99, 1287 (1955).

[12] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford U. P., London 1965), p. 802.

[13] From Ref. 2, Fig. 1 (b): The data labeled Ne^+-Ne included Ne^{++}-Ne data also. According to Lichten (Ref. 8) only one Auger electron can be produced by a Ne^+-Ne collision. This being true, it was incorrect to calculate α for Ne^+-Ne collision using the same formula as was appropriate for the Ar^+-Ar Collisions. The correct maximum probability for such an excitation is approximately 10% if one assumes that only one vacancy per Ne^+-Ne collision is possible.

[14] R. J. Fortner, B. P. Curry, R. C. Der, T. M. Kavanagh, and J. M. Kahn, Phys. Rev. 185, 164 (1969).

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Total Cross Sections for the Excitation of the Triplet States in Molecular Nitrogen*

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A consistent set of total cross sections for electron impact excitation of the $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, $W\,^3\Delta_u$, $B'\,^3\Sigma_u^-$, $C\,^3\Pi_u$, $E\,^3\Sigma_g^+$, and $D\,^3\Sigma_u^+$ triplet states of molecular nitrogen from the $X\,^1\Sigma_g^+$ state has been calculated quantum mechanically for incident electron energies from threshold to 80 eV. The Ochkur-Rudge exchange scattering and Franck-Condon approximations were employed to obtain these cross sections. Minimum and double-minimum basis-set LCAO-MO wave functions centered on the nuclei were used, and the multicenter terms in the scattering amplitude were evaluated using a ζ-function expansion. Rotationally averaged cross sections were calculated for excitation from $v''=0$ to individual v' levels of the excited electronic states. The calculated total cross section for excitation of the $B\,^3\Pi_g$ state is in good agreement with that deduced from recent experimental data for the process. The cross section for excitation of the $C\,^3\Pi_u$ state agrees well with one pair of experimental measurements and is a factor of 2 larger than another pair of measurements and about a factor of 4 larger than a fifth experimental determination and the previous calculations. The calculated cross section for excitation of the $A\,^3\Sigma_u^+$ state is a good deal larger than previous theoretical and experimental estimates. However, a comparison with recent experimental differential cross-section data indicates that the theoretical $A\,^3\Sigma_u^+$ total cross section is correct for incident energies greater than about 35 eV. The relative magnitude of these excitation cross sections leads to interesting predictions concerning N_2 processes in the upper atmosphere.

I. INTRODUCTION

In any detailed study of phenomena involving charged particles and gaseous molecular nitrogen, it is necessary to have reliable cross sections for the various excitation processes of molecular nitrogen by electrons. In addition to the central role these inelastic processes play in atmospheric physics,[1,2] these same collision processes are, for instance, important in explaining the operation of the recently developed molecular nitrogen-gas laser.[3] However, there has been no consistent set of cross sections for excitation of the individual electronic states previously reported, experimental or theoretical, and the sets of cross sections which have been employed to describe the effect of electron collisions in gaseous N_2 have generally been incomplete and, in some cases, inaccurate.

In this paper, total cross sections for the electron impact excitation of the seven lowest triplet states of molecular nitrogen from the lowest vibrational level of the ground electronic state are reported.[4] The calculations were done in the framework of a modified first-order perturbation approximation (Ochkur-Rudge) which has been successful in describing similar processes in molecular hydrogen. The calculated cross section for excitation of the $B\,^3\Pi_g$ state agrees well with that implied by recent data on the excitation of the second positive system by electron impact. The calculated excitation cross section for the $C\,^3\Pi_u$ state agrees well with two experimental determinations but is larger than another set of measurements for the same process. The cross sections for excitation to the $W^3\Delta_u$, $E^3\Sigma_g^+$, and $D^3\Sigma_u^+$ states, for which few or no data exist, are found to be large enough to play an important role in the population of the lower electronic states in the triplet system of N_2.

In Sec. II a brief discussion is given of the derivation of the first-order portion of the exchange amplitude from the many-body scattering formalism. The bound-state wave functions and the numerical techniques used are presented in Secs. III and IV, respectively. Section V contains the comparison of the calculated cross sections with the available experimental and other theoretical results and a discussion of the quality of the calculated cross sections.

II. THEORY

In describing the scattering of a free electron by a particle composed of N_0 electrons, it is essential that the $(N=N_0+1)$-particle system be properly antisymmetrized in accordance with the Pauli principle. In doing so, it is convenient to write the time-independent unsymmetrized initial state (χ_a) in terms of the electron space-spin variables as (suppressing for the moment any other degrees of freedom)

$$\chi_a(\xi_0\xi_1\cdots\xi_{N_0})=\zeta_{S1}(\xi_0)\Psi_{S2}(\xi_1\cdots\xi_{N_0}) , \quad (1)$$

where $S1$ and $S2$ denote the quantum state of the incident and target particle, respectively, including spin. The function Ψ_{S2}, denoting the target particle, is assumed to be the correctly antisymmetrized solution of the N_0-electron problem, and ζ_{S1} is the free-electron wave function. The complete antisymmetrized wave function for the (N_0+1)-electron system is then given by[5]

$$\mathcal{A}(a)\equiv\mathcal{A}\chi_a=[(N_0+1)^{1/2}/(N_0+1)!]\times\sum_Q\epsilon_Q\hat{Q}\zeta_{S1}(\xi_0)\Psi_{S2}(\xi_1\cdots\xi_{N_0}) , \quad (2)$$

where $\hat{Q}$ is one of the $N!$ permutations of the N particles and ϵ_Q is the parity of the permutation. When the number of identical particles (N) is the same in both the incident and final channels, the T matrix for the collision process can be written as[5]

$$\langle\mathcal{A}(b)|\mathcal{T}|\mathcal{A}(a)\rangle=(1/N_0!)\sum_Q\epsilon_Q\langle\hat{Q}\chi_b|\mathcal{T}|\chi_a\rangle , \quad (3)$$

where the symbol $\mathcal{A}(b)$ denotes the antisymmetrized N-particle final state and $\mathcal{T}$ is the transition operator for the process. If the additional restriction is made that the final channel also contains N_0 bound electrons and one free electron, the unsymmetrized final-channel wave function can be taken to have the same form as the initial channel:

$$\chi_b=\zeta_{S'1}(\xi_0)\Psi_{S'2}(\xi_1\cdots\xi_{N_0}) . \quad (4)$$

When Eq. (4) is inserted into Eq. (3) and use is made of the fact that $\Psi_{S'2}$ is antisymmetric with respect to its N_0 particles, Eq. (3) can be rewritten in the form

$$\langle\mathcal{A}(b)|\mathcal{T}|\mathcal{A}(a)\rangle=\langle\chi_b|\mathcal{T}|\chi_a\rangle-\sum_{\lambda=1}^{N_0}\langle\hat{Q}_{0\lambda}\chi_b|\mathcal{T}|\chi_a\rangle . \quad (5)$$

In Eq. (5) the symbol $\hat{Q}_{0\lambda}$ denotes interchange of the incident electron and the jth bound electron.

A. Pure Exchange Excitation

The first term in Eq. (5) represents the contribution due to direct scattering and the second term that due to exchange scattering. In the remainder of the discussion, only the exchange amplitude will be discussed since the processes of interest here are pure exchange in character.

In the above treatment, the bound-state wave functions are assumed to be known, and in the general case the free-electron wave functions (ζ) are determined in terms of these known functions. General expressions for the free-electron wave functions can be written in terms of the N_0-electron wave functions by using properties of the symmetric group (tableaux) for N_0+1 electrons.[6] This method of dealing with the (N_0+1)-particle system ensures that the solutions obtained are correct eigenfunctions of the total spin and z component of the spin for the (N_0+1)-electron system. The practical extension of these techniques based on the symmetric group to the case where $(N_0+1)>3$ is made possible by observing that many cases of interest can be reduced to that corresponding to $(N_0+1)=2-5$ electrons by using the properties of closed orthogonal shells. Thus for the processes of interest here in the (e, N_2) system, the 15-electron problem can be reduced to either a three- or a five-electron problem, depending on the particular excitation process. However the close-coupling and distorted-wave methods, which arise naturally from the formulation using the symmetric group, were considered to be too complicated to be used for this study of the exchange excitation of N_2 because of the mathematical difficulties associated with the lack of spherical symmetry in the N_2 molecule. Consequently, a modified first-order description of the exchange excitation process was used in these calculations in which the distortion of the free-electron wave function by the bound system is neglected. The spin variables in Eq. (5) can be treated as follows.

Since the interactions producing the exchange excitation are taken to be independent of spin and only the lowest-order term in the exchange transition amplitude is to be treated, the integration over spin variables can be performed in a number of equivalent ways. One may reduce the general expressions for the N-electron problem derived from the symmetric group to those terms of lowest order in the exchange interaction. The correct factors from the spin integration then appear as coefficients of these first-order terms, expressed as functions of the tableaux shape.[6] As a good approximation, one may also assume that the complete wave function for both the target and the incident electron can be explicitly factored into a product of two terms, one involving only spatial variables, and the other the spin eigenfunction of the particle. Then since channel spin[7] is conserved, the spin integration can be performed with the aid of vector-coupling techniques and without having to manipulate explicit spin wave functions. This is particularly straightforward when the initial spin state of the bound state is a singlet, for then the incident-channel spin state $|S, S_z\rangle$, in terms of the two-particle spin states $|s, s_z\rangle_i$, $i = b$ or e, is

$$|\tfrac{1}{2}\tfrac{1}{2}\rangle_{\text{initial}} = |00\rangle_b |\tfrac{1}{2}\tfrac{1}{2}\rangle_e . \tag{6}$$

In Eq. (6) the subscripts b and e denote, respectively, the bound- and free-particle spin states and the incident-particle beam has been assumed, for the moment, to be polarized. When the final spin state of the bound particle is a triplet, the final-channel spin state, in terms of the target and free-particle spin states, is

$$|\tfrac{1}{2}\tfrac{1}{2}\rangle_{\text{final}} = \sqrt{\tfrac{2}{3}}\, |11\rangle_b |\tfrac{1}{2}\, -\tfrac{1}{2}\rangle_e - (1/\sqrt{3})|10\rangle_b |\tfrac{1}{2}\tfrac{1}{2}\rangle_e . \tag{7}$$

