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Excitation of the Electronic States of the Nitrogen Molecule by Electron Impact*

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The electron-impact excitation cross sections of the $a\,^1\Pi_g$, $c'\,^1\Sigma_u^+$, $a''\,^1\Sigma_g^+$, $w\,^1\Delta_u$, $b'\,^1\Sigma_u^+$, $b\,^1\Pi_u$, $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, $C\,^3\Pi_u$, $D\,^3\Sigma_u^+$, $W\,^3\Delta_u$, and $E\,^3\Sigma_g^+$ states of N_2 have been calculated over the range of 0–2000 eV for the singlet states and 0–40 eV for the triplet states by means of the Born approximation with Ochkur's and Rudge's scheme for treating the electron-exchange-scattering amplitude. The Franck-Condon-factor approximation was used to obtain the excitation cross sections to each vibrational level of the electronic states. The computation of the scattering-amplitude integrals was greatly facilitated by expressing the molecular wave functions in terms of atomic Gaussian-type orbitals. Four sets of self-consistent-field molecular wave functions have been employed for the calculations in order to test the sensitivity of the calculated cross sections to the choice of the wave functions. With the exception of the $c'\,^1\Sigma_u^+$ state, the cross sections based on three of the four sets vary by typically about 15%. As a test of the Born cross sections for singlet-singlet excitation, comparison between the theoretical and the available experimental values shows 25% agreement for the $a\,^1\Pi_g$ state at 900 eV and 50% for the $a''\,^1\Sigma_g^+$ state at 80 eV. In the case of triplet excitation, the theoretical cross sections of the $C\,^3\Pi_u$ state agree very well with the experimental data, but for the $A\,^3\Sigma_u^+$ and $B\,^3\Pi_g$ states the discrepancy is generally as large as a factor of 2.

I. INTRODUCTION

Although a great deal of efforts have been directed toward characterizing the electron-excitation functions of atoms and comparing the experimental excitation cross sections with the theoretical values in recent years,[1–3] similar studies for molecules are rather sparse in the literature. Even with the simplification of using the Born approximation, computation of the cross sections of electron excitation of the electronic states of diatomic molecules is complicated by the necessity of evaluating multicenter integrals. Indeed, calculations of cross sections for diatomic molecules using accurate molecular wave functions have been reported for only a few cases.[4–6] The introduction of the Gaussian-type orbitals (GTO), which has been used extensively in the calculations of electronic structure of molecules[7,8] and more recently of crystalline solids,[9] has circumvented the difficulty of multicenter integration to the point that the computational procedure for electron-excitation cross sections of molecules is no more complex than the corresponding atomic cases.[6,10]

A large part of the experimental efforts of measuring electron-excitation cross sections of the electronic states of molecules has been devoted to the N_2 molecule. Experimental studies of a number of triplet states have been reported from several laboratories.[11–16] Recently the excitation functions of the Lyman-Birge-Hopfield bands ($a\,^1\Pi_g$) and of the $a''\,^1\Sigma_g$ state have been measured.[17–20] The availability of these experimental data makes it possible to conduct a comprehensive comparison between theoretical calculations and experiments.

In this paper we present our calculations with the Born-type approximations of the electron-excitation cross sections of the $a\,^1\Pi_g$, $c'\,^1\Sigma_u^+$, $a''\,^1\Sigma_g^+$, $w\,^1\Delta_u$, $b'\,^1\Sigma_u^+$, $b\,^1\Pi_u$, $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, $C\,^3\Pi_u$, $D\,^3\Sigma_u^+$, $W\,^3\Delta_u$, and $E\,^3\Sigma_g^+$ states of N_2 by means of the technique of GTO. We have computed the cross sections by using different sets of wave functions to test how sensitively the former depend on the accuracy of the latter. Theoretical Born-type cross sections of the $a\,^1\Pi_g$ and $b\,^1\Pi_u$ states have been reported by Rozsnyai,[21] and those of the six triplet states by Cartwright.[5] In both Refs. 21 and 5, the molecular wave functions were expressed as linear combinations of the Slater-type orbitals (STO), thus certain approximations were made in order to evaluate the Born integrals. In some cases, quite substantial differences are found between the results of the previous workers and those of ours. Moreover, in comparing the algebraic expressions of cross sections given in Cartwright's paper to those of ours, we find that Eq. (17) of Ref. 5 leads to cross sections which are twice larger than the ones computed according to our formulation, as noted in our previous paper.[22] This discrepancy is due to an error in the integration over spin variables in Cartwright's work, and the correction for this error has been given.[23]

The experimental data of the $a\,^1\Pi_g$ state furnish a test of the accuracy of the Born approximation (without exchange) as applied to electronic excitation of diatomic molecules since the measurements extended to incident energies as high as 2000 eV. For the sake of completion our calculated cross sections (Born approximation) are given for incident energies down to the threshold;

however, our interests lie mainly in the high-energy region, since the plane-wave approximation is no longer valid in the near-threshold region. It may be mentioned that while systematic comparisons of theoretical excitation cross sections calculated by the Born approximation with the experimental values have been made for atoms, similar studies for electronic excitation of molecules are very sparse in the literature.

For calculations of singlet-triplet excitation cross sections, modifications of the Born-Oppenheimer approximation have been introduced by Ochkur[24] and by Rudge.[25] Although the use of the plane-wave approximation is expected to be valid only at high energies, these modifications could possibly provide sufficient degree of improvement over the Born-Oppenheimer scheme so that their applicability may extend to much lower energies than does the Born-Oppenheimer approximation. The singlet-triplet excitation functions fall off with energy much more rapidly than the singlet-singlet counterparts; indeed in most of the experimental work, the energy range of interest lies between threshold and about 50 eV rather than the high-energy region where the triplet cross sections become very small. Accordingly, our discussions of calculated triplet cross sections (by Ochkur's and Rudge's modifications) and their comparison with the experimental data will be confined to incident energies below 40 eV.

II. FORMULATION

The process of our prime interest is the excitation of N_2 from the ground electronic and ground vibrational state to a particular vibrational level of a certain excited electronic state. The rotational structure of the molecule will be neglected; instead, we shall average the excitation cross sections over the orientation of the molecular axis with respect to the direction of incident electron. This is essentially equivalent to summing over the rotational levels of the final state and averaging over those of the initial state.

Let us consider a system of an incident electron and a diatomic molecule with N electrons (N being even) and denote the spatial and spin coordinates of the incident electron by $\vec{r}_1$ and σ_1, respectively, those of the molecular electrons by $\vec{r}_2$, $\vec{r}_3$, $\cdots$, σ_2, σ_3, $\cdots$, and the interatomic distance of the molecule by R. To derive a general expression for the excitation-scattering amplitude, we adopt a procedure similar to that of Seaton[26] for treating an $(N+1)$-electron system corresponding to an electron-molecule collision process. The first step is to couple the electronic part of the molecular wave functions with the spin of the incident (or scattered) electron to form a set of basis functions $\psi_m(S, M_S | \vec{r}_2, \vec{r}_3, \cdots \vec{r}_{N+1};\ \sigma_1 \cdots \sigma_{N+1};\ R)$ which is characterized by the total spin quantum numbers S, M_S of the entire system. For instance, the initial state (0) of the N_2 molecule is a spin-singlet from which we obtain a basis function ψ_0 with $S=\frac{1}{2}$, $M_S=\frac{1}{2}$. The final state (n) may be a singlet or triplet. However, in setting up the scattering equations we need to consider only those ψ_n corresponding to $S=\frac{1}{2}$, $M_S=\frac{1}{2}$. In this work, each electronic state is represented by the one-configuration picture, and the wave functions are constructed from the appropriate antisymmetrized products of the self-consistent-field (SCF) molecular orbitals ϕ_i's.

For electron excitation of the N_2 molecule from the ground electronic and ground vibrational state to the vth vibrational state of the excited electronic state (n), we denote the wave vector of the incident and of the scattered electron as $\vec{k}_{00}$ and $\vec{k}_{nv}$, respectively. The wave function of the entire $(N+1)$-electron system is expanded as a series (with proper antisymmetrization) of the form $F_{mv}(\vec{r}_1) \times \psi_m(\frac{1}{2}, \frac{1}{2} | \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_{N+1};\ \sigma_1 \cdots \sigma_{N+1}; R)\, \chi_{mv}(R)$ where $\chi_{mv}(R)$ stands for the vibrational wave functions and $F_{mv}(\vec{r}_1)$ is to be determined by solving the scattering equations. By using the Born approximation it is straightforward to show that the direct-excitation collision amplitude[1] is

$$f_{nv}(\theta\phi) = -(2\pi)^{-1} \int e^{i(\vec{k}_{00}-\vec{k}_{nv})\cdot\vec{r}_1}\, V_{nv,00}(\vec{r}_1)\, d\vec{r}_1, \tag{1}$$

where

$$V_{nv,00}(\vec{r}_1) = \sum_{\sigma} \int \chi_{nv}^{*}\, \psi_n^{*}(\tfrac{1}{2}, \tfrac{1}{2} | \vec{r}_2, \cdots, \vec{r}_{N+1};\ \sigma_1 \cdots \sigma_{N+1};\ R) \times \left(-\frac{Z}{r_{1A}} - \frac{Z}{r_{1B}} + \sum_{i=2}^{N+1} |\vec{r}_1 - \vec{r}_i|^{-1} \right) \chi_{00} \times \psi_0(\tfrac{1}{2}, \tfrac{1}{2} | \vec{r}_2, \cdots, \vec{r}_{N+1};\ \sigma_1 \cdots \sigma_{N+1};\ R) R^2 \times dR\, d\vec{r}_2 \cdots d\vec{r}_{N+1}. \tag{2}$$

In the above equation, $\sum_\sigma$ signifies summation over all spin coordinates, Z is the charge of each nucleus, and r_{1A} is the distance of the electron from the nucleus A. When the wave functions are given by the one-configuration approximation as described previously, the collision amplitude reduces to that of a two-electron molecule with the excitation of one electron from the molecular orbital ϕ_λ to ϕ_μ, i.e.,

$$f_{nv}(\theta\phi) = -2K^{-2} \int (1/\sqrt{2})[\phi_\lambda(\vec{r}_1, R)\phi_\mu(\vec{r}_2, R) + \phi_\lambda(\vec{r}_2, R)\, \phi_\mu(\vec{r}_1, R)]^{*} (e^{i\vec{K}\cdot\vec{r}_1} + e^{i\vec{K}\cdot\vec{r}_2}) \times \phi_\lambda(\vec{r}_1, R)\, \phi_\lambda(\vec{r}_2, R)\, \chi_{nv}^{*}(R)\, \chi_{00}(R)\, R^2\, dR\, d\vec{r}_1\, d\vec{r}_2, \tag{3}$$

where $\vec{K} = \vec{k}_{00} - \vec{k}_{nv}$.

