PHYSICAL REVIEW VOLUME 163, NUMBER 1 5 NOVEMBER 1967

# Electron-Impact Excitation Cross Section for the Two Lowest Triplet States of Molecular Hydrogen*

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(Received 8 May 1967)

Calculations for the electron-impact excitation cross sections of molecular hydrogen from its ground ($X^1\Sigma_g^+$) to its first ($b^3\Sigma_u^+$) and second ($a^3\Sigma_g^+$) triplet states were performed using the Ochkur (O) and Ochkur-Rudge (OR) approximations. All nuclear motions were taken into account. It was found that the first triplet cross section is sensitive to the choice of the ground-state wave function whereas the second one is not. The former is also sensitive to the excited-state wave function used. The results using the O approximation are significantly larger than those of the OR approximation, and the maximum cross section occurs at a somewhat lower energy. Use of the separated-atom approximation produced results significantly lower than those arising from inclusion of all the multicenter terms in the scattering amplitude. The sum of the first and second OR triplet cross sections agrees well with a recent approximate experimental determination of the cross section for the electron-impact dissociation of $H_2$ into 2H. More accurate experiments are now needed to further test the OR approximation.

## 1. INTRODUCTION

THE calculation of meaningful cross sections for the electronic excitation of atoms and molecules by electron impact has been largely limited to electron-atom processes because of the mathematical complexities associated with the noncentral nature of the molecular field. The first detailed calculation of the electronic exchange excitation of a molecular system was done by Massey and Mohr,[1] who considered the first triplet excitation process ($X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$) in molecular hydrogen. By applying the Born-Oppenheimer (BO) approximation[2] to describe the scattering process and estimating the contribution from the multicenter terms which appear in the scattering amplitude, they obtained a total cross section which violated conservation of particle flux. Their predicted maximum cross section exceeds recent experimental data[3] for the process by a factor of about 7. Recently, a modification of the basic BO approximation was introduced by Ochkur[4] (O), who considered the exchange excitation of helium. The results of his calculation show good agreement with the available experimental data. Shortly after, Rudge[5,6] modified the O treatment to make it consistent with the variational principles of scattering theory, and applied his method to describe the exchange excitation of atomic hydrogen. The modifications by Ochkur (O) and Rudge (OR) have removed a major failing of the BO approximation. In the O and OR modifications the prior core terms (those due to the interaction of the incident electron with the nuclei) will not contribute to the exchange-scattering amplitude, as is also the case in an exact theory.[7] In the BO approximation the contribution of the core terms does not vanish. It is commonly believed that this contribution is large in the $H_2$ case and in part responsible for the anomalously large values of the calculated triplet excitation cross sections. In addition, the scattering amplitude for the excitation process in the OR modification contains in general nonvanishing real and imaginary parts, which is not the case for the O theory. This complex nature of the scattering amplitude is a necessary condition for conservation of particles to be satisfied.[6,8] In the present paper, the OR approximation is used for the calculation of the total cross sections for the exchange excitation of the first ($b^3\Sigma_u^+$) and second ($a^3\Sigma_g^+$) triplets from the ground state ($X^1\Sigma_g^+$) of molecular hydrogen. Polarization and higher-order effects are neglected. The effects of the nuclear motions are included and shown to be significant. The results show good agreement with available experimental data.[3] The calculations are done using exponent-optimized minimum basis set two-center wave functions for the molecule and include all the multicenter terms that appear in the scattering amplitude. In addition, three different ground-state wave functions and two different $b^3\Sigma_u^+$ wave functions are tried in the calculations

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* Work supported in part by the U. S. Atomic Energy Commission; Report Code: CALT-532-11.

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[1] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A135**, 258 (1932).

[2] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[3] S. J. B. Corrigan, J. Chem. Phys. **43**, 4381 (1965). The authors would like to thank Dr. Corrigan for sending us details of his experimental measurements.

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

[5] M. R. H. Rudge, Proc. Phys. Soc. (London) **85**, 607 (1965). O. Bely has pointed out [Proc. Phys. Soc. (London) **87**, 1010 (1966); Joint Institute for Laboratory Astrophysics Report No. 66, 1966 (unpublished)] that in the case of direct-plus-exchange excitation the scattering cross section containing the Rudge approximation for the exchange contribution suffers from lack of detailed balancing. However, in the case of pure exchange excitation this discrepancy disappears.

[6] M. R. H. Rudge, Proc. Phys. Soc. (London) **86**, 763 (1965).

[7] (a) T. B. Day, L. S. Rodberg, G. A. Snow, and J. Sucher, Phys. Rev. **123**, 1051 (1961); (b) I. J. Kang and J. Sucher, Phys. Letters **20**, 22 (1966); (c) T.-Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), p. 334.

[8] Y. N. Demkov, *Variational Principles in the Theory of Collisions* (Pergamon Press, London, 1963), pp. 97–102.

in order to determine the effect on the total cross sections of using different approximate wave functions. Calculations were also done using the simple Ochkur (O) theory and compared with the OR results.

After the present work was well under way, Khare and Moiseiwitsch[9] (KM) published a calculation of the total cross section for the exchange excitation to the first triplet state of molecular hydrogen using the O and first-order exchange (E1) method coupled with the separated-atom (SA) approximation. In addition, Khare (K) has completed a calculation[10] for the same excitation processes using one-center molecular wave functions and the O approximation. We have compared our complete calculations with the results of the KM and K calculations and with O and OR calculations using the SA approximation. The latter comparison indicates the inaccuracies introduced by the SA approximation.

## 2. GENERAL THEORY

### A. Exchange-Scattering Amplitude in the Born-Oppenheimer Approximation

Let $n$, $\nu$, $J$, and $M$ be the electronic, vibrational, and rotational quantum numbers for the initial state of the hydrogen molecule and $n'$, $\nu'$, $J'$, and $M'$ the corresponding final-state ones. The molecular wave function can be written as[11]

$$\begin{aligned}\Phi(\boldsymbol{\zeta}_1,\boldsymbol{\zeta}_2;R,\chi,\phi)&=\Psi(\mathbf{r}_1,\mathbf{r}_2;R,\chi,\phi)S(\mathbf{s}_1,\mathbf{s}_2)\,,\\ \Psi(\mathbf{r}_1,\mathbf{r}_2;R,\chi,\phi)&=\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)\xi_{n\nu J}(R)Y_J{}^M(\chi,\phi)\,.\end{aligned}\tag{1}$$

Here $\Psi$ and $S$ are the total space and electronic spin wave functions; $\psi$, $\xi$, and $Y$ are the electronic-space, vibrational, and rotational (spherical-harmonic) wave functions; $\boldsymbol{\zeta}_1\equiv(\mathbf{r}_1,\mathbf{s}_1)$ and $\boldsymbol{\zeta}_2\equiv(\mathbf{r}_2,\mathbf{s}_2)$ are the space and spin coordinate pairs for the bound electrons in a molecule-fixed coordinate system; $R$ is the internuclear distance; and $\chi$, $\phi$ are the spherical polar angles of the molecular axis with respect to a space-fixed system of reference. In the BO approximation,[2] the differential cross section (per unit solid angle) for scattering of an electron into a given direction after the exchange excitation of the molecule from the initial state $i(n\nu JM)$ to the final state $f(n'\nu'J'M')$ can be written in the prior interaction form as[12]

$$I_i{}^f(k_0,\theta,\varphi)=\frac{3}{(2\pi)^2a_0{}^2}\frac{k'}{k_0}\left|\int e^{-i\mathbf{k}'\cdot\mathbf{r}_1}\Psi_f{}^*(\mathbf{r}_3,\mathbf{r}_2;R,\chi,\phi)\times\left(\frac{1}{r_{31}}+\frac{1}{r_{32}}-\frac{1}{r_{3A}}-\frac{1}{r_{3B}}\right)\times e^{i\mathbf{k}_0\cdot\mathbf{r}_3}\Psi_i(\mathbf{r}_1,\mathbf{r}_2;R,\chi,\phi)d\mathbf{R}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3\right|^2,\tag{2}$$

where $a_0=\hbar^2/me^2$ is the Bohr radius; $\mathbf{r}_3$ and $(\mathbf{r}_1,\mathbf{r}_2)$ denote the positions of the incident and bound electrons in a molecular-fixed coordinate system; $r_{31}$, $r_{32}$ $r_{3A}$, and $r_{3B}$ are the distances of the incident electron to the molecular electrons (1,2) and nuclei (A,B); $d\mathbf{R}$ and $d\mathbf{r}_j$ are the internuclear and $j$th electron volume elements; $\mathbf{k}_0$ and $\mathbf{k}'$ are the wave vectors for the incident and scattered electrons; $\theta$ and $\varphi$ are the spherical polar angles which define the direction of the scattered electron in a laboratory-fixed system whose $z$ axis is in the direction of $\mathbf{k}_0$; and the subscripts $i$ and $f$ denote the initial- and final-state wave functions. The contribution of the core terms $-1/r_{3A}-1/r_{3B}$ to the cross section vanishes in an exact theory,[12] but this is not the case in the usual BO approximation.[13] The factor of 3 in the right-hand side of Eq. (2) results from the spin degeneracy of the final triplet state.

It should be noted that $k'$ is determined by $k_0$ and the excitation energy according to

$$k'(k_0,i,f)=[k_0{}^2-(2m/\hbar^2)(E_f-E_i)]^{1/2}\,,\tag{3}$$

where $E_f$, and $E_i$ are the final and initial energies of the molecule and $m$ is the mass of the electron. Because of the energy degeneracy of the rotational levels with respect to $M$ and $M'$, $k'$ (for a given electronic transition) is a function of $k_0$, $n$, $\nu$, $J$, $n'$, $\nu'$, and $J'$ only.

Substitution of Eq. (1) into Eq. (2) gives

$$I_i{}^f(k_0,\theta,\varphi)=3\frac{k'}{k_0}\left|\int\xi_{n'\nu'J'}{}^*(R)Y_{J'}{}^{M'*}(\chi,\phi)\times T_{fi}\xi_{n\nu J}(R)Y_J{}^M(\chi,\phi)R^2dRd\Omega\right|^2,\tag{4}$$

where $d\Omega$ is the element of solid angle corresponding to $\chi$, $\phi$. $T_{fi}$ is the prior electronic scattering amplitude defined by

$$T_{fi}(k_0,\theta,\varphi;R,\chi,\phi)\equiv\frac{1}{2\pi a_0}\int e^{-i\mathbf{k}'\cdot\mathbf{r}_1}\psi_{n'}{}^*(\mathbf{r}_3,\mathbf{r}_2;R)\times\left(\frac{1}{r_{31}}+\frac{1}{r_{32}}-\frac{1}{r_{3A}}-\frac{1}{r_{3B}}\right)\times e^{i\mathbf{k}_0\cdot\mathbf{r}_3}\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3.\tag{5}$$

Once the initial and final wave functions are known,

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[9] S. P. Khare and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **88**, 685 (1966).

[10] S. P. Khare, Phys. Rev. **157**, 107 (1967). The authors wish to thank Dr. Khare for making this paper available to them prior to its publication

[11] M. Born and J. R. Oppenheimer, Ann. Physik. **84**, 457 (1927).

[12] (a) J. D. Craggs and H. S. W. Massey, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, p. 333; (b) H. S. W. Massey, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 36, p. 369.

[13] It has been suggested (see Ref. 12a) that even in the BO approximation the core terms should be dropped, although there is some disagreement on this point (see Ref. 12b). For $H_2$, a BO calculation including core terms has been published (see Ref. 1). Unfortunately, no corresponding calculation excluding core terms has been reported, and therefore a direct comparison between the two approaches is not yet available.

Eqs. (4) and (5) furnish the differential cross section $I_i^f$.