From the conservation of channel spin, the orthonormality of the free-particle spin states, and the normalization of the channel spin state, the inner product of the initial- and final-channel spin states given by Eqs. (6) and (7) reduces to

$$\langle\tfrac{1}{2}\tfrac{1}{2}|\tfrac{1}{2}\tfrac{1}{2}\rangle_e \langle 10|00\rangle_b = -\sqrt{3} , \tag{8}$$

which is the result of the spin integration for a singlet-triplet transition. The first-order T matrix for the exchange-excitation process, in terms of spatial variables only, now follows directly from Eqs. (5) and (8) as

$$\begin{aligned} \mathcal{T}_{ex}^{(1)} &= -\sum_{\lambda=1}^{N_0} \langle \hat{Q}_{0\lambda}\chi_b | \mathcal{T}^{(1)} | \chi_a \rangle \\ &= \sqrt{3} \sum_{\lambda=1}^{N_0} \langle \hat{Q}_{0\lambda} \Phi_f(\vec{r}_0) \Psi_f(\vec{r}_1 \cdots \vec{r}_{N_0}) | \mathcal{T}^{(1)} | \Phi_i(\vec{r}_0) \\ &\quad \times \Psi_i(\vec{r}_1 \cdots \vec{r}_{N_0}) \rangle , \end{aligned} \tag{9}$$

where the permutation $\hat{Q}_{0\lambda}$ now involves only the spatial variables and the superscript (1) means only the first-order term in the exchange interaction is retained. In Eq. (9), Φ and Ψ are used to denote the spatial portions of the free- (plane-wave) and bound-particle wave functions, and the subscripts i and f denote initial and final states, respectively. As a third equivalent procedure for treatment of the spin variables, one may form the differential cross section in terms of the spatial portions of the transition amplitude and merely sum this cross section over the spin projections of the final bound particle (triplet) and average over the initial spin projections of the bound particle.[7] One then obtains a cross section which is proportional to the square of (9). The normal experimental situation of an unpolarized beam yields the same result as given in Eq. (9) since the two possible free-electron spin states are weighted equally.[7]

The complete $\mathcal{T}$ operator for the (e, N_2) system is[5]

$$\mathcal{T} = V + V_{\hat{Q}_{0\lambda}} [1/(E - i\eta - H)]\, V , \tag{10}$$

where H and E, respectively, are the Hamiltonian and total energy of the system and V is (in a.u.)

$$V = -\frac{7}{r_{A0}} - \frac{7}{r_{B0}} + \sum_{i=1}^{14} \frac{1}{|\vec{r}_i - \vec{r}_0|} . \tag{11}$$

The subscripts A and B, i, and 0 in Eq. (11) refer, respectively, to the two nuclei, the ith bound electron, and the incident electron. The first-order transition amplitude is obtained by the substitution $\mathcal{T}^{(1)} = V$ in Eq. (9).

B. Ochkur-Rudge Modification

The Born-Oppenheimer (BO) scattering amplitude as given in Eq. (9) possesses well-known difficulties[8] in describing the scattering process for low-energy electrons. Modifications of the

BO amplitude by Ochkur[9] and Rudge[10] have removed the major difficulties while still maintaining the first-order simplicity. The Ochkur-Rudge (OR) approximation to the exchange amplitude has been shown to predict reliable total cross sections for exchange-scattering processes involving H_2,[11] He, and H,[12] and therefore has been used with some confidence in this study of the (e, N_2) system. The OR approximation is obtained as follows. The nuclear and electronic motion are separated by writing the bound-state wave function as

$$\Psi_i \equiv \Psi_{n''v''J''M''} = \psi_i(\vec{r}_1 \cdots \vec{r}_{N_0};\, R) \times \xi_{n''v''}(R)\, Y_{J''M''}(\Theta,\, \phi)\ ,$$

$$\Psi_f \equiv \Psi_{n'v'J'M'} = \psi_f(\vec{r}_1 \cdots \vec{r}_{N_0};\, R) \times \xi_{n'v'}(R)\, Y_{J'M'}(\Theta,\, \phi)\ , \tag{12}$$

where n, v, (J, M); ψ, ξ, Y are, respectively, the electronic, vibrational, and rotational quantum numbers, and the corresponding wave functions of the molecule. The symbols $\vec{r}_i$ and $R = (R, \Theta, \phi)$ denote, respectively, the ith electronic and the nuclear coordinates with respect to a space-fixed coordinate system. Equation (9) can be written using Eqs. (12) and $\mathcal{T}^{(1)} = V$ as

$$\mathcal{T}^{(1)}_{\epsilon x} = \langle \xi_{n'v'}\, Y_{J'M'} \,|\, T_{fi} \,|\, \xi_{n''v''}\, Y_{J''M''} \rangle\ , \tag{13}$$

where T_{fi}, the electronic portion of the transition amplitude, is given by

$$T_{fi} \equiv \sqrt{3} \sum_{\lambda=1}^{N_0} \langle Q_{0\lambda}\, \Phi_f(\vec{r}_0)\, \psi_f(\vec{r}_1 \cdots \vec{r}_{N_0}) \,|\, V \,|\, \Phi_i(\vec{r}_0) \times \psi_i(\vec{r}_1 \cdots \vec{r}_{N_0}) \rangle\ . \tag{14}$$

The integration in Eq. (13) is over nuclear coordinates while that in Eq. (14) is over electronic coordinates for fixed nuclei. Omitting the details of the derivation,[9,10] the OR modification of Eq. (14) generalized to N_0 bound electron is

$$T^{\mathrm{OR}}_{fi} = -\sqrt{3} \sum_{\lambda=1}^{N_0} \langle \psi_f(\vec{r}_1 \cdots \vec{r}_{N_0}) \,|\, 4\pi e^{i\vec{q}\cdot\vec{r}_\lambda} \times (k' - iI_{n''}{}^{1/2})^{-2} \,|\, \psi_i(\vec{r}_1 \cdots \vec{r}_{N_0}) \rangle\ , \tag{15}$$

where the wave number k' is related to the incident electron energy k_0^2 and the energy difference between the molecular states by

$$k' = [\, k_0^2 - 2(E_f - E_i)\,]^{1/2}\ , \tag{16}$$

and E_i (E_f) denotes the energy of the initial (final) molecular state. The quantities q and $I_{n''}$ are, respectively, the magnitude of the momentum transfer defined as $\vec{q} \equiv \vec{k}_0 - \vec{k}'$ and the ionization energy of the initial state in Ry. The subscript λ in Eq. (15) denotes the electron with which the exchange takes place and the summation runs over all N_0 bound electrons.

Additional simplifications of Eq. (15) can be made when specific configurations are chosen for the initial electronic states and their respective electronic wave functions are expressed as single Slater determinants. Then if the orbitals used for the initial and final electronic states, customarily obtained by energy minimization, are transformed by unitary transformations such that the overlap matrix between the two sets of orbitals used in the wave functions is diagonal,[13] Eq. (15) reduces to

$$T^{\mathrm{OR}}_{fi} = -\sqrt{3}\ 4\pi (k' - iI_{l''}{}^{1/2})^{-2} \times \langle \varphi_{l'}(\vec{r}) \,|\, e^{i\vec{q}\cdot\vec{r}} \,|\, \varphi_{l''}(\vec{r}) \rangle D^{1/2}_{l'l''}\ . \tag{17}$$

The symbol $\varphi_{l''}$ ($\varphi_{l'}$) has been used to denote the initial (final) nondegenerate "corresponding orbital"[13] involved in the excitation process for the chosen pair of configurations, and $I_{n''}$ has been replaced by the theoretical orbital eigenvalue of the $\varphi_{l''}$ orbital, denoted as $I_{l''}$. The multiplicative factor $D^{1/2}_{l'l''}$ results from the diagonalization of the overlap matrix between the initial and final electronic states.[13] In writing Eq. (17), the additional phase factors of the electronic transition amplitude introduced by the unitary transformation of the orbitals have been omitted since they are not important for a pure-exchange process. It should be noted that the simplification of the summation in Eq. (15) to the single term in Eq. (17) is a result of the orthogonality of the "corresponding orbitals," the choice of specific single configurations for the initial and final electronic states, and the fact that the transition operator ($e^{i\vec{q}\cdot\vec{r}}$) is a single-particle operator. This simplification is the usual Slater-Condon rule except for the factor $D^{1/2}_{l'l''}$ and the fact that the orbitals $\varphi_{l''}$ and $\varphi_{l'}$ are "corresponding" orbitals. These two modifications are necessary whenever the molecular orbital (MO) sets used to describe the ground and excited electronic states are nonorthogonal. The extension to multiconfigurational wave functions can be made without difficulty.

C. Rotationally Averaged Cross Sections

The differential cross section (in units of πa_0^2) for the excitation process I_i^f is related to the transition amplitude Eq. (13) by[5]

$$I_i^f(k_0,\theta,\varphi)=\frac{1}{4\pi^3}\frac{k'}{k_0}\left|\mathcal{T}_{\text{ex}}^{(1)}(T_{fi})\right|^2 , \tag{18}$$

with T_{fi} as given in Eq. (14). Since transitions between specific rotational levels are not of interest here and because under most experimental conditions the energy resolution is not sufficient to resolve the specific ΔJ transitions, Eq. (18) is summed over final rotational states and averaged over the $2J''+1$ degenerate initial states. The differential cross section can be written in the OR approximation as[11]

$$I_{n''v''}^{n'v''}(k_0,\theta,\varphi)=(1/4\pi^3)(k''/k_0)| \times\langle\xi_{n'v'}|T_{n''v''}^{n'v'}|\xi_{n''v''}\rangle|^2_{\text{av}} , \tag{19}$$

where $k''\equiv[k_0^2-2(E_{n'v'}-E_{n''v''})]^{1/2}$ and $T_{n''v''}^{n'v'}\equiv T_{fi}^{\text{OR}}(k'')$ are both now independent of the rotational quantum numbers. The subscript "av" in Eq. (19) is used to indicate that the square of the transition amplitude is averaged over all orientations of the molecular axis with respect to the incident electron beam ($\vec{k}_0$).

For certain of the transitions of interest here, the final electronic state is degenerate [in the approximation of Eq (12)] because of Λ doubling. The wave function used to describe such a state is usually taken as a single configuration corresponding to one of the two degenerate Λ states. Since the totality of all rotational transitions is considered, the possibility of the Λ degeneracy can be accounted for by multiplying Eq. (19) by a factor equal to the Λ degeneracy of the final state:

$$\omega_f=2-\delta_{0,\Lambda} ,$$

where δ is the Kronecker δ and Λ the projection of the total electronic orbital angular momentum on the internuclear axis. Equation (19) then becomes

$$I_i^f(k_0,\theta,\varphi)=(1/4\pi^3)(k''/k_0)\omega_f| \times\langle\xi_{n'v'}|T_{n''v'}^{n'v'}|\xi_{n''v''}\rangle|^2_{\text{av}} . \tag{20}$$

It should be pointed out that no additional factor need be introduced for the case of the four equivalent π_u electrons in the ground state. This equivalence, and any similar equivalence in the excited states, is accounted for when the symmetry of the final state is specified.

Two useful approximations which can be applied to Eq. (20) will now be discussed.

