Cross sections for electron-impact excitation of the electronic states of N_2

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Distorted-wave cross sections are presented for the excitations of the $w\,^1\Delta_u$, $W\,^3\Delta_u$, $A\,^3\Sigma_u^+$, $b'\,^1\Sigma_u^+$, and $c'\,^1\Sigma_u^+$ states of N_2 by low-energy electron impact. The distorted waves are obtained in the static-exchange field of the ground electronic state. Differential and integral cross sections are presented from near threshold up to 60-eV impact. Comparison is made with available experimental data and with other calculations.

I. INTRODUCTION

Elastic and inelastic differential cross sections (DCS's) for electron-molecule collisions provide a great deal of information on the nature of the electron-target interaction. For this and other reasons, it is important to develop and test formulations which can reproduce the magnitude and shape of the angular distributions at all incident particle energies and all scattering angles.

Recently, considerable effort[1–8] has been directed toward the study of electronic excitation processes of molecules by electron impact. However, only a few comparisons[6,8] between the theoretical and experimental DCS's have been made. Generally, only intergal cross sections have been compared with experimental data, although DCS's provide a more severe test of the theory. This is probably owing to the lack of experimental absolute DCS in the literature for these inelastic processes. Indeed, very few experimental measurements[9,10] of these electronic excitation cross sections have been carried out at low energies (below 100 eV). A study of such inelastic cross sections for N_2 would hence be a very useful test of theoretical methods because it is one of the few molecules for which extensive experimental measurement of differential and integral inelastic cross sections has been carried out.[11–14]

Several studies of the electron impact excitation of N_2 have been reported previously in the literature. The Born-Ochkur-Rudge approximation has been applied by Cartwright[15] and recently by Chung and Lin[16] to study the cross sections for excitation of several states of N_2. Although in some cases (e.g., $X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$) the calculated DCS's agree reasonably well with experimental data[11] at very small scattering angles, these Born-type theories do not generally reproduce either the shape or magnitude of the experimental DCS. This is particularly true for singlet-triplet transitions. More recently, Fliflet *et al.*[6] have calculated the DCS for several singlet-triplet excitations in N_2 using a distorted-wave (DW) method. Although these results generally reproduced the shape of the DCS (except for the $X\,^1\Sigma_g^+ \rightarrow E\,^3\Sigma_g^+$ transitions at 30 and 50 eV), the DW method in general overestimated the cross sections for excitation of these triplet states by a factor of 2 to 4. The impact-parameter-approximation studies of Hazi[17] (excitation of the b' and $c'\,^1\Sigma_u^+$ states) and the two-state close-coupling calculation of Holley *et al.*[3] (excitation of the a $^1\Pi_g$ state) did not report any DCS's.

Recently, we have studied the cross sections for the excitation and dissociation processes of many states of H_2 utilizing the DW approximation.[18] The results agreed quite well with the available experimental data and also with other calculated results. As a more extensive and rigorous test of the DW method, we apply this DW method to calculate the differential and integral cross sections for excitation of the $w\,^1\Delta_u$, $A\,^3\Sigma_u^+$, $W\,^3\Delta_u$, $b'\,^1\Sigma_u^+$, and $c'\,^1\Sigma_u^+$ states of N_2.

In Sec. II, we give a very brief outline of the theory. A comparsion with the experimental results is given in Sec. III, and finally, conclusions are presented in Sec. IV.

II. THEORY

Using the Born-Oppenheimer and Franck-Condon approximations, and treating the target rotational level as essentially degenerate, the DCS for electronic excitation by electron impact can be written as

$$\frac{d\sigma}{d\Omega}(n\leftarrow 0;E,\hat{r}') = SM_n \sum_{\nu'} \frac{k_{\nu'}}{k_0} q_{\nu' 0} \frac{1}{8\pi^2} \int d\hat{R}' \, |f_{k_0}(n\leftarrow 0;\vec{R}',\hat{r}')|^2 , \quad (1)$$

where E is the impact energy, k_0 and $k_{\nu'}$ the momentum of the incoming and outgoing electron, respectively, $q_{\nu'0}$ the Franck-Condon factor for the $\nu=0$ level of the initial electronic state and the ν' vibrational level of the excited state. The factor S results from summing over final, and averaging over initial, spin sublevels. For singlet-to-singlet excitations S equals $\frac{1}{2}$ and for singlet-to-triplet excitations S equals $\frac{3}{2}$. For linear molecules, M_n is the orbital angular momentum projection degeneracy factor of the final target state (1 for a Σ state and 2 for a Π state). The $f(n\leftarrow 0;\vec{R}',r')$ is the laboratory-frame scattering amplitude and can be related to the fixed-nuclei dynamical coefficients as follows:

$$f_{k_0}(n\leftarrow 0;\vec{R}',\hat{r}')=\sum_{ll'mm'm''} a_{ll'mm'}(n\leftarrow 0;k_0,R)D^{(l')*}_{m''m}(\hat{R})D^{(l')}_{0m'}(\hat{R})Y_{lm''}(\hat{r}') , \tag{2}$$

where $D^{(l')}_{m''m}(\hat{R}')$ is a rotational harmonic, and the fixed-nuclei dynamical coefficients $a_{ll'mm'}$ can be written in terms of fixed-nuclei partial-wave components of the electronic portion ofthe transition matrix elements as

$$a_{ll'mm'}(n\leftarrow 0,k_0,R)=-\tfrac{1}{2}\pi[4\pi(2l'+1)]^{1/2}i^{l'-l}\langle k_n lm,n \mid T_{el} \mid k_0 l'm',0\rangle . \tag{3a}$$