### B. Ochkur and Rudge Modifications

The scattering amplitude of Eq. (5) furnishes the electronic excitation cross section of the hydrogen molecule for a fixed position of the two nuclei. This BO $T_{fi}$ is known to fail at low incident energy.[14] Ochkur[4] has pointed out that the BO approximation to the exchange-scattering amplitude is in error and that to maintain consistency with first-order perturbation theory, this amplitude should be expanded in powers of $k_0^{-1}$ and only the leading term retained. By performing an integration by parts on each term of the interaction potential (including core terms) and keeping only the lowest-order terms in $k_0^{-1}$, Ochkur showed that $T_{fi}$ should be

$$T_{fi}(k_0,\theta,\varphi;R,\chi,\phi)=\frac{2}{a_0k_0^2}\int e^{i\mathbf{q}\cdot\mathbf{r}_1}\psi_{n'}^*(\mathbf{r}_1,\mathbf{r}_2;R)\times\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)d\mathbf{r}_1d\mathbf{r}_2,\quad(6)$$

where

$$\mathbf{q}\equiv\mathbf{k}_0-\mathbf{k}'\quad(7)$$

is the wave-number vector transferred from the incident to the scattered electron. As part of his derivation he verified that the contribution of the core terms was of order $k_0^{-6}$ and therefore they were dropped. Consequently, Eq. (6) is obtained whether or not core terms are included in the BO scattering amplitude, from which the derivation starts.

Rudge[5,6] has proposed an improved version of the Ochkur modification of the BO approximation by considering the variational expression[15]

$$T_{fi}=\frac{1}{2\pi a_0e^2}\int f(\mathbf{r}_1)\psi_{n'}^*(\mathbf{r}_3,\mathbf{r}_2;R)V_{\text{int}}\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)e^{i\mathbf{k}_0\cdot\mathbf{r}_3}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3,\quad(8)$$

where $e$ in the electronic charge and $V_{\text{int}}$ is the interaction potential between the incident electron and the atom or molecule. $f(\mathbf{r}_1)$, the wave function for the scattered electron, was determined by a variational method[15] under the constraint that for very large incident energy, the form of $T_{fi}$ reduce to the O result except for allowing a different energy-dependent factor outside of the integral in Eq. (6). Rudge obtained an expression for the wave function of the scattered electron which behaves asymptotically as

$$f(\mathbf{r}_1)\underset{r_1\to\infty}{\sim}e^{i\mathbf{k}'\cdot\mathbf{r}_1}+\frac{8\pi a_0}{[a_0k'-(I_n/\mathcal{R})^{1/2}i]^2}\delta(\hat{k}'+\hat{r}_1)\frac{e^{ik'r_1}}{r_1},\quad(9)$$

where $I_n$ is the ionization potential of state $n$, $\mathcal{R}$ is Rydberg's constant, and $\hat{k}'$ and $\hat{r}_1$ are unit vectors in the $\mathbf{k}'$ and $\mathbf{r}_1$ directions, respectively. The scattering amplitude which results from the Rudge modification is

$$T_{fi}=\frac{2a_0}{[a_0k'-(I_n/\mathcal{R})^{1/2}i]^2}\times\int e^{i\mathbf{q}\cdot\mathbf{r}_1}\psi_{n'}^*(\mathbf{r}_1,\mathbf{r}_2;R)\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)d\mathbf{r}_1d\mathbf{r}_2.\quad(10)$$

Both the O and OR modifications have removed a major failing of the BO approximation in that there is no contribution from the core terms. In addition, the final state for the scattered electron contains, in the Rudge modification, a scattered spherical wave as well as the usual plane one, and leads to a complex scattering amplitude with nonvanishing real and imaginary parts, a property which is necessary if particle flux is to be conserved.[8]

### C. Rotationally Averaged Cross Section

Under most experimental conditions, the target molecules are not all in the same quantum state. For the case of molecular hydrogen at temperature $T$ (around room temperature) essentially all of the molecules are in the ground electronic and vibrational states, but many rotational states are represented, their relative populations being determined by the Boltzmann distribution for this temperature. Furthermore, as a result of electron impact on a molecule in a given initial rotational state, several rotational states of the electronically excited molecule can be produced. In the present paper, we are interested in the sum of the cross sections for excitation to all accessible rotational states. In the derivation which follows, the two nuclei will, for simplicity, be considered distinguishable, as in HD. In the actual case for $H_2$, we should treat it as a 3 to 1 mixture of ortho- and parahydrogen, with only odd-odd rotational transitions allowed for the ortho hydrogen and only even-even ones for the parahydrogen. Since the rotational characteristic temperature $\theta_r$ of $H_2$ is 85.4°K, $T$ is appreciably larger than $\theta_r$ at room temperature and above. Under these conditions we may, as is done in the calculation of the thermodynamic properties of $H_2$, assume that the appropriate statistical-mechanical sums over even values of $J$ equal the corresponding ones over odd $J$. This leads to the same expression for the rotationally averaged cross section as for a heteronuclear diatomic molecule. Let us define the rotationally averaged cross section

$$I_{n\nu}^{n'\nu'}(k_0,\theta,\varphi;T)\equiv\langle I_{n\nu JM}^{n'\nu'}(k_0,\theta,\varphi)\rangle_T,\quad(11)$$

where

$$I_{n\nu JM}^{n'\nu'}(k_0,\theta,\varphi)=\sum_{J'=0}^{J_{\text{max}}'}\sum_{M'=-J'}^{J'}I_i^f(k_0,\theta,\varphi).\quad(12)$$

The averaging indicated by the angular brackets of Eq. (11) refers to a statistical-mechanical average over initial rotational states $J$ and $M$, the weighting factors

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[14] D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, Phil. Trans. Roy. Soc. London A243, 93 (1950).

[15] Reference 7c, Chap. 1.

being the Boltzmann populations of those states at temperature $T$. The double sum over $J'$ and $M'$ in Eq. (12) extends over the accessible final rotational states for given initial and final electronic and vibrational quantum numbers $n$, $\nu$, $n'$, and $\nu'$ and a given initial wave number $k_0$. $J_{\max}'$ is the maximum $J'$ for which $k'$, as given by Eq. (3), remains real. Therefore, it depends on $k_0$, $n$, $\nu$, $J$, $n'$, and $\nu'$.

Next, let us show how $I_{n\nu}{}^{n'\nu'}$ can be determined. If $G_j(u)$ is any complete orthonormal set of functions of a variable $u$ (which may be multidimensional) and $F(u)$ is any well-behaved function of $u$, the following expression is valid:

$$\sum_{j'}\left|\int G_{j'}{}^*(u)F(u)G_j(u)du\right|^2=\int|F(u)G_j(u)|^2du. \quad (13)$$

This property is easily proven by expanding $FG_j$ in the right side of Eq. (13) in terms of the $G_j$. Applying Eq. (13) to the particular case in which $G_j$ is $Y_J{}^M(\chi,\phi)$ furnishes

$$\sum_{J'=0}^{\infty}\sum_{M'=-J'}^{J'}\left|\int Y_{J'}{}^{M'*}(\chi,\phi)F(\chi,\phi)Y_J{}^M(\chi,\phi)d\Omega\right|^2 =\int|Y_J{}^M(\chi,\phi)|^2|F(\chi,\phi)|^2d\Omega. \quad (14)$$

Substitution of Eq. (4) into Eq. (12), replacement of $T_{fi}$ by the quantity $T_{n\nu}{}^{n'\nu'}$ defined below, and use of Eq. (14) with $F=\int\xi_{n'\nu'}{}^*T_{n\nu}{}^{n'\nu'}\xi_{n\nu}R^2dR$ furnishes

$$I_{n\nu JM}{}^{n'\nu'}(k_0,\theta,\varphi) =\frac{3\bar{k}'}{k_0}\int_\Omega\left|\int_R \xi_{n'\nu'}{}^*(R)T_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi;R,\chi,\phi) \times\xi_{n\nu}(R)R^2dR\right|^2|Y_J{}^M(\chi,\phi)|^2d\Omega. \quad (15)$$

Here, $\bar{k}'(k_0,n,\nu,J,n',\nu')$ represents some mean value of $k'(k_0,n,\nu,J,n',\nu',J')$ over the accessible $J'$. The scattering amplitude $T_{fi}$ depends on $J'$ through $k'$. Because of their small mass, electrons are not effective in producing rotational excitation. Therefore, the change in the wave number of the incident electron due to rotational excitation is negligible compared to that due to electronic and vibrational excitation. As a result, $k'$ should deviate very little from

$$k''=[k_0{}^2-(2m/\hbar^2)(E_{n'\nu'}-E_{n\nu})]^{1/2}, \quad (16)$$

where the energies $E_{n\nu}$ and $E_{n'\nu'}$ do not include rotational contributions. Since $T_{fi}$ is not a very rapidly varying function of $k'$, we can substitute $T_{fi}(k')$ by $T_{n\nu}{}^{n'\nu'}\equiv T_{fi}(k'')$ to a very good approximation. This quantity is not a function of $J$ or $J'$ and depends on $\nu$ and $\nu'$ only through $k''$. To get Eq. (15), the sum over $J'$ in Eq. (12) was assumed to extend to infinity. The justification for this assumption is that for the reasons just stated, $I_i{}^f$ is expected to be negligible for $J'$ very different from $J$. Therefore, the additional terms introduced in going from $J_{\max}'$ to $\infty$ should be negligible. On the same basis, since only relatively small values of $J$ and $J'$ are being considered, the radial wave functions $\xi_{n'\nu'J'}(R)$ and $\xi_{n\nu J}(R)$ were assumed to be independent of $J'$ and $J$, respectively.

Substituting Eq. (15) into Eq. (11) and using the sum rule for spherical harmonics gives the result

$$I_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi;T)=\frac{3\langle\bar{k}'\rangle_T}{k_0}\int_\Omega\left|\int_R[R\xi_{n'\nu'}(R)]^* \times T_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi;R,\chi,\phi)[R\xi_{n\nu}(r)]dR\right|^2\frac{d\Omega}{4\pi}, \quad (17)$$

where

$$\langle\bar{k}'\rangle_T\equiv\frac{\sum_J(2J+1)e^{-E_{n\nu J}/kT}\bar{k}'(k_0,n,\nu,J,n',\nu')}{\sum_J(2J+1)e^{-E_{n\nu J}/kT}}. \quad (18)$$

To a first very good approximation, $\langle\bar{k}'\rangle_T$ can be replaced by the quantity $k''$ defined by Eq. (16), for the same reasons used to justify the replacement of $k'$ by $k''$. This substitution is even more reasonable if the incident electron beam is not monoenergetic enough to resolve rotational transitions, which is the usual case in the experiments performed to date. The resulting expression for the differential, rotationally averaged, excitation cross section is

$$I_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi) =\frac{3k''}{k_0}\int_\Omega\left|\int_R[R\xi_{n'\nu'}(R)]^*T_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi;R,\chi,\phi) \times[R\xi_{n\nu}(R)]dR\right|^2\frac{d\Omega}{4\pi}. \quad (19)$$

As a result of the replacement of $\langle\bar{k}'\rangle_T$ by $k''$, the temperature $T$ has been dropped as a variable in $I_{n\nu}{}^{n'\nu'}$. As pointed out above, this same Eq. (19) is obtained for $H_2$ when $T\gg\theta_r$. For temperatures around $\theta_r$ or less, this expression would be wrong. It is, however, relatively simple to modify it appropriately by treating the ortho and para components in a manner analogous to that indicated above, but without recourse, in this case, to the simplifications introduced by Eq. (14).

In Eq. (19), $\nu'$, the quantum number for the vibrational level of the excited state, is implicitly assumed to be discrete. However, if some of the symbols are redefined, this equation still holds when $\nu'$ is continuous, i.e., when $E_{n'\nu'}-E_{n'0}$ is larger than the dissociation energy of electronic state $n'$ or when that state is a repulsive one. In such cases, $I_{n\nu}{}^{n'\nu'}$ is to be interpreted as a cross section per unit range of $\nu'$, such that $I_{n\nu}{}^{n'\nu'}d\nu'$ represents the differential, rotationally averaged, excitation cross section from state $n$, $\nu$ into any state in the range $n'$, $\nu'$ to $n'$, $\nu'+d\nu'$. In addition, the radial wave function $R\xi_{n'v'}(R)$, which now represents a state in the continuum, is assumed to be normalized according to[16]

$$\lim_{\eta\to 0}\left[\frac{1}{\eta}\int_0^\infty\left|\int_{v'}^{v'+\eta}R\xi_{n'v''}(R)dv''\right|^2 dR\right]=1. \quad (20)$$

It should be noted that Eq. (19) states that the differential scattering cross section $I_{n\nu}{}^{n'\nu'}$ for excitation from state $(n\nu)$ to state $(n'\nu')$ can be obtained by assuming the molecular axis fixed at some orientation $(\chi,\phi)$, averaging the electronic transition amplitude $T_{n\nu}{}^{n'\nu'}$ over the vibrational wave functions $\xi_{n\nu}$ and $\xi_{n'\nu'}$, and then performing an angular average on the square of this quantity over all possible orientations.

