

## Excitation of Hydrogen Molecule by Electron Impact. III. Singlet-Triplet Excitations

S. P. KHARE\*†

*Laboratory for Theoretical Studies, National Aeronautics and Space Administration,  
Goddard Space Flight Center, Greenbelt, Maryland*

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One-center wave functions of Huzinaga along with the Ochkur approximation have been employed to investigate the exchange excitation of the hydrogen molecule by electron impact from the ground electronic state  $X(1s\sigma^1\Sigma_g^+)$  to the triplet  $a(2s\sigma^3\Sigma_g^+)$ ,  $b(2p\sigma^3\Sigma_u^+)$ , and  $c(2p\pi^3\Pi_u)$  electronic states. Since the lowest triplet state  $b(3\Sigma_u^+)$  is a repulsive state and the intercombination of the triplet and the singlet states are optically forbidden, the singlet-triplet excitations give rise to the dissociation of the hydrogen molecule into two hydrogen atoms. The shape of the theoretical curve for the dissociation cross section is in general accord with the experimental data of Corrigan. Theoretical efficiencies of the dissociation of the hydrogen molecule by electron impact and of the emission of the continuous radiation due to  $a(3\Sigma_g^+) \rightarrow b(3\Sigma_u^+)$  transitions have also been computed and are compared with the available experimental data.

### I. INTRODUCTION

THE excitation of the ground-state hydrogen molecule  $X(1s\sigma^1\Sigma_g^+)$  to the triplet states due to the electron impact proceeds only with the exchange of the incident electron with one of the molecular electrons. Since optical intercombination of triplet-singlet is forbidden and the lowest triplet state  $b(2p\sigma^3\Sigma_u^+)$  is a repulsive state, all the singlet-triplet excitations give rise to the dissociation of the hydrogen molecule into two hydrogen atoms moving apart with certain kinetic energy. Massey and Mohr<sup>1</sup> employed the Born-Oppenheimer approximation along with Wang's<sup>2</sup> two-center wave functions to compute the total collisional cross section for the excitation of the ground-state hydrogen molecule to the lowest triplet state by electron impact. However, it is now well known that the Born-Oppenheimer approximation overestimates such a cross section. Edelstein<sup>3</sup> reinvestigated the problem variationally; however, his cross-section curve has two peaks, which is not reconcilable with the experimental data of Corrigan<sup>4</sup> for the dissociation of the hydrogen molecule. The recent investigation of Khare and Moiseiwitsch,<sup>5</sup> who employed the Born-Oppenheimer, the Ochkur,<sup>6</sup> and the first-order exchange<sup>7</sup> approximations along with Wang's wave functions, shows that the latter two approximations yield values of the excitation cross sections considerably smaller than those obtained by employing the Born-Oppenheimer approximation and thereby

improves the agreement between the theory and the experiment. However, no investigation seems to be available for the excitation of the hydrogen molecule to the other low-lying triplet states; namely, the attractive  $a(2s\sigma^3\Sigma_g^+)$  and  $c(2p\pi^3\Pi_u)$  excited states—which may give appreciable contribution to the dissociation of the hydrogen molecule by electron impact.

Recently, the author<sup>8,9</sup> has employed one-center wave functions given by Huzinaga<sup>10</sup> to investigate the excitation of the hydrogen molecule to the low-lying singlet  $B(2p\sigma^1\Sigma_u^+)$ ,  $C(2p\pi^1\Pi_u)$ , and  $D(3p\pi^1\Pi_u)$  excited states by electron impact. For these optically allowed excitations, the agreement between the theoretical values and the experimental data has been encouraging. Hence it seems interesting to use the same type of wave functions along with the Ochkur approximation or the first-order exchange approximation to investigate the singlet-triplet excitations.

### II. THEORY

Within the Born-Oppenheimer approximation, the averaged value of the differential cross section for the excitation of the ground-state hydrogen molecule to the triplet states is given by<sup>11</sup>

$$I(\omega) = (k_n/k_0) \langle |g(R_0)|^2 \rangle_{av}, \quad (1)$$

where  $\mathbf{k}_0$  and  $\mathbf{k}_n$  are, respectively, initial and final wave vectors of the free electron, which lies after the scattering between the solid angles  $\omega$  and  $\omega+d\omega$ ,  $R_0$  is the equilibrium internuclear distance for the ground state, and

$$\langle |g(R_0)|^2 \rangle_{av} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} |g(R_0, \delta, \xi)|^2 \sin \delta \, d\delta \, d\xi, \quad (2)$$

<sup>8</sup> S. P. Khare, Phys. Rev. **149**, 33 (1966), hereafter referred to as I.

