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BY
ELECTRON IMPACT, III

Singlet-Triplet Excitations

BY

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EXCITATION OF HYDROGEN MOLECULE BY ELECTRON IMPACT, III

- SINGLET - TRIPLET EXCITATIONS -

by

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Greenbelt, Maryland

ABSTRACT

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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 excititions 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 emmission of the continuous radiation due to $a({}^3\Sigma_g^+) \rightarrow b({}^3\Sigma_u^+)$ transions have

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also been computed and are compared with the available experimental data.

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1. 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 ~~to the~~ into two hydrogen atoms moving apart with certain kinetic energy. Massey and Mohr[1] employed the Born - Oppenheimer approximation along with Wang's[2] 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 cross section. Edelstein[3] reinvestigated the problem variationally, however, his cross section curve has two peaks and does not reconcile with the experimental data of Corrigan[4] for the dissociation of the hydrogen molecule. The recent investigation of Khare and Moiseiwitsch[5], who employed the Born - Oppenheimer, the Ochkur[6] and the first-order exchange[7] approximations along with Wang's wave functions, shows that the later two approximations yield the values of the excitation cross sections considerably smaller than that 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[8,9] has employed one - center wave functions given by Huzinaga[10] 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 differetial cross - section for the excitation of the ground state hydrogen molecule to the triplet states is given by[11]

$$I(\omega) = \frac{k_n}{k_0} \left\langle \left| g\,(R_0) \right|^2 \right\rangle_{av} , \qquad (1)$$

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

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

where δ and ξ fix the orientation of $\underline{R_0}$ with respect to $\underline{K}$, the change in the wave vector due to the scattering, and the exchange scattering amplitude for the inter nuclear distance R is given by

$$g(R,\delta,\xi) = -\frac{\sqrt{3}}{4\pi}\int e^{-i\underline{k_n}\cdot\underline{r_1}}\, d\underline{r_1} \iint \psi_n^*(\underline{r_2},\underline{r_3})\,\psi_0(\underline{r_1},\underline{r_3}) \times V(\underline{r_2};\underline{r_1},\underline{r_3})\, d\underline{r_2}\, d\underline{r_3} \, , \qquad (3)$$

where ψ_0 and ψ_n are respectively the initial and the final wave functions of the hydrogen molecule: $\underline{r_1}$, $\underline{r_2}$ and $\underline{r_3}$ are the co-ordinates of the electrons referred to the center of the molecule and the interaction potential is given by

$$V(\underline{r_2};\underline{r_1},\underline{r_3}) = \frac{2}{|\underline{r_2}-\underline{r_1}|} + \frac{2}{|\underline{r_2}-\underline{r_3}|} - \frac{2}{|\underline{r_2}-\underline{R}/2|} - \frac{2}{|\underline{r_2}+\underline{R}/2|} \, . \qquad (4)$$

Enq. (1) is obtained by making the same assumptions as 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 remains unresolved and the square of the vibrational wave function $|\chi_v(R)|^2$ has a strong maximum at the equilibrium inter nuclear distance R_0.

It may be noted that in the Born - Oppeheimer approximation the interaction potential given by (4) includes core term i.e.

the term representing the Coulomb interaction between the free electron and the protons. However, in the first-order exchange approximation[7], which includes all the first-order terms in the interaction energy and in the Ochkur approximation[6], 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 above two mentioned approximations are respectively given by

$$g(R, \delta, \xi) = -\frac{\sqrt{3}}{2\pi}\int e^{-i\underline{k}_n\cdot\underline{r}_1}\,d\underline{r}_1\int \Psi_n^*(\underline{r}_2, \underline{r}_3)\,\Psi_0(\underline{r}_1, \underline{r}_3)\,e^{i\underline{k}_0\cdot\underline{r}_2}$$

$$\times\left\{\frac{1}{r_{12}} + \frac{1}{r_{32}} - 2\iint \frac{|\Psi_0(\underline{r}_{1'}, \underline{r}_{3'})|^2}{r_{21'}}\,d\underline{r}_{1'}\,d\underline{r}_{3'}\right\} d\underline{r}_2\,d\underline{r}_3, \qquad (5)$$

and

$$g(R, \delta, \xi) = -\frac{2}{k_0^2}\sqrt{3}\int e^{i\underline{K}\cdot\underline{r}_1}\,\Psi_n^*(\underline{r}_1, \underline{r}_3)\,\Psi_0(\underline{r}_1, \underline{r}_3)\,d\underline{r}_1\cdot d\underline{r}_3. \qquad (6)$$

Enq. (6) can be easily obtained from (5) by putting

$$\frac{1}{r_{12}} = \frac{4\pi}{k_0^2}\,\delta(\underline{r}_1 - \underline{r}_2), \qquad (7)$$

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[12] 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 singlet He (^{1}S) to the triplet He (^{3}S) and the He (^{3}P) states[6,13] and also due to its simplicity.