In a similar manner, the exchange-excitation collision amplitude can be treated by Ochkur's or by Rudge's modification of the Born-Oppenheimer approximation with the results

$$g_{nv}^{+}(\theta\phi)=2T^{-2}\int(1/\sqrt{2})\,[\phi_\lambda(\vec{r}_1,R)\,\phi_\mu(\vec{r}_2,R)+\phi_\lambda(\vec{r}_2,R)\,\phi_\mu(\vec{r}_1,R)]^{*}\,e^{i\vec{K}\cdot\vec{r}_2}\,\phi_\lambda(\vec{r}_1,R)\times\phi_\lambda(\vec{r}_2,R)\,\chi_{nv}^{*}(R)\chi_{00}(R)\,R^2\,dR\,d\vec{r}_1\,d\vec{r}_2\,, \quad (4)$$

$$g_{nv}^{-}(\theta\phi)=2\sqrt{3}\;T^{-2}\int(1/\sqrt{2})[\phi_\lambda(\vec{r}_1,R)\,\phi_\mu(\vec{r}_2,R)-\phi_\lambda(\vec{r}_2,R)\,\phi_\mu(\vec{r}_1,R)]^{*}\,e^{i\vec{K}\cdot\vec{r}_2}\,\phi_\lambda(\vec{r}_1,R)\times\phi_\lambda(\vec{r}_2,R)\,\chi_{mv}^{*}(R)\,\chi_{00}(R)\,R^2\,dR\,d\vec{r}_1\,d\vec{r}_2\,, \quad (5)$$

where g^{+} and g^{-} are the exchange amplitude for singlet and triplet excitation, respectively, and

$$T^2=\begin{cases}k_{00}^2, & \text{excitation}\\ k_{nv}^2, & \text{deexcitation}\end{cases}\quad\text{(Ochkur)}$$
$$T^2=(k_{nv}-i\epsilon^{1/2})^2\quad\text{(Rudge)}, \quad (6)$$

and ϵ is the ionization potential of the initial state in *Rydberg units*. To further simplify the calculation it is customary to use the "Franck-Condon-factor approximation" with which we neglect the dependence of the molecular orbitals on the internuclear distance in Eqs. (3)–(5), so that the R integration leads directly to the Franck-Condon factor. This procedure is satisfactory for excitation from the ground vibrational state whose wave function has a localized form. With this approximation Eq. (3) becomes

$$f_{nv}=2K^{-2}\mathcal{E}_{0n}(K,\Theta,\Phi)\int\chi_{nv}^{*}(R)\chi_{00}(R)R^2\,dR\,, \quad (7)$$

where

$$\mathcal{E}_{0n}(K,\Theta,\Phi)=-\int(1/\sqrt{2})[\phi_\lambda(\vec{r}_1,R_0)\,\phi_\mu(\vec{r}_2,R_0)+\phi_\lambda(\vec{r}_2,R_0)\,\phi_\mu(\vec{r}_1,R_0)]^{*}(e^{i\vec{K}\cdot\vec{r}_1}+e^{i\vec{K}\cdot\vec{r}_2})\times\phi_\lambda(\vec{r}_1,R_0)\,\phi_\lambda(\vec{r}_2,R_0)\,d\vec{r}_1\,d\vec{r}_2\,, \quad (8)$$

Θ and Φ specify the orientation of the molecular axis relative to $\vec{K}$, and R_0 is the equilibrium bond length of the molecule in the ground electronic state. Likewise, the exchange amplitudes can be factored in a similar way. The differential cross sections for singlet and triplet excitation are

$$I_{nv}^{S}(\theta\phi)=(\omega_n k_{nv}/4\pi k_{00})\int d\Omega\,|f_{nv}+g_{nv}^{+}|^2=(\omega_n k_{nv}q_{nv}/\pi k_{00})\int d\Omega\,|(K^{-2}-\tfrac{1}{2}T^{-2})\times\mathcal{E}_{0n}(K,\Theta,\Phi)|^2\,, \quad (9)$$

$$I_{mv}^{T}(\theta\phi)=(3\omega_n k_{nv}q_{nv}/\pi k_{00})\int d\Omega\,|-\tfrac{1}{2}T^{-2}\mathcal{E}_{0n}(K,\Theta,\Phi)|^2\,, \quad (10)$$

respectively, where q_{nv}, the Franck-Condon factor, is

$$q_{nv}=|\int\chi_{nv}^{*}(R)\chi_{00}(R)R^2\,dR|^2\,, \quad (11)$$

ω_n is the degeneracy of the excited state, and the integration over Ω results from averaging over the orientation of the molecular axis with respect to $\vec{K}$. Integration of the differential cross sections over K from $K_{\min}$ $(=k_{00}-k_{nv})$ to $K_{\max}$ $(=k_{00}+k_{nv})$ gives the total electronic-vibrational excitation cross section $Q(00\to nv)$. The total excitation cross section of an electronic state is obtained by summing $Q(00\to nv)$ over all v, viz.,

$$Q(0\to n)=\sum_v Q(00\to nv)=2\pi\sum_v q_{nv}\int_{\bar{K}_{\min}}^{\bar{K}_{\max}}I_{nv}(K)\,K\,dK\,, \quad (12)$$

where $I_{nv}(K)$ has the following forms for singlet and triplet excitation:

$$I_{nv}^{S}(K)\,K\,dK=(\omega_n K\,dK/\pi k_{00}^2)\times\int d\Omega\,|(K^{-2}-\tfrac{1}{2}T^{-2})\mathcal{E}_{0n}(K,\Theta,\Phi)|^2\quad\text{for singlet excitation}, \quad (13)$$

$$I_{nv}^{T}(K)\,K\,dK=(3\omega_n K\,dK/\pi k_{00}^2)\times\int d\Omega\,|-\tfrac{1}{2}T^{-2}\mathcal{E}_{0n}(K,\Theta,\Phi)|^2\quad\text{for triplet excitation}. \quad (14)$$

Although in principle the values of $K_{\max}$ and $K_{\min}$ depend on v, except near the threshold one can ignore their variations due to the difference of vertical excitation energies to different vibrational levels of the upper electronic state and simply use some mean value $\bar{K}_{\max}$ and $\bar{K}_{\min}$ for all the vibrational components, i.e.,

$$Q(0\to n)\simeq 2\pi\sum_v q_{nv}\int_{\bar{K}_{\min}}^{\bar{K}_{\max}}I_n(K)\,K\,dK=2\pi\int_{\bar{K}_{\min}}^{\bar{K}_{\max}}I_n(K)\,K\,dK\,. \quad (15)$$

The error in the total cross section due to this approximation is about 2% at 40 eV, and at energy greater than 100 eV the error is completely negligible. However, the use of Eq. (12) requires reliable Franck-Condon factors, whereas the use of Eq. (15) does not. In this paper we used Eq. (12) to compute cross sections for all triplet states and the $a\,^1\Pi_g$ state. The Franck-Condon factors used in this paper are from the work of Benesch *et al.*[27] for $a\,^1\Pi_g$, $B\,^3\Pi_g$, $C\,^3\Pi_u$, and $A\,^3\Sigma_u^+$; and from the work of Cartwright[5] for $W\,^3\Delta_u$, $E\,^3\Sigma_g^+$, and $D\,^3\Sigma_u^+$. For the other singlet states ($b\,^1\Pi_u$, $b'\,^1\Sigma_u^+$, $w\,^1\Delta_u$, $a''\,^1\Sigma_g^+$, $c'\,^1\Sigma_u^+$), we used Eq. (15) to compute the cross sections. It is convenient to introduce the quantity

$$G_{0n}(K)=(2\omega_n/4\pi K^2)\int|\mathcal{E}_{0n}(K,\Theta,\Phi)|^2\,d\Omega\,, \quad (16)$$

from which one can easily obtain both the singlet and triplet excitation cross sections. Here $G_{0n}(K)$ depends only on the wave functions of the initial and final electronic states; therefore, it is especially suitable for testing the sensitivity of cross sections to the accuracy of the wave functions used. The generalized oscillator strength $\mathcal{F}_{0n}(K)$ is related to $G_{0n}(K)$ as

$$\mathcal{F}_{0n}(K)=(\Delta E)\,G_{0n}(K)\,, \quad (17)$$

where ΔE is the vertical excitation energy.