It is customary to introduce an additional approximation[17] into Eq. (19) by assuming that $T_{n\nu}{}^{n'\nu'}(R)$ is a very slowly varying function of $R$ and replacing it by its value at the equilibrium internuclear distance $R_e{}^{(n\nu)}$ of the $(n\nu)$ initial state. As will be seen in Sec. 5 B2, this approximation is not always justified. However, it significantly simplifies Eq. (19) to

$$I_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi)=(3k''/k_0)g_{n\nu}{}^{n'\nu'} \times\langle|T_{n\nu}{}^{n'\nu'}(R_e{}^{(n\nu)})|^2\rangle, \quad (21)$$

where

$$\langle|T_{n\nu}{}^{n'\nu'}(R)|^2\rangle\equiv\int|T_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi;R,\chi,\phi)|^2\frac{d\Omega}{4\pi} \quad (22)$$

is the average of $|T_{n\nu}{}^{n'\nu'}|^2$ over all orientations of the internuclear axis and

$$g_{n\nu}{}^{n'\nu'}\equiv\left|\int_0^\infty[R\xi_{n'\nu'}(R)]^*[R\xi_{n\nu}(R)]dR\right|^2 \quad (23)$$

is the Franck-Condon factor for the $(n\nu)\rightarrow(n'\nu')$ electronic-vibrational transition. The quantity $\langle|T_{n\nu}{}^{n'\nu'} \times(R_e{}^{(n\nu)})|^2\rangle$ is a function of the transition $(n\nu)\rightarrow(n'\nu')$, the incident electron wave number $k_0$, and the scattering direction only.

The total cross section for the $(n\nu)\rightarrow(n'\nu')$ transition can be obtained by integrating Eq. (19) [or its approximate equivalent Eq. (21)] over all scattering angles:

$$\sigma_{n\nu}{}^{n'\nu'}(k_0)=\int_{\theta,\varphi}I_{n\nu}{}^{n'\nu'}(k_0,\theta,\varphi)\sin\theta d\theta d\varphi. \quad (24)$$

The total electronic excitation cross section from the initial $(n\nu)$ state to *all* accessible vibrational states of the excited electronic state $(n')$ is given by

$$\sigma_{n\nu}{}^{n'}(k_0)=\mathbf{S}_{\nu'}\sigma_{n\nu}{}^{n'\nu'}(k_0), \quad (25)$$

where $\mathbf{S}_{\nu'}$ is used to represent a sum over the discrete values of $\nu'$ plus an integral over its continuum value which are energywise accessible in the sense that $k''^2\geqslant 0$.

## 3. MOLECULAR WAVE FUNCTIONS

We will consider the excitation of $H_2$ from its ground electronic vibrational state $(X^1\Sigma_g{}^+;\nu=0)$ to its first and second triplet states ($b^3\Sigma_u{}^+$ and $a^3\Sigma_g{}^+$, respectively). For the ground state, three different approximate wave functions[18] were used: the two-parameter wave function of Weinbaum[19]:

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2)=N_0[(1s_A{}^z(1)1s_B{}^z(2)+1s_A{}^z(2)1s_B{}^z(1)) +C(1s_A{}^z(1)1s_A{}^z(2)+1s_B{}^z(1)1s_B{}^z(2))], \quad (26)$$

the valence bond wave function of Wang[20]:

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2)=N_0[1s_A{}^z(1)1s_B{}^z(2)+1s_A{}^z(2)1s_B{}^z(1)], \quad (27)$$

and the simple molecular-orbital wave function of Coulson[21]:

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2)=N_0[(1s_A{}^z(1)+1s_B{}^z(1)) \times(1s_A{}^z(2)+1s_B{}^z(2))]. \quad (28)$$

For the first triplet state $(b^3\Sigma_u{}^+)$ the two-parameter wave function of Phillipson-Mulliken[22] was used:

$$\psi_3(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\{\varphi_g(1)\varphi_u(2)-\varphi_g(2)\varphi_u(1)\}, \quad (29)$$

where

$$\varphi_g\equiv N_g(1s_A{}^{z_1}+1s_B{}^{z_1}) \quad (30)$$

and

$$\varphi_u\equiv N_u(1s_A{}^{z_2}-1s_B{}^{z_2}); \quad (31)$$

and the less accurate Hurley[23] two-parameter wave function

$$\psi_3(r_1,r_2)=N_3[1s_{A'}{}^{z_1}(1)1s_{B'}{}^{z_1}(2) -1s_{A'}{}^{z_1}(2)1s_{B'}{}^{z_1}(1)]. \quad (32)$$

In the latter, the centers $A'$, $B'$ are permitted to be displaced from the nuclei $A$, $B$, the displacement being the second variational parameter which, however, turns out to be practically zero for this state. Finally, for the second triplet state $(a^3\Sigma_g{}^+)$ we calculated a two-parameter Hartree-Fock function using computer programs furnished to us by W. A. Goddard of the California Institute of Technology. The form of this function was

$$\psi_3(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\{\varphi_{1g}(1)\varphi_{2g}(2)-\varphi_{1g}(2)\varphi_{2g}(1)\}, \quad (33)$$

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[16] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover Publications, Inc., New York, 1958), pp. 162–170.

[17] E. N. Lassettere and M. E. Krasnow, J. Chem. Phys. **40**, 1248 (1964).

[18] The optimized values of the screening constants for the experimental equilibrium distance of the ground states were made available to us by Dr. G. O. Hultgren, now at Battelle Institute, Columbus, Ohio.

[19] C. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

[20] S. C. Wang, Phys. Rev. **31**, 579 (1929).

[21] C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937).

[22] P. E. Phillipson and R. S. Mulliken, J. Chem. Phys. **28**, 1248 (1958).

[23] A. C. Hurley, Proc. Roy. Soc. (London) **A226**, 187 (1954).

TABLE I. Parameters of molecular wave functions.

| Wave function | Parameters | | | | Energy (rydbergs) |
|---|---|---|---|---|---|
| Ground state[a] ($X^1\Sigma_g^+$) | $R(a_0)$ | $N_0^2(a_0^{-6})$ | $z$ | $C$ | |
| | 1.20 | 0.0802 | 1.2493 | 0.2606 | |
| Weinbaum[b] | 1.40 | 0.0668 | 1.2005 | 0.2647 | $-2.2956$ |
| | 1.60 | 0.0571 | 1.1592 | 0.2589 | |
| | 1.20 | 0.1099 | 1.2226 | 0 | |
| Wang[c] | 1.40 | 0.0881 | 1.1695 | 0 | $-2.2780$ |
| | 1.60 | 0.0731 | 1.1257 | 0 | |
| | 1.20 | 0.0310 | 1.2412 | 1.0 | |
| Coulson[d] | 1.40 | 0.0255 | 1.1895 | 1.0 | $-2.2564$ |
| | 1.60 | 0.0214 | 1.1449 | 1.0 | |
| Accurate[e] | $R_e=1.40a_0$ | | | | $-2.3490$ |
| First triplet ($b^3\Sigma_u^+$) | $R(a_0)$ | $N_g^2N_u^2(a_0^{-6})$ | $z_1$ | $z_2$ | |
| Phillipson-Mulliken[f] | 1.20 | 0.0908 | 1.3868 | 0.5055 | |
| | 1.40 | 0.0720 | 1.3250 | 0.5754 | $-1.5638$ |
| | 1.60 | 0.0588 | 1.2715 | 0.6412 | |
| | 1.20 | 0.1466 | 1.0 | | |
| Hurley[g] | 1.40 | 0.1170 | 1.0 | | $-1.0574$ |
| | 1.60 | 0.0977 | 1.0 | | |
| Accurate[h] | | | | | $-1.5910$ |
| Second triplet ($a^3\Sigma_g^+$) | $R(a_0)$ | $N_{1g}^2N_{2g}^2(a_0^{-6})$ | $z_1$ | $z_2$ | |
| | 1.20 | 0.00020 | 1.4463 | 0.4733 | |
| Hartree-Fock | 1.40 | 0.00027 | 1.3497 | 0.5120 | $-1.3830$ |
| | 1.60 | 0.00033 | 1.2399 | 0.5477 | |
| Accurate[i] | $R_e=1.864a_0$ | | | | $-1.4258$ |

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.
[d] Reference 21.
[e] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).
[f] Reference 22.
[g] Reference 23.
[h] A. S. Coolidge and H. M. James, J. Chem. Phys. 6, 730 (1938).
[i] Reference 24d.

where

$$\varphi_{1g}=N_{1g}(1s_A^{z_1}+1s_B^{z_2})\,, \tag{34}$$

and

$$\varphi_{2g}=N_{2g}(2s_A^{z_2}+2s_B^{z_2})-N_{1g}'(1s_A^{z_1}+1s_B^{z_1})\,. \tag{35}$$

In Eqs. (26) through (34), the symbol $1s_X^z(j)\equiv e^{-zr_{jX}/a_0}$ stands for a 1s atomic orbital for electron $j(=1,2)$ centered on nucleus $X(=A,B)$ with screening parameter $z$; and $2s_X^z(j)\equiv(r_{jX}/a_0)e^{-zr_{jX}/a_0}$ is a similar 2s Slater atomic orbital.

To perform cross-section calculations, it is necessary to know the molecular electronic wave functions of the ground and excited states as well as the vertical excitation energies from the ground to the appropriate excited state as parametric functions of the internuclear distance $R$. In all cases considered in this paper, these parametric functions varied quite slowly over the pertinent range of $R$ determined by the classical turning points of the ground electronic vibrational state ($1.20a_0<R<1.67a_0$), and it was possible to use, with a high degree of accuracy (error$<3\%$), polynomial representations of this $R$ variation obtained from least-squares fitting to values calculated for a few $R$ values. The $R$ variation of the screening parameters for the first triplet states were found in the literature,[22,23] while for the ground states the $R$ dependence was obtained from unpublished work.[18] The $R$ variation of the parameters for the second triplet state was determined in our calculation of the wave function. The values used in determining the $R$ variation of the excitation energies were taken from theoretical calculations of the potential energy as a function of the internuclear distance for the ground and the two excited triplet states.[24] Figure 1 illustrates the potential-energy curves for these and some additional states. The classical range of $R$ variation and the Franck-Condon region are indicated by the shading.

In Table I are summarized some of the important parameters for the wave functions used. The last column gives the variationally determined energy at $R_e=1.40a_0$. Included in this table is a listing of the $R$ variation of the screening parameters and normalization constants for the wave functions used.

## 4. EVALUATION OF MULTICENTER INTEGRALS

The scattering amplitude $T_{fi}$ was calculated for fixed $q$, $R$, and orientation $(\chi,\phi)$ in the following manner. When the two-center molecular wave functions are inserted into Eqs. (6) or (10), two- and three-center one-electron integrals appear. The two-center integrals

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[24] (a) For the ionization energy: V. A. Johnson, Phys. Rev. **60**, 373 (1941); (b) for the states $X^1\Sigma_g^+$, $b^3\Sigma_u$, and $c^1\Pi_u$: W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965); (c) for the $B^1\Sigma_u^+$ state: W. Kolos and L. Wolniewicz, Laboratory for Molecular Structure and Spectra Technical Report, University of Chicago, 1965 (unpublished); (d) for the $a^3\Sigma_g^+$ state: C. B. Wakefield and E. R. Davidson, J. Chem. Phys. **43**, 834 (1965); (e) for the $c^3\Pi_u$ state: J. C. Browne, J. Chem. Phys. **40**, 43 (1964).