In the DW approach, $\mid k_n lm\rangle$ and $\mid k_0 l'm'\rangle$ represent the final and initial Hartree-Fock continuum partial waves, satisfying incoming-wave, outgoing-wave boundary conditions, respectively, and n and 0 designate the excited and initial electronic states of the target, respectively. The transition matrix element of Eq. (3a) is treated in a form of the DW approximation in which (i) the initial target state is the Hartree-Fock ground state and the final target state is equivalent to the single-channel Tamm-Dancoff approximation,[8] and (ii) the incident and outgoing one-electron continuum orbitals are both calculated in the field of the static-exchange potential of the ground state and hence are orthogonal to the occupied Hartree-Fock orbitals of that state. This single-channel Tamm-Dancoff approximation is equivalent to an independent-electron picture in which the excited electron orbital is an eigenfunction of the V_{N-1} potential due to the $N-1$ "frozen-core" electrons. Since in this formulation the initial and final target states differ by only one orbital, the transition matrix element is given by

$$\langle \vec{k}_n,n \mid T_{el} \mid \vec{k}_0,0\rangle=\langle \bar{\phi}_n \psi^{(-)}_{\vec{k}_n} \mid v \mid \psi^{(+)}_{\vec{k}_n}\phi_\alpha\rangle , \tag{3b}$$

where $\langle ij \mid v \mid kl\rangle$ is a Coulomb two-electron matrix element. Here $\psi^{(+)}_{\vec{k}_0},\psi^{(-)}_{\vec{k}_n}$ are Hartree-Fock continuum orbitals satisfying outgoing-wave, incoming-wave boundary conditions; ϕ_α is a Hartree-Fock occupied orbital; $\bar{\phi}$ is an orbital of the V^{N-1} potential formed by removing an electron from the target orbital α. This choice of bound and continuum one-electron orbitals leads to the particularly simple form of the DW approximation of Eq. (3b).

The laboratory-frame DCS's in the j_t-basis expansion, after carrying out the orientation average, have the form

$$\frac{d\sigma}{d\Omega}(n\leftarrow 0)=SM_n\sum_{\nu'}\frac{k_{\nu'}}{k_0}q_{\nu'0}\sum_{j_t m_t m_t'}\frac{1}{2j_t+1}\mid B^{j_t}_{m_t m_t'}(n\leftarrow 0,k_0,k',\hat{r}')\mid^2 , \tag{4}$$

where j_t is the angular momentum transfer during the collision, defined as

$$\vec{j}_t=\vec{l}-\vec{l}' , \tag{5}$$

and $B^{j_t}_{m_t m_t'}(n\leftarrow 0,k_0;k',\hat{r}')$ is the j_t-basis expansion coefficient, which can be related to the fixed-nuclei dynamical coefficients by

$$B^{j_t}_{m_t m_t'}(\Omega')=\sum_{ll'mm'}(-1)^m a_{ll'mm'}(l'l0m_t \mid j_t m_t)(l'lm'm \mid j_t m_t')Y_{lm_l}(\Omega') . \tag{6}$$

For linear molecules, m_t' is determined by the electronic transition.

TABLE I. Basis sets used in the initial step for scattering wave functions.

	$^2\Sigma_g$, $^2\Sigma_u$ symmetry					$^2\Pi_g$, $^2\Pi_u$ symmetry			
Type	l	m	n	Exponent	Type	l	m	n	Exponent
N[a]	0	0	0	7.0	N	1	0	0	5.0
N	0	0	0	3.0	N	1	0	0	2.0
N	0	0	0	1.2	N	1	0	0	0.5
N	0	0	0	0.5	N	1	0	0	0.2
N	0	0	0	0.2	N	1	0	1	1.0
N	0	0	1	1.0	N	1	0	1	0.5
N	0	0	1	0.5	N	1	0	1	0.2
N	0	0	1	0.2					
N	0	0	2	0.5					
		$^2\Delta_g$					$^2\Delta_u$		
N	1	1	0	3.0	N	1	1	0	3.0
N	1	1	0	1.0	N	1	1	0	1.0
N	1	1	0	0.5	N	1	1	0	0.5
N	1	1	0	0.1	N	1	1	0	0.1
N	1	1	0	0.05	N	1	1	0	0.05
CM[b]	2	2		0.5					

[a]Cartesian-Gaussian function of the form $\mu_{lmn}=N(x-A_x)^l(y-A_y)^m(z-A_z)^n e^{-\alpha(r-r_A)^2}$ on the nuclei.