<sup>9</sup> S. P. Khare, Phys. Rev. **152**, 74 (1966).

<sup>10</sup> S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **17**, 162 (1957).

<sup>11</sup> We use atomic units unless specified otherwise.

\* National Academy of Sciences—National Research Council Resident Research Associate.

† On leave of absence from the Department of Applied Physics, University of Allahabad, Allahabad, India.

<sup>1</sup> H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A135**, 258 (1932).

<sup>2</sup> S. C. Wang, Phys. Rev. **31**, 579 (1928).

<sup>3</sup> L. A. Edelstein, Nature **182**, 932 (1958).

<sup>4</sup> S. J. B. Corrigan, J. Chem. Phys. **43**, 4381 (1965).

<sup>5</sup> S. P. Khare and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **88**, 605 (1966).

<sup>6</sup> V. I. Ochkur, Zh. Eksperim. i Teor. Fiz. **45**, 734 (1963) [English transl.: Soviet Phys.—JETP **18**, 503 (1964)].

<sup>7</sup> K. L. Bell and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A276**, 346 (1963).

where  $\delta$  and  $\xi$  fix the orientation of  $\mathbf{R}_0$  with respect to  $\mathbf{K}$ , the change in the wave vector due to the scattering, and the exchange scattering amplitude for the internuclear distance  $R$  is given by

$$g(R, \delta, \xi) = -\frac{\sqrt{3}}{4\pi} \int e^{-i\mathbf{k}_n \cdot \mathbf{r}_1} d\mathbf{r}_1 \int \int \psi_n^*(\mathbf{r}_2, \mathbf{r}_3) \psi_0(\mathbf{r}_1, \mathbf{r}_3) e^{i\mathbf{k}_0 \cdot \mathbf{r}_2} \times V(\mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3, \quad (3)$$

where  $\psi_0$  and  $\psi_n$  are, respectively, the initial and the final wave functions of the hydrogen molecule;  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$  are the coordinates of the electrons referred to the center of the molecule; and the interaction potential is given by

$$V(\mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_3) = \frac{2}{|\mathbf{r}_2 - \mathbf{r}_1|} + \frac{2}{|\mathbf{r}_2 - \mathbf{r}_3|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}/2|} - \frac{2}{|\mathbf{r}_2 + \mathbf{R}/2|}. \quad (4)$$

Equation (1) is obtained by making the same assumptions as was made in the derivation of (3) of Paper I, namely, that the  $k_n$  and  $K$  do not depend upon the final rotational and vibrational states which remain unresolved and the square of the vibrational wave function  $|\chi_v(R)|^2$  has a strong maximum at the equilibrium internuclear distance  $R_0$ .

It may be noted that in the Born-Oppenheimer approximation, the interaction potential given by (4) includes the core term, i.e., the term representing the Coulomb interaction between the free electron and the protons. However, in the first-order exchange approximation,<sup>7</sup> which includes all the first-order terms in the interaction energy, and in the Ochkur approximation,<sup>6</sup> which considers only the leading term of the exchange scattering amplitude when expanded in a series in the inverse power of  $k_0^2$ , the core term drops out and the exchange scattering amplitude in the two above-mentioned approximations are, respectively, given by

$$g(R, \delta, \xi) = -\frac{\sqrt{3}}{2\pi} \int e^{-i\mathbf{k}_n \cdot \mathbf{r}_1} d\mathbf{r}_1 \times \int \psi_n^*(\mathbf{r}_2, \mathbf{r}_3) \psi_0(\mathbf{r}_1, \mathbf{r}_3) e^{i\mathbf{k}_0 \cdot \mathbf{r}_2} \left\{ \frac{1}{r_{12}} + \frac{1}{r_{32}} - 2 \int \int \frac{|\psi_0(\mathbf{r}_1, \mathbf{r}_3)|^2}{r_{21'}} d\mathbf{r}_1 d\mathbf{r}_3 \right\} d\mathbf{r}_2 d\mathbf{r}_3, \quad (5)$$

and

$$g(R, \delta, \xi) = -(2/k_0^2)\sqrt{3} \times \int e^{i\mathbf{K} \cdot \mathbf{r}_1} \psi_n^*(\mathbf{r}_1, \mathbf{r}_3) \psi_0(\mathbf{r}_1, \mathbf{r}_3) d\mathbf{r}_1 \cdot d\mathbf{r}_3. \quad (6)$$