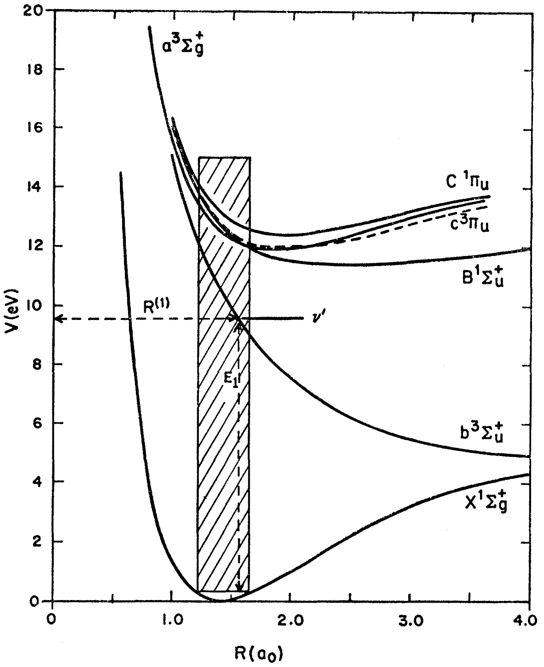

FIG. 1. Potential energy as a function of internuclear distance for low-lying states of $H_2$ (see Ref. 24). Quantities $R^{(1)}$ and $E_1$ are defined in Sec. 5 B.1. The shaded area represents the Franck-Condon region for excitation from the ground vibrational state. The horizontal full line to the right of the $b^3\Sigma_u^+$ curve represents a continuum vibrational energy level $\nu'$.

can be performed analytically while the three-center ones require numerical evaluation. The general form of these three-center one-electron integrals is

$$I=N_pN_t\int e^{i\mathbf{q}\cdot\mathbf{r}_1}r_{1A}^{p-1}e^{-zr_{1A}}r_{1B}^{t-1}e^{-z'r_{1B}}d\mathbf{r}_1, \qquad (36)$$

where $p$, $t=1$, 2; $N_p$ and $N_t$ are the normalization constants for the corresponding atomic orbitals; $\mathbf{r}_1$ is the position vector of electron 1 with respect to the center (0) of the molecule; $r_{1A}$ and $r_{1B}$ are the distances of this electron from the nuclei (see Fig. 2); and $z$ and $z'$ are the screening parameters of the atmoic wave functions considered. These integrals are evaluated by expanding the plane wave as

$$e^{i\mathbf{q}\cdot\mathbf{r}_1}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}i^lj_l(qr_1)Y_l^{m*}(\hat{q})Y_l^m(\hat{r}_1), \qquad (37)$$

where $j_l$ is the spherical Bessel function of order $l$, $Y_l^m$ is the spherical harmonic, and $\hat{q}$ and $\hat{r}_1$ are the unit vectors in the $\mathbf{q}$ and $\mathbf{r}_1$ directions. The atomic orbitals are expanded in Legendre polynomials about the center of the molecule according to the $\zeta$-function expansion[25] which for the wave functions used in these calculations takes the form

$$r_{1X}^{p-1}e^{-zr_{1X}}=\sum_{u=0}^{\infty}\frac{(2u+1)}{(r_1R/2)^{1/2}}$$
$$\times P_u(\cos\theta_1)\zeta_{p,u}(z,r_1;R/2), \qquad (38)$$

where $(r_1,\theta_1)$ are the coordinates of the electron measured from the diatomic center as indicated in Fig. 2 [26]; $r_{ij}$ is the distance of the electron from nucleus $j=A,B$; $P_u$ is the Legendre polynomial of order $u$; and $\zeta_{p,u}$ is the $\zeta$ function.[25] Although the integrals $I$ of Eq. (36) can be reduced to two-center integrals about the nuclei, an expansion about their midpoint has the advantage that it enables the averaging over all orientations of the molecular axis to be performed easily and without any great increase in the complexity of the numerical work. When the expansions are inserted into this equation, one obtains, after choosing the laboratory-fixed $z$ axis along $\mathbf{q}$ and performing the integration over $\varphi_1$ (the angle of rotation of $\mathbf{r}_1$ around $AB$),[26] the following:

$$I=\sum_{l=0}^{\infty}(2l+1)i^lP_l(\cos\chi)\sum_{u=0}^{\infty}\sum_{u'=0}^{\infty}N_pN_t(-1)^{u'}(2u+1)(2u'+1)\int j_l(qr_1)\zeta_{p,u}(z,r_1;R/2)\zeta_{t,u'}(z',r_1;R/2)$$
$$\times\left(\frac{2}{r_1R}\right)P_l(\cos\theta_1)P_u(\cos\theta_1)P_{u'}(\cos\theta_1)2\pi r_1^2dr_1\sin\theta_1d\theta_1\equiv\sum_{l=0}^{\infty}(2l+1)i^lP_l(\cos\chi)Z_{t,z'}^{p,z}(l;q,R). \qquad (39)$$

Equation (39) serves to define the quantity $Z_{t,z'}^{p,z}$ as used in these calculations.

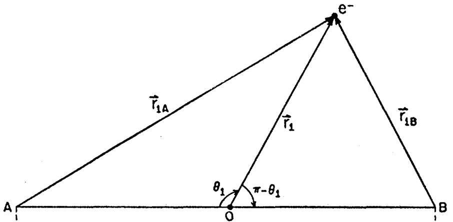

FIG. 2. Diagram indicating distances and angles for the evaluation of multicenter integrals.

Our three-center scattering integral program for Eq. (36) was developed using the methods just described. It was generated by modification of a three-center energy integral program kindly supplied by R. M. Pitzer of the California Institute of Technology. In the actual computation the terms for each $l$ in Eq. (39) decreased rapidly in magnitude with in-

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[25] M. P. Barnett, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, pp. 95–120.

[26] The angles $\theta_1,\varphi_1$ bear no relationship to the polar angles $\theta,\varphi$ which define the direction of the wave-number vector $\mathbf{k}'$ of the scattered electron in a laboratory-fixed system of reference.

creasing $l$ so the series was truncated after $l=2$. The error due to this truncation is less than 5%. For fixed $q$, $R$, and $\chi$, each $Z_{t,z'}{}^{p,z}$ function can be evaluated with 5 or 6 decimal place accuracy in about 7 sec on an IBM 7094. This includes an integration over $\theta_1$ using the recursion relations of the $P_u$ functions and a numerical integration over $r_1$ by a Gauss-Legendre integration.[25]

## 5. METHOD OF CALCULATING CROSS SECTIONS

Total cross sections for the exchange excitation of the hydrogen molecule from the ground state $(X^1\Sigma_g{}^+)$ to the first $(b^3\Sigma_u{}^+)$ and second $(a^3\Sigma_g{}^+)$ triplet states have been calculated. The OR and O approximations to the scattering amplitude $T_{fi}$ [Eqs. (10) and (6), respectively] have been used, the necessary integrals, including the three-center ones, having been evaluated as indicated in the previous section. Even though the OR approximation is superior to the O one, calculations with the latter were also performed for comparison with the OR results, since this O approximation appears frequently in the literature. The difference in computational efforts between these two approximations is very small, since they differ only in the energy-dependent factors which appear outside of the integral in the expressions for the corresponding scattering amplitudes.

In addition, the calculations were repeated using the ER and O approximations with the separated-atom (SA) approximation to the scattering amplitude. This latter approximation, introduced by Khare and Moiseiwitsch,[27] consists in neglecting the two- and three-center integrals in the expression for $T_{n\nu}{}^{n'\nu'}$ as if the two atoms wese infinitely separated. Except for this, the molecule is treated as if the nuclei were at a finite distance $R$. Although this SA approximation greatly simplifies the calculations by eliminating the need to evaluate the difficult three-center integrals, there seems to be little physical justification for it, as shown in Sec. 6 B. However, since such an approximation has appeared in the literature, the cross sections were calculated using it for comparison with the complete calculations.

### A. Electronic Scattering Amplitude

Using the wave functions described in Sec. 3, the OR and O scattering amplitudes for the transition from the ground vibrational-electronic state $(X^1\Sigma_g{}^+)$ to the first $(b^3\Sigma_u{}^+)$ and second $(a^3\Sigma_g{}^+)$ states are given, respectively, by

$$T_{\nu'}{}^{(1)}\equiv 2^{1/2}\pi a_0 N_0 N_g N_u(1+C)\beta F(k_0,k')i \times[H_1\sin(\tfrac{1}{2}qR\cos\chi)-6M_1\cos\chi], \tag{40}$$

$$T_{\nu'}{}^{(2)}\equiv 2^{1/2}\pi a_0 N_0 N_{1g} N_{2g}(1+C)\epsilon F(k_0,k') \times[H_2\cos(\tfrac{1}{2}qR\cos\chi)+2K_2-10L_2P_2(\cos\chi)]. \tag{41}$$

In the expressions above the laboratory-fixed system of coordinates was chosen so that its $z$ axis is parallel to $\mathbf{q}$. With this choice the values of $T_{\nu'}{}^{(1)}$ and $T_{\nu'}{}^{(2)}$ are independent of $\phi$, which is now the angle of rotation of $\mathbf{R}$ around $\mathbf{q}$. The new quantities in Eq. (40) are defined by Eqs. (42) through (46) and those in Eq. (41) by Eqs. (47) through (52):

$$H_1(q,R)\equiv\frac{16(z+z_2)}{[(z+z_2)^2+(a_0q)^2]^2}+W_1\frac{16(z+z_1)}{[(z+z_1)^2+(a_0q)^2]^2}, \tag{42}$$

$$W_1(R)\equiv\gamma(1-C)/\beta(1+C), \tag{43}$$

$$\gamma(R)\equiv a_0^3\int 1s_A{}^z(r_{2A})1s_A{}^{z2}(r_{2A})d\mathbf{r}_2-a_0^3\int 1s_A{}^z(r_{2A})1s_B{}^{z2}(r_{2B})d\mathbf{r}_2, \tag{44}$$

$$\beta(R)\equiv a_0^3\int 1s_A{}^z(r_{2A})1s_A{}^{z1}(r_{2A})d\mathbf{r}_2+a_0^3\int 1s_A{}^z(r_{2A})1s_B{}^{z1}(r_{2B})d\mathbf{r}_2, \tag{45}$$

$$M_1(q,R)\equiv\frac{\pi}{(zz_2)^{3/2}}Z_{1,z_2}{}^{1,z}(1;q,R)+W_1\frac{\pi}{(zz_1)^{3/2}}Z_{1,z}{}^{1,z1}(1;q,R), \tag{46}$$

$$H_2(q,R)\equiv\frac{16(z+z_1)}{[(z+z_1)^2+(a_0q)^2]^2}-W_2\frac{16[3(z+z_2)^2-(a_0q)^2]}{[(z+z_2)^2+(a_0q)^2]^3}, \tag{47}$$

$$W_2(R)\equiv\alpha/\epsilon, \tag{48}$$

$$\alpha(R)\equiv a_0^3\int 1s_A{}^z(r_{2A})1s_A{}^{z1}(r_{2A})d\mathbf{r}_2+a_0^3\int 1s_A{}^z(r_{2A})1s_B{}^{z1}(r_{2B})d\mathbf{r}_2, \tag{49}$$

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[27] S. P. Khare and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **85**, 821 (1965).

$$\epsilon(R)\equiv a_0^3\int 1s_A{}^{z}(r_{2A})2s_A{}^{z2}(r_{2A})d\mathbf{r}_2+a_0^3\int 1s_A{}^{z}(r_{2A})2s_B{}^{z2}(r_{2B})d\mathbf{r}_2\,, \tag{50}$$

$$K_2(q,R)\equiv\frac{\pi}{(zz_1)^{3/2}}Z_{1,z}{}^{1,z1}(0;q,R)-W_2\left(\frac{3\pi^2}{z^3z_2{}^5}\right)^{1/2}Z_{2,z_2}{}^{1,z}(0;q,R)\,, \tag{51}$$

$$L_2(q;R)\equiv\frac{\pi}{(zz_1)^{3/2}}Z_{1,z}{}^{1,z1}(2;q,R)-W_2\left(\frac{3\pi^2}{z^3z_2{}^5}\right)^{1/2}Z_{2,z_2}{}^{1,z}(2;q,R)\,. \tag{52}$$

The quantity $F(k_0,k')$ is defined by

$$\begin{aligned}&(\mathrm{OR}): && F=[a_0k'-(I_0/\mathcal{R})^{1/2}i]^{-2}\,,\\ &(\mathrm{O}): && F=(a_0^2k_0^2)^{-1}\,,\end{aligned} \tag{53}$$

where $I_0=15.279$ eV[24a] and the value of $C$ depends on which ground-state function is used. It is 0 for the Wang function, 1 for the Coulson function, and given in Table I as a function of $R$ for the Weinbaum function. The quantities $H_1$, $H_2$, $\alpha$, $\beta$, $\gamma$, $\epsilon$, $W_1$, and $W_2$ depend on $R$ because of the dependence of the molecular wavefunction parameters on this quantity, as indicated in Table I.

