham-Ochkur-Rudge approximation at incident energies ≤ 1000 eV and by the distorted-wave method at incident electron energies ≤ 100 eV both considerably underestimated what was then the best experimental data for the *total* production of H(2*s*) as reported by Vroom and de Heer [7]. This discrepancy with experiment was not understood until recently, when Shemansky, Ajello, and Hall [8] measured an absolute dissociative cross section $\sigma(2p)$ for H Lyman-α production from H_2 by electron impact and found that the experimental data reported by Vroom and de Heer [7] and Mohlmann, Shima, and de Heer [9] were too large by 31%. In this connection, we note also that the error bars on the experimental $\sigma(2s)$ dissociative cross-section values were also fairly large.

Early theoretical values [4,5] were calculated using very simple molecular wave functions of the self-consistent-field (SCF) type. The discrepancy, of course, may be attributed to a number of factors including (i) the use of overly simple molecular wave functions, (ii) the use of an approximate vibrational wave function and failure to include double excitation and predissociation in the theoretical model, and (iii) the experimental errors. In our early study of the effect of electron correlations on the GOS for excitations to $B'\,^1\Sigma_u$, it was shown that up to a 10% error in the GOS at momentum transfers $K=0$ due to the level of electron correlation included was possible (see Table VI of Ref. [3] for details). In addition, it was pointed out that the error due to the use of approximate nuclear vibrational wave functions can be very significant. In this work, we will investigate the errors due to the use of simple target wave functions.

The earlier study [10] of the total cross section of H_2 using fast electrons has shown the Bethe-Born approximation to be valid at incident energies above 500 eV, even though the approximation is not designed to account for the effect of electron exchange. It would be interesting to calculate a dissociative Bethe cross section using more accurate wave functions for comparison with other theoretical results [4,5] that include the effect of electron exchange.

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The purpose of this work is to calculate accurately the dissociative cross section in the Bethe approximation for production of H(1s) and H(2s) using the methodology reported earlier [2,3]. The calculated theoretical values are given for comparison with earlier theoretical values [4,5] and experimental data for total production of H(2s) [7,9] (applying the correction recommended in the recent literature [8]).

II. THEORETICAL BACKGROUND

For electron-impact spectra at high incident energies, the rotational excitation is usually unresolved. Due to their small mass, electrons are not effective in producing rotational excitations; therefore, the change in the wave function of the incident electron due to rotational excitation is negligible compared to that due to electronic and vibrational excitations. Here we assume that the molecule is in the ground vibrational and rotational states and that the momentum transfer is independent of the final rotational quantum number.

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 a continuum manifold. The Franck-Condon (FC) approximation is usually used to treat the excitation between two bound electronic states. For electron-impact excitation to a repulsive state, the reflection approximation [11] has been successfully used to describe dissociative processes on many occasions [2,4,12]. The reflection approximation is used here also, as it has considerably simplified the calculation. Only one-electron excitation processes will be considered; hence we neglect the contribution from double excitations and predissociation.

The differential cross section as a function of internuclear distances R for excitation from the ground state to electronic state n can be written as [1,2]

$$d\sigma_n(R)=\frac{4\pi a_0^2}{[T\ (\mathrm{Ry})]}\frac{f_n(K,R)}{[\Delta E_n\ (\mathrm{Ry})]}d(Ka_0)^2/(Ka_0)^2\ , \quad (1)$$

where k is the momentum transfer, $f_n(K,R)$ is the generalized oscillator strength [2], T is the incident electron energy in Rydberg units (Ry), and ΔE_n is the energy of excitation from the ground state to excited state n. Accordingly, the integrated cross section is given by [1,2]

$$\sigma_n(R)=\frac{4\pi a_0^2}{[T\ (\mathrm{Ry})]}\{M_n^2(R)\ln[4T\ (\mathrm{Ry})]+I_{1n}(R)-I_{2n}(R)-2L_n(R)\}\ , \quad (2)$$

where the oscillator strength moment (transition dipole moment squared) for an optically allowed transition $M_n^2(R)$ is defined by [see Eq. (8), Ref. [3] for the explicit definition of H_2]

$$M_n^2(R)=f_n(R)/\Delta E_n(R)\mathrm{Ry}\ ,$$

with the optical oscillator strength $f_n(R)$ defined by

$$f_n(R)=f_n(K,R)|_{K=0}\ ,$$

$$L_n(R)=M_n^2(R)\ln[\Delta E_n(R)\ (\mathrm{Ry})]\ ,$$

$$I_{1n}(R)=\int_0^\infty\frac{f_n(K,R)}{[\Delta E_n\ (\mathrm{Ry})]}d\ln[(Ka_0)^2]\ ,$$

and

$$I_{2n}(R)=\int_{-\infty}^0\left|M_n^2(R)-\frac{f_n(K,R)}{[\Delta E_n\ (\mathrm{Ry})]}\right|d\ln[(Ka_0)^2]\ .$$

As shown earlier [2], it is seen that the values of $M_n^2(R)$, $L_n(R)$, $I_{1n}(R)$, and $I_{2n}(R)$ can be calculated once $f_n(K,R)$ for a given excitation is known.