Equation (6) can be easily obtained from (5) by putting

$$(1/r_{12}) = (4\pi/k_0^2)\delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (7)$$

and neglecting the last two terms within the curly bracket. It may be noted that the first-order exchange approximation and the Ochkur approximation are in accord with the recent investigation of Kang and Sucher<sup>12</sup> who have shown that the exchange scattering amplitude should not include the core term. In the present investigation, we have employed the Ochkur approximation due to its relative success in the explanation of the excitation of the singlet He(<sup>1</sup>S) to the triplet He(<sup>3</sup>S) and the He(<sup>3</sup>P) states<sup>6,13</sup> and also due to its simplicity.

For the molecular wave functions, we take Huzi-naga's<sup>10</sup> one-center wave functions. The ground-state wave function is identical to that given by (11) and (13) of Paper I and the excited-state wave functions are given by

$$\psi_n(\mathbf{r}_1, \mathbf{r}_2) = (1/\sqrt{2}) [\phi_{\text{in}}^n(\mathbf{r}_1) \phi_{\text{out}}^n(\mathbf{r}_2) - \phi_{\text{in}}^n(\mathbf{r}_2) \phi_{\text{out}}^n(\mathbf{r}_1)], \quad (8)$$

where  $\phi_{\text{in}}^n(\mathbf{r})$  is again identical to  $\phi_{\text{in}}^{\text{B.C.}}(\mathbf{r})$  of Paper I and  $\phi_{\text{out}}^n(\mathbf{r})$  for the excited states  $a(^3\Sigma_g^+)$ ,  $b(^3\Sigma_u^+)$ , and  $c(^3\Pi_u)$  are, respectively, given by

$$\begin{aligned} \phi_{\text{out}}^a(\mathbf{r}) &= N(2, \eta_2^a) r \exp(-\eta_2^a r) Y_{00}, \\ \phi_{\text{out}}^b(\mathbf{r}) &= N(2, \eta_2^b) r \exp(-\eta_2^b r) Y_{10}, \\ \phi_{\text{out}}^c(\mathbf{r}) &= N(2, \eta_2^c) r \exp(-\eta_2^c r) 1/\sqrt{2} (Y_{11} + Y_{1-1}), \end{aligned} \quad (9)$$

where  $Y_{lm}$  are normalized spherical harmonics and

$$N(n, x) = \frac{(2x)^{n+1/2}}{[(2n)!]^{1/2}}. \quad (10)$$

The parameter  $\eta_2$  is determined variationally for  $R=1.4$ , the equilibrium internuclear distance for the ground state of the hydrogen molecule. After determining  $\eta_2$  for the  $a(^3\Sigma_g^+)$  state, the wave function was renormalized to unity.

Changing the variable of integration from  $\omega$  to  $K$  in (1) and integrating over  $K$  we obtain the total excitation cross section

$$Q_n = \frac{2\pi}{k_0^2} \int_{K_{\text{min}}}^{K_{\text{max}}} \langle |g(R_0)|^2 \rangle_{\text{av}} K dK, \quad (11)$$

where

$$K_{\text{max}} = k_0 + k_n$$

and

$$K_{\text{min}} = k_0 - k_n. \quad (12)$$

### III. RESULTS AND DISCUSSIONS

In Table I we present the values of  $\eta_2$  and the energies obtained variationally for  $R=1.4$ . A comparison of the

<sup>12</sup> I. J. Kang and J. Sucher, Phys. Letters **20**, 22 (1966).

<sup>13</sup> K. L. Bell, H. Eissa, and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **88**, 57 (1966).