[b]Spherical Gaussian function of the form $\mu_{lm}=N\exp(-\alpha r^2)Y_{lm}(\theta,\varphi)$ at the midpoint of the molecule.

III. CALCULATION AND RESULTS

A. Continuum wave functions

In this work, the elastic static-exchange continuum orbitals are obtained by the iterative Schwinger variational method.[19] The static potential is generated using the ground state of N_2 with the electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$. The Hartree-Fock wave function at the equilibrium internuclear separation of 2.068 a.u. was determined by a self-consistent-field (SCF) calculation using a $(9s5p2d)$ primitive Gaussian function contracted to a $(4s3p2d)$ basis set. The basis set gives a total energy of $-108.973\,235$ a.u.

The details of the iterative Schwinger variational method have been given previously by Lucchese *et al.*[19] We have obtained the continuum wave functions for partial waves with $l\leq 10$ and $m\leq 2$. In these calculations the partial-wave expansion of the direct and exchange potentials are carried out to $l=54$ and $l=36$, respectively. The initial basis set used in the calculations for the continuum wave functions is shown in Table I. Both the initial and final continuum wave functions are determined in the static-exchange field of the ground state of the molecule and are hence orthogonal to the occupied SCF orbitals of that state.[20] Only one iteration was needed in the Schwinger iterative procedure.[21] Calculations have been done for incident energies in the 10—60-eV range. To determine the energy of the scattered electron for a given impact energy, we used the experimental values for the vertical excitation energy from the $v=0$ vibrational level of the initial state.

B. Excitation of the $W\,^3\Delta_u$ and $A\,^3\Sigma_u$ states

The $W\,^3\Delta_u$ and $A\,^3\Sigma_u^+$ excited states correspond essentially to a single-electron transition from the occupied $1\pi_u$ orbtial to the $1\pi_g$ unoccupied orbital. The experimentally determined excitation energies for these transitions are 8.08 and 7.49 eV,[15,22] respectively. For these states, the excited $1\pi_g$ orbital is taken as an eigenfunction of the V_{N-1} potential formed by removing an electron from the $1\pi_u$ occupied orbital. We solved for these excited states with the same Gaussian basis used in the SCF calculation, using the computer codes developed by Goddard and co-workers.[23]

The excitation of these triplet excited states of N_2 involves only the exchange part of the DW matrix element. These matrix elements are calculated by use of the single-center expansion of the distorted waves, the target orbitals, and the Coulomb interaction. In this expansion, we have included sufficient

terms to ensure the convergence of all matrix elements. The resulting radial integrals are evaluated numerically by Simpson's rule. The single-center expansion of the DW matrix element converges rapidly for exchange-type excitation processes. In this calculation we included partial-wave matrix elements for $l,l' \leq 10$ and $m,m' \leq 2$. No higher-order corrections were included.[8] We estimate that the contribution to the differential cross sections from these higher partial-wave contributions to be less than 5% at the impact energies in this work.

For these transitions, we used the Franck-Condon factors calculated by Cartwright.[15] The sum over final vibrational states in Eq. (1) was adequately converged by including only the discrete vibrational levels.

Our DCS's for the impact excitation of these states at incident energies of 20 and 50 eV are shown in Figs. 1 and 2, along with the experimental DCS results of Trajmar *et al.*[11,12] The agreement is quite good both in shape and magnitude for such a simple theory. Our DCS shown in Figs. 1 and 2 are backward peaked as expected for excitation of triplet states and in agreement with the experimental data of Trajmar *et al.*[11,12] In Fig. 1, the DCS for excitation of the $W\,^3\Delta_u$ state at 20 eV agrees well both in shape and in magnitude over the entire range. The agreement between our DCS and the experimental results at 50 eV is still good away from very small angles and up to 140°. Some of the difference between the calculated DCS and the experimental DCS at smaller and larger scattering angles can be due to the fact that experimental values for these angles were obtained by extrapolation of the measured DCS.

In Fig. 2, we compare our DCS for the transition $X\,^1\Sigma_g^+ \rightarrow A\,^3\Sigma_u^+$ with the available experimental data. At both impact energies (20 and 50 eV) our DCS reproduces the shape of the experimental curves quite well. The agreement with the measured magnitude is also good at large scattering angles. However, the calculated cross sections at small angles are in poor agreement with the experimental DCS. The Born-Ochkur-Rudge (BOR) DCS (see Figs. 26 and 27 of Ref. 11) are also in poor agreement with these experimental results both in shape and magnitude.