Within the Franck-Condon (FC) approximation, the cross section σ_{nv} for excitation to a discrete vibrational level v of an electronic state n is approximated by

$$\sigma_{nv}=q_{nv}\sigma_n(R_0)\ , \quad (3)$$

where R_0 is the equilibrium bond length of the initial state and q_{nv} is the Franck-Condon factor given by

$$q_{nv}=\left|\int x_{nv}(R)x_{00}(R)R^2dR\right|^2\ , \quad (4)$$

$x_{00}(R)$ is the ground vibrational wave function for the ground electronic state, and $x_{nv}(R)$ is the vibrational wave function for the vth vibrational level in the excited electronic state n. If the excited electronic state contains continuum vibrational levels as well as discrete vibrational levels, the sum of the FC factors of the discrete levels S_d and the integral of FC factors for the continuum levels S_c, must add up to 1, where S_d is given by

$$S_d=\sum_v q_{nv} \quad (5)$$

and

$$S_c=\int d\epsilon\left|\int x_{n_\epsilon}(R)x_{00}(R)R^2dR\right|^2\ , \quad (6)$$

where $x_{n_\epsilon}(R)$ is the continuum vibrational wave function with energy ϵ. The value of S_d and S_c can be used to estimate the relative excitation cross sections to discrete levels and to continuum levels, respectively, of a given electronic state.

The electron-impact excitation to the following four excited states $B'\,{}^1\Sigma_u$, $e\,{}^3\Sigma_u$, $E\,{}^1\Sigma_g$, and $a\,{}^3\Sigma_g$ all lead to dissociation of H_2 with production of H(1s) and H(2s). According to the study [10] of the total cross section for electron scattering by H_2 at incident energies above 500 eV, the effect of electron exchange on the total cross section is not important. Consequently, at high incident energies used here, the effect of electron exchange on dissociation cross sections is neglected. According to Chung, Lin, and Lee [4], the dissociative excitation via $E\,{}^1\Sigma_g$ fails to account for more than 2% of the total dissociative cross section at incident electron energies above 100 eV, which is much smaller than the magnitude of the uncertainty of the measured cross section reported elsewhere [7–9]. This dissociative excitation is also neglected here. Moreover, the contribution due to the excitation via

$B'\,^1\Sigma_u$ accounts for more than 95% of the total dissociation at incident electron energies above 100 eV. Therefore, in the sequel we consider only the contribution of the $B'\,^1\Sigma_u$ state to the dissociative excitation cross section for production of H(1*s*) and H(2*s*).

In order to simplify the calculation for excitation to the vibrational continuum, the reflection or δ approximation [2,11,12] is used to approximate the continuum vibrational wave function, i.e.,

$$x_{n_\epsilon}(R)=(A/\epsilon)\delta(R-R_c)/R_c \ , \tag{7}$$

where R_c is the internuclear distance at the classical turning point and A is the normalization constant. According to the reflection approximation, S_c can be given by

$$S_c=|A|^2\int_0^{1/D_0}|x_{\infty}(R)|^2/R^2dR \ , \tag{8}$$

where D_0 is the dissociation energy of H_2 for $B'\,^1\Sigma_u$ (i.e., -0.75 a.u.). Since $S_c+S_d=1$, normalization constant A can be obtained if S_d is accurately given. The vibrational wave functions $x_{nv}(R)$ for $B'\,^1\Sigma_u$ and $x_{00}(R)$ for $X\,^1\Sigma_g$ are computed using accurate Born-Oppenheimer (BO) potential-energy curves given by Kolos and Rychlewski [13] and Wolniewics and Dressler [14], respectively. In Table I, the FC factors q_{nv} computed by using these accurate potential-energy curves are given for comparison with the less accurate ones reported by Spindler [15]. The value of S_d calculated using Spinder's FC factors [15] are smaller than our accurate value by about 8%. Therefore, an error of 8% for the calculated dissociative cross sections can result from using approximate vibrational wave functions. Note that normalization constant A defined in Eq. (7) can be computed once S_d is given. Finally, the total dissociative cross section (for excitation via $B'\,^1\Sigma_u$) can be written

$$\sigma_d=|A|^2\int_0^{1/D_0}\sigma_n(R)|x_{00}(R)|^2/R^2dR \ . \tag{9}$$

TABLE I. Franck-Condon factor q_{nv} for the $B'\,^1\Sigma_u$-$X\,^1\Sigma_g$ excitation .