For the molecular wave functions, we take Huzinaga's[10] 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

$$\Psi_n(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\phi^n_{in}(r_1)\,\phi^n_{out}(r_2) - \phi^n_{in}(r_2)\,\phi^n_{out}(r_1)\right], \quad (8)$$

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

$$\phi^a_{out}(r) = N(2, \eta_2^a)\, r \exp(-\eta_2^a r)\, Y_{00}$$

$$\phi^b_{out}(r) = N(2, \eta_2^b)\, r \exp(-\eta_2^b r)\, Y_{10}$$

$$\phi^c_{out}(r) = N(2, \eta_2^c)\, r \exp(-\eta_2^c r)\, \frac{1}{\sqrt{2}}\left(Y_{11} + Y_{1-1}\right), \quad (9)$$

where $Y_{\ell m}$ are normalized spherical harmonics and

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

The parameter η_2 is determined variationally for $R = 1.4$, the equilibrium inter nuclear distance for the ground state of the hydrogen molecule. After determining η_2 for the $a({}^3\Sigma_g^+)$ state the wave function was renormalized to unity.

Changing the variable of intergration from ω to K in (1) and intergrating over K we obtain the total excitation cross section

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

where

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

and

$$K_{min} = k_0 - k_n \, . \qquad (12)$$

III. RESULTS AND DISCUSSIONS

In table I we present the values of η_2 and the energies obtained variationally for $R = 1.4$. A comparison of the present energy values with the values obtained by more elaborate calculations[14,15,16,17] and the experimental data [18,19] shows satisfactory agreement, similar to that obtained for singlet states[8]. From the figures 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 eV, 11.7 eV 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 comparison 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 dissociation of the hydrogen molecule. Such a statement is supported by the experimental results of Corrigan and vonEngel[20]. Lunt and Meek[21] 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 the figure 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 Edelstein[3] shows quite different behaviour. First, the cross section curve has a delayed onset region. From the threshold of excitation potential (assumed to 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 the figure 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 figure 3 we campare 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[4]. The discontinuities in the theoretical curve occurs at the threshold of the excitation potentials of the $a(^3\Sigma_g^+)$ and the $c(^3\Pi_u)$ states. Although the experimental threshold ponential 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. Further, 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[22], under the assumption that all the produced H_2^+ undergo dissociative recombination yielding two hydrogen atoms (cf. 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 η_d, determined experimentally by Poole[23] in a swarm experiment, which gives the number of the 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[4]. Assuming the velocity distrubution 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 (cf. Ref.5)

$$\eta_d = \frac{(54\pi)^{1/2} N_o}{p_o} \, \frac{1}{c^3 u} \, \frac{1}{X p^{-1}} \int_0^\infty Q_d(v)\, v^3 \exp\left(-1.5\, v^2/c^2\right) dv, \qquad (13)$$

where No is the Loschmidst number 2.687 x 10^{19}, p_o is the standard pressure 760mm of Hg, 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[24], originally determined by Townsend.

Replacing Q_d 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 η_g due to $a(^3\Sigma_g^+) \rightarrow b(^3\Sigma_u^+)$ transitions. The relative measurements of η_g in a swarm experiment by Lunt, Meek and Smith[25] are shown in figure 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 the figure 4 we notice that the agreement between the computed and the normalized value of η_g is satisfactory, but in most of the region the present investigation overestimates the values of η_d. Further, the experimental study of Corrigan and von Engel[20] 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[21]. However, while making 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.

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TABLE I

Energy E, threshold of excitation potential ΔE and η_2 (see text for definition) values of the low lying triplet excited states of the hydrogen molecule for the inter nuclear distance of $R = 1.4$ a.u.