The integral cross sections for excitation of the $W\,^3\Delta_u$ and $A\,^3\Sigma_u^+$ states are shown in Figs. 3 and 4 along with the experimental[13] and BOR results.[16] The agreement between our integral cross sections and experimental data is quite good for impact energies above 15 eV. In contrast, the BOR cross sections for these states agree poorly with the measured cross sections. In both cases, the discrepancy diminishes with increasing energy. At higher energies

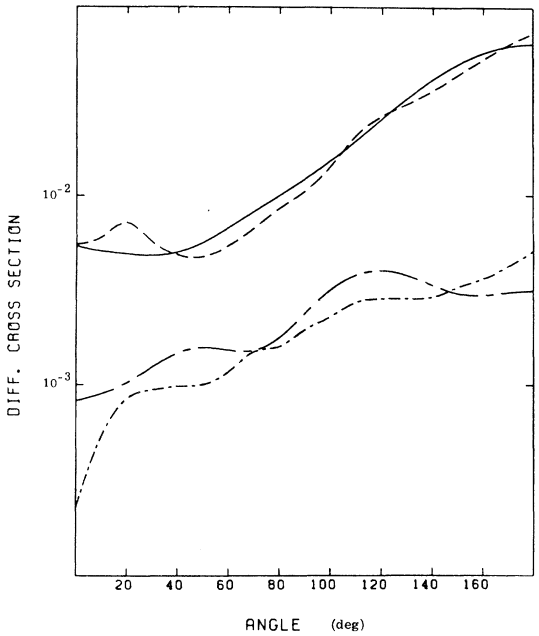

FIG. 1. DCS (in 10^{-16} cm/sr) for the excitation $X\,^1\Sigma_g^+ \rightarrow W\,^3\Delta_u$ in N_2: DW result at 20 eV (solid line); experimental results of 20 eV of Ref. 12 (dashed line); DW results at 50 eV (long-short dashed line); and experimental data at 50 eV (dashed-dot line).

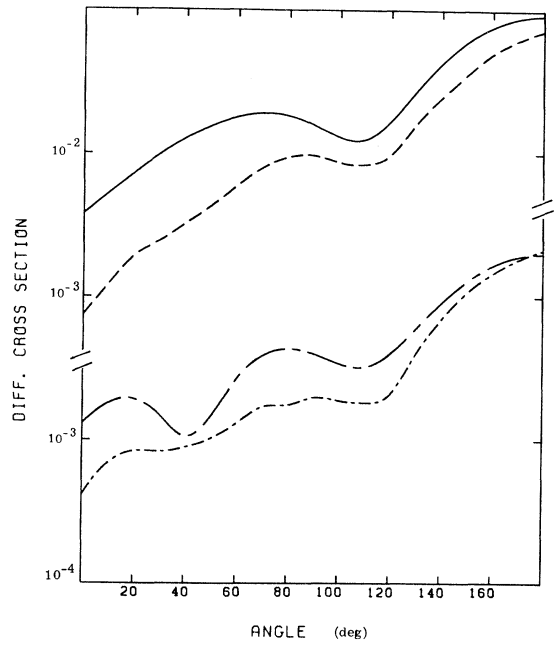

FIG. 2. DCS (in 10^{-16} cm/sr) for the excitation $X\,^1\Sigma_g^+ \rightarrow A\,^3\Sigma_u^+$. The labels are the same as in Fig. 1.

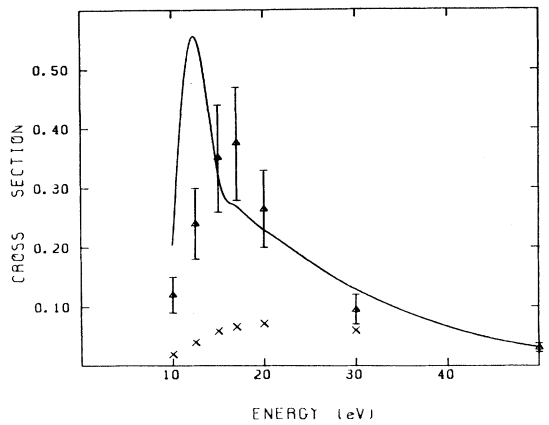

FIG. 3. Integral cross sections (in 10^{-16} cm^2) for the excitation of the $W\,^3\Delta_u$ state: the DW results (solid line); the BOR results of Ref. 16 (crosses); and experimental data of Ref. 13 (open triangles with error bar). The error bars shown as claimed by the authors of Ref. 13.

such as 50 eV, the BOR results agree well both with our integral cross sections and also the experimental results, although the corresponding DCS's are very different.

Near threshold our total cross sections for excitation of these states in the DW approximation show a large enhancement. The same feature has been observed by Fliflet *et al.*[6] in their study of the cross sections for the excitation of the $B\,^3\Pi_g$, $C\,^3\Pi_u$, and $E\,^3\Sigma_g^+$ states of N_2. This resonancelike feature near threshold in the integral cross section is caused by the shape resonance in the $^2\Pi_g$ elastic scattering wave function. In this DW model, the outgoing waves are determined in the potential field of the initial target state and the resonance behavior in the elastic scattering wave functions, i.e., at the final energies and not at incident energies, can clearly lead to enhancement of the inelastic excitation cross section. This enhancement can be unphysical. This feature of the DW model limits its applicability in the near-threshold region for many molecular systems since many of them show such shape resonances in the elastic cross sections.