III. METHOD OF COMPUTATION

To obtain the excitation cross sections, we first compute $\mathcal{E}_{0n}$ [as defined in Eq. (8)] which, on account of the orthonormality of the molecular orbitals, reduces to

$$\mathcal{E}_{0n}(K,\Theta,\Phi) = -\sqrt{2}\int \phi_\mu^*(\vec{r})\,e^{i\vec{K}\cdot\vec{r}}\,\phi_\lambda(\vec{r})\,d\vec{r}\ . \tag{18}$$

We use the Franck-Condon–factor approximation throughout this paper; thus, the molecular orbitals are taken to be at a fixed internuclear distance corresponding to the equilibrium bond length of the ground electronic state. Each of the molecular orbitals is written as a linear combination of atomic orbitals centered at the two nuclei A and B as

$$\phi_\lambda = \sum_l C_l\,[u_l(\vec{r}_A) + M_{\lambda l}\,u_l(\vec{r}_B)]\ , \tag{19}$$

where $\vec{r}_A$ and $\vec{r}_B$ are the radius vectors of the electron extended from A and B, respectively, and $M_{\lambda l}$ is either 1 or -1. If the atomic orbitals u_l are expressed in terms of the STO, Eq. (18) contains a series of multicenter integrals of the type

$$\int r_A^p\,e^{-\alpha r_A}\,Y_{lm}^*(\theta_A\phi)\,e^{i\vec{K}\cdot\vec{r}}\,r_B^q\,e^{-\beta r_B}\,Y_{l'm'}(\theta_B\phi)\,d\vec{r}\ . \tag{20}$$

The evaluation of such integrals is quite difficult. An approximation scheme of using ζ-function expansion has been given by Cartwright and Kuppermann.[4] Even with this expansion technique the computational complexity increases rapidly with inclusion of atomic orbitals of higher quantum numbers. On the other hand, GTO's have been employed to great advantage in evaluating the multicenter integrals in molecular-structure calculations, and application of the GTO to the studies of electron excitation of molecules has been made by Miller and Krauss.[6] In fact, if the STO's in Eq. (20) were replaced by the GTO's, the resulting multicenter integral can be evaluated in closed forms.[6,10] A detailed account of the method of integration can be found in Ref. 10. In this paper we shall adopt the GTO approach. Although the molecular orbitals are generally given in terms of the STO's in published works on the SCF calculations of the electronic structure of N_2, they can be converted into the form of linear combinations of GTO's by a curve-fitting procedure. For each molecular orbital we used seven $1s$-type, seven $2p$-type, and seven $3d$-type GTO's and the optimum choice of the Gaussian exponents and their weighting coefficients is determined by a nonlinear least-squares curve-fitting technique of Marquardt.[28] Typically in the region where the value of the wave function is greater than 10^{-2} of its peak value, the fit is accurate to within a few tenths of a percent. As the wave function decreases to 10^{-3} of its peak value, the accuracy of the curve fitting reduces to about 1%. The fit becomes poorer (about 10%) as the wave function decreases to 10^{-5} of the peak value. To get an idea of how sensitively the calculated cross sections depend on the "goodness" of the GTO expansion of an STO, we note that the accuracy of the curve fitting indicated above is considerably higher than the six-term GTO expansions of the $1s$ and $2p$ wave functions of the hydrogen atom (Fig. 1 of Ref. 10) which give excitation cross sections within 1% of those calculated by the exact hydrogenic wave functions.

Following the procedure outlined in Ref. 10, one can express $\mathcal{E}_{0n}(K,\Theta,\Phi)$ in analytic forms. To facilitate the integration of $\mathcal{E}_{0n}(K,\Theta,\Phi)$ over the orientation of the molecular axis, it is convenient to choose the coordinate axes such that $\vec{K}$ lies on the y-z plane. Equation (16) then gives $G_{0n}(K)$ from which one can obtain the generalized oscillator strengths, the differential cross sections, and the total cross sections.

IV. RESULTS AND DISCUSSION

A. Generalized Oscillator Strengths

Before making an extensive comparison between the theoretical and experimental excitation cross sections of the N_2 molecule, it is important to ascertain how sensitively the theoretical values vary with the choice of the electronic wave functions. To this end we have used the wave functions given by Nesbet,[29] Richardson,[30] Ransil,[31] Sahni and De Lorenzo,[32] and Lefebvre-Brion and Moser.[33] The wave functions of Ransil and those of Sahni and De Lorenzo contain in the basis functions $n=1$ and $n=2$ atomic orbitals, with the difference that the exponents of atomic orbitals were optimized in the former set, whereas they were not in the latter. The wave functions of Richardson differ from those above in that the number of $n=2$ atomic orbitals were doubled. The $3d$ atomic orbitals were included in Nesbet's wave functions which give better energies. For comparison we have performed an SCF calculation of the electronic structure of N_2 using 13 s-type and seven p-type GTO's as the basis functions. The exponents and the "contractions" of the Gaussians were taken from the work of Huzinaga and Sakai[34]; however, the "contractions" on the $2p$ GTO's were relaxed to gain more variational freedom. For convenience we shall designate by set (i) Nesbet's wave functions for both the ground and excited states, by set (ii) Richardson's wave functions, and by set (iii) the GTO functions. In the cases of excitation to the Rydberg excited states (c'^1, $D\,^3\Sigma_u^+$, and a''^1, $E\,^3\Sigma_g^+$), we used the wave functions of the excited orbitals by Lefebvre-Brion and Moser in combination with Nesbet's, Richardson's, and our GTO ground-state functions. However, we shall continue to use the same designations without confusion, since those wave functions by Lefebvre-Brion and Moser are the only ones used for the Rydberg excited orbitals of $(3s)\sigma_g$ and $(3p)\sigma_u$. By set (iv) we shall refer to the combinations of Ransil's ground-state and the excited-state functions of Sahni and De Lorenzo's "restricted treatment."

Since both the singlet and triplet excitation cross sections are proportional to the generalized oscillator strength, we have examined in some detail the various versions of the functions $G_{0n}(K)$ computed by different sets of wave functions.[35] The singlet cross sections are particularly sensitive to the behavior of $G_{0n}(K)$ for small values of K ($\lesssim 1.0$), whereas the triplet cross sections are governed mainly by $G_{0n}(K)$ for larger values of K [see Eqs. (13) and (14)]. When the electronic states of the molecule are represented by those of a single electron configuration, each excitation can be characterized as a one-electron transition from one molecular orbital to another. In this subsection we discuss the $3\sigma_g \rightarrow 1\pi_g$, $2\sigma_u \rightarrow 1\pi_g$, $1\pi_u \rightarrow 1\pi_g$, $3\sigma_g \rightarrow (3s)\sigma_g$, and $3\sigma_g \rightarrow (3p)\sigma_u$ transitions which are the underlying one-electron transitions of all the excitation processes considered in this paper.

1. $3\sigma_g \rightarrow 1\pi_g$

This transition corresponds to the $a\,^1\Pi_g$ and $B\,^3\Pi_g$ of the $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(1\pi_g)$ configuration.[36] We have calculated $G_{0n}(K)$ by using all four sets of wave functions. Figure 1 shows the curves of $G_{0n}(K)$ calculated by sets (i), (iii), and (iv) along with the experimental values of Lassettre and Krasnow.[37] The results of set (ii) lie between sets (i) and (iii) and are left out for clarity. The theoretical values calculated using sets (i)–(iii) agree very well with one another (within 10%) and also show a reasonable agreement with the experimental data for small values of K. The theoretical generalized oscillator strengths have been reported by Rozsnyai (based on Ransil's functions with *unoptimized* exponents for both the ground and excited states).[21] His values are lower than all four sets of theoretical values mentioned above (Fig. 1). Although Rozsnyai's scheme of computation involves some approximations, this discrepancy of a factor greater than 2 is difficult to explain. As we shall see in Sec. IV A 2, his values for the $2\sigma_u \rightarrow 1\pi_g$ transition agree much better (20%) with ours. Rozsnyai was able to increase the value of the oscillator strengths by dropping the $1s$ and $2s$ constituents from the $3\sigma_g$ molecular orbital, but the theoretical justification for this step is not clear. The close agreement between the theoretical values calculated from the wave functions of Nesbet, Richardson, and our GTO wave functions is especially encouraging.

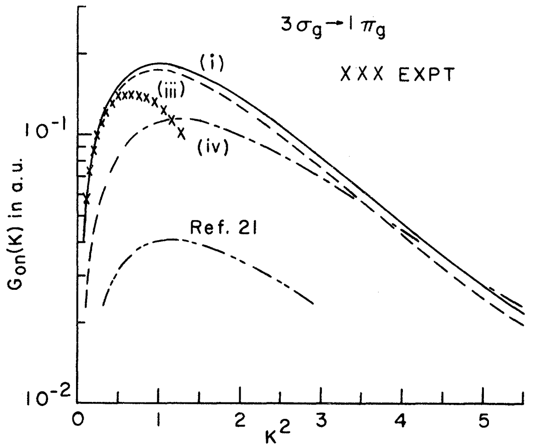

FIG. 1. Values of $G_{0n}(K)$ [defined in Eq. (16)] for the $3\sigma_g \rightarrow 1\pi_g$ transition computed by using wave-function set (i) (solid line), set (iii) (even dashed line), and set (iv) (long-short dashed line). Also included are Rozsnyai's (Ref. 21) computed values (long-short-short dashed line), and the experimental data of Lassettre and Krasnow given in Ref. 37 (×).

2. $2\sigma_u \rightarrow 1\pi_g$

The electronic configuration $(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$ gives rise to the $C\,^3\Pi_u$ state[38] and to one $^1\Pi_u$ state; the latter $(b\,^1\Pi_u)$, however, is believed to be mixed with the $(2\sigma_u)^2(3\sigma_g)(1\pi_u)^3(1\pi_g)^2$ configuration.[39] The graphs of $G_{0n}(K)$ calculated by sets (i) and (iv) along with Rozsnyai's values[21] and Lassettre and Krasnow's experimental values[37] are displayed in Fig. 2. The results of sets (ii) and (iii), which are not shown in Fig. 2, differ from those of set (i) by no more than 8.5 and 2.6%, respectively. All four calculated $G_{0n}(K)$ curves show a maximum at $K = 0$, characteristic of the generalized oscillator strengths of a dipole-allowed transition. Moreover, they are not very sensitive to the choice of wave functions for this transition. From electron-impact energy-loss experiments, Lassettre and Krasnow obtained the generalized oscillator strengths for the energy loss $\Delta E = 12.85$ eV.[37] It was suggested that the spectrum of this energy loss probably includes contributions from vibrational levels of $c'\,^1\Sigma_u^+$, $b'\,^1\Sigma_u$ as well as $b\,^1\Pi_u$.[40] Because of these uncertainties no comparison between theory and experiment will be made for this transition.