1. *R-Centroid Approximation*

This approximation consists of replacing

$$\langle\xi_{n'v'}|T_{n''v''}^{n'v'}(R)|\xi_{n''v''}\rangle \text{by } T_{n''v''}^{n'v'}(\bar{R}_{v'v''})$$

$$\langle\xi_{n'v'}|\xi_{n''v''}\rangle ,$$

where $\bar{R}_{v'v''}$ is called the R centroid[14] of the (v',v'') transition and is defined by

$$\bar{R}_{v'v''}=\langle\xi_{n'v'}|R|\xi_{n''v''}\rangle .$$

Equation (20) then reduces to

$$I_{n''v''}^{n'v'}(k_0,\theta,\varphi)=(1/4\pi^3)(k''/k_0)\omega_f \times|T_{n''v''}^{n'v'}(k_0,\theta,\varphi;\bar{R}_{v'v''})|^2_{\text{av}}q_{v'v''} , \tag{21}$$

where $q_{v'v''}$, called the Franck-Condon factor, is defined by $q_{v'v''}=\langle\xi_{n'v'}|\xi_{n''v''}\rangle$. This R-centroid approximation has been quite useful in the analysis of molecular spectra, but has recently been criticized[15] as to its validity for certain molecular transitions, and, in particular, for transitions in N_2. It would have been interesting to test this approximation for the transitions of interest here, but unfortunately not enough molecular information is known. That is, while the R centroids and Franck-Condon factors are readily available, the necessary excited-state wave functions optimized at various values of the internuclear distance have not yet been published. Consequently, the R-centroid approximation could not be applied in this work.

2. *Frank-Condon Approximation*

The Franck-Condon approximation[14] is based on the assumption that the electronic transition amplitude Eq. (14) is a slowly varying function of the internuclear distance over the normal range of the variable and consequently can be replaced by a constant $T_{n''v''}^{n'v'}(R_e)$ in the integration over R. Equation (20) then takes the form

$$I_{n''v''}^{n'v'}(k_0,\theta,\varphi)=(1/4\pi^3)(k''/k_0)\omega_f \times|T_{n''v''}^{n'v'}(k_0,\theta,\varphi;R_e)|^2_{\text{av}}q_{v'v''} . \tag{22}$$

Except for those transitions from $v''=0$ or to $v'=0$, the choice of R_e is not obvious, and as might be expected, the Franck-Condon approximation is not always reliable for all (v',v'') transitions. However, for processes originating from $v''=0$, the Franck-Condon approximation has been shown to be quite good[16] (in most cases accurate to within 10%). This result is due to the fact that the initial vibrational wave function ($\xi_{n'',v''}=0$) is Gaussian in character, centered at the R_e of the initial electronic state, and consequently the major contribution to $\mathcal{T}_{ex}^{(1)}$, Eq. (13), must occur at this same R_e. Since the processes of interest in this study originate from $v''=0$, the Franck-Condon approximation has been employed and is expected to be a reliable approximation to the more complicated expression, Eq. (20).

The total cross section for the transition $n'v' \leftarrow n''v''$ is obtained from the differential cross section by

$$\sigma_{n''v''}^{n'v'}(k_0)=\int I_{n''v''}^{n'v'}(k_0,\theta,\varphi)\,d\Omega_{\theta,\varphi} \;. \tag{23}$$

A useful quantity in many applications is the total cross section for excitation of a particular electronic state ($\sigma_{n''v''}^{n'}$) and is obtained from Eq. (23) by summing over all v' values as

$$\sigma_{n''v''}^{n'}(k_0)=\sum_{v'}\sigma_{n''v''}^{n'v'} \;. \tag{24}$$

III. WAVE FUNCTIONS

There have been a number of accurate, extended and/or fully optimized basis-set calculations reported for the $X\,^1\Sigma_g^+$ state of N_2.[17] However, these results did not include wave functions for the various excited states of N_2 of interest in this work. In addition, the programs employed in the present calculations for the evaluation of the multicenter terms which appear in the transition amplitude were not able to include atomic orbitals with principal quantum numbers $\geqq 3$. Consequently, an elaborate ground-state wave function could not be used, and to be consistent the present calculations were limited whenever possible to wave functions for the ground and excited states which were formed from atomic orbitals with principal quantum number equal to 1 and 2.

In Table I are given the electronic configurations of the ground and excited states of interest, in order of increasing energy above the ground electronic state. The occupancy of each molecular orbital (MO) is indicated by + and − symbols appropriate to the z component of the electron spin. The symbol $Q_{m\lambda}$ denotes the mth Rydberg orbital of symmetry λ which gives the proper state symmetry when combined with the N_2^+ electronic core.

TABLE I. Electronic configurations of the ground and excited triplet states of molecular nitrogen.[a]

	$(1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2)$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$	$1\bar{\pi}_u$	$1\pi_g$	$1\bar{\pi}_g$	$\cdots$	$Q_{m\lambda}$
$X\,^1\Sigma_g^+$		+ −	+ −	+ −	+ −				
$A\,^3\Sigma_u^+$		+ −	+ −	+ −	+		+		
$B\,^3\Pi_g$		+ −	+	+ −	+ −	+			
$W\,^3\Delta_u$		+ −	+ −	+ −	+	+			
$B'\,^3\Sigma_u^-$		+ −	+ −	+ −	+		+		
$C\,^3\Pi_u$		+	+ −	+ −	+ −	+			
$E\,^3\Sigma_g^+$		+ −	+	+ −	+ −				+
$D\,^3\Sigma_u^+$		+ −	+	+ −	+ −				+

[a] Occupancy of each MO is indicated by giving the spin projection of each electron in the MO.

For $B\,^3\Pi_g$ and $C\,^3\Pi_u$ electronic states, the self-consistent-field (SCF)–MO set of wave functions constructed from minimum-basis-set Slater-type atomic orbitals by Sahni and De Lorenzo[18] (SDL) were used. Since the B and C excited states are open-shell states, the wave functions for these states were determined within the framework of a "restricted" SCF treatment[18] in order to issue a pure spin state. The resulting wave functions used were in the form of single Slater determinants in which the spin degrees of freedom in the calculation of the transition amplitude were treated separately as outlined in Sec. II. In the SDL wave functions, the values used for the screening constants were those given by Slater's rules,[19] and all the wave functions were calculated at one internuclear distance – that of the ground electronic state. A detailed discussion of the symmetry structure of the N_2 MO's can be found in work of Scherr.[19] For the excitation of the B and C state, the wave function used for the $X\,^1\Sigma_g^+$ ground electronic state was the exponent-optimized minimum-basis wave function of Ransil[20] constructed of orthogonal atomic orbitals (AO's).

For excitation of the $A\,^3\Sigma_u^+$ and $W\,^3\Delta_u$[21] states from the $X\,^1\Sigma_g^+$ ground state, the double minimum-basis-set SCF-MO wave functions of Richardson[22] were used. Richardson's calculations are similar to those carried out by SDL except that the number of basis functions centered on each nucleus was doubled. The screening constants employed in the Richardson wave functions were determined from calculations on the N atom for the $1s$ atomic orbital and by a slight modification of the customary Slater rules for the $2s$ and $2p$ atomic orbitals. As for the SDL and Ransil wave functions, the calculations were done only at the equilibrium internuclear separation of the $X\,^1\Sigma_g^+$ state. Based on the energy criteria for the quality of a wave function, the Richardson results should be as good as any single-ζ set of wave functions in which the screening constants were independently optimized.[22]

SDL[18] also reported wave functions for the $X\,^1\Sigma_g^+$ ground and $A\,^3\Sigma_u^+$ excited state, so the effect of improved wave functions on the calculated cross section could be determined in this case by comparing the excitation cross section to the $A\,^3\Sigma_u^+$ state obtained from the SDL set with that obtained using the Richardson double-ζ wave functions. The results obtained from this comparison are discussed in Sec. V.

TABLE II. Screening constant (z) and coefficients of the primitive-symmetry orbitals for the Rydberg MO's of the $E\,^3\Sigma_g^+$ and $D\,^3\Sigma_u^+$ states of N_2 (Ref. 23). The E- and D-state MO's are abbreviated g and u, respectively.

MO	$1s\sigma$	$2s\sigma$	$3s\sigma$	$4s\sigma$	$2p\sigma$	$3p\sigma$	$4p\sigma$	$3d\sigma$	$4d\sigma$
z	6.70	1.95	0.70	0.35	1.95	0.70	0.35	0.70	0.35
g	−0.057 70	0.315 661	−0.557 553	−0.075 635	−0.181 345	−0.074 023	−1.342 060	0.125 241	−0.153 941
u	−0.046 697	0.276 244	−0.282 549	5.434 09	−0.029 711	0.184 171	0.684 517	−0.048 868	0.173 989

For excitation to the two Rydberg states $E\,^3\Sigma_g^+$ and $D\,^3\Sigma_u^+$ the wave functions calculated by Lefebvre-Brion and Moser[23] (LBM) were used. The E and D Rydberg states converge to the $X\,^2\Sigma_g^+$ state of N_2^+ and were represented by a single configuration in which the core was assumed to be the same for all the Rydberg states. The screening constants for the orbitals were chosen by Slater's rules, and the calculations were carried out at the internuclear separation of the $X\,^1\Sigma_g^+$ state of N_2. The coefficients of each Rydberg orbital were found by minimizing the energy of the Rydberg orbital in the field of the fixed core. Of the three nearly equivalent wave functions reported by LBM for each Rydberg state, the wave function corresponding to set B was used in these calculations to describe the E and D Rydberg states. The coefficients and screening constants of the atomic orbitals comprizing the Rydberg MO's for these two states are given in Table II.

In the calculation of the transition amplitudes, the quantity $(I_{l''})$ in Eq. (17) was taken to be the orbital eigenvalue energy of the $\varphi_{l''}$ orbital as calculated for the particular ground-state wave function employed.

As discussed in Sec. II, the simplification of Eq. (15) to the form of Eq. (17) requires orthonormality between the orbital sets used to construct the initial and final electronic states. Since the MO sets of SDL, Ransil, and Richardson were not published in the required orthogonal form, it was necessary to transform certain of the MO sets to the required form. This was performed numerically[24] by employing the unitary transformation of King *et al.*,[13] which is based on the diagonalization of the Hermitian product of the overlap matrix between the ground and excited MO sets. For those transitions for which the initial and final orbitals were π MO's ($W, A \leftarrow X$), or in which the core was the same for the ground and excited states ($D, E \leftarrow X$), only the $D_{l'l''}^{1/2}$ factor had to be calculated. This is because that portion of the overlap matrix involving the initial orbitals for these transitions is already diagonal. However, for the wave functions used in the $B, C \leftarrow X$ transitions, the transformation of MO's themselves was also important because the initial orbitals for these transitions are σ_g (or σ_u) symmetry and this portion of the overlap matrix is not diagonal. The diagonalization procedure in this case causes the σ_g (and σ_u) orbitals to mix among themselves. The coefficients of the transformed Ransil best-limited (BL) initial orbitals are given in Table III for the $B \leftarrow X$ and $C \leftarrow X$ transitions. Included in Table III are the appropriate $D_{l'l''}^{1/2}$ factors used in the calculation of the transition amplitude Eq. (17) for all the excitation processes discussed here.