C. Excitation of $w\,^1\Delta_u$ state

Then $w\,^1\Delta_u$ state is also characterized by the single-electron transition from the $1\pi_u$ orbital to the unoccupied $1\pi_g$ orbital. The vertical experimental excitation energy from the $v=0$ level of the ground state to the excited state is 9.99 eV.[22]

In this excitation process, both direct and exchange parts of partial-wave transition matrix elements are included with $l,l' \leq 10$ and $m,m' \leq 2$. The contribution from higher partial-wave terms in the direct matrix elements are included in the Born approximation, as described by Fliflet and McKoy.[8] No higher-order corrections are included in the exchange matrix elements. For this transition, we used the Franck-Condon factors calculated by Benesch *et al.*[24]

In Fig. 5, we show our DCS at impact energies of 20 and 50 eV, and compare them with the experimental data of Trajmar *et al.*[11,12] for this excitation. The calculated DCS's are very different from the experimental results. Our DCS's show a relatively smooth angular behavior, whereas the experimental

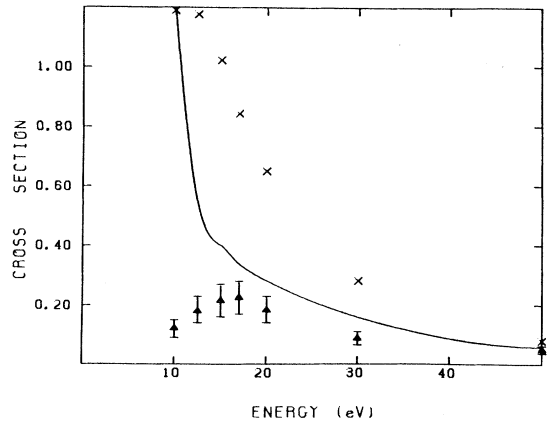

FIG. 4. Integral cross sections (in 10^{-16} cm^2) for the excitation of the $A\,^3\Sigma_u^+$ state. The labels are the same as in Fig. 3.

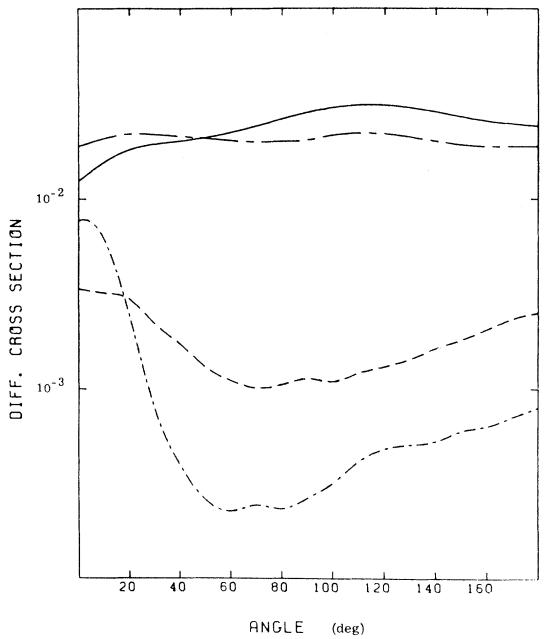

FIG. 5. DCS (in 10^{-16} cm^2/sr) for the $X\,^1\Sigma_g^+ \rightarrow w\,^1\Delta_u$ excitation. The labels are the same as in Fig. 1.

TABLE II. Comparison of excitation energies (in eV) and optical oscillator strengths for the $X\,^1\Sigma_g^+ \rightarrow b'$, $c'\,^1\Sigma_u^+$ transitions in N_2.

State	Experiment[a]		Random-phase approximation[b]		CI-I[c]		CI-II[c]		Single configuration[d]		CI[d]	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
b'	14.4		15.0	0.49	15.2	0.19	15.1	0.47	16.8	0.67	15.4	0.34
c'	12.9	0.14	12.1	0.11	14.6	0.41	12.8	0.11	15.3	0.02	14.5	0.23

[a]Reference 30.
[b]Calculated by Rose *et al.*, Ref. 28.
[c]Hazi, Ref. 17.
[d]This work.

data are strongly forward and backward peaked, especially at 50 eV. The integral cross section for the excitation of the $^1\Delta_u$ state is shown in Fig. 6. Here the agreement with the experimental cross section is also very poor. The DW integral cross sections are also very different from those of the BOR approximation.

This severe disagreement between the DW cross sections and the experimental cross sections is unusual. There are several electronic states which are close to the $w\,^1\Delta_u$ state, e.g., the $a'\,^1\Sigma_u^-$, $B'\,^3\Sigma_u^+$, and $a\,^1\Pi_g$ states.[13] This discrepancy may suggest that there is some channel coupling between the $w\,^1\Delta_u$ and other states. The measured cross sections for excitation of the $w\,^1\Delta_u$ and $a'\,^1\Sigma_u^-$ are both quite small, and moreover, the cross section for excitation of the $a'\,^1\Sigma_u$ state is exactly zero in the DW approximation. The coupling between these channels can be due to resonances which are clearly not included in the present treatment.