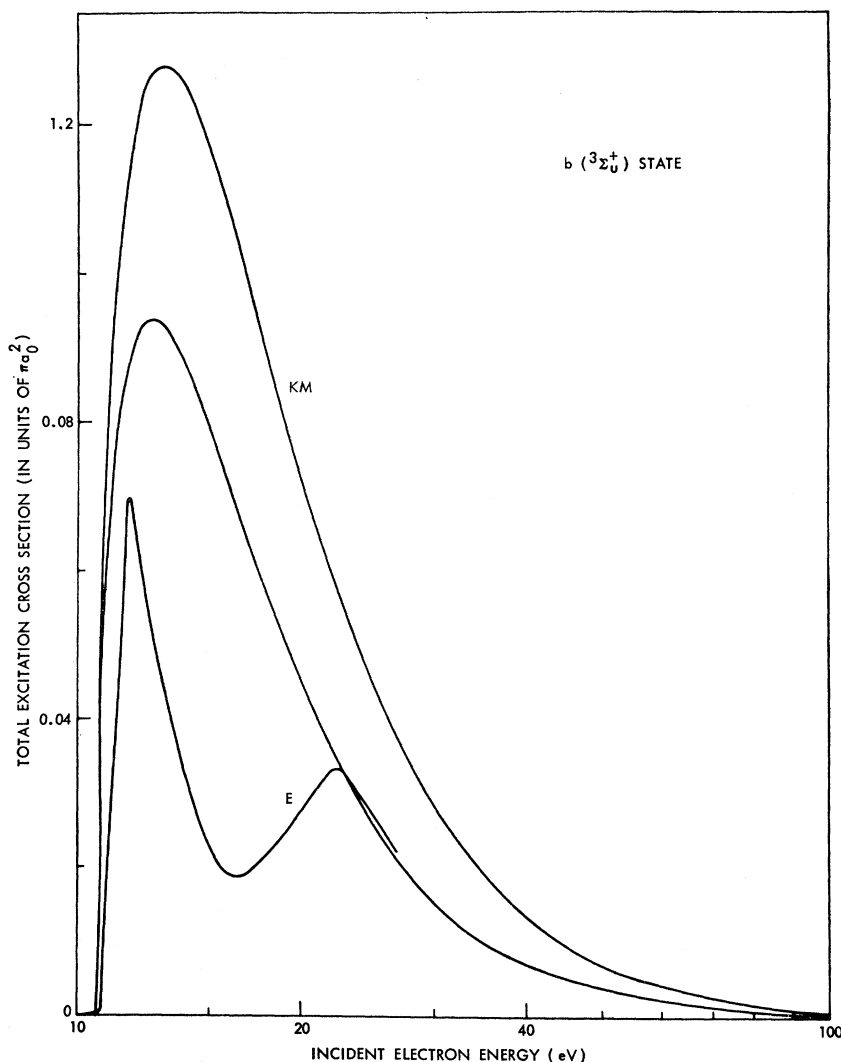


FIG. 1. Total cross section for the excitation of the ground-state hydrogen molecule to the  $b(^3\Sigma_u^+)$  electronic state by electron impact. The unmarked curve gives the value of the cross section obtained in the present calculations; the curves marked E and KM give the values of the cross section obtained by Edelstein (Ref. 3) and by Khare and Moiseiwitsch (Ref. 5), respectively. The curve marked KM is obtained by employing Ochkur approximation and assuming the threshold of excitation potential to be 10.6 eV, equal to that employed in the present investigation, instead of 11.0 eV assumed by Khare and Moiseiwitsch.

present energy values with the values obtained by more elaborate calculations<sup>14-17</sup> and the experimental data<sup>18,19</sup> shows satisfactory agreement, similar to that obtained for singlet states.<sup>8</sup> From Figs. 1 and 2 we notice that the shapes of the curves for the excitation cross sections, which are obtained by taking the threshold of the excitation potentials to be 10.6, 11.7, and 11.9 eV for the  $b(^3\Sigma_u^+)$ ,  $a(^3\Sigma_g^+)$ , and  $c(^3\Pi_u)$  excitations, respectively, are as expected, i.e., they have a sharp maximum close to the threshold of the excitation and then fall off quite rapidly with the increase of the impact energy. For high impact energies, the cross sections fall as  $k_0^{-6}$ . A com-

parison of the excitation cross sections for the three states shows that the excitation of the molecule to the  $b(^3\Sigma_u^+)$  state has the largest cross section, hence this process would give dominant contribution to the dis-

TABLE I. Energy  $E$ , threshold of excitation potential  $\Delta E$ , and  $\eta_2$  (see text for definition) values of the low-lying triplet excited states of the hydrogen molecule for the internuclear distance of  $R=1.4$  a.u.