As seen in Sec. 2 C [Eq. (21)], it is also useful to calculate the quantity $\langle|T_{\nu'}{}^{(j)}(R)|^2\rangle$. This can be done using the above equations and gives

$$\begin{aligned}\langle|T_{\nu'}{}^{(1)}|^2\rangle=&\,2\pi^2a_0^2N_0^2N_g^2N_u^2(1+C)^2\beta^2|F(k_0,k')|^2\\ &\times[H_1^2\Theta_{11}-(12/\pi)H_1M_1\Theta_{12}\\ &+(36/\pi^2)M_1^2\Theta_{13}]\,,\end{aligned} \tag{54}$$

$$\begin{aligned}\langle|T_{\nu'}{}^{(2)}|^2\rangle=&\,2\pi^2a_0^2N_0^2N_{1g}^2N_{2g}^2(1+C)^2\epsilon^2|F(k_0,k')|^2\\ &\times[H_2^2\Theta_{21}+(4/\pi)H_2K_2\Theta_{22}-(20/\pi)H_2L_2\Theta_{23}\\ &+(4/\pi^2)K_2^2\Theta_{24}+(100/\pi^2)L_2^2\Theta_{25}]\,.\end{aligned} \tag{55}$$

The quantities $\Theta_{ij}$ result from the orientation averaging process and are defined by

$$\Theta_{11}\equiv\langle\sin^2(\tfrac{1}{2}qR\cos\chi)\rangle=(\tfrac{1}{2})(1-\sin\tfrac{1}{2}qR)\,, \tag{56}$$

$$\begin{aligned}\Theta_{12}\equiv&\,\langle\sin(\tfrac{1}{2}qR\cos\chi)\cos\chi\rangle\\ &=(2/qR)^2\sin\tfrac{1}{2}qR-\tfrac{1}{2}qR\cos\tfrac{1}{2}qR)\,,\end{aligned} \tag{57}$$

$$\Theta_{13}\equiv\langle\cos^2\chi\rangle=\tfrac{1}{3}\,, \tag{58}$$

$$\Theta_{12}\equiv\langle\cos^2(\tfrac{1}{2}qR\cos\chi)\rangle=(\tfrac{1}{2})(1+\sin\tfrac{1}{2}qR)\,, \tag{59}$$

$$\Theta_{22}\equiv\langle\cos(\tfrac{1}{2}qR\cos\chi)\rangle=(2/qR)\sin\tfrac{1}{2}qR\,, \tag{60}$$

$$\begin{aligned}\Theta_{23}\equiv&\,\langle\cos(\tfrac{1}{2}qR\cos\chi)P_2(\cos\chi)\rangle=3(2/qR)^2\cos\tfrac{1}{2}qR\\ &+(2/qR)[1-3(2/qR)^2]\sin\tfrac{1}{2}qR\,,\end{aligned} \tag{61}$$

$$\Theta_{24}\equiv\langle P_0{}^2(\cos\chi)\rangle=1\,, \tag{62}$$

$$\Theta_{25}\equiv\langle P_2{}^2(\cos\chi)\rangle=\tfrac{1}{5}\,. \tag{63}$$

The actual calculations were done using atomic units throughout.

### B. Excitation Cross Sections

To calculate the total cross sections for the electronic excitation processes of interest we must evaluate the quantities defined by Eqs. (19), (24), and (25). It is convenient to consider the two triplet-state excitations separately.

#### *1. $X^1\Sigma_g{}^+\rightarrow b^3\Sigma_u{}^+$ Excitation*

The first triplet state ($b^3\Sigma_u{}^+$) is a nonbound one. Let its continuum vibrational wave function be $\xi_{\nu'}{}^{(1)}(R)$ and let $\xi_0{}^{(0)}(R)$ be the $\nu=0$ vibrational wave function of the ground electronic state. According to Eq. (19) we must evaluate the quantity

$$\begin{aligned}J_{\nu'}{}^{(1)}(k_0,\theta,\varphi;\chi,\phi)\equiv\Bigg|\int_0^\infty&[R\xi_{\nu'}{}^{(1)}(R)]^*\\ &\times T_{\nu'}{}^{(1)}(k_0,\theta,\varphi;R,\chi,\phi)[R\xi_0{}^{(0)}(R)]dR\Bigg|^2\,.\end{aligned} \tag{64}$$

Similar type quantities for $H_2$ have been considered in the past[28] in connection with spectral intensities in optical emissions from the $a^3\Sigma_g{}^+$ to the $b^3\Sigma_u{}^+$ state. As above, this was a discrete to continuum state transition. The integrals in question involved either the product of the radial wave functions alone [28a] or this product times the electric dipole transition moment.[28b] In either case it was shown that these integrals could be evaluated with good accuracy by substituting the radial function of the continuum state by a $\delta$ function at the classical turning point for the transition energy being considered. We will use here the same approximation and replace $R\xi_{\nu'}{}^{(1)}(R)$ in Eq. (64) by $A\delta(R-R^{(1)})$[29]:

$$J_{\nu'}{}^{(1)}=|A|^2|T_\nu{}^{(1)}(k_0,\theta,\varphi;R^{(1)},\chi,\phi)R^{(1)}\xi_0{}^0(R^{(1)})|^2\,. \tag{65}$$

In this expression, $A$ is a proportionality constant to be determined as indicated below. $R^{(1)}$ is the classical turning point and, as depicted in Fig. 1, is a function of the excitation energy $E_1$, determined by the relation

$$V^{(1)}(R^{(1)})=E_1=E_{\nu'}{}^{(1)}-E_0{}^{(0)}\,, \tag{66}$$

where $E_0{}^{(0)}$ is the energy of the ground vibrational-

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[28] (a) A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. 4, 193 (1936); (b) H. M. James and A. S. Collidge, Phys. Rev. **55**, 184 (1939).

[29] In Ref. 28, the replacement was $A'E^{1/4}\delta(R-R_c)$, where $E$ was the energy of the continuum state above its value at infinite internuclear separation. However, the continuum wave function was normalized so as to have unit amplitude at large $R$. It is simple to show from the information in Ref. 16 that if the normalization of Eq. (20) is used, the $E^{1/4}$ factor should be omitted.

electronic state and $E_{\nu'}^{(1)}$ that of the $\nu'$ level of the first triplet state. $V^{(1)}=V^{(1)}(R)$ is the equation for the potential-energy curve for the first triplet state, measured with respect to the ground vibrational-electronic state. Therefore, the function $R^{(1)}=R^{(1)}(E_1)$ is simply the inverse of the function $V^{(1)}=V^{(1)}(R)$. Since Eq. (66) relates $\nu'$ and $E_1$, either of them can be considered as the variable which defines the continuum vibrational level under consideration. We shall use them interchangeably.

The proportionality constant $A$ can be evaluated from the condition that replacement of $R\xi_{\nu'}^{(1)}(R)$ by $A\delta(R-R^{(1)})$ should also furnish a very good approximation[28a] to the Franck-Condon factor

$$g_{\nu'}^{(1)}\equiv\left|\int_0^\infty [R\xi_{\nu'}^{(1)}(R)]^*[R\xi_0^{(0)}(R)]dR\right|^2. \quad (67)$$

Expanding the normalized square integrable function $R\xi_0^{(0)}(R)$ in terms of the complete orthonormal set of wave functions $R\xi_{\nu'}^{(1)}(R)$ and using the orthonormality properties of such continuum functions,[16] it is easy to prove that

$$\int g_{\nu'}^{(1)}d\nu'=1. \quad (68)$$

Introducing into Eq. (67) the $\delta$-function substitution just mentioned, and requiring that the approximate $g_{\nu'}^{(1)}$ which results still be normalized according to Eq. (68) furnishes

$$|A|^2=\left[\int_{D_0}^\infty |R^{(1)}(E_1)\xi_0^0(R^{(1)}(E_1))|^2dE_1\right]^{-1}, \quad (69)$$

where $D_0$ is the dissociation energy of the $X^1\Sigma_g^+$ state measured from its lowest vibrational level.

Substitution of Eqs. (65), (66), and (69) into Eq. (19) furnishes for the rotationally averaged differential cross section per unit energy range:

$$I_{\nu'}^{(1)}(k_0,\theta,\varphi)=(3k''/k_0)P^{(1)}(E_1) \times\langle|T_{\nu'}^{(1)}[R^{(1)}(E_1)]|^2\rangle, \quad (70)$$

where

$$P^{(1)}(E_1)\equiv|A|^2|R^{(1)}(E_1)\xi_0^{(0)}[R^{(1)}(E_1)]|^2 \quad (71)$$

satisfies the normalization relation

$$\int_{D_0}^\infty P^{(1)}(E_1)dE_1=1, \quad (72)$$

as can easily be seen from Eq. (69). In addition to depending on the excitation energy $E_1$ (and hence $\nu'$) through $R^{(1)}$, the quantity $\langle|T_{\nu'}^{(1)}[R^{(1)}(E_1)]|^2\rangle$ [defined for arbitrary $R$ by Eq. (22)] is also a function of $k_0$, $\theta$, and $\varphi$.

The product $R\xi_0^{(0)}(R)$ is well represented by a ground linear-harmonic-oscillator wave function,[30] which was used in our calculations:

$$R\xi_0^{(0)}(R)=(\mu/\pi)^{1/4}\exp[-\tfrac{1}{2}\mu(R-R_e)^2]. \quad (73)$$

Here, $\mu=18.4a_0^{-2}$, $R_e$, the ground-state equilibrium internuclear distance, is $1.40a_0$.[30] The range of $R$ for which this wave function contributes non-negligibly to the total cross section $\sigma^{(1)}(k_0)$ is relatively small. Over this range, Eq. (66) can be represented to within 3% accuracy by

$$E_1=a^{(1)}-b^{(1)}R^{(1)}, \quad (74)$$

where $a^{(1)}=21.01$ eV and $b^{(1)}=7.40$ eV$/a_0$.

Substitution of Eq. (70) into Eq. (24) furnishes

$$\sigma_{\nu'}^{(1)}(k_0)=(3k''/k_0)P^{(1)}(E_1) \times\int\langle|T_{\nu'}^{(1)}[R^{(1)}(E_1)]|^2\rangle\sin\theta d\theta d\varphi. \quad (75)$$

Although $\langle|T_{\nu'}^{(1)}[R^{(1)}(E_1)]|^2\rangle$ depends in principle on both $\theta$ and $\varphi$, it can be seen from Eqs. (54) and (56) through (63) that this dependence occurs through the quantity $q$, which according to Eqs. (7) and (16) depends only on $\theta$:

$$q=[k_0^2+k''^2-2k_0k''\cos\theta]^{1/2}. \quad (76)$$

Therefore, the integration over $\varphi$ results in a multiplicative factor $2\pi$, whereas the $\theta$ integration can be easily calculated by changing to variable $q$. Since, from Eq. (76)

$$\sin\theta d\theta=qdq/k_0k'', \quad (77)$$

we get

$$\sigma_{\nu'}^{(1)}(k_0)=(6\pi^2/k_0^2)P^{(1)}(E_1) \times\int_{q_{\min}(E_1)}^{q_{\max}(E_1)}\langle|T_{\nu'}^{(1)}[R^{(1)}(E_1)]|^2\rangle qdq, \quad (78)$$

where

$$\begin{aligned}q_{\min}(E_1)&\equiv k_0-k''(E_1),\\ q_{\max}(E_1)&\equiv k_0+k''(E_1).\end{aligned} \quad (79)$$

The quantity $P^{(1)}(E)$ was calculated from Eqs. (69), (71), (73), and (74), whereas $\langle|T_{\nu'}^{(1)}|^2\rangle$ was obtained from Eq. (54). The most convenient method of evaluating numerically the integral over $q$ in Eq. (78) is to perform a Simpson integration taking advantage of the fact that as the incident energy increases, $q_{\min}$ and $q_{\max}$ monotonically decrease and increase, respectively. Therefore, it is convenient to start at the lowest desired incident energy and for each new energy value just add the contributions of the two new integration regions to the integral which has already been calculated. This is the method we adopted.

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[30] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Inc. New York, 1953), 2nd ed., pp. 76–78, 532.