3. $1\pi_u \rightarrow 1\pi_g$

When an electron in the degenerate $1\pi_u$ is promoted to another degenerate $1\pi_g$ orbital, four different assignments may be made, which are responsible for a Σ_u^+, a Σ_u^-, and a doubly degenerate Δ_u state.[41] The $^1\Sigma_u^+$ state (designated as $b'\,^1\Sigma_u^+$) is an optically allowed one, and its triplet counterpart is the $A\,^3\Sigma_u^+$ state. The other states $(a'\,^1\Sigma_u^-$, $B'\,^3\Sigma_u^-$, $w\,^1\Delta_u$, $W\,^3\Delta_u)$ are all dipole forbidden. The

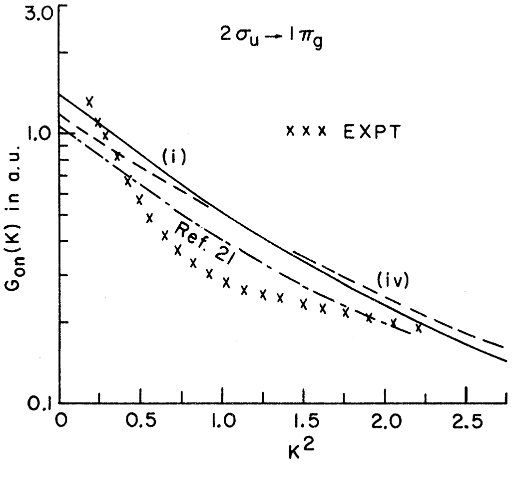

FIG. 2. Values of $G_{0n}(K)$ [defined in Eq. (16)] for the $2\sigma_u \rightarrow 1\pi_g$ transition computed by using wave-function set (i) (solid line) and set (iv) (even dashed line), including the Rozsnyai's (Ref. 21) computed values (long-short dashed line), and the experimental data of Lassettre and Krasnow given in Ref. 37 (×).

shape of the $G_{0n}(K)$ curves indeed properly reflect the optical nature of the transitions as may be seen in Figs. 3 and 4 [$G_{0n}(K)$ is identically zero for *symmetry*-forbidden transition to Σ_u^-]. Figure 3 shows the $G_{0n}(K)$ appropriate to ${}^{1,3}\Sigma_u^+$ computed by sets (i) and (iv), and the results by set (ii) are represented simply by dots for clarity. Set (iii) gives values which are between sets (i) and (ii) except near $K=0$ where they are about 5% larger than those of set (ii). Sets (i) and (iv) differ most, but the difference is within 25% for $K \lesssim 3.0$. We observed an interesting feature of the secondary extrema (not shown in Fig. 3) beyond $K=3.5$ (by all sets of wave functions). However, these extrema occur at too large values of K and the magnitude is too small (less than 10^{-3} of the value at $K=0$) to affect the total cross sections in any appreciable way.

Figure 4 shows $G_{0n}(K)$ appropriate for ${}^{1,3}\Delta_u$ computed by sets (i), (iv) and (iii) (by dots). The results by set (ii) are smaller by 10% at $K=0.1$ and larger by 10% at $K=6.0$ compared with those of set (i). We note the much broader peak in this curve compared with other optically forbidden transitions. As we shall see later, this broad peak is responsible for a broad peak in the excitation functions of the $w\,{}^1\Delta_u$ and $W\,{}^3\Delta_u$ states.

4. $3\sigma_g \rightarrow (3p)\sigma_u$ and $3\sigma_g \rightarrow (3s)\sigma_g$

The $3\sigma_g \rightarrow (3p)\sigma_u$ transition corresponds to excitation to the Rydberg $c'\,{}^1\Sigma_u^+$ and $D\,{}^3\Sigma_u^+$ states. In Fig. 3 we present the $G_{0n}(K)$ curves for the $3\sigma_g \rightarrow (3p)\sigma_u$ transition. As designated before, for this and the $3\sigma_g \rightarrow (3s)\sigma_g$ excitations, sets (i)–(iii) refer to the $3\sigma_g$ orbitals of Nesbet, Richardson, and GTO, respectively, in combination with $(3p)\sigma_u$ and $(3s)\sigma_g$ orbitals of Lefebvre-Brion and Moser. The generalized oscillator strengths depend more sensitively on the $3\sigma_g$ orbital in the low-K region as seen in Fig. 3. This will be reflected much more strongly in the singlet cross sections than in the triplet cross sections.

From the measurements of absorption spectrum, Lawrence, Mickey, and Dressler[42] obtained the absolute optical oscillator strength to be 0.14 ± 0.04 for the $p'\,{}^1\Sigma_u^+$ band which is the first vibrational member of $c'\,{}^1\Sigma_u^+$ state.[39] By comparing the transition probability deduced from their oscillator strength and the one from the lifetime measurement, they conclude that the Franck-Condon factor for the p' level to be very close to unity. Assuming the Franck-Condon factor to be unity, our computed $G_{0n}(K=0)$ leads to an optical oscillator strength of 0.0607 which is about 2.3 times smaller than the measured value. Unlike other transitions studied in this work, the $G_{0n}(K)$ function for $c'\,{}^1\Sigma_u^+$ shows an unusual behavior of decreasing very rapidly from $K=0$ to $K \cong 0.84$ by a factor greater than 200 and then rising again to a broad maximum around $K=1.3$ (Fig. 3). This sharp decrease in $G_{0n}(K)$ indicates a strong angular dependence of the differential cross section. The

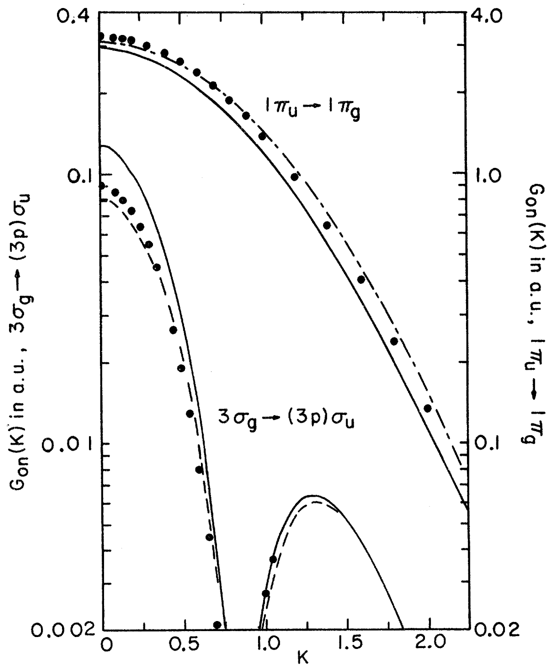

FIG. 3. Values of $G_{0n}(K)$ [defined in Eq. (16)] for the $1\pi_u \rightarrow 1\pi_g$ (appropriate for ${}^{1,3}\Sigma_u^+$ states) and $3\sigma_g \rightarrow (3p)\sigma_u$ transitions computed by using wave-function set (i) (solid line), set (ii) (dots), set (iii) (even dashed line), and set (iv) (long-short dashed line).

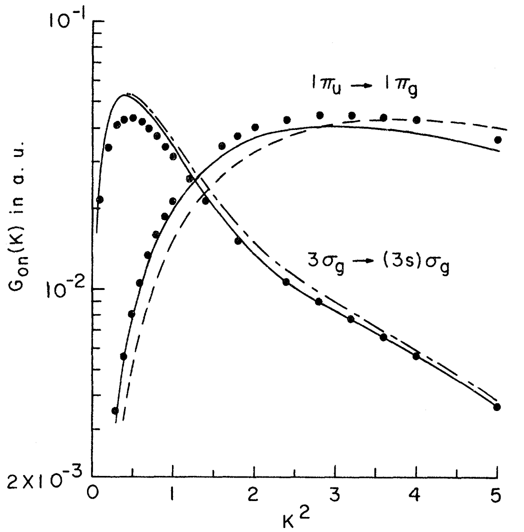

FIG. 4. Values of $G_{0n}(K)$ [defined in Eq. (16)] for the $1\pi_u \rightarrow 1\pi_g$ (appropriate for ${}^{1,3}\Delta_u$ states) and $3\sigma_g \rightarrow (3s)\sigma_g$ transitions computed by wave-function set (i) (solid line), set (ii) (long-short dashed line), set (iii) (dots), and set (iv) (even dashed line).

relative intensity measurements of electron-impact energy-loss spectra also show the strong angular dependence. The point is discussed in fuller detail in Sec. IV B 3.

The generalized oscillator strengths of the $3\sigma_g \rightarrow (3s)\sigma_g$ transition, which yields[43] the $a''\,{}^1\Sigma_g^+$ and $E\,{}^3\Sigma_g^+$ states, are seen to have the qualitative behavior of those of a dipole-forbidden state (Fig. 4). Compared with the values obtained by set (i), set-(ii) results are about 7% larger for $K \gtrsim 1.0$, whereas set (iii) gives values which are about 20% smaller for $K \lesssim 0.5$, but practically identical for $K \gtrsim 2.0$.