State	$\eta_2$	$-E$ (a.u.)		$\Delta E$ (eV)	
		Present	Others	Present	Others
$a(^3\Sigma_g^+)$	0.465	0.69056	0.64438 <sup>a</sup> 0.71294 <sup>b</sup>	11.7	11.7 <sup>a</sup> 11.8 <sup>c</sup>
$b(^3\Sigma_u^+)$	0.886	0.74251	0.78315 <sup>d</sup>	10.3	10.6 <sup>d</sup> 8.8 <sup>e</sup>
$c(^3\Pi_u)$	0.566	0.68482	0.702 <sup>f</sup>	11.9	...

<sup>14</sup> A. K. Bhatia and A. Temkin, J. Chem. Phys. 44, 3656 (1966).

<sup>15</sup> C. B. Wakefield and E. R. Davidson, J. Chem. Phys. 43, 834 (1965).

<sup>16</sup> W. Kolos and C. C. J. Roothan, Rev. Mod. Phys. 32, 19 (1960).

<sup>17</sup> J. C. Browne, J. Chem. Phys. 40, 43 (1964).

<sup>18</sup> H. Ramien, Z. Physik 70, 353 (1931).

<sup>19</sup> W. Finkelnburg and W. Weitzel, Z. Physik 68, 577 (1931).

<sup>a</sup> Reference 14.

<sup>b</sup> Reference 15.

<sup>c</sup> Reference 18.

<sup>d</sup> Reference 16.

<sup>e</sup> Reference 19.

<sup>f</sup> Reference 17, interpolated value.