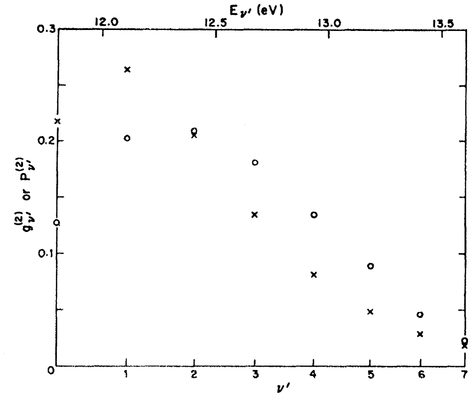

FIG. 3. Energy dependence of Franck-Condon factor $g_{\nu}'^{(2)}$ (×) and of δ-function factor $P_{\nu'}^{(2)}$ (○) for transition to second triplet state. Energy scale on top of graph is linear, but $\nu'$ scale is not because of anharmonicity effects.

Finally, the total cross section $\sigma^{(1)}(k_0)$ for excitation from the ground vibrational-rotational state of $H_2$ to all vibrationally accessible levels of the first triplet state by electrons of initial energy $E_0=\hbar^2k_0^2/2m$ can be obtained by substitution of Eq. (78) into Eq. (25), and use of $E_1$ rather than $\nu'$ as the vibrational-state label. The resulting expression is

$$\sigma^{(1)}(k_0)=\frac{6\pi}{k_0^2}\int_{D_0}^{E_0}P^{(1)}(E_1)\times\left[\int_{q_{\min}(E_1)}^{q_{\max}(E_1)}\langle|T_{\nu'}^{(1)}(R^{(1)}(E_1))|^2\rangle q dq\right]dE_1. \quad (80)$$

It is convenient to change integration variables from $E_1$ to $R^{(1)}$ through Eq. (66) [and specifically Eq. (74)]. The resulting expression is

$$\sigma^{(1)}(k_0)=\frac{6\pi}{k_0^2}\int_{R(E_0)}^{\infty}P^{(1)}[E_1(R)]\times\left[\int_{q_{\min}(R)}^{q_{\max}(R)}\langle|T_{\nu'}^{(1)}(R)|^2\rangle q dq\right]\left(-\frac{dE_1}{dR}\right)dR, \quad (81)$$

where we have dropped the superscript on the new integration variable. The integral over $R$ in this equation was performed by a three-point Gauss-Hermite quadrature[31] to 4 significant digit accuracy.

### 2. $X^1\Sigma_g^+\rightarrow a^3\Sigma_g^+$ *Excitation*

The second triplet state is a shallow (dissociation energy of 2.91 eV) bound state which has a minimum at $R_e^{(2)}=1.864a_0$. It has 16 bound vibrational states and no continuum states whose left classical turning points fall within the Franck-Condon vertical band depicted in Fig. 1. In principle, the calculation of the total cross section for the excitation of this state [according to Eqs. (19), (24), and (25)] requires inserting expressions for the $\xi^{(0)}$ and $\xi_{\nu'}^{(2)}$ vibrational wave functions, and performing the integration over $R$. Then the absolute value of the result obtained must be squared and averaged over all possible orientation angles of the molecular axis. This process requires very extensive numerical work in view of the large number of vibrational states involved, but is unnecessary within the scope of this paper, since we are attempting to calculate only the total electronic excitation cross section as defined by Eq. (25). Instead of using Eq. (19), we used two approximate methods. In one of them, Eq. (19) was replaced by Eq. (21). We shall discuss the validity of this approximation later in this section. The total excitation cross section which results from Eqs. (21), (24), and (25), after making the change of variables defined by Eq. (76), is

$$\sigma^{(2)}(k_0)=(6\pi/k_0^2)\mathsf{S}_{\nu'}g_{\nu'}^{(2)}\times\left[\int_{q_{\min}(\nu')}^{q_{\max}(\nu')}\langle|T_{\nu'}^{(2)}(R_e)|^2\rangle q dq\right], \quad (82)$$

where $R_e$ is the equilibrium internuclear distance of the ground electronic-vibrational state, and $q_{\min}$ and $q_{\max}$ are defined by Eq. (79) with $\nu'$ replacing $E_1$. $\langle|T_{\nu'}^{(2)}|^2\rangle$ was calculated using Eq. (55). For each incident energy $E_0=\hbar^2k_0^2/2m$, the integral over $q$ in Eq. (82) was calculated for all of the allowed $\nu'$ [for which $k''$, defined by Eq. (16), is real]. The corresponding Franck-Condon factors $g_{\nu'}^{(2)}$ were calculated by numerical integration[32] and the total cross section obtained by performing the sum over $\nu'$ indicated in Eq. (82). Because these Franck-Condon factors decrease rapidly with increasing $\nu'$, essentially all the contribution to $\sigma^{(2)}(k_0)$ comes from the first 8 vibrational levels ($\nu'=0, \cdots, 7$). In addition, contributions to $\sigma^{(2)}(k_0)$ from continuum values of $\nu'$ were neglected since the corresponding values of $g_{\nu'}^{(2)}$ are very small.

The assumption used to derive Eq. (21), and hence Eq. (82), was that $T_{n\nu}^{n'\nu'}$ was approximately inde-

TABLE II. Comparison of δ-function and Franck-Condon methods.

| Incident energy $E_0$ (eV) | Total cross section $\sigma^{(2)}(\pi a_0^2)$ δ function [Eq. (83)] | Franck-Condon [Eq. (82)] |
|---|---|---|
| 11.90 | 0.0072 | 0.0117 |
| 12.30 | 0.0376 | 0.0418 |
| 12.70 | 0.0710 | 0.0841 |
| 13.43 | 0.1312 | 0.1321 |
| 15.00 | 0.1783 | 0.1787 |
| 18.00 | 0.1602 | 0.1634 |
| Computer time (min) | 125 | 350 |

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[31] A. Kopal, *Numerical Analysis*, (John Wiley & Sons, Inc., New York, 1961), 2nd ed., p. 569.

[32] R. N. Zare, J. Chem. Phys. **40**, 1934 (1964); University of California Radiation Laboratory Report No. 10925, 1963 (unpublished). The authors would like to thank Dr. Zare for providing the programs necessary for this calculation.

pendent of $R$ over the important range of $R$ as determined by the ground vibrational state. To test this assumption we computed $\langle | T_{\nu'}^{(2)}(R) | \rangle$ for different values of the momentum transfer $q$, by using Eqs. (41) and (47) through (52). We found that it varied linearly over this range of $R$ with a slope that decreased rapidly with increasing $q$. From these considerations, the error introduced in this approximation is expected to be largest in the threshold region where it might be as high as 15%. Above 20-eV incident energy, the error associated with this approximation is estimated to be less than 8%.

An alternate approximation to Eq. (19) was used which is much faster computationally while still giving essentially the same total cross section as Eq. (82). This approximation consists of replacing the function $R\xi_{\nu'}^{(2)}(R)$ by a $\delta$ function at the classical turning point of the $\nu'$ state in a manner analogous to that done for the first triplet excitation. The total cross section for excitation of the second triplet is then given by expressions analogous to Eqs. (81), (71), and (69), with the superscript and subscript (1) replaced everywhere by (2). In particular, the expression corresponding to Eq. (81) is

$$\sigma^{(2)}(k_0)=\frac{6\pi}{k_0^2}\int_{R^{(2)}(E_0)}^{\infty} P^{(2)}[E_2(R^{(2)})] \times\left[\int_{q_{\min}(R^{(2)})}^{q_{\max}(R^{(2)})} \langle | T_{\nu'}^{(2)}(R^{(2)}) |^2 \rangle q dq\right] \times\left(-\frac{dE_2}{dR^{(2)}}\right) dR^{(2)}. \quad (83)$$

Although this is a rather drastic approximation, especially for small $\nu'$, it does not assume that $T_{\nu'}^{(2)}$ is independent of $R$, as the previous method did.

Over the region of $R$ of importance, the counterpart of Eq. (74) was obtained by a least-squares fit to the potential-energy curve for the second triplet state as calculated by Wakefield and Davidson,[24d] yielding (to within 1%)

$$E_2=a^{(2)}-b^{(2)}R^{(2)}+c^{(2)}[R^{(2)}]^2, \quad (84)$$

where $a^{(2)}=20.22$ eV, $b^{(2)}=7.48$ eV$/a_0$, and $c^{(2)}=1.44$ eV$/a_0^2$.

A comparison of the total electronic excitation cross section obtained from Eqs. (82) and (83) is given in Table II for a few energies in the threshold region. The total computing time necessary to obtain the cross section by Eq. (83) was 125 min, while that using Eq. (82) was 350 min. Therefore, the $\delta$-function method is faster than the Franck-Condon one but the results are equivalent. For this reason, all other calculations done for the second triplet state used the faster method. The good agreement of the two methods could be due in part to errors of the same size and in the same direction in the two different approximations. More likely, it is a consequence of the fact that the general behavior of the total electronic cross section is determined primarily by the parameters of the electronic states involved. In other words, the range of excitation energies due to excitation of different vibrational states is relatively small and hence the integral over $q$ varies slowly over the range of $\nu'$. The distributions $g_{\nu'}^{(2)}$ and $P^{(2)}(E_2)$ are both normalized:

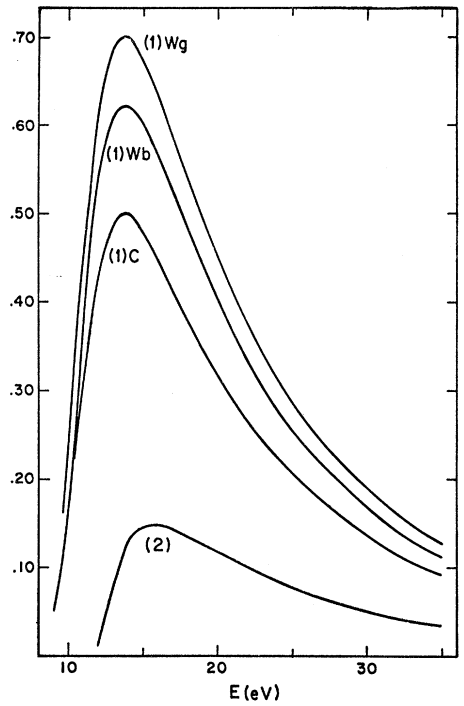

FIG. 4. Effect of ground-state wave function on cross section for excitation to first and second triplets: (1) Wg—first triplet, Wang; (1) Wb—first triplet, Weinbaum; (1) C—first triplet, Coulson; (2)—second triplet (curves corresponding to the three different ground-state wave functions coincide within plotting accuracy).

$$\mathbf{S}_{\nu'} g_{\nu'}^{(2)}=1 \quad (85)$$

and

$$\int P^{(2)}(E_2)dE_2=\sum\nolimits_{\nu'} P_{\nu'}^{(2)}=1, \quad (86)$$

where

$$P_{\nu'}^{(2)}\equiv\int_{E_2(\nu')}^{E_2(\nu'+1)} P^{(2)}(E_2)dE_2. \quad (87)$$

These relationships can be proved in a manner analogous to that used to verify Eqs. (68) and (72). In addition to being normalized, $g_{\nu'}^{(2)}$ and $P_{\nu'}^{(2)}$ have approximately the same shape, as can be seen from Fig. 3. Therefore, the result of Stiltjes integrating over $\nu'$ (or $E_2$) is relatively insensitive to the details of the $\nu'$ dependence of $\sigma_{\nu'}^{(2)}(k_0)$.

As for the first triplet, the integration over $R$ in Eq. (83) was performed by a Gauss-Hermite quadrature.[31]

TABLE III. Moments of the charge distribution of the ground electronic state.[a]

| Ground-state wave functions | Binding energy (eV) | $\langle x^2\rangle=\langle y^2\rangle$ ($a_0^2$) | $\langle z^2\rangle$ ($a_0^2$) | $\langle r^2\rangle$ ($a_0^2$) |
|---|---|---|---|---|
| Weinbaum[b] | 4.04 | 0.738 | 1.082 | 2.558 |
| Wang[b] | 3.76 | 0.767 | 1.131 | 2.665 |
| Coulson[b] | 3.47 | 0.742 | 1.073 | 2.557 |
| Experiment[c] | 4.476[d] | 0.7663 | 1.0604 | 2.593 |

[a] T. P. Das and R. Bersohn, Phys. Rev. **115**, 897 (1959).
[b] Calculated at $R_e=1.40a_0$.
[c] N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956).
[d] Reference 30.