STATE	η_2	$-E$ (a. u.)		ΔE (eV)	
		Present	Others	Present	Others
$a(^3\Sigma_g^+)$	0.465	0.69056	0.64438[a] 0.71294[b]	11.7	11.7[a] 11.8[c]
$b(^3\Sigma_u^+)$	0.886	0.74251	0.78315[d]	10.3	10.6[d] 8.8[e]
$c(^3\Pi_u)$	0.566	0.68482	0.702[f]	11.9	-

[a] Reference 14.

[b] Reference 15.

[c] Reference 18.

[d] Reference 16.

[e] Reference 19.

[f] Reference 17 , interpolated value.

Figure Captions:

Figure 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 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.

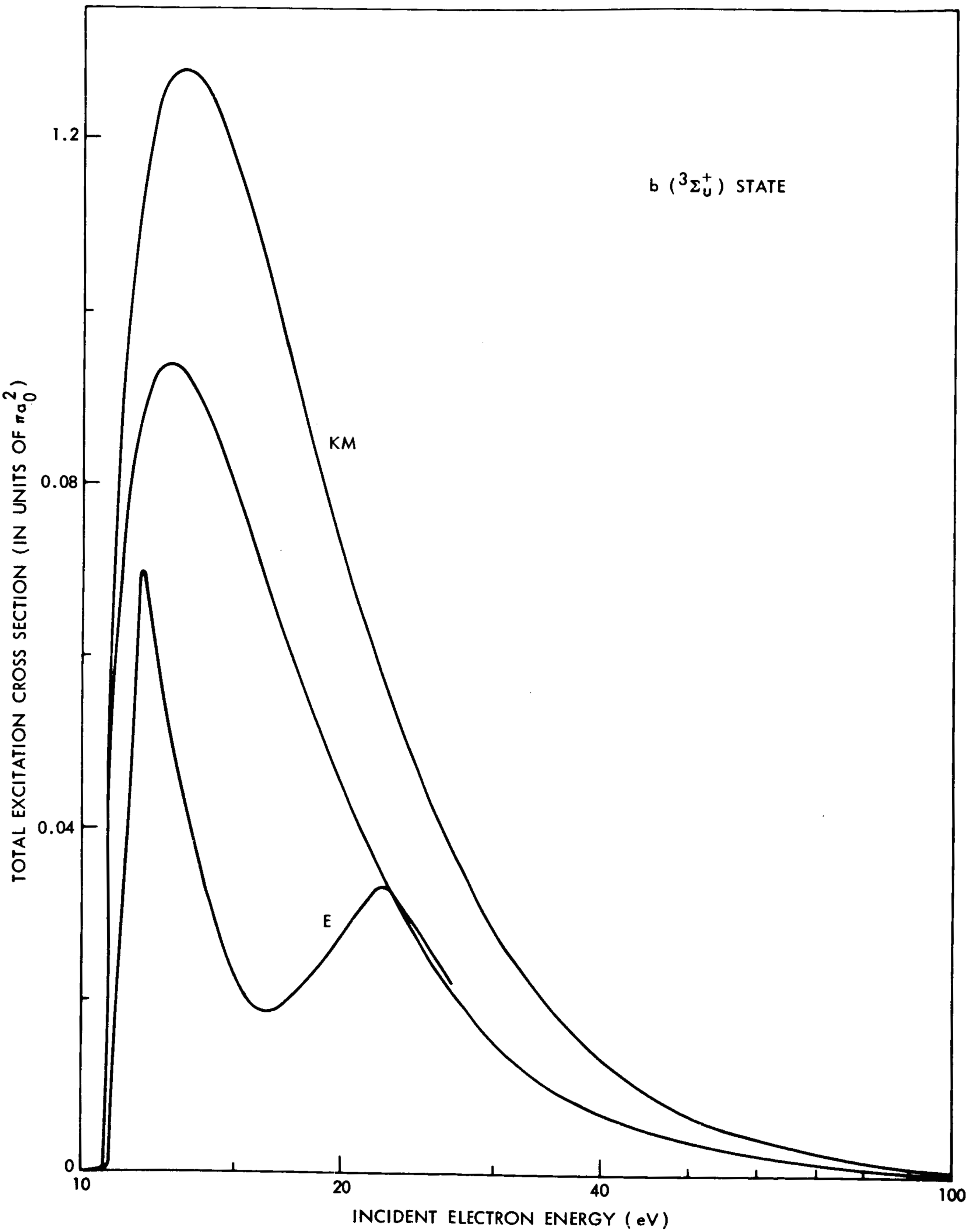
Figure 2. Total cross section for the excitation of the ground-state hydrogen molecule to the $a(^3\Sigma_g^+)$ and $c(^3\Pi_u)$ electronic states by electron impact.