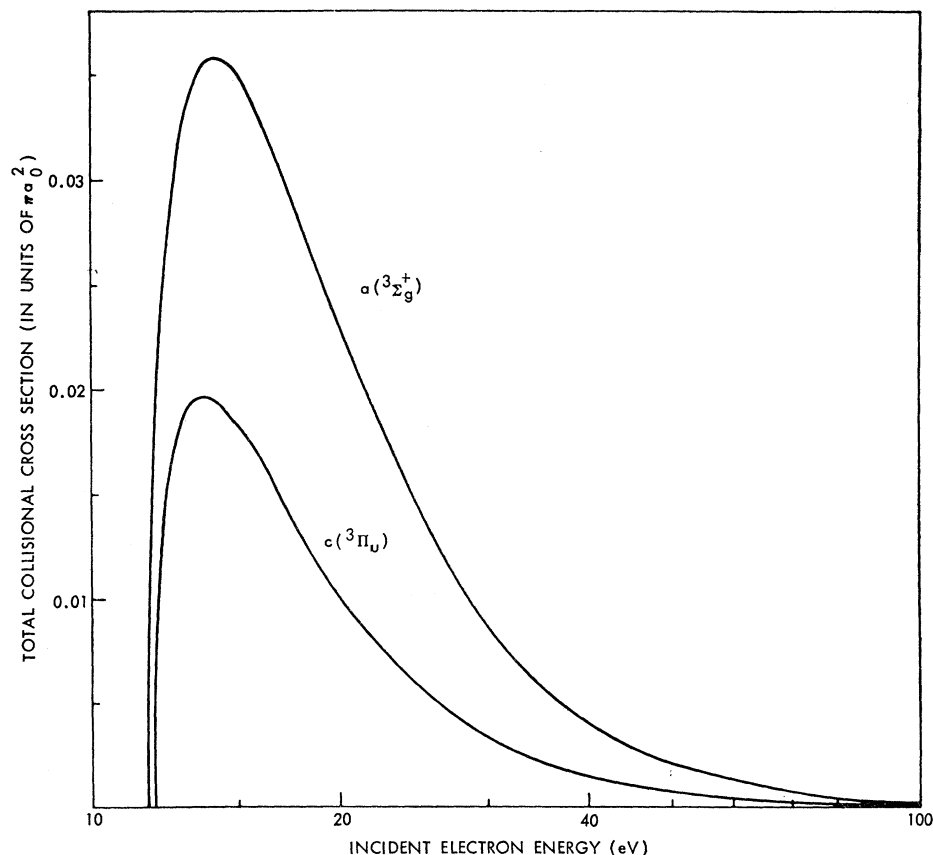


FIG. 2. Total cross section for the excitation of the ground-state hydrogen molecule to the  $a(^3\Sigma_g^+)$  and  $c(^3\Pi_u)$  electronic states by electron impact.

sociation of the hydrogen molecule. Such a statement is supported by the experimental results of Corrigan and von Engel.<sup>20</sup> Lunt and Meek<sup>21</sup> assumed the value of the  $Q(^3\Sigma_g^+)$  to be one-third of the value of the  $Q(^3\Sigma_u^+)$ ; however, the present investigation shows that the ratio of the two cross sections is energy-dependent and has a value of 0.41 at the electron impact energy of 14.0 eV, where  $Q(^3\Sigma_g^+)$  attains its maximum value. Further, from Fig. 1 we find that the effect of employing Wang's two-center wave functions instead of Huzinaga's one-center wave functions is to increase the excitation cross section throughout the energy range under investigation, but the shapes of the curves obtained by employing two different types of wave functions are very similar. However, the variational calculation of Edelman<sup>3</sup> shows quite different behavior. First, the cross-section curve has a delayed onset region. From the threshold of excitation potential (assumed to be 10.0 eV), the cross section remains very small but finite until the electron energy reaches 10.9 eV. Secondly, the cross-section curve has two peaks, one at 11.7 eV and another at 22 eV. Referring back to Fig. 2, we find no other

investigation for the excitation of the hydrogen molecule to the  $a(^3\Sigma_g^+)$  and  $c(^3\Pi_u)$  states which can be compared with the present investigation.

In Fig. 3 we compare the present value of the dissociation cross section  $Q_d$ , assumed to be equal to the sum of the excitation cross sections for all the three excited triplet states, with the experimental result of Corrigan.<sup>4</sup> The discontinuities in the theoretical curve occur at the threshold of the excitation potentials of the  $a(^3\Sigma_g^+)$  and the  $c(^3\Pi_u)$  states. Although the experimental threshold potential for the dissociation is 8.8 eV, as expected from the potential-energy curves of the hydrogen molecule, the value of the dissociation cross section up to 10.6 eV, the theoretically assumed single sharp value of the energy loss for the  $b(^3\Sigma_u^+)$  excitation, is relatively small. Furthermore, it may be pointed out that the estimated error in the experimental data for the electron impact energies below the threshold potential of ionization of  $H_2$  is about 30%, and above the ionization threshold the dissociation cross section due to the singlet-triplet excitations is taken to be the difference between the measured dissociation cross section and the ionization cross section for the same impact energy, experimentally measured by Tate and Smith,<sup>22</sup> under the assumption that all the produced  $H_2^+$  undergo

<sup>20</sup> S. J. B. Corrigan and A. von Engel, Proc. Roy. Soc. (London) **A245**, 335 (1958).

<sup>21</sup> R. W. Lunt and C. A. Meek, Proc. Roy. Soc. (London) **A157**, 146 (1936).

<sup>22</sup> J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

FIG. 3. Cross section for the dissociation of the ground-state hydrogen molecule due to singlet-triplet excitations produced by electron impact. The unmarked curve gives the value of the cross section obtained in the present calculations and the curve marked C give the experimental value of the cross section obtained by Corrigan (Ref. 4).