B. Excitation Cross Sections for Singlet States

1. $a\,{}^1\Pi_g$ *State (Lyman-Birge-Hopfield Bands)*

The $a\,{}^1\Pi_g$ state is the only singlet state for which a considerable amount of experimental work on the measurements of the absolute excitation cross sections has been reported in the literature; therefore, it is a particularly good case for testing the Born cross sections. In applying the Born approximation to the singlet-singlet excitation problems, it had been customary to ignore the exchange effect. By means of the Ochkur[24] and Rudge[25] modifications, the exchange effect can be taken into account more satisfactorily than by the Born-Oppenheimer approximation. Accordingly we have calculated the excitation cross sections by these two versions of exchange treatment and by neglecting exchange, using wave functions set (i), and compared the results in Fig. 5. It is seen that the Ochkur exchange tends to decrease the computed cross sections in the low-energy region, whereas the use of the Rudge formula reduces only slightly the cross sections above 40 eV but gives a substantial increase over the nonexchange values as the incident-electron energy is decreased. In fact, it is easy to see from Eqs. (6) and (13) that for incident-electron energy less than $\epsilon + \Delta E$ (in Ry) the Rudge exchange term tends to increase the cross sections. We also observe a similar increase of cross sections (at low energies) associated with the use of the Rudge modification for all the other singlet states studied in this paper. (Parenthetically we may add that the same kind of behaviors were also noted in the excitation functions of the ${}^1P$ and ${}^1D$ states of He.[44]) From the available experimental data of N_2, we find it difficult to decide which version of the exchange approximation works better for singlet-singlet excitation. Moreover, the difference between the nonexchange Born approximation and the two modifications is appreciable only at relatively low energies where such effects as polarization and distortion, which were not included in all the Born-type theory, may play important roles in determining the cross sections. Without a quantitative measure of these effects,

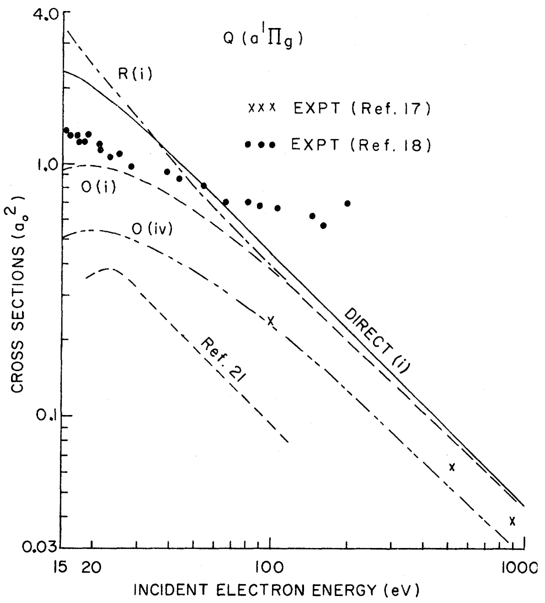

FIG. 5. Excitation functions of the $a\,{}^1\Pi_g$ state (Lyman-Birge-Hopfield bands) computed by using wave-function set (i) without exchange [direct (i), solid line]; set (i) including exchange by Ochkur's modification [O(i), even dashed line]; set (i) including exchange by Rudge's modification [R(i), long-short dashed line]; and set (iv) including exchange by Ochkur's modification [O(iv), long-short-short dashed line]. Also included are Rozsnyai's computed values (dashed line labeled Ref. 21), and experimental data of Holland, given in Ref. 17 (x), and of Ajello, given in Ref. 18 (dots).

it is impractical to attempt a critical appraisal of the two versions of exchange formula by comparing the theoretical values with experimental data. However, the steep rise of cross sections with reducing energies below 30 eV according to Rudge's modification could be somewhat unrealistic. For this reason and the reason that Rudge's modification lacks the detailed balancing in the case of singlet-to-singlet excitations,[45] we shall adopt the Ochkur modification to include the exchange effect. Unless otherwise specified, all singlet cross sections presented in this paper are computed with exchange by the Ochkur modification.

The theoretical excitation cross sections calculated by using the wave functions of sets (i)–(iii) agree very well with one another, of which the results of set (i) are shown in Fig. 5. The excitation functions by the other two sets are about 5% smaller than the one shown. The excitation function computed with set (iv) is markedly smaller, however (see Fig. 5). The sensitivity of cross sections on the choice of wave functions for this and other singlet states is summarized in Table I.

The theoretical cross sections based on wave functions (i)–(iii) are somewhat larger than the experimental values reported by Holland[17]; above 500 eV the agreement is within 25%. This provides an experimental test of the accuracy of the first Born approximation for electron-molecule excitation since at energies above 500 eV the exchange effect is entirely negligible.

Experimental measurements of the excitation cross sections have been reported also by Ajello[18] for the energy range 10–200 eV. His cross sections are much larger than those of Holland in the energy range where the two sets of data overlap. Between 100 and 200 eV, Ajello's cross sections are substantially larger than the theoretical values.

Aarts and De Heer[19] have studied the electron-impact emission of the $a\,^1\Pi_g \rightarrow X\,^1\Sigma_g^+$ transitions, and by normalizing the cross sections to the experimental data of Lassettre and Krasnow[37] at 500 eV, obtained the excitation cross sections of the $a\,^1\Pi_g$ state. Their results are in very good agreement with those of Holland.[17] Brinkmann and Trajmar[20] reported electron-excitation measurements for a number of states of N_2. By normalizing to the absolute cross sections of other workers and by extrapolation they gave an electron-excitation function of the $a\,^1\Pi_g$ state which agrees well with Holland's values. Other cross-section measurements of the $a\,^1\Pi_g$ state include the work of Borst[16] and of Freund[46] in the region 0–40 eV.

It should be mentioned that the measured cross sections of Holland and Ajello were not corrected for cascade contributions. Ajello[18] estimated the probable cascade to be less than 10%. In Holland's work evidence has been cited to indicate that the cascade contribution is not large.[17] However, it was pointed out in Ref. 17 that if the radiative lifetime of the $a\,^1\Pi_g$ state is as short as 40 μsec, the cross sections may include a cascade contribution of 25–35%. Recent measurements of Borst and Zipf give the lifetime of the $a\,^1\Pi_g$ state of N_2 as (115 ± 20) μsec,[47] supporting the idea of a small cascade contribution to the observed cross sections.

TABLE I. Peak electron-excitation cross sections ($Q_{\max}$), energies of the peak [$E(Q_{\max})$], and cross sections at 1000 eV [$Q(10^3\text{ eV})$] for six singlet states of N_2 calculated by wave-function sets (i)–(iv). Cross sections are in units of a_0^2 and energies in eV.

States	Sets	$Q_{\max}$	$E(Q_{\max})$	$Q(10^3$ eV)
$a\,^1\Pi_g$	(i)	0.980	18.5	0.0442
	(ii)	0.945	18.5	0.0427
	(iii)	0.931	18.5	0.0417
	(iv)	0.551	19.0	0.0276
$a''\,^1\Sigma_g^+$	(i)	0.253	26	0.0134
	(ii)	0.255	26	0.0134
	(iii)	0.210	26	0.0110
$c'\,^1\Sigma_u^+$	(i)	0.148	60	0.0383
	(ii)	0.104	60	0.0272
	(iii)	0.101	60	0.0249
$w\,^1\Delta_u$	(i)	0.0674	30	0.00715
	(ii)	0.0664	32	0.00751
	(iii)	0.0733	30	0.00783
	(iv)	0.0553	34	0.00708
$b'\,^1\Sigma_u^+$	(i)	8.287	40	1.241
	(ii)	9.392	40	1.391
	(iii)	9.409	40	1.411
	(iv)	9.324	40	1.347
$b\,^1\Pi_u$	(i)	4.875	34	0.620
	(ii)	5.275	34	0.670
	(iii)	4.950	34	0.625
	(iv)	4.442	32	0.542

Included in Fig. 5 are the theoretical cross sections reported by Rozsnyai.[21] His values are much lower than our theoretical cross sections calculated from all four sets of wave functions as was noted in Sec. IV A 1. There also exist other calculations of cross sections by semiempirical means,[48] but the methods employed were quite different from the one used here, hence no comparison of the results will be made.

2. $a''\,^1\Sigma_g^+$ *State*

The $a''\,^1\Sigma_g^+$ state arises from the $(1\pi_u)^4(3\sigma_g)(3s\sigma_g)$ configuration.[43] In Fig. 6 are shown the theoretical excitation functions of $a''\,^1\Sigma_g^+$ computed using sets (i) and (iii). The excitation cross sections do not seem to depend too sensitively on the choice of wave functions, sets (i) and (iii) differing by about 20%. The theoretical cross sections show

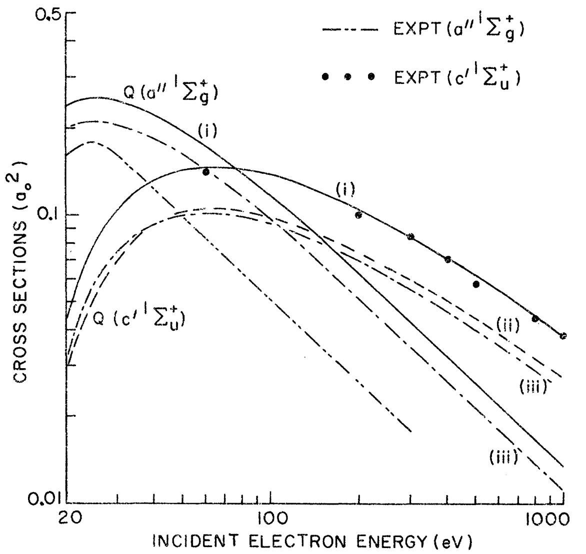

FIG. 6. Excitation functions of the $a''\ {}^1\Sigma_g^+$ and the $c'\ {}^1\Sigma_u^+$ states computed by means of Ochkur's modification and using wave-function set (i) (solid line), set (ii) (even dashed line), and set (iii) (long-short dashed line), including the experimental data ($a''\ {}^1\Sigma_g^+$) by Brinkmann and Trajmar, given in Ref. 20 (long-short-short dashed line), and the experimental data ($c'\ {}^1\Sigma_u^+$) by Aarts and De Heer, given in Ref. 19, (dots) which is normalized to the theoretical cross section of set (i) at 2000 eV.

an E^{-1} dependence beyond 250 eV. The experimental excitation function reported by Brinkmann and Trajmar[20] is about 50% of our theoretical counterpart above 80 eV, although agreement is considerably better at lower energy. The E^{-1} dependence of their excitation function starts at much lower energy than 250 eV found in this theoretical work. Brinkmann and Trajmar studied electron-impact energy-loss spectra at 15, 20, 30, 60, and 80 eV of incident-electron energy. They have normalized their data to different known experimental cross sections according to the incident-electron energy. At incident-electron energies greater than 80 eV, they extrapolated to obtain the cross sections. Their procedures of reducing experimental data may account for some of the discrepancy found between the theory and experiment.