## 6. RESULTS AND DISCUSSIONS

### A. The Effect of Different Approximate Wave Functions

Figure 4 shows the effect on the calculated total excitation cross sections of using different approximate wave functions for the ground state of the molecule. Only the results using the complete OR approximation are illustrated, since the O curves show the same relative differences. It can be seen from this figure that the first triplet cross section is quite sensitive to the choice of the ground-state wave function while the second-triplet one is not, which is at first surprising. In addition, the relative magnitude of the first triplet cross section does not change monotonically as the qualtity of the ground-state wave function is improved. Indeed, in order of increasing quality (from an energy-criterion viewpoint), the ground-state wave functions are Coulson, Wang, and Weinbaum, but in order of increasing relative cross section they are Coulson, Weinbaum, and Wang. This suggests that the relative sizes of two cross sections calculated from two different ground-state wave functions depends on properties of the wave functions other than those optimized by the energy minimization. This is indeed the case and both the relative magnitudes and ordering of the calculated cross sections can be qualitatively understood as follows. From the expression for the sctttering amplitude $T_{fi}$ [Eq. (10)], it is seen that the effect of the electronic wave functions on the excitation cross section is entirely contained in the one-electron overlap charge density defined as

$$\rho_{n'n}(\mathbf{r}_1;R)\equiv\int\psi_{n'}^*(\mathbf{r}_1,\mathbf{r}_2;R)\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)d\mathbf{r}_2. \qquad (88)$$

Therefore, any change in the ground-state wave function also produces a change in the overlap charge density. The nature and magnitude of this effect is expected to depend on the symmetries of the ground- and excited-state wave functions.

Consider the excitation to the first triplet state. The ground and first-triplet-state wave functions are both symmetric with respect to reflection of one of the electrons (electron 2, for example) through a plane containing the internuclear axis. However, the former one is even with respect to inversion of one electron through the center of the molecule whereas the latter one is odd. Therefore the plane passing through the origin and perpendicular to the internuclear axis is a one-electron plane of symmetry for the ground-state function and a nodal plane for the first triplet state. The effect of this nodal plane is to reduce the contribution to $\rho$ of spatial regions of the ground-state wave function close to it, i.e., of regions for which $|z_2|$ is small (Oz being the direction of the internuclear axis). As a result, the relative importance of the spatial extent of the ground-state wave function in the $x$ and $y$ directions is greatly reduced whereas the contribution to $\rho$ from regions of large $|z_2|$ is relatively enhanced. Consequently, slight differences in the $z$-direction tails (outer regions) of different ground-state wave functions will have their effect on $\rho$ amplified by this nodal plane, and appreciable differences in the resulting cross sections might be expected, as is indeed found to be the case. From these arguments, the ground-state wave function with largest extent in the $z$ direction might be expected to give the largest excitation cross section since the region in which $\rho$ is appreciable has then the largest spatial extent. Table III contains the values of the second-order moments of the ground-state charge density of the hydrogen molecule as calculated for the three ground-state wave functions used and as determined experimentally. As suggested by these qualitative considerations, the relative ordering of the values of $\langle z^2\rangle$ for the three ground-state wave functions used is indeed

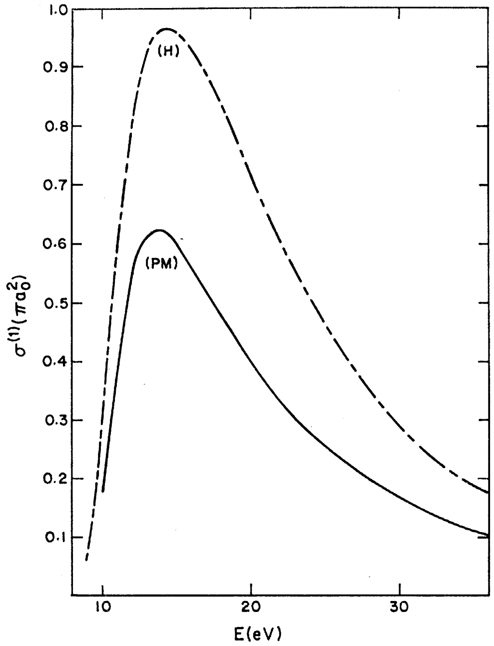

FIG. 5. Effect of different excited-state wave functions on the cross section for excitation to the first triplet. Ground state is Weinbaum for both. PM—Phillipson-Mulliken, H—Hurley.

TABLE IV. Comparison between complete and separated-atom OR calculations of the total cross section for excitation to the first triplet state ($R=1.40a_0$, $E_0=14.0$ eV, $E_f-E_i=8.8$ eV).

| Calculation | I<br>$N_0^2$<br>($a_0^{-6}$) | II<br>$N_g^2N_u^2$<br>($a_0^{-6}$) | III<br>$12\pi^2N_0^2N_g^2N_u^2(1+C)^2\beta^2$ | IV<br>$(\lvert F\rvert^2/k_0^2)\cdot$<br>$\int H_1^2\Theta_{11}qdq$ | V<br>$(\lvert F\rvert^2/k_0)\cdot$<br>$\int \frac{12}{\pi^2}H_1M_1\Theta_{12}qdq$ | VI<br>$(\lvert F\rvert^2/k_0^2)\cdot$<br>$\int \frac{36}{\pi^2}M_1^2\Theta_{13}qdq$ | VII<br>Sum of columns IV,V,VI | VIII<br>Cross section ($\pi a_0^2$) |
|---|---|---|---|---|---|---|---|---|
| Complete | 0.0668 | 0.0720 | 0.9610 | 1.274 | −0.734 | 0.106 | 0.646 | 0.621 |
| Separated atom | 0.1417 | 0.0056 | 0.1165 | 3.517 | 0.000 | 0.000 | 3.517 | 0.410 |

the same as the relative ordering of the magnitude of the corresponding cross sections for excitation to the first triplet state.

In the case of excitation to the second triplet, the excited-state wave function has the same one-electron symmetry characteristics as the ground-state wave function, that is, no one-electron nodal planes. As a result, the second triplet wave function does not strongly emphasize the importance of the ground-state wave function along any one axial direction over the other two. Consequently, the relative differences in $\rho_{nn'}(\mathbf{r}_1)$ as calculated for different ground-state wave functions is expected to be much smaller than in the first triplet case, and the resulting cross sections are expected to be much less sensitive to the choice of ground-state wave function. Figure 4 shows that this is indeed the case.

The cross section for excitation to the first triplet state was also calculated using the best (Weinbaum) ground-state wave function and the Hurley[23] wave function for the excited state. This excited-state wave function is much less accurate than the Phillipson-Mulliken one (from an energy standpoint) and from the above arguments should predict a significantly different cross section. This is indeed the case as shown in Fig. 5, which illustrates the first triplet cross section as calculated using the Weinbaum ground state and the two different excited-state wave functions, in the complete OR approximation. The large discrepancy between the two curves further serves to indicate the magnitude of errors which can result from the use of excessively inaccurate wave functions.

### B. Comparison of Ochkur, Ochkur-Rudge, and Separated-Atom Approximations

Figure 6 shows the theoretical cross sections for excitation to the first triplet state from the ground state as calculated in the complete Ochkur-Rudge (ORC), complete Ochkur (OC), the separated-atom Ochkur-Rudge (ORSA), and the separated-atom–Ochkur (OSA) approximations. The wave functions used for the ground and excited states were the Weinbaum and Phillipson-Mulliken ones, respectively (see Sec. 3). From the curves in this figure it can be seen that the OR and O calculations give significantly different results. As will be indicated in Sec. 6 C, the ORC results agree better with experiment than the OC ones. Two differences between the OR and the O approximations can be noted. First, in either the complete or the SA approximations the cross sections obtained using the O form for the transition amplitude [Eq. (6)] are about two times the corresponding OR cross sections [Eq. (10)], a result that might be expected from a comparison of the energy-dependent coefficients which precede the integral in Eqs. (6) and (10). Second, the location of the maximum in the O cross sections occurs at a lower energy (by about 0.5 to 0.75 eV) than the corresponding OR cross sections. In addition, the SA approximation, applied to either the O or the OR transition amplitudes, produces cross sections that have the proper shape but whose magnitude will generally be significantly smaller (by about 30%) than those predicted by the corresponding complete calculations. This is due to the fact that in the SA approximation all multicenter terms that appear in

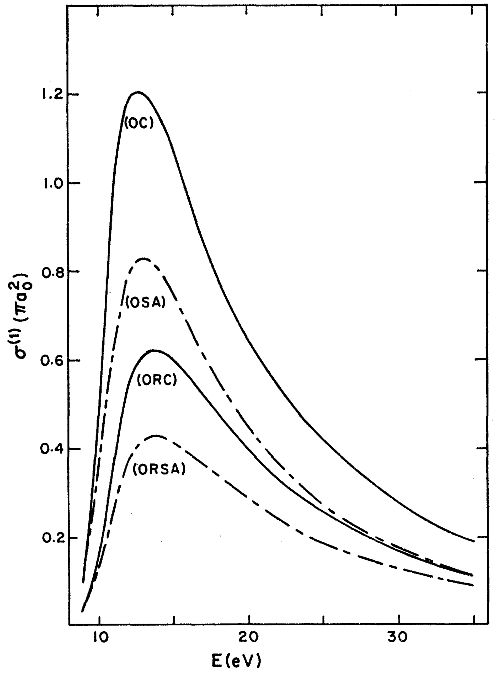

FIG. 6. Energy dependence of excitation cross section to first triplet: OC—Ochkur, complete; OSA—Ochkur, separated atom; ORC—Ochkur Rudge, complete; ORSA—Ochkur Rudge, separated atom.

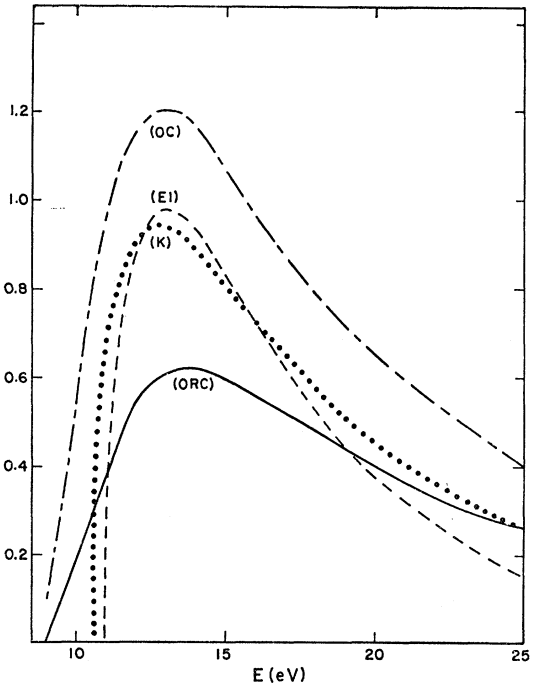

FIG. 7. Energy dependence of excitation cross section to first triplet: ORC—Ochkur Rudge, complete; OC—Ochkur complete; E1—first-order exchange; K—Khare one-center Ochkur.

the normalization constants and scattering amplitude are ignored. For purposes of illustration of the effect of multicenter terms, the following approximations were applied to Eq. (80): The quantity $\langle|T_{v'}^{(1)}\times(R^{(1)}(E_1))|^2\rangle$ was evaluated at $R_e=1.40a_0$ only and the excitation was assumed to occur at only one energy (8.8 eV). From these approximations and the normalization property of $P(E_1)$ [see Eq. (72)] we get

$$\sigma^{(1)}(k_0)\cong\frac{6\pi}{k_0^2}\int_{q_{\min}}^{q_{\max}}\langle|T^{(1)}(R_e)|^2\rangle q\,dq, \qquad (89)$$

where $\langle|T^{(1)}(R_e)|^2\rangle$ can be calculated from Eq. (54). Table IV gives the contribution to the total cross section of the various terms in this equation as obtained in the complete and SA calculations for an incident energy of 14.0 eV. The OR approximation was used along with the Weinbaum and Phillipson-Mulliken wave functions for the ground and excited states. Columns I, II, and III contain the energy-independent constants associated with the molecular (electronic) wave functions. Columns IV, V, and VI show, respectively, the values of each of the three terms in the bracket of Eq. (54) after they have been multiplied by $q$, integrated over $q$, and finally multiplied by $|F|^2/k_0^2$. Column VII is the sum of the three preceding columns and column VIII gives the total cross section (column III times column VII) in units of $\pi a_0^2$. Note that in the SA approximation, the second and third terms in this bracket are zero because they are three-center terms. It is evident from Table IV that application of the SA approximation leads to significant changes in all of the quantities involved in the scattering amplitude, some increasing and some decreasing. These changes are not justifiable on either physical or mathematical grounds, and as a result, the SA approximation should not be relied on to give more than order of magnitude results.