v	Ref. [15]	This work
0	0.0332	0.0490
1	0.0737	0.1000
2	0.1023	0.1228
3	0.1144	0.1175
4	0.1053	0.0939
5	0.0674	0.0543
6	0.0155	0.0060
Sum	0.5119	0.5436

III. CALCULATED RESULTS AND DISCUSSIONS

A. Wave functions

The ground-state $X\,^1\Sigma_g$ and excited-state $B'\,^1\Sigma_u$ wave functions for various internuclear distances were computed by the method described previously [3]. In Table II, the total energies obtained for the ground state and excited state $B'\,^1\Sigma_u$ are shown for comparison with the accurate values given by Kolos and Rychlewski [13] and Wolniewics and Dressler [14]. Our wave function for the ground state at $R=1.4$ a.u. was found to be sufficiently accurate for the calculation of the GOS. The error due to the ground-state electron correlation effect on the GOS was earlier shown [3] to be not very significant. Our total energies for excited state $B'\,^1\Sigma_u$ are in very close agreement with the Wolniewics and Dressler values [14], being in error by less than 100 μhartree for all internuclear distances. In our previous study [3], the effect on the GOS of excited-state electron correlation was shown to be less significant than the ground-state electron correlation. It

TABLE II. The total energies, in hartrees, for the ground state $X\,^1\Sigma_g$ and excited state $B'\,^1\Sigma_u$.

	$X\,^1\Sigma_g$ $-E_X$		$B'\,^1\Sigma_u$ $-E_{B'}$	
R	Ref. [14]	This work	Ref. [14]	This work
1.0	1.124 539 660	1.124 347 901	0.508 615 279	0.508 585 779
1.2	1.164 935 191	1.164 754 528	0.586 645 941	0.586 613 814
1.4	1.174 475 668	1.174 304 368	0.628 688 112	0.628 649 135
1.6	1.168 583 330	1.168 427 226	0.650 860 353	0.650 832 298
1.8	1.155 068 695	1.154 924 789	0.661 564 428	0.661 517 222
2.0	1.138 132 913	1.138 000 497	0.665 475 877	0.665 420 542
2.4	1.102 422 553	1.102 312 852	0.662 773 051	0.662 704 742
2.6	1.085 791 176	1.085 691 485	0.658 863 777	0.658 787 624
2.8	1.070 683 158	1.070 593 956	0.654 283 714	0.654 205 273
3.0	1.057 326 175	1.057 247 935	0.649 501 965	0.649 410 926
4.0	1.016 389 951	1.016 346 816	0.631 328 087	0.631 271 978
5.0	1.003 785 204	1.003 732 254	0.626 634 038	0.626 613 265
6.0	1.000 835 535	1.000 666 210	0.626 266 512	0.626 254 879

TABLE III. Electronic transition dipole moment squared $M^2_{XB'}$ and total energy $E_{B'}$, in hartrees, for the $B'\,{}^1\Sigma_u - X\,{}^1\Sigma_g$ excitation.

	Ref. [16]		This work	
R	$M^2_{XB'}$	$-E_{B'}$	$M^2_{XB'}$	$-E_{B'}$
1.4	0.1048	0.628 564 389	0.1054	0.628 649 135
1.8	0.1265	0.661 382 278	0.1252	0.661 517 222
2.0	0.1283	0.665 246 604	0.1270	0.665 420 542
2.2	0.1229	0.665 084 305	0.1215	0.665 263 154

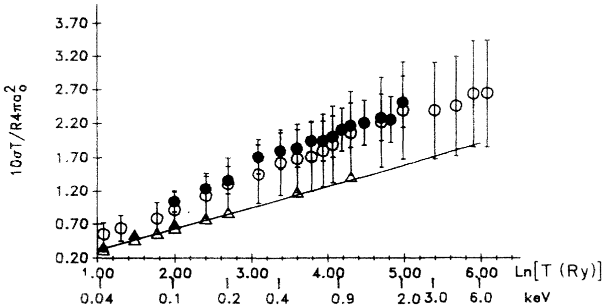

FIG. 1. ○, the experimental data of Vroom and de Heer with the correction detailed in the text; ●, the experimental data of Mohlmann *et al.* with the correction detailed in the text; △, the theoretical values of Chung *et al.*; ▲, the theoretical values of Lee *et al.*; ——, the present theoretical values.

was concluded that three figures of the GOS at $R = 1.4$ a.u. were accurate. Therefore, we believe at least three figures of the GOS calculated at $R = 14$ a.u. are accurate. In Table III, the values of the transition dipole moment squared, $M^2_{XB'}$ are given for comparison with the values computed by Wolniewics [16]. Our values are presumably more accurate than his since our wave functions for $B'\,{}^1\Sigma_u$ give lower total energies.