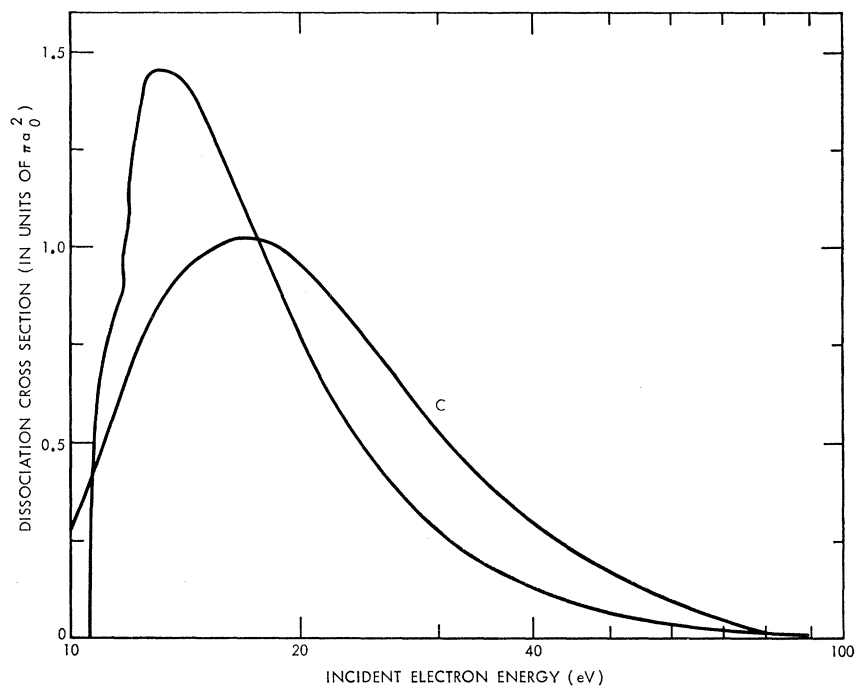
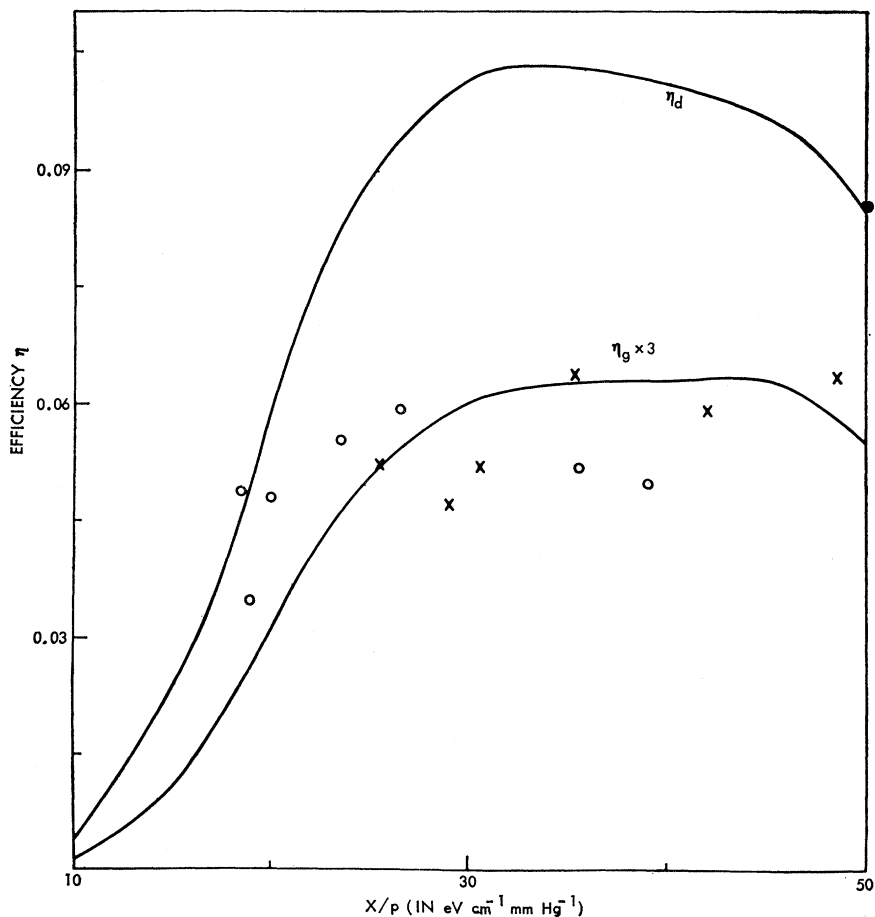