Figure 7 is a comparison of the OC and ORC calculations (using the Weinbaum and Phillipson-Mulliken wave functions) with two other recent calculations of the excitation cross section to the first triplet state. The curve labeled (E1) is the first-order exchange approximation of Khare and Moisiewitsch[9] in which the excitation was assumed to occur for a fixed energy loss of 11.0 eV and at the fixed internuclear distance $R_e=1.404a_0$. This is equivalent to assuming that the ground-state vibrational wave function $R\xi_0^{(0)}(R)$ is a $\delta$ function centered at $R_e$ instead of being given by Eq. (73). This is a drastic assumption at energies close to excitation threshold. In addition, the authors found it necessary to apply the SA approximation in order to evaluate the cross section. The curve labeled K is a recent calculation by Khare[10] in which the O approximation was employed along with the assumption that the excitation occurred at a fixed energy loss of 10.62 eV and at a fixed internuclear distance $R_e=1.40a_0$. To facilitate the evaluation of the integrals, only one-center molecular (electronic) wave functions were used in this last calculation. From Fig. 7, it is apparent that the assumption of fixed energy loss for the incident electrons and fixed internuclear distance predicts a steeper rise of the excitation cross section as a function of energy than either the ORC calculation, the OC calculation, or experiment (see Sec. 6 C).

Figure 8 is a comparison of the total cross section for excitation of the second triplet as calculated in the ORC and ORSA approximations using the three different ground-state wave functions. Included for comparison is the corresponding K cross section calculated by Khare[10] in the O approximation using one-center molecular (electronic) wave functions, a single energy loss (11.7 eV), and single internuclear distance $R_e=1.40a_0$. As can be seen from the figure, the cross sections calculated with the ORSA approximation are smaller and more sensitive to the choice of ground-state wave function than those calculated in the ORC approximation. In this latter calculation, the cross sections obtained from the three ground-state wave functions coincide with the plotting accuracy of Fig. 8. It is difficult to explain the large difference between the K and the ORC results but it is probably due to the use by Khare of the O approximation [which always leads to larger results than the OR one] and of one-center electronic wave functions which are less accurate than the two-center ones employed in the ORC calculations. It is interesting to note that the threshold energy in the K curve was normalized to the approximately correct value of 11.7 eV by using this as the single excitation energy, although the excitation energy consistent with the equilibrium internuclear distance used is 12.55 eV.[24d] This mode of normalization makes the maximum cross section occur at an energy about 1.2 eV lower than the ORC one.

### C. Comparison with Experiment

The only experimental results with which these calculations can be directly compared are the approximate measurements by Corrigan[3] of the total cross section for the electron-impact dissociation of $H_2$ into two H atoms. This experiment essentially measured the sum of the total cross sections for the excitation to all the triplets in molecular hydrogen. These states then decay radiatively to the lowest repulsive triplet ($b^3\Sigma_u^+$), which dissociates into two ground-state H atoms. Since experimental evidence indicates that the magnitude of the total cross sections for electronic excitation to level ($n$) from the ground state falls off very rapidly with increasing $n$,[33] the sum of the total cross sections for excitation of the first two triplets should account for most of this experimentally measured dissociation cross section. There is also a $c^3\Pi_u$ state which lies close in energy to the $a^3\Sigma_g^+$ state. However, we were unable to find a minimum basis set wave function for this state in the literature. Because of its $\Pi$ symmetry, a calculation of this type of wave function and of the corresponding scattering amplitude would have involved an extensive amount of computer time. We decided not to undertake this expense because this state is not expected to contribute much to the dissociation cross section. Its total excitation cross section is expected to be smaller than that for the $a^3\Sigma_g^+$ state in view of its different symmetry.[4,33] This behavior is indicated by the one-center calculations of Khare,[10] which show the cross section for excitation to the $c^3\Pi_u$ state to be about 60% of that to the $a^3\Sigma_g^+$ state. Because of the relative smallness of the former cross section, the error in the total dissociation cross section due to the neglect of the contribution from the $c^3\Pi_u$ state should not exceed 5%.

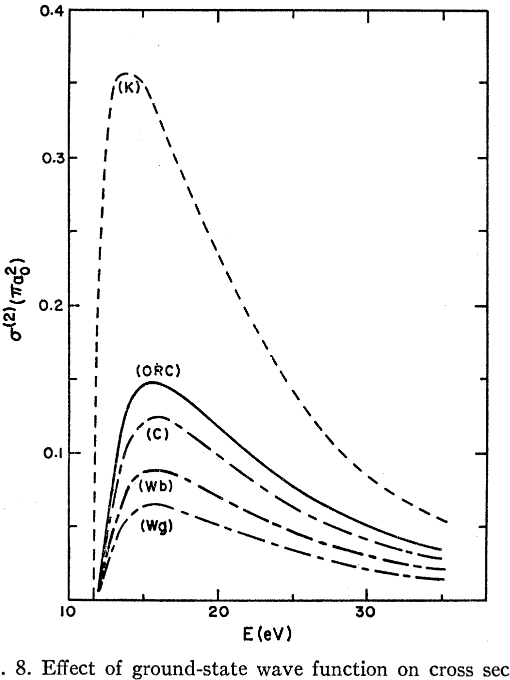

FIG. 8. Effect of ground-state wave function on cross section for excitation to second triplet state, for OR, complete and separated atom approximations: ----- separated atom SA: C—Coulson; Wb— Weinbaum; Wg—Wang; —— complete (curves corresponding to the three different ground-state wave functions coincide within plotting accuracy); ---- K, Khare one-center Ochkur.

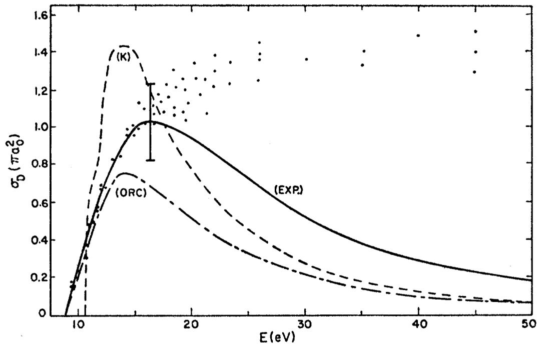

FIG. 9. Dissociation cross section of $H_2$ into 2H by electron impact. The points are experimental but include the effect of ionization (see Ref. 3). —— (Exp.), experimental curve (Ref. 3) after subtraction of molecular ionization cross section; ---- (ORC), present calculations of the sum of excitation cross sections to first two triplet states (using Weinbaum ground state), including effect of variation of excitation energy; ---- (K) Khare's one-center Ochkur dissociation cross section (see Ref. 10).

Figure 9 is a comparison of the experimental data (full curve) and the sum of the theoretical cross sections for the excitation to the first and second triplets (dash-dot curve) as calculated by us in the complete OR approximation, with the methods described above, and using the best (Weinbaum) ground-state wave function. The theory is seen to predict quite well the linear rise above threshold and the magnitude and general shape of the measured dissociation cross section. Although there actually exists a sudden change in slope of the theoretical curve at the onset of the second triplet excitation (~11.9 eV), this change is negligible within plotting accuracy of the figure and thus cannot be seen in the ORC curve. The discrepancy between the predicted and observed location (in energy) of the maximum of the cross section is perhaps due in part to the scatter in the experimental points (which are the dots shown in Fig. 9 before the effect of molecular ionization is subtracted), which is particularly bad for energies above 13 eV. In addition, neglect of the contribution of the $c^3\Pi_u$ to the cross section tends to make the theoretical maximum shift slightly towards lower energies. It is encouraging (but perhaps fortuitous) that the best agreement between the present ORC

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[33] A. H. Gabriel and D. W. O. Heddle, Proc. Phys. Soc. (London) **A258**, 124 (1960).

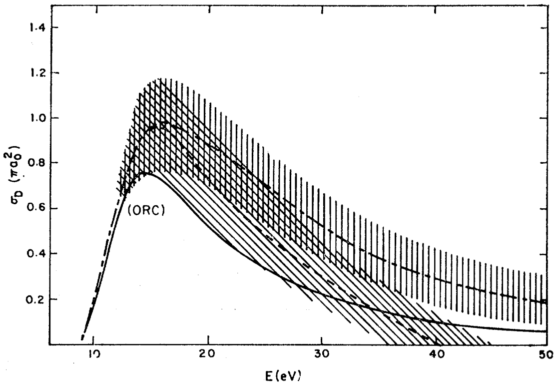

FIG. 10. Dissociation cross section of $H_2$ into 2H by electron impact. —— (ORC), present calculations (same as in Fig. 9); - - - - -, Corrigan data as modified by using ionization cross section of Golden and Rapp (Ref. 36); - - - - -, Corrigan data as modified using ionization data of Harrison (Ref. 37). The shading along the two experimental curves indicates the spread in experimental data as reported by Corrigan (Ref. 3).

calculations and experiment occurs in the energy region between threshold and maximum cross section, where the experimental points have highest accuracy.

Included in Fig. 9 is the dissociation cross-section curve reported by Khare,[10] in which his calculations for the cross sections for excitation of the $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, and $c^3\Pi_u$ states are added together. The high threshold energy and excessively steep rise between the threshold and maximum of this curve is due to the assumption that the excitation of each state occurs only at the most probable value of the internuclear distance (the equilibrium internuclear distance of the ground electronic state).

The ionization cross-section curve used by Corrigan to subtract the effect of ionization on his experimental results was that obtained in 1932 by Tate and Smith.[34] More recent measurements[35–37] furnish somewhat larger values for that ionization cross section, which would reduce the dissociation cross section of Corrigan and decrease the discrepancy between it and the ORC calculations at energies above 16 eV. In Fig. 10 are illustrated two dissociation cross sections obtained by modifying the Corrigan curve using the more recent experimental ionization data of Golden and Rapp,[36] and of Harrison.[37] The modification is a simple subtraction from the Corrigan curve of the difference between the more current data and that of Tate and Smith. The upper dash-dot curve represents the dissociation cross section obtained by modification with the Golden-Rapp[36] ionization cross section. The shaded area along this curve indicates the error in the experiment as determined by the spread in data points reported by Corrigan.[3] The lower dashed curve is the similar dissociation cross section obtained from the Corrigan and Harrison[36] data, with the experimental error in the former again denoted by the shading. It is apparent from this figure that more accurate measurements of the dissociation cross section are necessary before the quality of this exchange excitation model can be evaluated more precisely.

Finally, it should be stressed that all the calculations we made are completely *ab initio* and absolute, with no experimental parameters having been used and no normalization to experiment having been performed.

### D. Conclusions

The total cross section obtained in the OR model for exchange excitation appears to describe the dissociation excitation of the hydrogen molecule better than any other currently tractable model. When proper allowance for nuclear motion (vibration) is made, the results agree quite well with the experimental data in the threshold-to-maximum region. When the excitation is assumed to occur only at the equilibrium internuclear distance of the ground electronic state, an excessively high threshold energy results as well as too steep an increase in the cross section between this threshold and the energy of maximum cross section.

It is apparent from the results of these calculations that care should be exercised in the choice of the wave functions used to describe the bound system. In some cases the excitation cross sections for a molecular electronic excitation process may be quite sensitive to the "quality" of the wave functions used and in other cases not. It appears that the degree of this sensitivity on molecular (electronic) wave functions depends on the symmetries of the molecular states involved. The results of this investigation suggest that along with the energy, other properties such as moments of the one-electron charge density predicted by the approximate wave functions should be used to determine the "best" over-all approximate wave function.

In addition, it is evident from the calculations here reported that the SA approximation to the transition amplitude should be used with caution, since the cross sections predicted by it may differ by 30% from the more accurate results.

The results reported in this paper and elsewhere[4,6] show that the OR approximation describes reasonably well the exchange excitation processes and indicates that more accurate experiments are now needed in order to make a complete evaluation of this model.

## ACKNOWLEDGMENTS

The authors would like to thank Professor W. A. Goddard and Professor R. M. Pitzer of the California Institute of Technology for many interesting and helpful discussions concerning various aspects of these calculations and for supplying them with some useful computer programs.

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