D. Excitation of $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states

The $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states are characterized by the single-electron transitions $1\pi_u \rightarrow 1\pi_g$ and $3\sigma_g \rightarrow 3\sigma_u$, respectively. The transitions from the ground $X\,^1\Sigma_g^+$ state to both the $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states are optically allowed. Previous studies[25,26] indicate that configuration-interaction (CI) effects are important in determining the excitation energies, oscillator strengths[25,26] and excitation cross sections for these states.[17]

To describe the ground and these excited electronic states of N_2, we used the standard valence basis[27] of $(4s\,3p)$ Gaussian functions centered at each nuclei, augmented by $2pz$ ($\xi = 0.05$ and 0.01) functions and two $d\pi$ ($\xi = 0.3$ and 0.03) functions at the center of the molecule.[28]

With this basis the SCF energy of the ground state is -108.8878 a.u. For the $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states of N_2 we use a CI wave function with 31 configurations derived from all the single excitations of the type $2\sigma_g \rightarrow n\sigma_u$, $3\sigma_g \rightarrow n\sigma_u$, $2\sigma_u \rightarrow n\sigma_g$, and $1\pi_u \rightarrow 1\pi_g$. Table II compares the excitation energies and optical oscillator strengths obtained both by the single-configuration and CI calculations with experimental data and previous calculations of Hazi[17] and Rose *et al.*[18] Our CI optical oscillator strengths lie between the CI-1 and CI-2 results of Hazi,[17] whereas our single-configuration calculation overestimates the oscillator strength for the $X\,^1\Sigma_g^+ \rightarrow b'\,^1\Sigma_u^+$ transition and underestimates the oscillator strength for the transitions $X\,^1\Sigma_g^+ \rightarrow c'\,^1\Sigma_u^+$. This is expected since in the single-configuration calculation the $b'\,^1\Sigma_u^+$ state is essentially a valence state and the $c'\,^1\Sigma_u^+$ Rydberg-type state.

It is well known that strong perturbations[26] among several electronic states produce large anomalies in the spacings and associated intensities in many of the vibrational levels of the electronic states in this energy-loss region (12.9—14.2 eV) of N_2. To take this perturbation into account, we used the Franck-Condon factors which were determined

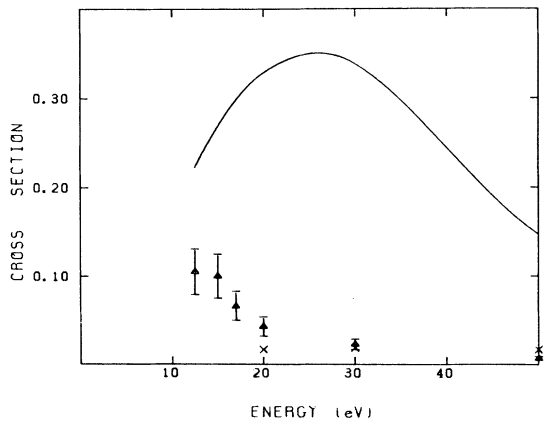

FIG. 6. Integral cross section (in 10^{-16} cm^2) for the excitation of the $w\,^1\Delta_u$ state. The labels are the same as in Fig. 3.

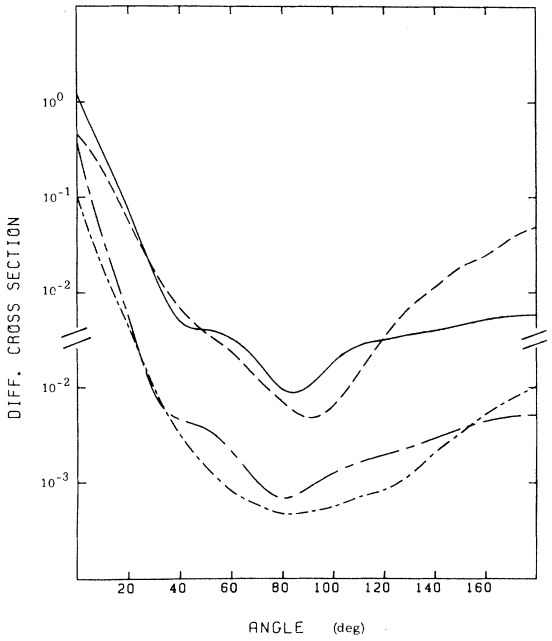

FIG. 7. DCS (in 10^{-16} cm/^{2}/sr) for the $X\,^1\Sigma_g^+ \rightarrow b'\,^1\Sigma_u^+$ excitation: the CI-DW results at 40 eV (solid line); the experimental data of 40 eV of Ref. 12 (dashed line); the CI-DW results at 60 eV (long-short dashed line); and experimental data at 60 eV (dashed-dot line).