Figure 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) .

Figure 4. Efficiencies of the dissociation of the hydrogen molecule and of the emission of the radiation due to $a(^3\Sigma_g^+) \rightarrow b(^3\Sigma_u^+)$ transition. The curves marked η_d and η_g give the efficiencies per electron volt of the dissociation and

of the radiation respectively obtained in the present calculation. ⊙ and X 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 is normalized to the theoretical curve.

FIGURE I.


b ($^3\Sigma_u^+$) STATE
KM
E
TOTAL EXCITATION CROSS SECTION (IN UNITS OF πa_0^2)
1.2
0.08
0.04
0
10
20
40
100
INCIDENT ELECTRON ENERGY (eV)

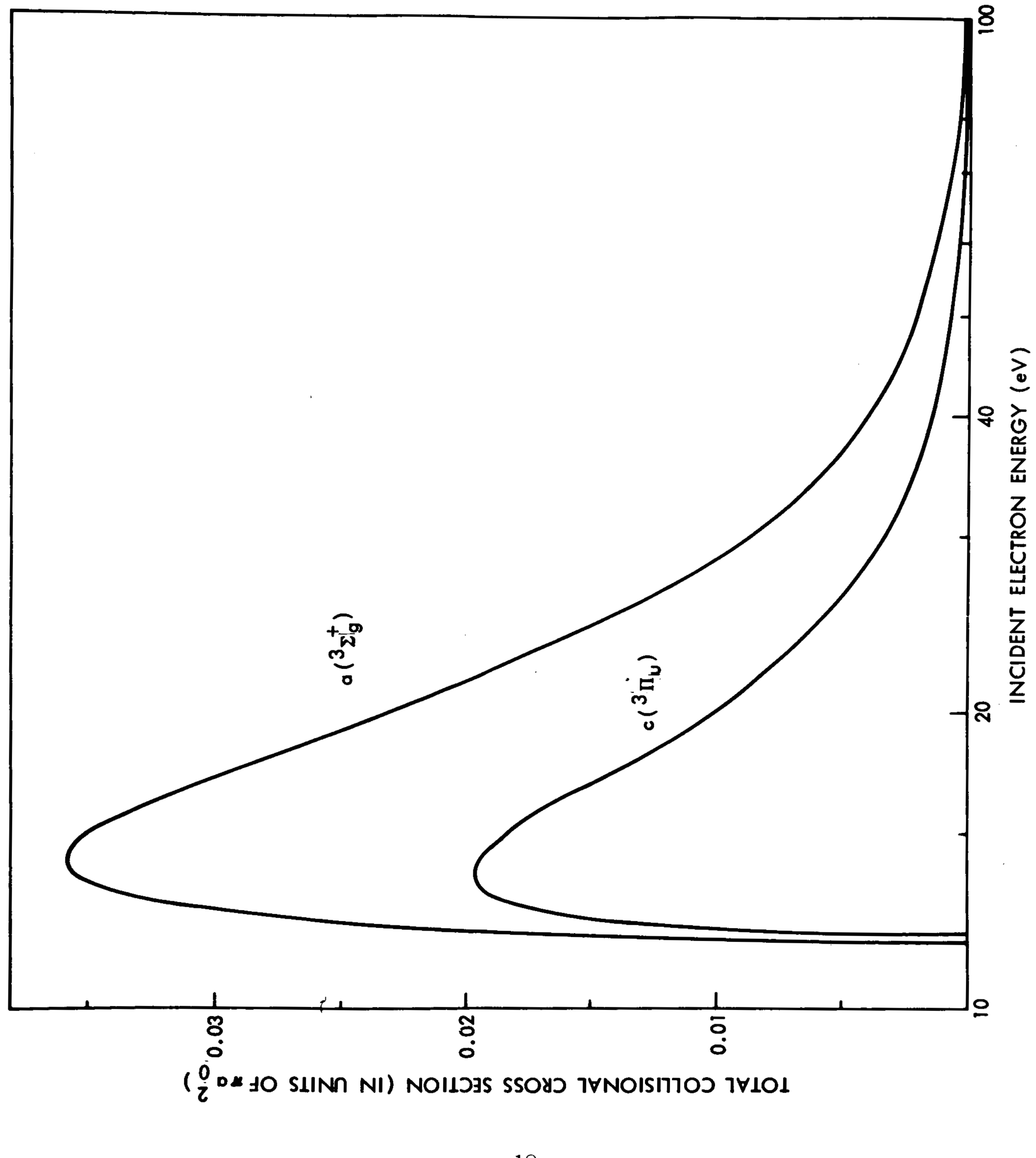

TOTAL COLLISIONAL CROSS SECTION (IN UNITS OF πa_0^2)
0.03
0.02
0.01
10
20
40
100
INCIDENT ELECTRON ENERGY (eV)
$a(^3\Sigma_g^+)$
$c(^3\Pi_u)$

FIGURE 11.