Configuration interaction (CI) may be important in certain of the excited electronic states,[25] and hence a single Slater determinant may not be an adequate representation of the true state. Of the excited states considered in this work, CI appears to be most important for the $A\,^3\Sigma_u^+$ state. An approximate test of the A-state wave functions to determine the importance of CI is discussed in Sec. V.

TABLE III. Transformed coefficients of the Ransil (BL) primitive-symmetry MO's for the $B \leftarrow X$ and $C \leftarrow X$ transitions in N_2 using the SDL excited states. The $D_{l'l''}^{1/2}$ values, those used in Eq. (17), are also given for these transitions as well as the W, $A \leftarrow X$ transitions calculated using the Richardson wave functions and the D, $E \leftarrow X$ transitions using the SDL and LB wave functions.

Transition	Transformed coefficients			$D_{l'l''}^{1/2}$
$B(1\pi_g) \leftarrow X(3\sigma_g)$	$+0.030\,50(\sigma_g 1s)$	$+0.484\,15(\sigma_g 2s)$	$-0.847\,99(\sigma_g 2p)$	0.988 42
$C(1\pi_g) \leftarrow X(2\sigma_u)$	$+0.027\,77(\sigma_g 1s)$	$+1.109\,99(\sigma_g 2s)$	$-0.328\,73(\sigma_g 2p)$	0.981 53
$W, A(1\pi_g) \leftarrow X(1\pi_u)$		None		0.973 65
$D, E \leftarrow X(3\sigma_g)$		None		1.000 00

TABLE IV. Excitation energies and Franck-Condon factors for the transition $A\,^3\Sigma_u^+\,(v'=0\cdots 20) \leftarrow X\,^1\Sigma_g^+\,(v'=0)$ as calculated from the spectroscopic data tabulated by Benesch *et al.* (Ref. 26).

v'	ΔE(eV)	$q_{v'0}$	v'	ΔE(eV)	$q_{v'0}$
0	6.169	0.000 98	11	7.931	0.075 62
1	6.346	0.005 21	12	8.070	0.065 25
2	6.521	0.014 82	13	8.205	0.054 59
3	6.691	0.030 08	14	8.335	0.044 52
4	6.859	0.048 63	15	8.462	0.035 66
5	7.023	0.067 22	16	8.585	0.028 06
6	7.183	0.081 75	17	8.704	0.021 73
7	7.340	0.091 45	18	8.819	0.016 59
8	7.493	0.094 57	19	8.930	0.012 49
9	7.643	0.091 80	20	9.036	0.009 27
10	7.789	0.085 09			

IV. NUMERICAL TECHNIQUES

Since the wave functions used to describe the ground and excited states were given only at R_e $(X\,^1\Sigma_g^+)$, the R-centroid concept could not be used. Thus, only the Franck-Condon factors, the $(v''=0, v')$ energy separations, and the electronic transition amplitudes were necessary to determine the total cross sections.

A. Potential-Energy Curves and Franck-Condon Factors

The potential-energy curves and vibrational-level spacings used for the $X\,^1\Sigma_g^+$, $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, and $C\,^3\Pi_u$ electronic states were those determined from spectroscopic constants by Benesch *et al.*[26] and Gilmore[27] from which the $(v''=0, v')$ energy separations were calculated. Benesch *et al.*[28] have reported Franck-Condon arrays for transitions from the X state to all v' levels of importance in the B and C states. However, it was necessary to extend their published arrays for the $A \leftarrow X$ transition to higher v' levels even though the extended portion of the array may be of somewhat lower accuracy. The Franck-Condon factors for these high v' levels of the A state were determined by using spectroscopic constants[26] to determine Rydberg-Klein-Rees (RKR) potential-energy curves for the X and A states, followed by numerical integration of the resulting nuclear wave functions to obtain the Franck-Condon[29] factors. The calculated energy levels and Franck-Condon factors for transitions to all v' levels of the A state from $v''=0$ of the X state are given in Table IV. The Franck-Condon factors for the lower v' levels are seen to agree well with those reported by Benesch *et al.*[28]

The potential-energy curves for the W, E, and D electronic states were calcultaed by a RKR method from spectroscopic constants determined as follows. The vibrational constants and T_e for the W state have recently been measured by Wu and Benesch.[21] The rotational constants used for the W state were taken from the theoretical work of Fraga and Ransil.[30] The spectroscopic constants used for the E state were taken from Lofthus[25] and ground-state $(X\,^2\Sigma_g^+)$ N_2^+ data.[31] For the D state, the data of Lofthus[25] were combined with those for the $p'\,^1\Sigma_u^+$ state.[32] The spectroscopic data used for the RKR ground state were those given by Benesch *et al.*[26] The spectroscopic constants used in the potential-energy curve calculations on the W, E, and D states are summarized in Table V.

Freund has recently reported[33] measurements on the radiation emitted from the E state; from an analysis of the relative intensities in the various bands he estimated the R_e and B_e values for this state to be 1.16 ± 0.02 Å and 1.77 ± 0.06 cm^{-1}, respectively. A potential-energy curve for the E state using these values and the corresponding Franck-Condon factors connecting this state with the ground electronic state were calculated but rejected in favor of those obtained from the constants given in Table V. The latter set of constants was determined to represent the E state better because the corresponding Franck-Condon factors for transitions from $v''=0$ of the ground-state agree much better with those determined from recent energy-loss spectra.[34]

The Franck-Condon factors for the $E \leftarrow X$ and $D \leftarrow X$ transitions were calculated in the same manner as described above to extend the $A \leftarrow X$ array. The excitation energies (eV) and Franck-Condon factors for transitions from $v''=0$ of the X state

TABLE V. The spectroscopic constants used to calculate the potential-energy curves for the $W\,^3\Delta_u$, $E\,^3\Sigma_g^+$, and $D\,^3\Sigma_u^+$ states. See text for a discussion of the data.

	$W\,^3\Delta_u$	$E\,^3\Sigma_g^+$	$D\,^3\Sigma_u^+$
$T_e(\text{cm}^{-1})$	59 738.00[a]	95 859.46[c]	103 652.22[c]
$\omega_e(\text{cm}^{-1})$	1 539.00[a]	2 185.00[c]	2217.00[e]
$\omega_e x_e(\text{cm}^{-1})$	17.00[a]	16.136[d]	19.00[e]
$\omega_e y_e(\text{cm}^{-1})$	⋯	−0.04[d]	⋯
$B_e(\text{cm}^{-1})$	1.546[b]	1.9322[d]	1.961[c]
$\alpha_e(\text{cm}^{-1})$	0.011 63[b]	0.020 2[d]	0.000 02[c]
R_e(Å)	1.248[a]	1.116 2[d]	1.108[c]

[a] Taken from Ref. 21.
[b] Taken from Ref. 30.
[c] Taken from Ref. 25.
[d] Taken from Ref. 31.
[e] Taken from Ref. 32.

TABLE VI. Excitation energies and Franck-Condon factors for the $W\,^3\Delta_u\,(v'=0,\ldots,12)$, $E\,^3\Sigma_g^+\,(v'=0,1)$, $D\,^3\Sigma_u^+\,(v'=0,1)$, $X\,^1\Sigma_g^+\,(v''=0)$ transitions in N_2 as calculated from potential-energy curves obtained using the spectroscopic constants in Table V. For each v' level, the first number is the excitation energy in eV, and the second is the Franck-Condon factor.

v'	$W\,^3\Delta_u$	$E\,^3\Sigma_g^+$	$D\,^3\Sigma_u^+$
0	7.355 0.0129	11.877 0.9278	12.841 0.9819
1	7.542 0.0522	12.139 0.0625	13.097 0.0176
2	7.724 0.1100		
3	7.902 0.1609		
4	8.076 0.1820		
5	8.246 0.1686		
6	8.412 0.1320		
7	8.573 0.0887		
8	8.730 0.0515		
9	8.883 0.0257		
10	9.031 0.0108		
11	9.176 0.0036		
12	9.316 0.0009		

to the W, E, and D states are given in Table VI and all the potential-energy curves are shown in Fig. 1.

B. Evaluation of Multicenter Terms

When Slater-type orbitals centered on the nuclei are used to represent the MO's, single-center and multicenter terms appear in the evaluation of the transition amplitude Eq. (17).[11] The single-center terms could be done analytically, and the methods used to evaluate the multicenter terms have been discussed in detail elsewhere.[11,35] To facilitate the averaging over orientations of the diatomic axis with respect to the incident electron beam, the atomic orbitals on each nucleus were expanded about the center of mass of the diatomic molecule using the ζ-function expansion. Multicenter terms composed of atomic orbitals of principal quantum number $n \leqq 2$ could be evaluated for any value of the momentum transfer q and internuclear distance R. Since the numerical methods used to evaluate the multicenter terms were not able to treat atomic orbitals of $n \geqq 3$, not all the multicenter terms appearing in the scattering amplitude describing excitation to the E and D states could be evaluated. Therefore, in order to be consistent in calculating the E- and D-state transition amplitudes, none of the multicenter terms appearing in the transition amplitude for excitation of the E and D states were evaluated. Because of the neglect of these multicenter terms, the cross sections corresponding to these excitations are of lower accuracy relative to the calculated cross sections for excitations of the A, B, W, and C electronic states. From previous work on the excitation of H_2,[11] the error in the $E \leftarrow X$, $D \leftarrow X$ cross sections due to the omission of the multicenter terms is not believed to exceed 60%.

The total cross sections in all cases were obtained by Romberg integration over q to a specified accuracy of three significant figures.

V. RESULTS

In these calculations, the initial vibrational level has been taken as $v''=0$ in all cases. Since $v''=1$ corresponds to an excitation temperature of about 3350 °K, this choice for the initial vibrational state corresponds to the situation encountered in many studies of processes involving N_2. Because of the generally weak dependence of k'' and q on v', only the total excitation cross sections ($\sigma_{00}^{n'}$) for the electronic states of interest will be given below. Except near threshold, the cross

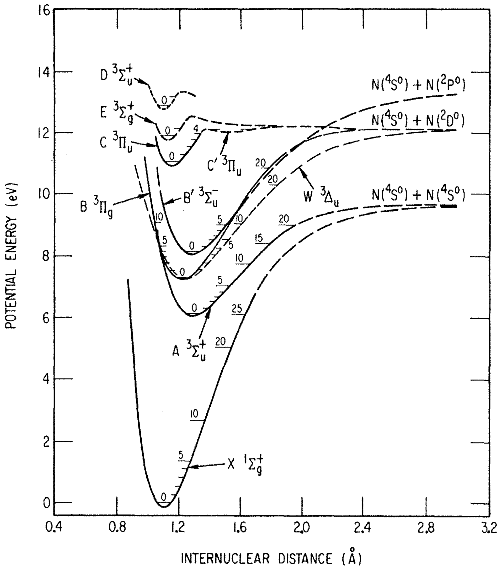

FIG. 1. Potential-energy curves for the ground and seven lowest triplet states of N_2 as functions of the internuclear distance. The curves for the $W\,^3\Delta_u$ and $D\,^3\Sigma_u^+$ were calculated as outlined in Sec. IV, the others were taken from Gilmore (Ref. 27).