3. $c'\ {}^1\Sigma_u^+$ *State*

The $c'\ {}^1\Sigma_u^+$ state, which belongs to the $(1\pi_u)^4(3\sigma_g)(3p\sigma_u)$ configuration, is a dipole-allowed state; thus it is of special interest to study its excitation properties. The excitation functions obtained by using wave functions (i)–(iii) are shown in Fig. 6. The broad peak of the excitation function reminds one of the corresponding case of the dipole-allowed excited states of atoms. For this state we see unusually large variations of the cross sections due to the choice of wave functions (as large as 50%), the shape of the theoretical curves remaining nearly the same. Recently the $p'\ {}^1\Sigma_u^+$ state has been identified as the lowest vibrational level of the $c'\ {}^1\Sigma_u^+$ state.[39] The optical excitation function of $p'\ {}^1\Sigma_u^+ \rightarrow X\ {}^1\Sigma_g^+\ (v''=1)$ has been measured by Aarts and De Heer,[19] and the shape of their excitation function is in good agreement with our calculations. Since only one vibrational component ($v'=0 \rightarrow v''=1$) of the $c'\ {}^1\Sigma_u^+ \rightarrow X\ {}^1\Sigma_g^+$ transitions and one component of $c'\ {}^1\Sigma_u^+ \rightarrow a\ {}^1\Pi_g$ were reported in the measurements of Aarts and De Heer,[19] we are unable to compare the magnitude of our theoretical cross sections with experiments. Instead, we normalized the optical cross sections of Aarts and De Heer to the theoretical cross section [by set (i)] at 2000 eV in order to compare the shape of the excitation functions. The normalized cross sections of Aarts and De Heer are included in Fig. 6. The agreement is seen to be quite good.

Like the case of a dipole-allowed *atomic* excited state, the differential excitation cross sections of $c'\ {}^1\Sigma_u^+$ are sharply peaked in the forward direction as illustrated in Fig. 7 where we have plotted the differential cross sections at various incident-electron energies, including that of $a\ {}^1\Pi_g$ at 20 eV for comparison. This is in qualitative agreement with the experiment by Williams and Doering.[49] Lassettre[50] has pointed out the sharp decrease in relative intensity at zero angle of the 12.93-eV transition of the electron-impact spectra of Heideman,

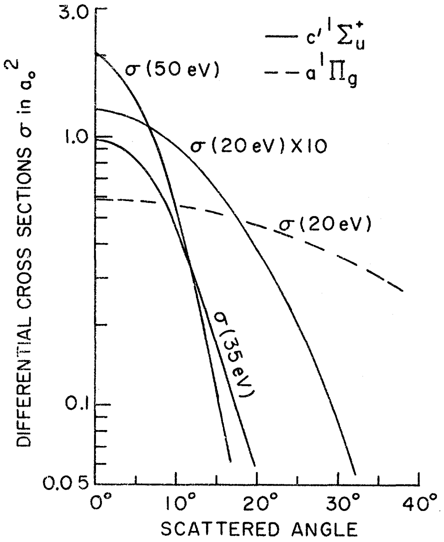

FIG. 7. Differential cross sections σ of the $c'\ {}^1\Sigma_u^+$ state at various incident electron energies (solid lines). Also included are the differential cross sections of the $a\ {}^1\Pi_g$ state (dashed line) at incident-electron energy of 20 eV for comparison. Wave-function set (i) was used for all computation.

Kuyatt, and Chamberlain,[51] and identified this peak as $p'\,^1\Sigma_u^+$ state. Our calculations give a theoretical value of 8 for the ratio of the differential cross section at $\theta = 0$ of the $p'\,^1\Sigma_u^+$ state at 35 eV to that at 20 eV in qualitative agreement with the observation cited above.

4. $w\,^1\Delta_u$ and $b'\,^1\Sigma_u^+$ States

The configuration $(1\pi_u)^3\,(3\sigma_g)^2(1\pi_g)$ gives rise to three singlet states $w\,^1\Delta_u$, $b'\,^1\Sigma_u^+$, and $a''\,^1\Sigma_u^-$. We are not aware of any direct experimental measurements of electron excitation of the $w\,^1\Delta_u$ state; however, Freund has pointed out a possible experimental evidence of such an excitation process.[52] The excitation functions of the $w\,^1\Delta_u$ state computed by using wave-function set (i) is displayed in Fig. 8. Compared with the results shown, the cross sections by set (ii) are about 5% smaller at low energy but 5% larger at high energy. Set (iii) gives cross sections which are uniformly larger by 10% than the ones shown. Below 40 eV, the cross sections by set (iv) are about 20% smaller than the ones by set (i), but above 200 eV the agreement is within 5%. The broad shape of $G_{0n}(K)$ for this transition is reflected in the broad peak of the excitation function with E^{-1} dependence starting around 400 eV.

The $b'\,^1\Sigma_u^+$ state is another dipole-allowed state. However, theoretical calculations here are complicated by the mixing with the $(1\pi_u)^4\,(3\sigma_g)\,(3\sigma_u)$ configuration (35%) and possible vibrational perturbation of the high vibrational levels.[53,39] The latter will not be treated in this paper, but the former can be analyzed in some detail. In Fig. 8, we have shown theoretical cross sections to the pure $(1\pi_u)^3\,(3\sigma_g)^2\,(1\pi_g)^1\Sigma_u^+$ state, to the pure $(1\pi_u)^4\,(3\sigma_g)\,(3\sigma_u)^1\Sigma_u^+$ state, and to the state of 65–35% weighted mixture of the above two (using Richardson's functions). Although the pure cross sections of $1\pi_u \rightarrow 1\pi_g$ and $3\sigma_g \rightarrow 3\sigma_u$ excitations are quite similar both in magnitude and shape, the severe destructive interference in $\mathcal{E}_{0n}(K)$ results in the "mixed" cross sections being about one tenth of either of the pure cross sections. The sensitivity of the "mixed" cross sections indicates that in order to obtain reliable excitation cross sections of $b'\,^1\Sigma_u^+$ state, it would be necessary to conduct an accurate analysis of the configuration mixing.

Under the first Born approximation (including Ochkur's or Rudge's exchange term), the excitation cross sections of the $a'\,^1\Sigma_u^-$ state becomes zero. To analyze theoretically excitation to this state, one must consider the indirect coupling between $X\,^1\Sigma_g^+$ and $a'\,^1\Sigma_u^-$ through the various intermediate states. Calculations of excitation cross sections involving indirect coupling are beyond the scope of this paper. Nevertheless, we may point out a somewhat similar case of excitation of neon atoms in which the Born cross sections (exclusive of exchange terms) of a number of the excited states of the $2p^5np$ and $2p^5nd$ configuration are zero.[3]

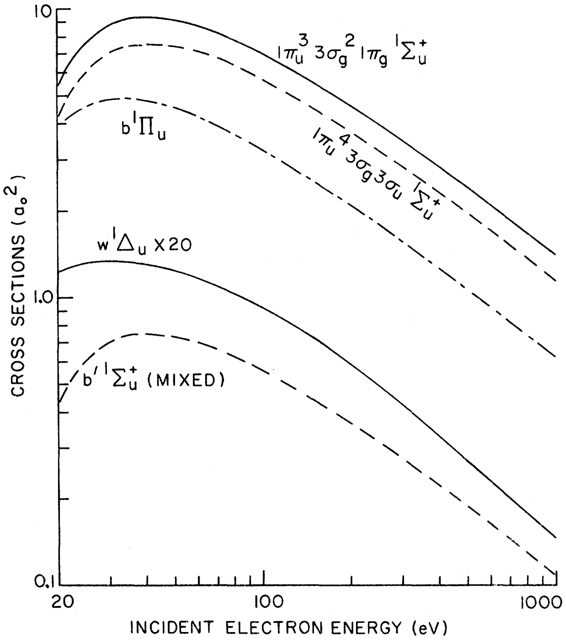

FIG. 8. Excitation functions of the $b\,^1\Pi_u$ state and the $w\,^1\Delta_u$ (enlarged by a factor of 20) state computed by using wave-function set (i) and excitation functions calculated from wave-function set (ii) for the pure $(1\pi_u)^3(3\sigma_g)^2(1\pi_g)\,^1\Sigma_u^+$, for the pure $(1\pi_u)^4(3\sigma_g)(3\sigma_u)\,^1\Sigma_u^+$, and for the $^1\Sigma_u^+$ state consisting of 65–35% weighted mixture of the above two configurations. Exchange by Ochkur's modification is included in all results.

5. $b_1\Pi_u$ State

The $b\,^1\Pi_u$ state may be described as deriving from the $(2\sigma_u)(1\pi_u)^4(1\pi_g)$ configuration mixed with $(1\pi_u)^3\,(3\sigma_g)(1\pi_g)^2$. Since we are not able to find wave functions for the latter configuration, our discussions for this state are only qualitative in nature. Nevertheless, we have computed the excitation cross sections for the pure $(2\sigma_u)(1\pi_u)^4\,(1\pi_g)\,^1\Pi_u$. In Fig. 8 is shown the excitation function calculated by using set (i). The sensitivity to the choice of wave function is not too great (see Table I). The excitation function exhibits the broad maximum characteristic of the dipole-allowed states. The shape of the excitation function is in fact rather similar to that of the $b'\,^1\Sigma_u^+$ state.

The singlet excitation functions (computed by using Nesbet's functions) for the dipole-allowed $b'\,^1\Sigma_u^+$ (pure $1\pi_u \rightarrow 1\pi_g$), $b\,^1\Pi_u$, and $c'\,^1\Sigma_u^+$ states show within 5% $E^{-1}\ln E$ dependence from 500, 700, and 1400 eV on, respectively. For the dipole-forbidden $a\,^1\Pi_g$, $a''\,^1\Sigma_g^+$, and $w\,^1\Delta_u$ states, the E^{-1} dependence becomes apparent at incident energies above 300, 250, and 400 eV, respectively.