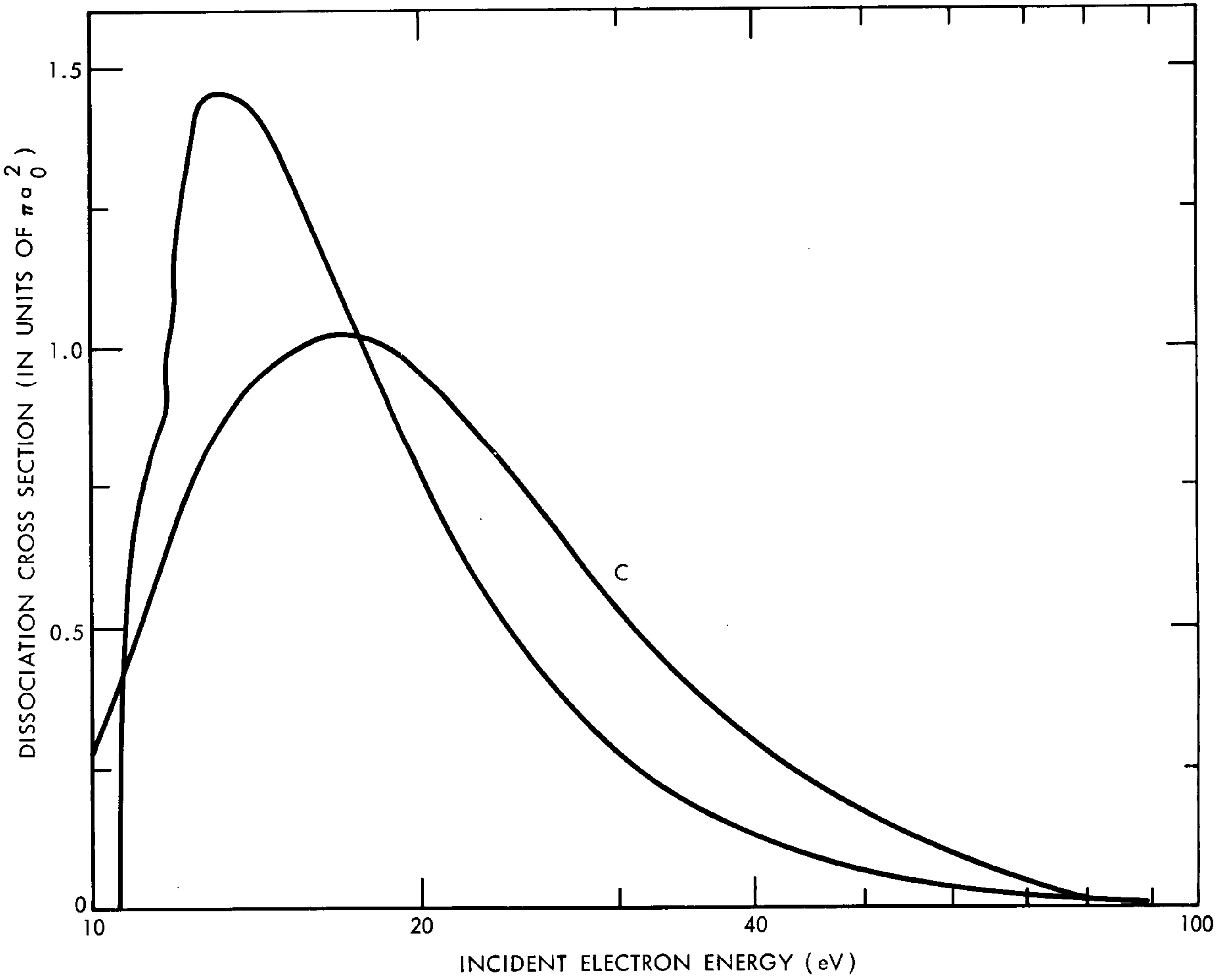
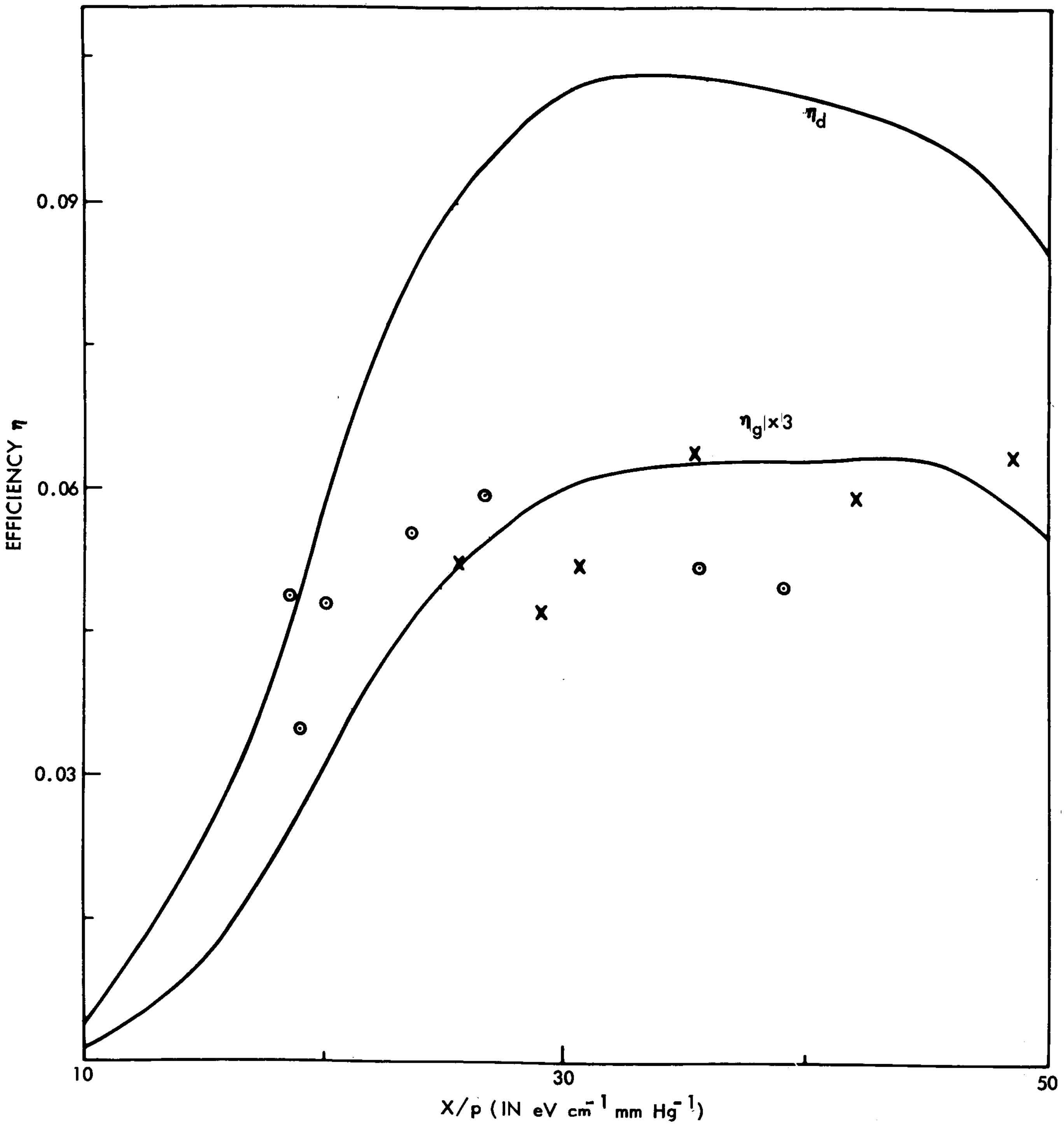

1.5
1.0
0.5
0
DISSOCIATION CROSS SECTION (IN UNITS OF πa_0^2)
C
10
20
40
100
INCIDENT ELECTRON ENERGY (eV)

FIGURE III.

FIGURE IV.


EFFICIENCY η
0.09
0.06
0.03
10
30
50
X/p (IN eV cm^{-1} mm Hg^{-1})
η_d
η_g x 3