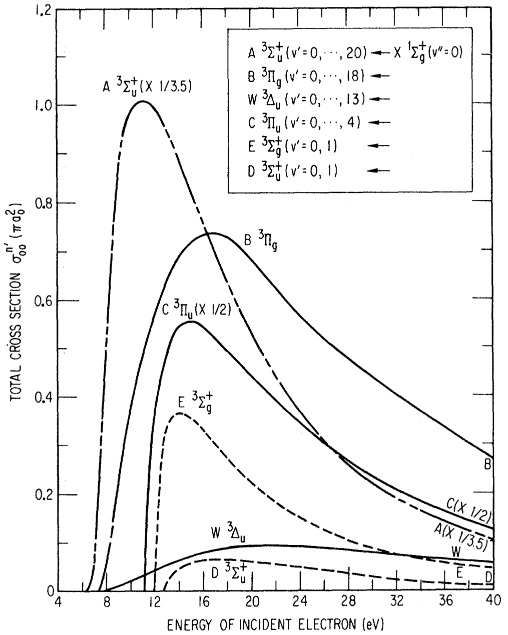

FIG. 2. Total cross sections ($\sigma_{00}^{n'}$), as defined by Eq. (24), for excitation of the seven lowest triplet electronic states of N_2 from $v''=0$ of the ground state as a function of the incident electron energy. The cross section for excitation of the $B'\,^3\Sigma_u^-$ state is zero in this model and hence does not appear in the figure. The cross sections for excitation of the $A\,^3\Sigma_u^+$ and $C\,^3\Pi_u$ states shown here have been *reduced* by factors of 3.5 and 2.0, respectively.

section for excitation of a single v' level ($\sigma_{00}^{n'v'}$) can be obtained with reasonable accuracy from the $\sigma_{00}^{n'}$ given below by multiplication with the appropriate Franck-Condon factor.

In Fig. 2 are shown the total cross sections ($\sigma_{00}^{n'}$) for excitation of the A, B, W, C, E, and D triplet states of N_2 from $X\,^1\Sigma_g^+$ ($v''=0$). These total cross sections all exhibit the steep rise to a maximum near threshold followed by the rapid k_0^{-6} fall-off characteristic of pure exchange excitation except that for the W state. The total cross section for excitation of the $B'\,^3\Sigma_u^-$ state from $X^1\ \Sigma_g^+$ is identically zero in the model used here to describe the scattering process[36] and consequently does not appear in Fig. 2.

No experimental determination of the $W \leftarrow X$ excitation cross section has been reported. Peaks corresponding to excitation of the W state will not easily be seen in conventional electron-impact spectra because the W-state vibrational levels are nearly degenerate in energy with v' levels of the $B\,^3\Pi_g$ and $A\,^3\Sigma_u^+$ states (see Fig. 1), whose cross sections are 5 to 10 times larger than that for the W state at all incident-electron energies. However, knowledge of the $W \leftarrow X$ total cross section is useful in the analysis of radiation from electron-impact-excited N_2. That is, since $W\,^3\Delta_u \rightarrow B\,^3\Pi_g$ is dipole allowed and the W-state excitation cross section is fairly large and broad in shape, the $W \rightarrow B$ radiation (in the 3.0→5.3μ region) should be relatively strong in processes such as the aurora. A detailed analysis of the effect of the $W \rightarrow B$ transitions in the population of the A and B states under auroral conditions is the subject of a future publication.

In the following sections a comparison of these theoretical cross sections is made with the limited amount of experimental data and other theoretical calculations available for these processes. An argument based on a comparison of a theoretical and a experimental energy-loss spectrum is given to indicate that these calculated cross sections comprise a consistent set for the description of the excitation of the lowest seven triplet states of N_2.

A. $C^3\Pi_u \leftarrow X^1\Sigma_g^+$

The excitation processes of the $C\,^3\Pi_u$ state have been the most extensively studied of any excited state of the N_2 triplet system. This can be attributed to (i) the fact that the radiation in the second positive system ($C\,^3\Pi_u \rightarrow B\,^3\Pi_g$) is in a region of the electromagnetic spectrum which is easily measured, and (ii) there is little or no cascade population of the C state from higher electronic states, and therefore when electrons of known energy are passed through N_2 gas, the resulting radiation in the second positive system can be used to estimate the corresponding C-state excitation cross section. The technique which is usually employed is one of calibrating the photon detection system against a standard lamp and/or some other radiation from electron-impact-excited N_2 for which the cross section is assumed known (such as the 3914-Å band from N_2^+). However, there are a good many experimental difficulties in determining the excitation cross sections from optical data, and, as will be discussed below, the cross sections obtained by different investigators using essentially the same technique do not accord with each other.

The results to which the theoretical $C\,^3\Pi_u$ excitation cross section can be compared[37] are those of Jobe, Sharpton, and St. John (JSSJ),[38] Burns, Simpson, and McConkey (BSM),[39,40] Skubenich and Zapesochny (SZ),[41] and Legler (L).[42] These investigators used the intensity of the second positive system for known incident electron energy as a measure of the excitation cross section. There is also a determination of this cross section by Engelhardt *et al.*[43] based on an analysis of electron transport coefficient data.

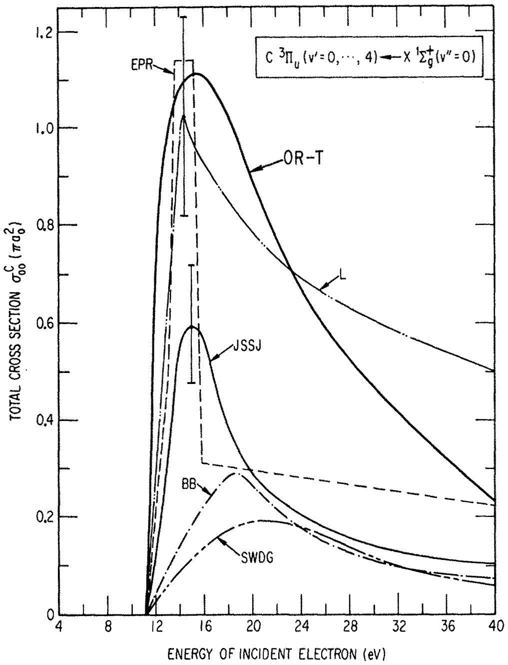

FIG. 3. Total cross section for excitation of the $C\,^3\Pi_u$ state from $X\,^1\Sigma_g^+(v''=0)$ as a function of the incident electron energy. The present results are labeled OR-T and the other cross sections are Engelhardt *et al.* (EPR, Ref. 43), Legler (L, Ref. 42), Jobe *et al.* (JSSJ, Ref. 38), Bauer and Bartky (BB, Ref. 44), and Stolarski *et al.* (SDWG, Ref. 45). The experimental cross sections of Burns *et al.* (Ref. 39) and Skubenich and Zapesochny (Ref. 41) have been omitted for clarity but are discussed in the text. The vertical bar drawn on the L and JSSJ curves represent the quoted experimental uncertainty.

Figure 3 shows the comparison between the calculated total excitation cross section, the experimentally determined values for the cross section, and the semiempirical results of Bauer and Bartky[44] (BB) and Stolarski *et al.*[45] (SDWG). (For purposes of clarity the experimental results of BSM and SZ, respectively, 15% and a factor of 2 smaller than the JSSJ curve at 15 eV, are not shown in Fig. 3.) From the figure, one notes that the maximum of the excitation cross section determined in the various experiments falls into one of two groups for which the quoted error bars do not overlap. The maximum value as determined by EPR and by L, is greater than $1.0\pi a_0^2$ and in good agreement with the calculated cross section. The more recent experimental determinations of the cross section by SZ, BSM, and JSSJ are a factor of 2 or more smaller and have maxima less than $0.6\pi a_0^2$. However, there is disagreement within this latter group of experimental data in that the SZ cross section (not shown in Fig. 3) is about a factor of 2 smaller at maximum than that obtained by JSSJ and BSM although the same experimental technique was employed. This discrepancy coupled with the fact that the cross-section determination by Legler was also based on photon collection of the second positive bands makes a meaningful comparison between theory and experiment difficult.

Approximations which could lead to a theoretical total cross section which is too large are the relatively simple wave-function representations used to describe the ground and excited states (see Sec. V F) and/or the scattering model used to describe the excitation process. However, previous calculations involving similar processes in H, He, and H_2 employing comparably accurate wave functions and the same scattering model have generally been in good agreement with the corresponding experimental measurements. All that can be concluded from the above comparison is that the theoretical excitation cross section for the $C^3\Pi_u$ state shown in Fig. 3 is probably larger than the true cross section, but most likely accurate to within a factor of 2. The resolution of the differences between the various experimental determinations must await the results of further experimental work or a more elaborate theoretical study.

B. $B_3\Pi_g \leftarrow X_1\Sigma_g^+$

There have been no published measurements of the absolute cross section for excitation of the v' levels of the $B\,^3\Pi_g$ state which do not include cascade contributions from the $A\,^3\Sigma_u^+$, $W^3\Delta_u$, $C\,^3\Pi_u$, $C'^3\,\Pi_u$, and $D\,^3\Sigma_u^+$ electronic states. This is because the experimental method usually employed is the optical technique similar to that used to determine the $C\,^3\Pi_u$ cross section. However, the cascade contributions to the measured B-state cross section cannot be accounted for without knowledge of the excitation cross section for the A, W, C, C', and D electronic states and their transition probabilities to the B state. The cross section for excitation of the C state has been discussed in Sec. IV ; but, with the exception of the first positive ($B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$) and second positive ($C\,^3\Pi_u \rightarrow B\,^3\Pi_g$) transition probabilities, the necessary quantities have not been reported. As a consequence, only a qualitative comparison with experiment will be made at this time.