C. Excitation Cross Sections for Triplet States

Compared with the singlet states, a considerably larger amount of experimental data are available for excitation cross sections of the triplet states. Particularly the $B\,^3\Pi_g$ (first positive system) and $C\,^3\Pi_u$ (second positive system) states have been investigated experimentally by several groups.[11-15] Unlike the case of some of the singlet states, there is no evidence of serious configuration mixing or of perturbation of vibrational levels in the triplet electronic states. Since the electron-exchange effect is entirely responsible for exciting the triplet states, one expects a much larger difference between the Ochkur-type and the Rudge-type calculations than in the singlet counterparts. From Eqs. (6) and (10) we see that if the vertical excitation energy ΔE is equal to the ionization potential ϵ of the initial state, the two modifications would give identical results. Thus for the excitation to the triplet states of the helium atom, for which the excitation energy is more than 80% of the ionization energy, one finds a close agreement between the results of two modifications.[25] However, for the $B\,^3\Pi_g$ state of N_2 which is about halfway between the ground state and the ionization limit, the Ochkur approximation gives markedly larger cross sections than does the Rudge modification.[10] The Rudge formula was derived in a first-principle manner based on the variational method, thus we will adopt it in our calculations of the triplet-excitation cross sections. Unless otherwise specified, all of our calculated cross sections of the triplet states reported in this section are of the Rudge type. We have used both theoretical and experimental values of the ionization energy ϵ in Eq. (6). We present the results using the latter only. The replacement of the latter by the former may reduce the cross sections by as much as 20% for $B\,^3\Pi_g$, $C\,^3\Pi_u$, $D\,^3\Sigma_u^+$, and $E\,^3\Sigma_g^+$, and increase by as much as 20% for $A\,^3\Sigma_u^+$ and $W\,^3\Delta_u$.

The sensitivity of the triplet cross sections to the choice of wave functions employed is summarized in Table II.

1. $C^3\Pi_u$ State (Second Positive System)

The excitation function of the $C\,^3\Pi_u$ state calculated by using Nesbet's wave functions (with Rudge's exchange) is shown in Fig. 9. For the purpose of comparison, we have also plotted the excitation function (scaled to one-half) calculated by means of the Ochkur exchange. The results by using wave-function sets (i)–(iii) agree within 4%, and the results of set (iv) differ no more than 10% from the above group (see Table II). The theoretical excitation function of Cartwright is uniformly twice as large as ours for the reason explained in Sec. I.

TABLE II. Peak electron-excitation cross sections ($Q_{\max}$), energies of the peak [$E(Q_{\max})$], and cross sections at 40 eV [Q(40 eV)] for six triplet states of N_2 calculated by wave-function sets (i)–(iv). Cross sections are in units of a_0^2 and energies in eV.

States	Sets	$Q_{\max}$	$E(Q_{\max})$	Q(40 eV)
$C\,^3\Pi_u$	(i)	1.609	14.5	0.367
	(ii)	1.676	14.5	0.365
	(iii)	1.615	14.5	0.364
	(iv)	1.613	15.0	0.403
$A\,^3\Sigma_u^+$	(i)	4.354	11.0	0.491
	(ii)	5.035	11.0	0.569
	(iii)	4.917	11.0	0.536
	(iv)	5.263	11.5	0.619
$B\,^3\Pi_g$	(i)	0.997	13.5	0.187
	(ii)	0.968	13.5	0.179
	(iii)	0.928	13.0	0.172
	(iv)	0.706	14.5	0.175
$D\,^3\Sigma_u^+$	(i)	0.0334	18	0.00713
	(ii)	0.0320	18	0.00701
	(iii)	0.0322	18	0.00709
$W\,^3\Delta_u$	(i)	0.257	21	0.148
	(ii)	0.275	22	0.169
	(iii)	0.284	21	0.163
	(iv)	0.273	24	0.183
$E\,^3\Sigma_g^+$	(i)	0.133	15	0.0257
	(ii)	0.142	15	0.0272
	(iii)	0.123	15	0.0247

Included in Fig. 9 are the experimental excitation functions (apparent) reported by Jobe, Sharpton, and St. John[11] and by Burns, Simpson, and McConkey.[13] The $C\,^3\Pi_u$ state receives little cascade contribution, thus it is particularly suited for making comparison between theory and experiment. The magnitude and the position of the peak of our theoretical curve ($1.61a_0^2$ at 14.5 eV) agree well with the experimental values of $1.85a_0^2$ at 15 eV by Jobe *et al.* and with $1.52a_0^2$ at 14.0 eV by Burns *et al.*, but the shape of the theoretical excitation function is somewhat broader than the experimental counterpart. The recent optical measurements by Shemansky and Broadfoot[54] show a peak cross section of $1.4a_0^2$ at 14.7 eV. The unnormalized optical excitation function of Freund[46] has a somewhat broader shape than those in Refs. 11 and 13. The cross sections reported by Skubenich and Zapesochny,[12] however, are much smaller than those of Refs. 11 and 13. The good agreement between our theoretical cross sections and the experimental results of two different groups[11,13] suggests the possibility that the Born-Rudge approximation may be reasonably adequate in de-

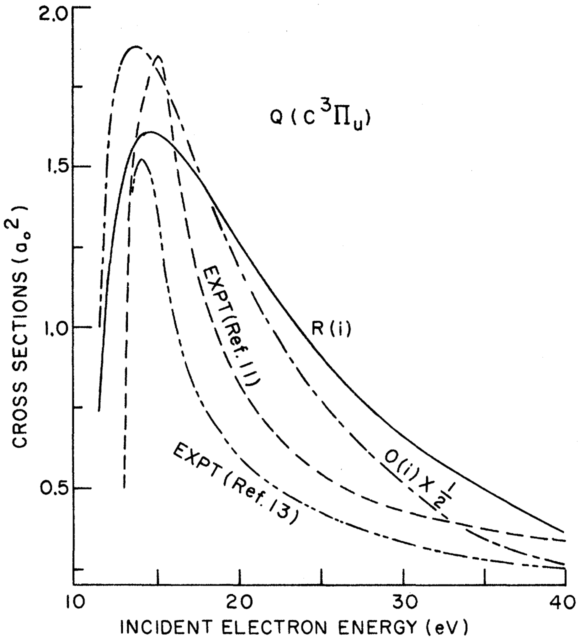

FIG. 9. Excitation function of the $C\,^3\Pi_u$ state computed by wave-function set (i) and by Rudge's modification [R(i), solid line], by Ochkur's modification (scaled to $\frac{1}{2}$) [O(i), long-short dashed line]. Included are also the experimental data of Jobe *et al.* given in Ref. 11 (even dashed line), and those of Burnes *et al.* given in Ref. 13 (long-short-short dashed line).

scribing electron-impact excitation for the triplet states of N_2. The Born-Ochkur cross sections, however, are more than two times greater than the Born-Rudge counterpart near the peak, and by 40% at 40 eV and 27% at 60 eV.

2. $A\,^3\Sigma_u^+$ *State (Vegard-Kaplan Bands)*

The transitions between $A\,^3\Sigma_u^+$ and $X\,^1\Sigma_g^+$ have been observed by various methods.[55,56] The mechanism of population of $A\,^3\Sigma_u^+$ is of aeronomical interest. In their analysis of auroral spectrum, Broadfoot and Hunten[57] suggested that the population of $A\,^3\Sigma_u^+$ is almost entirely due to cascade. Very recently Borst[16] has reported direct experimental measurements of the $A\,^3\Sigma_u^+$. In Fig. 10 we present our calculated cross sections (Nesbet's wave functions) along with Borst's experimental results. The excitation functions gotten by using other sets of wave functions are somewhat (15–20%) larger than the one shown in Fig. 10, but their shapes and the positions of peak agree very well with one another. While the peaks of both curves occur at about the same energy, the theoretical cross sections are substantially larger than the experimental ones, lying beyond the limits of uncertainty given by Borst. Cartwright's theoretical values are consistent with ours except for the difference of a factor 2 mentioned previously.

3. $B\,^3\Pi_g$ *State (First Positive System)*

The excitation function computed by using Nesbet's wave functions is shown in Fig. 11. It agrees with the theoretical curves resulted from sets (ii) and (iii) to within 8%. When the wave functions of set (iv) were used, the peak cross section is found to undergo a 30% reduction, while the cross sections above 40 eV are not much affected (8%). Although we had expected our cross sections to be about one-half of those of Cartwright,[5] the latter are found to be about three times larger than our values using similar wave functions.

Experimental measurements of the apparent excitation functions have been reported by Stanton and St. John,[15] by McConkey and Simpson,[14] and by Skubenich and Zapesochny.[12] The first two sets of data are quite close to each other, whereas the Skubenich and Zapesochny cross sections differ quite appreciably from those of Refs. 14 and 15 for incident energies below 16 eV. These apparent excitation functions contain, in addition to direct excitation, the cascade contributions from higher states. Among the states which may cascade to the $B\,^3\Pi_g$ state, it is clear that $C\,^3\Pi_u$ is an important contributor. By using the experimental data of the optical excitation function of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ transition reported by St. John and co-workers,[11] we have corrected the experimental data of Ref.

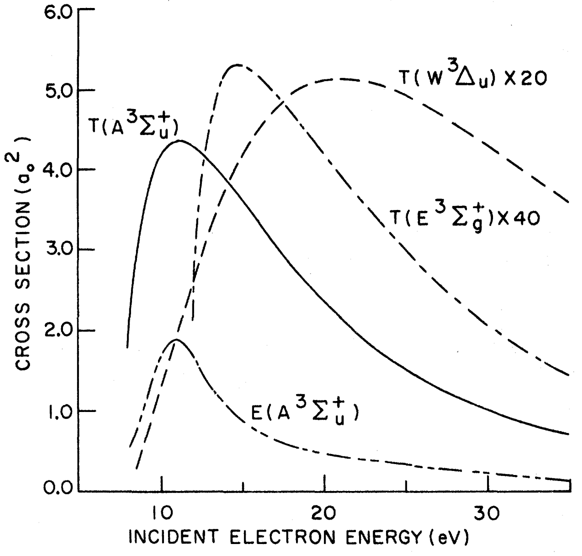

FIG. 10. Excitation functions of the $A\,^3\Sigma_u^+$ state (solid line), of the $W\,^3\Delta_u$ state enlarged by a factor of 20 (even dashed line), and of the $E\,^3\Sigma_g^+$ state enlarged by a factor of 40 (long-short dashed line) computed by Rudge's modification using wave-function set (i). Included are also the experimental data of $A\,^3\Sigma_u^+$ by Borst given in Ref. 16 (long-short-short dashed line).