FIG. 4. Efficiencies of the dissociation of the hydrogen molecule and of the emission of the radiation due to  $a(^2\Sigma_u^+) \rightarrow b(^2\Sigma_u^+)$  transition. The curves marked  $\eta_d$  and  $\eta_r$  give the efficiencies per electron volt of the dissociation and of the radiation, respectively, obtained in the present calculation.  $\circ$  and  $\times$  represent experimental data for the efficiencies of the dissociation and of the radiation, respectively, obtained by Poole (Ref. 23) and by Lunt, Meek, and Smith (Ref. 25). The relative data of Lunt *et al.* are normalized to the theoretical curve.



dissociative recombination yielding two hydrogen atoms (compare Ref. 4). Hence, considering the uncertainty of the experimental data and the simple nature of the wave functions and the approximations employed in the calculation, the agreement between the theory and the experiment may be regarded as satisfactory.

Another way of comparing the theory with the experiment is to compute the dissociation efficiency  $\eta_a$ , determined experimentally by Poole<sup>23</sup> in a swarm experiment, which gives the number of molecules dissociated per electron volt supplied to the positive column of a straited glow discharge in hydrogen as a function of the ratio of  $X/p$  of the electric-field strength  $X$  in the positive column to the gas pressure  $p$ . This has been the only way available for the comparison until the determination of the dissociation cross section by Corrigan.<sup>4</sup> Assuming the velocity distribution function of the electrons in the straited glow discharge to be Maxwellian (which, we recognize, is not likely to be a good approximation), we have (compare Ref. 5)

$$\eta_a = \frac{(54\pi)^{1/2} N_0}{p_0} \frac{1}{c^3 u} \frac{1}{X p^{-1}} \times \int_0^{\infty} Q_a(v) v^3 \exp(-1.5v^2/c^2) dv, \quad (13)$$

where  $N_0$  is the Loschmidt number  $2.687 \times 10^{19}$ ,  $p_0$  is the standard pressure 760 mm of Hg, and  $c$  and  $u$  are the root-mean-square velocity and the drift velocity, respectively. The values of  $c$  and  $u$  were taken from the data for hydrogen gas quoted by Emeleus *et al.*,<sup>24</sup> originally determined by Townsend.

<sup>23</sup> H. G. Poole, Proc. Roy. Soc. (London) **A163**, 424 (1937).

<sup>24</sup> K. G. Emeleus, R. W. Lunt, and C. A. Meek, Proc. Roy. Soc. (London) **A156**, 394 (1936).

Replacing  $Q_a$  by  $Q(^3\Sigma_g^+)$  in (13) and assuming that the  $a(^3\Sigma_g^+)$  state is mainly populated by the electron impact excitation, we obtain the efficiency of the emission of the continuous spectrum  $\eta_\theta$  due to  $a(^3\Sigma_g^+) \rightarrow b(^3\Sigma_u^+)$  transitions. The relative measurements of  $\eta_\theta$  in a swarm experiment by Lunt, Meek, and Smith<sup>25</sup> are shown in Fig. 4, after being normalized to the computed value at  $X/p=25.5$ , the lowest value of  $X/p$  for which the measurement exists. From Fig. 4, we notice that the agreement between the computed and the normalized value of  $\eta_\theta$  is satisfactory, but in most of the region the present investigation overestimates the values of  $\eta_a$ . Further, the experimental study of Corrigan and von Engel<sup>20</sup> indicates that at  $X/p=40$  the contribution of the higher triplet states to the dissociation of the hydrogen molecule is less than 6%, whereas the present investigation shows that the contribution of the  $a(^3\Sigma_g^+)$  and the  $c(^3\Pi_u)$  states at the above-mentioned value of  $X/p$  is about 31%, which is close to the assumed value of 25% by Lunt and Meek.<sup>21</sup> However, in the above comparisons, it should be kept in mind that there is great uncertainty about the form of the velocity distribution of the electrons in a straited glow discharge and the Maxwellian distribution is a crude approximation. Direct measurements of the excitation cross sections will be valuable.

#### ACKNOWLEDGMENTS

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<sup>25</sup> R. W. Lunt, C. A. Meek, and E. C. Smith, Proc. Roy. Soc. (London) **A158**, 729 (1937).