In Fig. 4 the calculated total cross section for excitation of the $B\,^3\Pi_g$ state from $X^1\Sigma_g^+(v''=0)$ is compared with the "apparent" excitation cross section as measured by Stanton and St. John[46] (SSJ) and Skubenich and Zapesochny[41] (SZ). The apparent excitation cross section measured by McConkey and Simpson[47] (MS) agrees well with the SSJ results and has been omitted from Fig. 4 for the

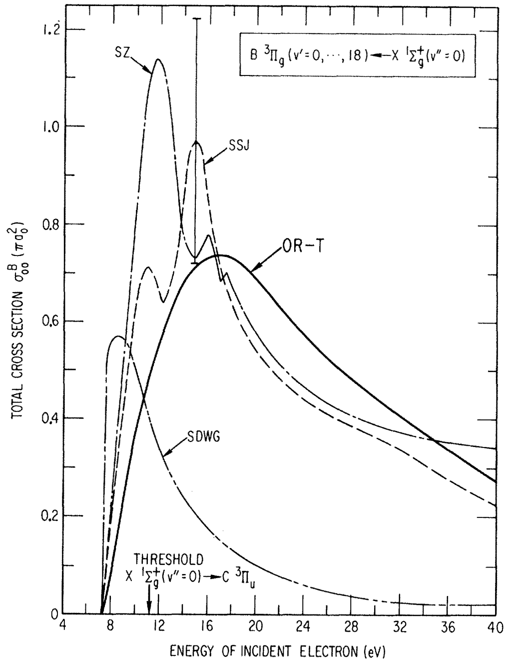

FIG. 4. Total cross section for excitation of the $B\,^3\Pi_g \times (v' = 0, \ldots, 18)$ state from $X\,^1\Sigma_g^+ (v'' = 0)$ as a function of incident electron energy. The present results are labeled OR-T and the other cross sections are Stanton and St. John (SSJ, Ref. 46), Skubenich and Zapesochny (SZ, Ref. 41), and Stolarski *et al.* (SDWG, Ref. 45). The apparent cross section measured by McConkey and Simpson (Ref. 47) agrees well with the SSJ results and is not shown. The vertical bar on the SSJ curve represents the ±25% uncertainty in the measured "apparent" excitation section estimated by MS for the case of the strongest first positive bands. The cross sections reported by SSJ, SZ, and MS are apparent cross sections, containing cascade effects, and therefore represent experimental upper bounds on the true excitation cross section.

sake of clarity. Even though the "apparent" excitation cross sections contain a variety of cascade contributions, the following comparison can be made with the calculated cross section. The first peak in the apparent cross sections for excitation of the lower ($v' \lesssim 5$) v' levels of the B state has been interpreted by MS as being due to direct excitation of these v' levels from the ground electronic state and the second peak (at about 15 eV) as due to cascading from the $C\,^3\Pi_u$ state. However, preliminary calculations using a reasonable value for the $A\,^3\Sigma_u^+$-state excitation cross section (see Sec. V C) and the known transition moment for the first positive system[48] indicate that the first peak at 10 eV in the apparent excitation cross section may be due to cascade from the higher vibrational levels of the A state to the particular v' level of interest in the B state rather than direct excitation from the ground state. This results from the fact that the A-state excitation cross section has its maximum near 10-eV incident energy, and has Franck-Condon factors such that its higher vibrational levels ($v' \geq 12$) are appreciably populated by direct excitation from the ground state (see Table IV). Since the second peak in the measured cross section (at about 15 eV) is probably due in part to cascade from the C state, the maximum of the "true" B-state excitation cross section most likely occurs near the feature observed by MS for incident energies between 15 and 16.5 eV. Similar calculations using the theoretical cross section for excitation of the $W\,^3\Delta_u$ state shown in Fig. 2 and a theoretical transition moment calculated by the author indicate that the shoulder at about 30-eV incident energy observed by SSJ and MS is due to the W state cascading into the B states. The details of these calculations will be reported in a subsequent publication.

With the cascade effects in mind, the comparison in Fig. 4 indicates that the calculated cross section will agree reasonably well with the "true" B-state excitation cross section, although the theoretical curve may peak at slightly too large an incident energy and be somewhat too broad. The cause of the discrepancy in the relative magnitudes of the first two peaks in the measured apparent excitation function of the B state as determined by SSJ and MS and that observed by SZ may be due to the fact that SZ used an extrapolation method to obtain the apparent cross section of the entire B state from the cross section for excitation of a few specific v' levels of the B state. Included in Fig. 4 for purposes of comparison is the semiempirical cross section estimated by Stolarski *et al.*[45] based on relative cross-section data obtained by Schulz[49] using the trapped-electron method.

C. $A\,^3\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$

To date there have been no published measurements of the absolute cross section for excitation of the $A\,^3\Sigma_u^+$ state. The long lifetime of the A state, together with the fact that the emissions from the A state ($A\,^3\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$; Vegard-Kaplan bands) are in the uv, makes the determination of the cross section by optical methods difficult. In Fig. 5 the theoretical cross section for excitation of the A state is compared with the semiclassical cross section of Bauer and Bartky,[44] and the semiempirical estimate of Stolarski *et al.*[45] The cross section deducted by Engelhardt *et al.*[43] from the trapped-electron experiments of Schulz[49] is not included in Fig. 5 because the cross section measured by Schulz in the energy region 6–9 eV contained contributions from the excitation of the A, B, and W states. One notes from the figure

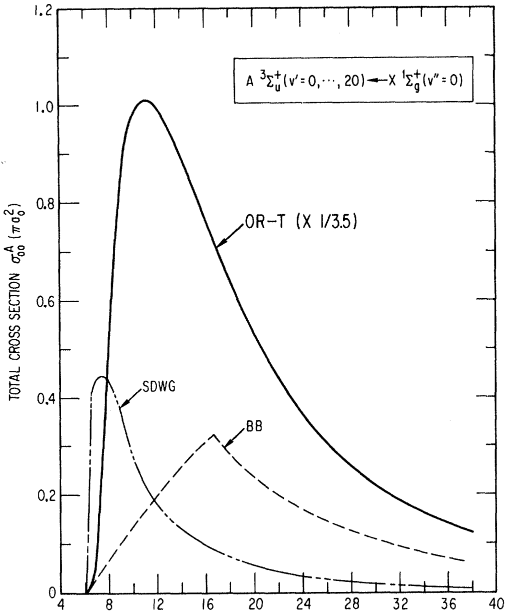

FIG. 5. Total cross section for excitation of the $A\,^3\Sigma_u^+\times(v'=0,\ldots,20)$ state from $X\,^1\Sigma_g^+(v''=0)$ as a function of incident electron energy. The present result is labeled OR-T and has been *reduced* by a factor of 3.5. The other curves are Bauer and Bartky (BB, Ref. 44) and Stolarski *et al.* (SDWG, Ref. 45).

that the A-state excitation cross section reported here is considerably larger than previously believed.

There are some recent energy-loss spectra to which these calculations can be compared to determine whether the theoretical A-state cross section is of the correct magnitude relative to that of the B and C states. This comparison, which is discussed in more detail in Sec. V E, indicates that the calculated A-, B-, and C-state cross sections are of the correct relative magnitudes at 35 eV. The cross section obtained in the OR approximation is much larger than that predicted by SDWG and BB not only for the A state but also for the B and C states. Because of the good agreement between the calculated and measured B-state cross section, the A-state cross section reported here is probably the most reliable estimate presently available at energies above about 30 eV.

The approximate wave functions used for the A state were examined to determine whether they are a particularly poor representation of the A state. As mentioned in Sec. III, the $A\,^3\Sigma_u^+$ state is not a pure state, but contains a mixture of other configurations (mainly $^1\Sigma$ and $^1\Pi$) due to the electron spin-orbit interaction.[50] This is evidenced by the fact that the radiation in the Vegard-Kaplan bands is electric dipole in character even though the transition is spin forbidden.[51] Therefore, to properly describe the excitation of the A state, it may be necessary to include the mixing-in of the other configurations in the A-state wave function. The modification of the available wave functions to include such configuration interaction was beyond the scope of this work, so the effect of the configuration mixing was estimated as follows. The square of the transition moment (D_{BA}^2) for the first positive system $(B\,^3\Pi_g\rightarrow A\,^3\Sigma_u^+)$ was calculated at an R-centroid value of $R=1.0941$ Å using the SDL wave functions and compared with the measurements of Jeunehomme[48a] and Turner and Nicholls.[48b] If the B-state wave function employed is assumed to be "pure," which appears valid for the B-state v' levels of importance here,[25] any discrepancy between the calculated and observed (D_{BA}^2) could be attributed to the inadequacy of the single-configuration A-state wave function. However, the calculated transition moment differed from the experimental value by less than 30%, and therefore no correction based on this comparison was believed to be justified.

The effect on the cross section of improving the wave functions was also determined in the case of the A-state excitation by calculating the excitation cross section using the SDL X- and A-state wave-function pair.[18] The cross section obtained using the SDL wave functions was found to be only 18% larger than that obtained with the Richardson wave functions. Thus for the $A\leftarrow X$ excitation, this significant improvement in the set of wave function used does not produce a significant change in the excitation cross section.

D. $E\,^3\Sigma_g^+, D\,^3\Sigma_u^+\leftarrow X\,^1\Sigma_g^+$

There have been no absolute experimental or theoretical determinations of the cross section for excitation of the $E\,^3\Sigma_g^+$ state and only two experimental estimates reported for the $D\,^3\Sigma_u^+$ excitation cross section.

Clampitt and Newton have reported[52] detection of the $E\,^3\Sigma_g^+$ state in a crossed-electron–N_2-beams experiment, but gave no quantitative estimate of the magnitude or energy dependence of the excitation cross section. Freund (F) has given[33] a relative "excitation function" for the excitation of the E state over the energy range from threshold to 23 eV based on measurements of the delayed-emission spectra observed from a beam of excited N_2 molecules. Figure 6 is a comparison between the theoretical $E\,^3\Sigma_g^+$ excitation cross section, calculated without the multicenter terms (see Sec. IVB), and the excitation function measured by Freund. The latter has been normalized to the theoretical curve at its maximum. Ehrhardt and Willmann

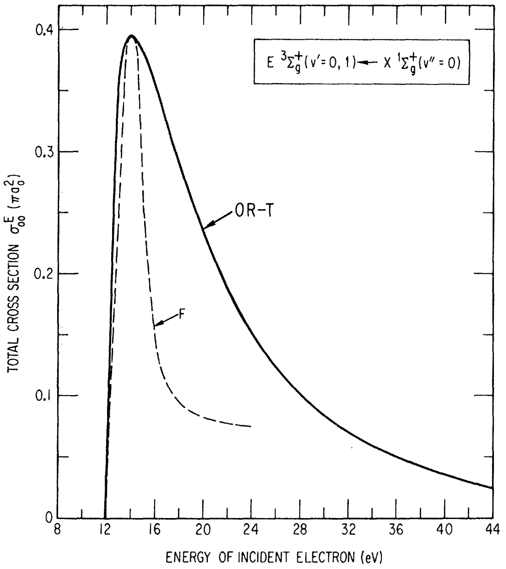

FIG. 6. Total cross section for excitation of the $E\,^3\Sigma_g^+ \times (v'=0, 1)$ state from $X\,^1\Sigma_g^+(v''=0)$ as a function of incident electron energy. The present results are labeled OT – T, and the relative cross section measured by Freund (F, Ref. 33) has been normalized to the theoretical curve at its maximum. See the text for a discussion of the cross section measured by Ehrhardt and Willmann (Ref. 53).