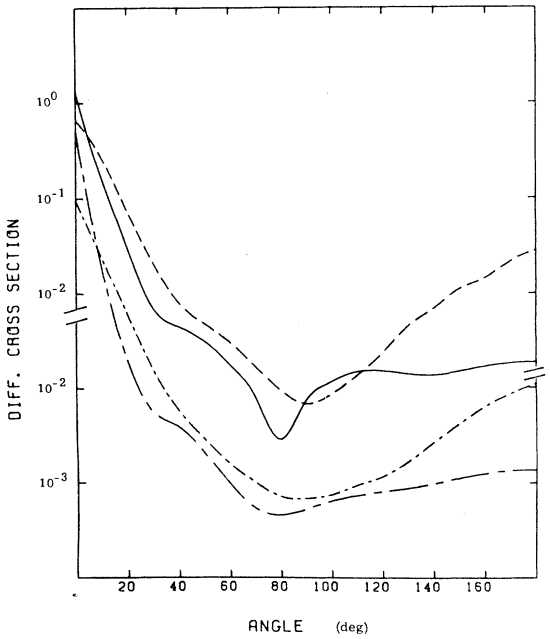

FIG. 8. DCS (in 10^{-16} cm^2/sr) for the $X\,^1\Sigma_g^+ \rightarrow c'\,^1\Sigma_u^+$ excitation in N_2. The labels are the same as in Fig. 7.

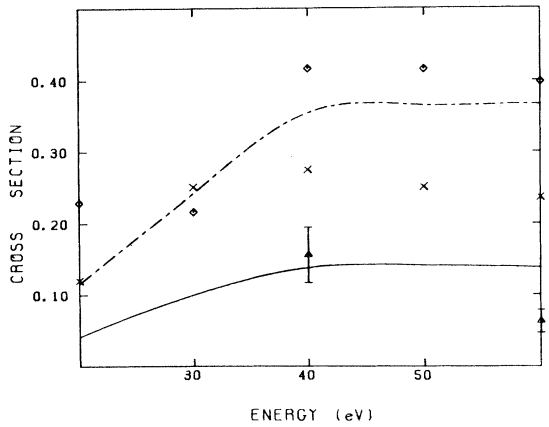

FIG. 9. Integral cross sections (in 10^{-16} cm^2) for excitation of the $b'\,^1\Sigma_u^+$ state: CI-DW results (solid line); single-configuration DW results (dashed-dot line); single-configuration BOR results of Ref. 16 (crosses); impact-parameter method of Ref. 17 (open diamonds); and experimental data of Ref. 14 (open triangle with error bar).

from the measured relative intensities of Geiger and Schröder.[29]

In Figs. 7 and 8 we compare our calculated DCS with the experimental results of Trajmar *et al.* for excitation of the $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states at the two impact energies (40 and 60 eV) reported.[13] The agreement is quite good both in shape and magnitude, except again for the large angle scattering. Some of this discrepancy between the calculated and measured differential cross sections at large angles could again be due to the extrapolation used to estimate the experimental values at these angles.[13,14]

In Figs. 9 and 10, we compare our CI-DW integral cross sections along with the integral cross sections obtained using the single-configuration wave function for these excited states with the experimental data, the single-configuration BOR results, and the impact-parameter results of Hazi.[17] The agreement between our CI-DW results and experimental data is good. For excitation of the $b'\,^1\Sigma_u^+$ state, our CI-DW cross section is close to the experimental value at 40 eV but is 30% above the measured value at 60 eV. As expected, the single-configuration DW calculation overestimates the total cross sections for this transition. The impact-parameter method of Hazi, using his CI-2 wave function shows a cross section 2—3 times larger than our CI-DW results. Some of the discrepancy between the CI-DW cross section and those of the impact-parameter method is probably due to diffeences reflected in the oscillator strengths associated with these calculations. For the $X\,^1\Sigma_g^+ \rightarrow c'\,^1\Sigma_u^+$ transition our CI-DW results agree well with the limited experimental data, but for this transition our

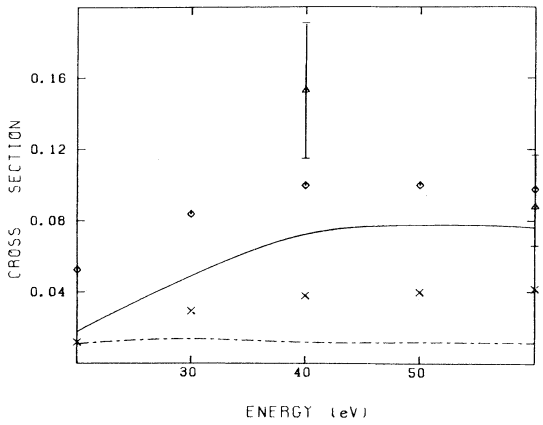

FIG. 10. Integral cross sections (in 10^{-16} cm^2) for excitation of the $c'\,^1\Sigma_u^+$ state. The labels are the same as in Fig. 9.