B. Dissociative cross sections

Using the methods presented in our previous work [3], the GOS's for excitation to $B'\,{}^1\Sigma_u$ for various internuclear distances are calculated here according to Eq. (2). In the reflection approximation, the dissociative cross section Eq. (9) becomes

$$\sigma_d = \frac{4\pi a_0^2}{[T\ (\mathrm{Ry})]}\{0.0317 \ln[T\ (\mathrm{Ry})] + 0.0006\}\ . \qquad (10)$$

The value of the slope of the Fano plot [17] calculated using the continuum vibrational wave function obtained from the potential-energy curve [14] for $B'\,{}^1\Sigma_u$ is also carried out according to Le Roy's method [18]. The value computed by using the δ approximation is in agreement within 1% of the values obtained by the exact treatment.

The value of the slope of the Fano plot [17] for the dissociative cross section also can be estimated from the experimental data of Shemansky, Ajello, and Hall [8] as follows. According to the FC approximation, the total (dissociative and nondissociative) cross section for excitation to the $B'\,{}^1\Sigma_u$ state from the ground state at $R_0 = 1.4$ a.u. is given by

$$\sigma(R_0) = \frac{4\pi a_0^2}{[T\ (\mathrm{Ry})]}\{0.1054 \ln[T\ (\mathrm{Ry})] + 0.1461\}\ . \qquad (11)$$

The experimental value of the sum of the oscillator strength moments for excitation to various discrete vibrational levels for $B'\,{}^1\Sigma_u$ was reported by Shemansky, Ajello, and Hall [8] (see Table III of Ref. [7]) and is equal to 0.065 45±15% a.u. Therefore, the slope of the Fano plot for the dissociative cross section is approximately equal to $0.04\pm0.01 = 0.1054 - 0.065\,45 \pm 15\%$, where we assume that the total oscillator strength moment is equal to the sum of the oscillator strength moments due to the dissociative continuum and all discrete excitations. Our value in Eq. (10) is in good agreement with the estimated values. The Fano plot of the dissociative cross section for the experimental data [7,9] and the present theoretical values are shown in Fig. 1. It was mentioned above that the experimental data at 100 eV reported by Vroom and de Heer [7] and Mohlmann, Shima, and de Heer [9] for Lyman-α production of H($2p$) are too large by 31% [8]. The experimental data [7,9] in Fig. 1 for the dissociative cross sections of H_2 for total production of H($2s$) have been accordingly reduced by 31%. Mohlmann, Shima, and de Heer [9] estimated the slope of the Fano plot for their data and the data of Vroom and de Heer [7]. The values, after a reduction of 31%, are, respectively, 0.0395 and 0.0377, which are consistent with the values 0.04±0.01 estimated in this study.

In addition to the reduction of 31% mentioned above, in Fig. 1 the experimental data of Vroom and de Heer [7] are reported with 30% error bars. The data of Mohlmann, Shima, and de Heer [9] with error bars of 15% (as inferred from their early work [19]) are shown for comparison with the theoretical values. The experimental data at high incident energies clearly exceed the present theoretical values and those of others [4,5]. In spite of the fact that other theoretical values [4,5] were calculated using ground- and excited-state wave functions not nearly as accurate as ours, those values are nevertheless still in very close agreement with the presented theoretical values. It is of interest to point out that the dissociative cross sections reported by Chung, Lin, and Lee [4] at 500 eV and 1 keV are, respectively, 1.13 and 0.674 (in units of 10^{-18} cm^2) while our values are respectively 1.10 and 0.0655 (in units of 10^{-18} cm^2), which are smaller than their values by 3%. The error due to use of simple target wave functions employed in the calculation by Chung, Lin, and Lee [4] can be unpredictable, large, and uncertain, and the reduced error in their calculation is mainly due to the cancellation of the errors resulting from the use of SCF wave functions and an approximate potential curve for $B'\,{}^1\Sigma_u$, as discussed early.

It is interesting to note that the effect of electron exchange is negligibly small for incident energies above 50 eV, which is in good agreement with the reported electron-impact dissociation of H_2^+ [2]. Although the theoretical value for the slope of the Fano plot lies within the values estimated from experiment, more accurate experimental data are needed to confirm the findings reported here since the error in the experimental data [7] is large. It is well known that optically allowed transitions are the main contribution to the slope of the Fano plot for high-energy electron-scattering data, and there is good agreement between theory and experiment in this report. Therefore, the discrepancy between theory and experiment may be due to the neglected contribution from double excitations [20], which are mainly optically forbidden transitions. This remains to be investigated. Due to the fact that the experimental data [7,9] were reported with large uncertainties, more accurate experimental data at high incident energies are urgently required to reconfirm the discrepancy reported here and/or to estimate the contribution due to double excitations, predissociation, cascading, etc.

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