(EW) have also reported[53] a relative cross section for excitation of the E state for incident-electron energies from 11 to 17 eV, based on the collection of those electrons which had lost 11.87-eV energy and been scattered into an angle of 20° or less. An energy loss of 11.87 eV corresponds to excitation of $v'=0$ of the E state which is about 93% of the complete cross section σ_{00}^E (see Table VI). The EW cross section is quite narrow, with a full width at half-maximum (FWHM) of less than 0.5 eV, and for that reason it is not shown in Fig. 6. The theoretical cross section is seen to be considerably broader than both the F and EW cross sections. This disagreement between the calculated and measured shape of the E-state cross section is not expected to be removed by the inclusion of the multicenter terms in the theoretical cross section. The extreme narrowness of the measured E-state excitation cross section relative to the cross sections for excitation of the other nitrogen triplet states implies that the E state may be excited by a resonant-type process rather than the simple exchange process used in these calculations.

Skubenich and Zapesochny (SZ) have reported[41] an apparent excitation cross section for the $D\,^3\Sigma_u^+$, and McConkey and Simpson[47] (MS) have estimated the maximum in the D-state cross section by assuming certain cascade contributions to the apparent cross section which they measure for the $B\,^3\Pi_g$ state. These experimental values are shown along with the theoretical excitation cross section for the $D\,^3\Sigma_u^+$ state in Fig. 7. As expected, because the multicenter terms were not included in the evaluation of the D-state transition amplitude, the calculated cross section is larger than the experimental values. Previous experience with the effect of the multicenter terms for a Σ_g^+ to Σ_u^+ transition indicates that omission of these terms from the scattering amplitude results in a cross section which is too large by about a factor of 2. When the multicenter terms are included in the calculation of the D-state transition amplitude, the resulting cross section is expected to agree well with the estimate of MS but perhaps still be slightly larger than the SZ result.

E. Relative Magnitudes of the Triple Excitation Cross Sections

The experimental determination of the magnitude of the total cross section for excitation of the $A\,^3\Sigma_u^+$ state has a large uncertainty, and that for the $W^3\Delta_u$ and $E\,^3\Sigma_g^+$ states has not yet been made. In this section a comparison is made between a calculated energy-loss spectrum, based on the theoretical differential cross sections, and recent experimental energy-loss spectra. The purpose

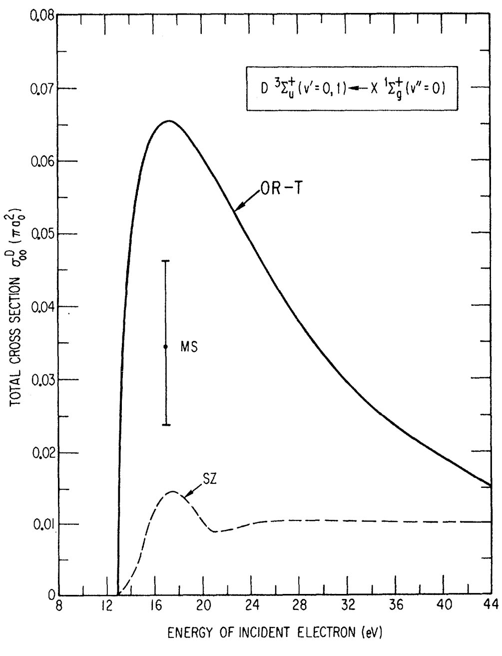

FIG. 7. Total cross section for excitation of the $D\,^3\Sigma_u^+ \times (v'=0, 1)$ state from $X\,^1\Sigma_g^+(v''=0)$ as a function of incident electron energy. The present results are labeled OR-T, and the experimental results of McConkey and Simpson (Ref. 47) and Skubenich and Zapesochny (Ref. 41) are labeled MS and SZ, respectively.

of this comparison is to show that the relative magnitudes of the theoretical cross sections, particularly those for the *A*, *B*, *W*, and *C* states, are consistent with those determined experimentally and therefore reliable within the accuracy provided by this comparison.

The energy-loss spectrum chosen for this comparison is that obtained by Rice[54] for an incident electron energy of 35 eV. Since the objective of this comparison is to show that the calculated *total* cross sections for excitation of the *A*, *B*, *W*, and *C* electronic states are of the correct relative magnitudes, the comparison with experimental energy-loss spectra is made for a scattering angle θ as close as possible to 90°. There are two other reasons for making this comparison at large scattering angles. The first is that for small scattering angles the differential cross sections for singlet-singlet transitions are larger than those for singlet-triplet transitions by an order of magnitude or more. As a result, it is difficult to resolve the singlet-triplet processes at small scattering angles. On the other hand, at larger scattering angles ($\theta \gtrsim 60°$) the singlet-triplet transitions have magnitudes comparable to or larger than the singlet-singlet ones and therefore are more easily studied. The second reason is that the OR scattering approximation is usually more reliable for scattering angles greater than 40° than it is in the range 0°–40°, the actual range of validity depending on the nature of the scatterer.[12,55] The choice of 35-eV incident energy, calculated from the theoretical differential cross sections assuming a resolution[56] of 0.080 eV, is shown in Fig. 8(a) and is to be compared with the experimental spectrum[54] shown in Fig. 8(b). In the experimental spectrum, for energy loss above 8.5 eV, peaks corresponding to excitation of the v' levels of the $a\,^1\Pi_g$ singlet state appear. Since only triplet excited states were treated in the calculations reported here, the corresponding peaks are absent in the synthetic spectrum. The energy-loss region 7.35–9.0 eV is composed of overlapping peaks due to excitation of the *A*- ($v' \geq 7$), *B*-, and *W*-state vibrational levels, and the experimental resolution was not sufficient to resolve the individual excitation processes. Since the experimental spectrum is relative, the peaks in this region of the spectrum, some corresponding to the overlap of two or more v' levels, should be compared to a standard peak. The $C\,^3\Pi_u$ ($v' = 0, 1$) peaks at 11.03- and 11.28-eV energy loss are the logical choices for reference peaks since they are the best resolved in the experimental spectrum. The essence of this comparison between theory and experiment is that for the synthetic spectra, the series of peaks between 6.6- and 8.5-eV energy loss have magnitudes relative to the $v' = 0$ and $v' = 1$ peaks of the *C* state which agree well with corresponding magnitudes in the measured spectrum when the background is subtracted from the latter.

From this comparison between the synthetic and measured spectra, the following points should be emphasized.

(i) Due to the Franck-Condon factors for excitation from the ground state, many more levels of the *A* state are excited with approximately equal intensity than in the *B* or *W* states. Consequently,

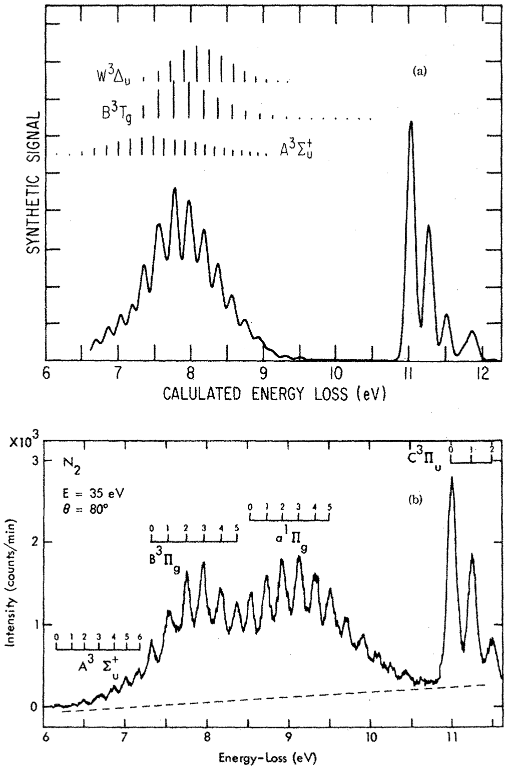

FIG. 8. (a) Synthetic energy-loss spectrum based on the theoretical differential cross sections for excitation of the lowest seven triplet states as calculated by the methods described in the text. The incident energy was taken as 35 eV, the scattering angle is 80°, and the resolution assumed to be 0.080 eV (Ref. 56). Note that no peaks corresponding to excitation of the singlet states appear in the spectrum since these states were not included in the calculations. The energy-loss locations and Franck-Condon factors of the various vibrational levels of the *A*, *B*, and *W* states are indicated by the vertical lines in the figure. All the Franck-Condon factors are relative to that for $v' = 2$ of the *B* state, and the dots represent v' levels whose Franck-Condon factors are zero on this scale. (b) Smoothed experimental energy-loss spectrum obtained by Rice (Ref. 54) for an incident energy of 35 eV, scattering angle of 80°, and unknown resolution. The identification of some of the vibrational levels is indicated above certain peaks although all of the peaks between 7 and 9 eV consist of more than one unresolved feature.

the low peaks corresponding to excitation of the A state for energy loss ≤ 7.34 eV actually result in a *total* cross section (summed over v' levels; σ_{00}^{A}) which is comparable to that for the B state at 35 eV (see Fig. 2).

(ii) By varying the magnitude of the A-state cross section, it was found that a change of about ± 50% in the value of the theoretical A-state differential cross section at 35 eV results in poorer agreement between the calculated and measured spectrum. Consequently, assuming that the OR scattering model properly predicts the differential cross sections at 35 eV and 80°, this comparison implies that the total cross sections for excitation of the A state is significantly larger than the estimates of Bauer and Bartky[44] and Stolarski *et al.*[45]

(iii) The cross sections for excitation of the vibrational levels of the W state are from 5 to 10 times smaller than those for the A and B states for an incident energy of 35 eV. Consequently the effect of excitation of the W state is indiscernible in the calculated and measured energy-loss spectra at a resolution of 0.080 eV. By varying the resolution used in the synthetic spectrum, it is estimated that a resolution of 0.045 eV or better at large scattering angles will be necessary to resolve the least blended peak corresponding to excitation of the W state. In any case, based on the comparison with experiment of the other calculated cross sections, the theoretical W-state excitation cross section is believed to be accurate to about a factor of 2.

Although this argument is not as quantitative as one would like, the general agreement between the synthetic and measured energy-loss spectra indicates that, at least at 35 eV, the calculated set of total cross sections displayed in Fig. 2 comprise a consistent set of excitation cross sections.

F. Effect of Approximate Wave Functions

As mentioned in Sec. III, there are a variety of ground-state wave functions available for the description of the nitrogen molecule ranging in complexity from the minimum-basis-set Scherr[19] wave function to the Hartree-Fock SCF-MO calculations of Nesbet and of Cade *et al.*[17] The characteristics of the electron charge distribution and of the individual MO's themselves has been shown by Smith and Richardson[57] (SR) to be sensitive to the degree of approximation used in constructing the wave function. In the case of the $2\sigma_u$ MO, the initial-state MO involved in the excitation of the $C\,^3\Pi_u$ state, the hybridization,[57] and spatial extent were found to vary considerably from one approximation to the other. It has been shown earlier[11] that the OR cross section may, for certain symmetry combinations of ground and excited states, be sensitive to the quality of the wave functions employed as measured by the spatial electron distribution it predicts. Consequently the B- and C-state excitation cross sections were calculated with the SDL excited-state wave functions and with the ground-state wave function of SDL and of Ransil in an effort to determine the effect on the calculated cross section of an improvement in the ground-state wave function. Use of the Ransil rather than the SDL ground-state wave function (with the appropriate transformations to allow use of the Slater-Condon rule) resulted in a 20% reduction in the maximum of the B-state cross section and a 5% increase in that for the C state. This indicates that the cross section calculated with the different wave functions is not as sensitive to the "quality" of the MO's as are other properties such as hybridization. Coupled with the comparison between the SDL and Richardson ground-state wave functions made in Sec. VC for excitation of the $A\,^3\Sigma_u^+$ state it can be concluded that although the theoretical cross sections are somewhat sensitive to the quality of the wave functions used, the magnitude and direction of the effect do not appear easily predictable.