CI-DW is lower than the measured value at 40 eV and close to it at 60 eV. As expected, in this transition the single-configuration DW cross section is very small, since the single-configuration wave function cannot correctly describe the $c'\,^1\Sigma_u^+$ state. This small cross section is in agreement with the small optical oscillator strength obtained with this kind of wave function for this $c'\,^1\Sigma_u^+$ state.

Finally, it is important to note that for these singlet-singlet transitions (i.e., $X\,^1\Sigma_g^+$ to $w\,^1\Delta_u$, $b'\,^1\Sigma_u^+$, and $c'\,^1\Sigma_u^+$ states), the elastic shape resonance feature which affects the cross sections in the energy region near threshold in singlet-triplet transitions has almost no effect on these singlet excitations.

IV. CONCLUSION

We have applied the DW method to study the electron impact excitation processes from the ground $X\,^1\Sigma_g^+$ state to the $w\,^1\Delta_u$, $W\,^3\Delta_u$, $A\,^3\Sigma_u^+$, $b'\,^1\Sigma_u^+$, and $c'\,^1\Sigma_u^+$ states of N_2. For the last two transitions, a DW theory has been applied with final-state CI wave functions. The results of these studies are generally encouraging except for the $X\,^1\Sigma_g^+ \rightarrow w\,^1\Delta_u$ transition where the DW results disagree dramatically with the measured cross sections. These results suggest the existence of strong interchannel coupling for this transition. The present study of the $X\,^1\Sigma_g^+ \rightarrow b'$, $c'\,^1\Sigma_u^+$ cross sections shows the importance of electron correlation in these transitions. In singlet-triplet transitions we again see the effect of the shape resonance feature, i.e., in the $^2\Pi_g$ channel of N_2, on the inelastic cross section near threshold. Nevertheless, these effects are not pronounced in singlet-singlet transitions. Application of this DW method to more complicated heteronuclear molecules (e.g., CO) and polyatomic linear molecules (e.g., CO_2), is in progress.

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[1]G. P. Arrighini, F. Biondi, C. Guidotti, A. Biagi, and F. Marinelli, Chem. Phys. 52, 133 (1980).
[2]S. Chung and C. C. Lin, Phys. Rev. A 17, 1874 (1978).
[3]T. K. Holley, S. Chung, C. C. Lin, and E. T. P. Lee, Phys. Rev. A 24, 2946 (1981).
[4]A. U. Hazi, Phys. Rev. A 23, 2232 (1981).
[5]T. N. Rescigno, C. W. McCurdy, and V. McKoy, J. Phys. B 8, L433 (1975).
[6]A. W. Fliflet, V. McKoy, and T. N. Rescigno, J. Phys. B 12, 3281 (1979).
[7]A. W. Fliflet, V. McKoy, and T. N. Rescigno, Phys. Rev. A 21, 788 (1979).
[8]A. W. Fliflet and V. McKoy, Phys. Rev. A 21, 1863 (1980).
[9]S. Trajmar, D. C. Cartwright, J. K. Rice, R. T. Brinkmann, and A. Kuppermann, J. Chem. Phys. 49, 5464 (1968).
[10]S. Trajmar, D. C. Cartwright, and W. Williams, Phys. Rev. A 4, 1482 (1971).
[11]D. C. Cartwright, A. Chutjian, S. Trajmar, and W. Williams, Phys. Rev. A 16, 1013 (1977).

[12]S. Trajmar, D. F. Register, and A. Chutjian, Phys. Rep. (in press and private communication).
[13]D. C. Cartwright, S. Trajmar, A. Chutjian, and W. Williams, Phys. Rev. A 16, 1041 (1977).
[14]A. Chutjian, D. C. Cartwright, and S. Trajmar, Phys. Rev. A 16, 1052 (1977).
[15]D. C. Cartwright, Phys. Rev. A 2, 1331 (1970).
[16]S. Chung and C. C. Lin, Phys. Rev. A 6, 988 (1971).
[17]A. U. Hazi, Phys. Rev. A 23, 2232 (1981).
[18]Lee Mu-Tao, R. R. Lucchese, and V. McKoy (unpublished).
[19]R. R. Lucchese and V. McKoy, J. Phys. B 12, L421 (1979).
[20]T. N. Rescigno, C. W. McCurdy, Jr., B. V. McKoy, J. Phys. B 7, 2396 (1974).
[21]R. R. Lucchese, D. Watson, and V. McKoy, Phys. Rev. A 22, 421 (1980).
[22]W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 142, 1227 (1965).
[23]W. J. Hunt and W. A. Goddard III, Chem. Phys. Lett. 24, 464 (1974).
[24]W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 143, 236 (1966).
[25]K. Dressler, Can. J. Phys. 47, 547 (1969).
[26]H. Lefebvre-Brion, Can. J. Phys. 47, 541 (1969).
[27]T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
[28]J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 58, 74 (1973).
[29]J. Geiger and B. Schröder, J. Chem. Phys. 50, 7 (1969).
[30]G. M. Lawrence, D. L. Mickey, and K. Dressler, J. Chem. Phys. 48, 1989 (1968).