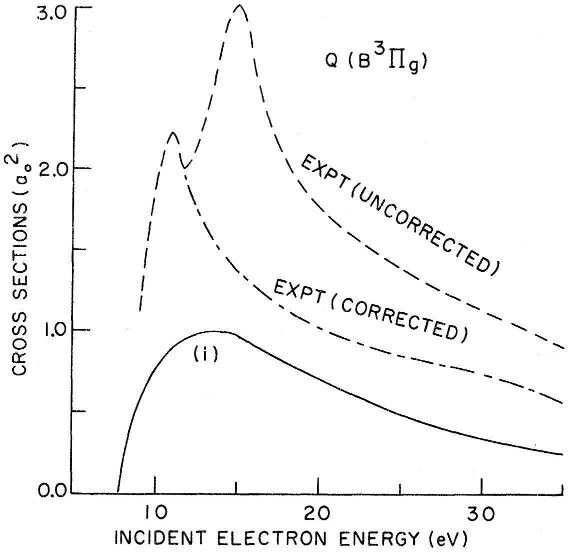

FIG. 11. Excitation function of the $B^3\Pi_g$ state computed by Rudge's modification using wave-function set (i) (solid line) along with the experimental apparent excitation function of Stanton and St. John given in Ref. 15 (even dashed line) and the one corrected for cascade from the $C^3\Pi_u$ state by means of the experimental data of Ref. 11 [long-short dashed line].

15 for cascade from $C^3\Pi_u$. This corrected excitation function along with the uncorrected apparent excitation function of Stanton and St. John is included in Fig. 11. We are not able to find experimental data of excitation cross sections of the $C'^3\Pi_u$ state to estimate its cascade contribution. The $C'^3\Pi_u$ state [configuration $(1\pi_u)^3(3\sigma_g)(1\pi_g)^2$] involves two electrons in excited orbitals; no accurate wave functions for this state have been published to our knowledge. Of the other triplet states which may cascade to $B^3\Pi_g$, the cross sections of the $W^3\Delta_u$ and $D^3\Sigma_u^+$ states are much smaller than the direct excitation cross sections of $B^3\Pi_g$ as will be seen in Sec. IV C 4 and IV C 5. Under the Born-Rudge (or Born-Ochkur) approximation, the collision amplitude of excitation of the $B'^3\Sigma_u^-$ vanishes. Thus no further cascade subtraction will be made to the "corrected" excitation function in Fig. 11. It is seen that the experimental excitation cross sections of $B^3\Pi_g$ are considerably larger than our calculated values. From their recent optical measurement, Shemansky and Broadfoot[54] estimate the peak cross section as $4.3a_0^2$ which is about two times larger than ones reported in Refs. 12, 14, and 15.

Gilmore[58] pointed out the interesting possibility of the cascade scheme of $A^3\Sigma_u^+$ (high v) → $B^3\Pi_g$ (low v) → $A^3\Sigma_u^+$ (low v). Our calculations indeed indicate that the excitation cross sections of $A^3\Sigma_u^+$ is about five times larger than those of $B^3\Pi_g$ and that the Franck-Condon factors of $A^3\Sigma_u^+$ favor excitation to the vibrational levels around $v=10$ which may cascade to the lower vibrational levels of $B^3\Pi_g$. Such a double-cascade mechanism may be responsible for at least part of the discrepancy between the theoretical and experimental curves.

4. $D^3\Sigma_u^+$ State

Our theoretical excitation function of the $D^3\Sigma_u^+$ state computed with set (i) is shown in Fig. 12 with the experimental data of Skubenich and Zapesochny,[12] and the optical excitation function of Freund[46] (normalized to theory at 18 eV). Wavefunctions sets (ii) and (iii) give results within 4% of the ones shown. The shape of the excitation function is markedly different between theory and experiment. The broad secondary peak around 25 eV reported in Ref. 12 is in distinct contrast with the present theoretical results. A recent experimental optical-excitation function by Freund[46] also shows somewhat similar shape to the one in Ref. 12. The theoretical cross sections of Cartwright[5] are some six to eight times larger than our values. It may be noted that in Cartwright's calculations of the excitation function of the $D^3\Sigma_u^+$ state,[5] the multicenter terms in the transition amplitude were neglected. Because of this difference in the computational scheme, we shall not make detailed comparisons of Cartwright's cross sections with ours for the $D^3\Sigma_u^+$ state.

5. $W^3\Delta_u$ and $E^3\Sigma_g^+$ States

The theoretical excitation function of the $W^3\Delta_u$ state shows a peak around 22 eV which is distinctly broader than those of the other triplet states

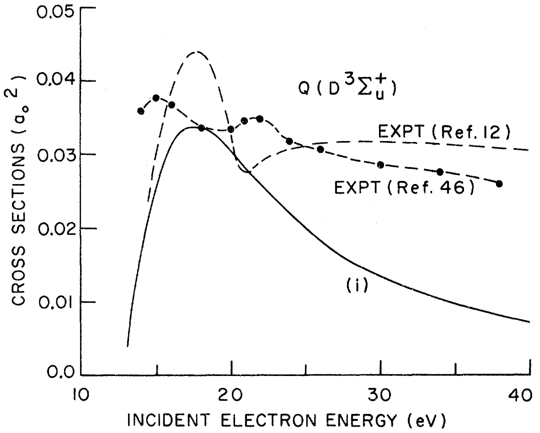

FIG. 12. Excitation function of the $D^3\Sigma_u^+$ state computed by Rudge's modification using wave-function set (i) (solid line) along with the experimental curve by Skubenich and Zapesochny given in Ref. 12 (dashed line) and the one by Freund given in Ref. 46 (dots) which is normalized to the theoretical value at 18 eV.

studied in this work (Fig. 10). The excitation function shown in Fig. 10 is obtained by using wave-function set (i). The other three sets of wave functions give cross sections which are somewhat larger (about 15%) than the ones shown. We have not been able to find any experimental measurements of the excitation cross sections of the $W^3\Delta_u$ in the literature to compare with our theoretical values. Although we expect a factor of 2 between ours and Cartwright's cross sections,[5] his excitation function for $W^3\Delta_u$ is virtually identical to ours.

In Fig. 10 is also included our calculated excitation function of the $E^3\Sigma_g^+$ by using set (i). Sets (ii) and (iii) give cross sections that are about 8% larger and smaller, respectively, than the ones shown in Fig. 10. In the cross-section calculations for the $E^3\Sigma_g^+$ state reported in Ref. 5, the multicenter terms in the transition amplitude were neglected (like the case of $D^3\Sigma_u^+$), and these cross sections are some four to nine times larger than ours. Several investigators[59] have found a sharp peak around 12.3 eV attributed to the $E^3\Sigma_g^+$ state in their excitation experiments, e.g., the experimental measurements by Borst[16] with the peak cross section of $0.25a_0^2$. Our theoretical excitation function shows a much broader shape with the peak cross section of $0.133a_0^2$ at 15 eV. Since the experimental evidence is suggestive of a resonance-type mechanism, no further comparison will be made.

All the triplet cross sections fall off as E^{-3} at high incident-electron energies. Our computed cross sections using Nesbet's functions show such energy dependence (within 5%) starting at 170 eV ($A^3\Sigma_u^+$), 190 eV ($B^3\Pi_g$), 160 eV ($C^3\Pi_u$), 85 eV ($D^3\Sigma_u^+$), 100 eV ($E^3\Sigma_g^+$), and 190 eV ($W^3\Delta_u$).

V. CONCLUSIONS

By using the GTO as basis functions of the molecular orbitals, the Born-approximation cross sections of electron-impact excitation of the electronic states of diatomic molecules can be calculated by a very simple procedure which is no more complicated than the corresponding case of excitation of atoms. In this paper we present the theoretical excitation functions for 12 states of the N_2 molecule. When molecular wave functions of sufficiently high accuracy are used, the computed cross sections do not appear to vary too sensitively with the choice of the wave functions.

For the excitation of the singlet states one can use the Born approximation for the direct-excitation scattering amplitude neglecting the exchange term, or alternatively include the exchange amplitude by the Ochkur or the Rudge scheme. At energies well above the threshold all three schemes (Ochkur, Rudge, and nonexchange) result in nearly the same cross sections. Near the threshold region, the Rudge-modification cross sections substantially exceed the other two types; however, at the low-energy range the Born approximation is not expected to be reliable for singlet-singlet excitation. Thus the difference among the three schemes is not of great interest to us. Comparison of our calculated singlet excitation cross sections with the available experimental data shows about 25% agreement for the $a^1\Pi_g$ state at 900 eV, but for the $a''\,^1\Sigma_g^+$ state at 80 eV the experimental cross section is 50% of the theoretical value.

In the case of singlet-triplet excitation, the low-energy range is of prime interest in most of the experimental work. For the theoretical calculations of the cross sections, we have adopted the Rudge modification. Our theoretical excitation cross sections of the $C^3\Pi_u$ state are in good agreement with the experimental values, whereas for the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states the discrepancy becomes considerably larger.

In conclusion we may state that with the use of the GTO, the Born approximation along with the Rudge modification provides a simple practical scheme to compute the electronic excitation cross sections of N_2, and the results are in reasonable agreement with the available experimental data.

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Angular Distribution of Electrons Elastically Scattered from N_2†

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The angular distribution of electrons elastically scattered from N_2 as a function of energy has been measured utilizing a crossed-beam technique. Measurements have been made of monoenergetic electrons with energies between 5 and 90 eV scattered from a collimated beam of N_2 at angles from $-114°$ to $+160°$. The wide angular range of the measurements has enabled the determination of the total elastic-scattering and momentum-transfer cross sections. The measurements are relative and have been normalized to Fisk's theoretical calculation at 5 eV. The results generally agree well with other published measurements and with theory.

INTRODUCTION

Scattering of electrons with energies in the range of a few eV to a few hundred eV from N_2 has been investigated by several authors. Normand[1] and Aberth *et al.*[2] have measured the total scattering cross section. Elastic-scattering cross sections for N_2 as a function of energy have been measured