VI. CONCLUSIONS

A consistent set of total exchange-excitation cross sections has been calculated for excitation of the $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, $W\,^3\Delta_u$, $B'\,^3\Sigma_u^-$, $C\,^3\Pi_u$, $E\,^3\Sigma_g^+$, and $D\,^3\Sigma_u^+$ triplet electronic states of molecular nitrogen from the ground $X\,^1\Sigma_g^+$ $(v''=0)$ state. The calculated total cross section for excitation of the $B^3\,\Pi_g$ state is expected to agree well with the available experimental data when the cascade effects from the higher electronic states to the measured B-state cross section are removed. The theoretical cross section for excitation of the C state is found to agree well with one group of measurements, but is a factor of 2 larger than another group of results. Unfortunately, the peculiarities found in the $2\sigma_u$ MO of the various approximate ground-state wave functions means that the agreement between the theoretical C-state excitation cross section and the larger experimental cross-section value may be fortuitous. When the multicenter terms are included in the calculation of the $D\,^3\Sigma_u^+$ excitation cross section, the theoretical results are expected to agree well with the recent experimental estimates of the cross section. A comparison between a synthetic energy-loss-spectrum calculated from theoretical differential cross sections and a scattering angle of 80° indicates that the relative magnitudes of the total cross sections are consistent among themselves and with the experimentally determined relative magnitudes. The results of this comparison indicate that the cross section for excitation of the $A\,^3\Sigma_u^+$ state is comparable to that for the $B\,^3\Pi_g$ state at 35 eV. However, for lower incident electron energy, the theoretical A-state excitation cross section may be too large owing to the approximate nature of the A-state wave functions used in which configuration interaction was neglected. No previous results for excitation of the $W\,^3\Delta_u$ state have been reported. The comparison between the calculated cross section for excitation of the $E\,^3\Sigma_g^+$ state with the available experimental data indicates that the theoretical curve is considerably broader than that which is measured. Although the OR scattering model appears generally to predict a total cross section which is slightly broader than that measured, the very large discrepancy in this case implies that the $E\,^3\Sigma_g^+$ state is excited by some other process than that described by the theory employed here.

It can be concluded that the general good agreement of the theoretical results with the available data, the cross-section magnitudes of which vary over two orders of magnitude, indicates that the OR exchange approximation can be expected to give reliable excitation cross sections, in most cases better than a factor of 2.

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[†] Present address.

[1] A review of the N_2 auroral emissions produced by electron impact is given by A. Omholt, in *Aurora and Airglow* (Reinhold, New York, 1967), p. 59.

[2] The various collision processes of importance involving N_2 are discussed in K. Takayanagi and T. Takahashi, Rept. Ions. Space Res. 20, 357 (1966) and more recently by various authors in Can. J. Chem. 47, 1703 (1969).

[3] See for instance E. T. Gerry, Appl. Phys. Letters 7, 6 (1965) and references therein.

[4] A preliminary set of cross sections for excitation of the A, B, W, and C electronic states of N_2 is published in Mem. Soc. Roy. Sci. Liége, Ser V, 17, 163 (1969). A brief summary of the results reported here is given in Bull. Am. Phys. Soc. 14, 941 (1969).

[5] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), pp. 138–160.

[6] G. F. Drukarev, in *The Theory of Electron-Atomic Collisions*, edited by J. B. Hasted (Academic, New York, 1965), Chap. 8.

[7] L. S. Rodberg and R. M. Thaler, *Introduction of the Quantum Theory of Scattering* (Academic, New York, 1967), pp. 297–303.

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

[9] V. I. Ochkur, Zh. Eksperim. i Teor. Fiz. 45, 734 (1963) [Soviet Phys. JETP 18, 503 (1964)].

[10] M. R. H. Rudge, Proc. Phys. Soc. (London) 85, 607 (1965).

[11] D. C. Cartwright and A. Kuppermann, Phys. Rev. 163, 86 (1967).

[12] D. G. Truhlar, D. C. Cartwright, and A. Kuppermann, Phys. Rev. 175, 113 (1968).

[13] H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, J. Chem. Phys. 47, 1936 (1967).

[14] R. W. Nicholls and A. T. Stewart, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962), Chap. 2

[15] T. C. James, J. Mol. Spectry. 20, 77 (1966); P. H. Krupenie and W. Benesch, J. Res. Natl. Bur. (U. S.) 72A, 495 (1968). See also J. Drake and R. W. Nicholls, Chem. Phys. Letters 3, 457 (1968).

[16] K. J. Miller and M. Krauss, J. Chem. Phys. 47, 3754 (1967); S. Rothenberg and E. R. Davidson, J. Mol. Spectry. 22, 1 (1967).

[17] R. K. Nesbet, J. Chem. Phys. 40, 3619 (1964); P. E. Cade, K. D. Sales, and A. C. Wahl, *ibid.* 44, 1973 (1966).

[18] R. C. Sahni and E. J. De Lorenzo, J. Chem. Phys. 42, 3612 (1965).

[19] C. W. Scherr, J. Chem. Phys. 23, 569 (1955).

[20] B. J. Ransil, J. Chem. Phys. 32, 245 (1960).

[21] The "W" notation used for this state is that suggested by H. L. Wu and W. Benesch, Phys. Rev. 172, 31 (1968), following their relocation of this state.

[22] J. W. Richardson, J. Chem. Phys. 35, 1829 (1961).

[23] H. Lefebvre-Brion and C. M. Moser, J. Chem. Phys. 43, 1394 (1965). The author would like to thank Mdme. Lefebvre-Brion for providing the details of their calculations and helpful comments concerning the interpretation of their results.

[24] The necessary programs were constructed using the IBM SSP matrix-algebra routines which contain an eigenvalue-eigenvector subroutine that orders the eigenvalues of the overlap matrix in the required decreasing order.

[25] A. Lofthus, University of Oslo, Spectroscopy Report No. 2, 1960 (unpublished). The author would like to thank Professor Lofthus for helpful correspondence.

[26] W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkenson, Astrophys. J. 142, 1227 (1965).

[27] F. R. Gilmore, J. Quant. Spectry. Radiative Transfer 5, 369 (1965).

[28] W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 143, 236 (1966).

[29] These results were obtained using modified versions of the original RKR and Franck-Condon programs written by R. N. Zare, UCRL Report No. 10925, 1963 (unpublished).

[30] S. Fraga and B. J. Ransil, J. Chem. Phys. 35, 669 (1961).

[31] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, N. J., 1957), p. 554.

[32] R. S. Mulliken, in *The Threshold of Space*, edited by M. Zelikoff (Pergamon, New York, 1957), p. 169; see K. Dressler, Can. J. Phys. 47, 547 (1969) for a new assignment of the p' state.

[33] R. S. Freund, J. Chem. Phys. 50, 3734 (1969).

[34] The ratio of the Franck-Condon factor for $v'=0$ to that for $v'=1$ can be determined directly from the high-resolution spectrum of A. Skerbele, M. A. Dillon, and E. N. Lassettre, J. Chem. Phys. 46, 4161 (1967). See the inset of Fig. 16 in their paper.

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

[36] This fact can be shown group theoretically by expressing $e^{i\vec{q}\cdot\vec{r}}$ in terms of spherical harmonics and examining the expansion of the angular momentum eigenfunctions in terms of the irreducible representations of the group $D_{\infty h}$. See F. H. Read, J. Phys. B 1, 893 (1968). This fact is also shown using a different approach by E. N. Lassettre and M. E. Krasnow, J. Chem. Phys. 40, 1248 (1964).

[37] Only the more recent measurements were chosen for comparison with theory. Reference 2 contains a discussion of the earlier measurements in their review.

[38] J. D. Jobe, F. A. Sharpton, and R. M. St. John, J. Opt. Soc. Am. 57, 106 (1967).

[39] D. J. Burns, F. R. Simpson, and J. W. McConkey, J. Phys. B 2, 52 (1969). I would like to thank Dr. Burns for making a preprint to this work available prior to publication.

[40] J. F. M. Aarts and F. J. De Heer, Chem. Phys. Letters 4, 116 (1969). They report a cross section for $v'=0$ which agrees in magnitude with BSM (Ref. 39) but has a somewhat different shape.

[41] V. V. Skubenich and I. P. Zapesochny in *Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, July*, 1967 (Leningrad Nauka Publishing House, Leningrad, U.S.S.R., 1967), p. 570.

[42] W. Legler, Z. Physik 173, 169 (1963).

[43] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Phys. Rev. 135, A1566 (1958).

[44] E. Bauer and C. E. Bartky, J. Chem. Phys. 43, 2466 (1965).

[45] R. S. Stolarski, V. A. L. Dulock, C. E. Watson, and A. E. S. Green, J. Geophys. Res. 72, 3953 (1967).

[46] P. N. Stanton and R. M. St. John, J. Opt. Soc. Am. 59, 252 (1969).

[47] J. W. McConkey and F. R. Simpson, J. Phys. B 2, 923 (1969).

[48] (a) M. Jeunehomme, J. Chem. Phys. 45, 1805 (1966); (b) R. G. Turner and R. W. Nicholls, Can. J. Phys. 32, 475, (1954).

[49] G. J. Schulz, Phys. Rev. 116, 1141 (1959).

[50] R. Schlapp, Phys. Rev. 39, 806 (1932).

[51] D. E. Shemansky, J. Chem. Phys. 51, 689 (1969).

[52] R. Clampitt and A. S. Newton, J. Chem. Phys. 50, 1997 (1969).

[53] H. Ehrhardt and K. Willmann, Z. Physik 204, 462 (1967).

[54] J. K. Rice, thesis, California Institute of Technology, 1969 (unpublished). This spectrum will appear in S. Trajmar, J. K. Rice, and A. Kuppermann, Advan. Chem. Phys. 18 (to be published).

[55] S. Trajmar, D. C. Cartwright, J. K. Rice, R. T. Brinkmann, and A. Kuppermann, J. Chem. Phys. 49, 5464 (1968).

[56] The resolution quoted here is based on the assumption of a Gaussian profile for the incident and scattered electron beams and is somewhat smaller than the corresponding FWHM value. See S. Trajmar, J. K. Rice, and A. Kuppermann, JPL Tech. Report No. 33-373, 1968, p. 14 (unpublished); see also Ref. 54.

[57] P. R. Smith and J. W. Richardson, J. Phys. Chem. 71, 924 (1967).