

AIR FORCE REPORT NO.
SAMSO-TR-70-263

AEROSPACE REPORT NO.
TR-0059(9260-01)-6

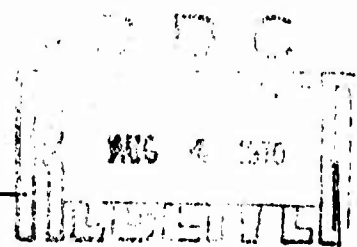
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TOTAL CROSS SECTIONS FOR THE EXCITATION
OF THE TRIPLET STATES IN MOLECULAR NITROGEN

Prepared by DAVID C. CARTWRIGHT
Space Physics Laboratory

70 AUG 05

Laboratory Operations
THE AEROSPACE CORPORATION



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AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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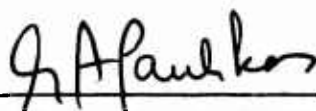
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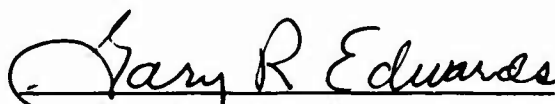
FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-70-C-0059. This report, which documents research carried out from 1 October 1969 through 1 March 1970, was submitted on 23 June 1970 to Lt. Gary R. Edwards, SMTAE, for review and approval.



G. A. Paulikas, Director
Space Physics Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



Gary R. Edwards, 1st Lt, USAF
Project Officer

ABSTRACT

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

indicates that the theoretical $A \ ^3\Sigma_u^+$ total cross section is correct for incident energies greater than about 35 eV. The relative magnitudes of these excitation cross sections lead to interesting predictions concerning N_2 processes in the upper atmosphere.

ACKNOWLEDGEMENTS

I extend my appreciation to NATO for a postdoctoral fellowship (1967-68) to the Max-Planck-Institute für Extraterrestrische Physik, Munich where this work was initiated. My thanks go to the director of the Institut, R. Lüst, and the members of the Institute for making the visit a pleasant one and particularly S. Drapatz and W. Michel for numerous stimulating discussions.

Thanks also go to M. Mizushima of the University of Colorado, Boulder for his encouragement; the computer center there for the computing time used to do some of the calculations reported here, and the Committee on University Scholarly Publications for their support. Finally I wish to thank B. Brinkmann, S. Trajmar and W. Williams of JPL for their enthusiastic cooperation in the acquisition and analysis of the energy loss spectra, and D. Truhlar of the University of Minnesota for carefully reading the manuscript.

CONTENTS

FOREWORD		ii
ABSTRACT		iii
ACKNOWLEDGEMENTS		v
I. INTRODUCTION		1
II. THEORY		3
A. Pure Exchange Excitation		4
B. The Ochkur-Rudge Modification		8
C. Rotationally Averaged Cross Sections		11
III WAVEFUNCTIONS		17
IV NUMERICAL TECHNIQUES		25
A. Potential Energy Curves and FC Factors		25
B. Evaluation of the Multicenter Terms		29
V. RESULTS		33
A. $C^3\Pi_u \leftarrow X^1\Sigma_g^+$		35
B. $B^3\Pi_g \leftarrow X^1\Sigma_g^+$		39
C. $A^3\Sigma_u^+ \leftarrow X^1\Sigma_g^+$		43
D. $E^3\Sigma_g^+, D^3\Sigma_u^+ \leftarrow X^1\Sigma_g^+$		46
E. The Relative Magnitudes of the Triplet Excitation Cross Sections		50
F. The Effect of Approximate Wavefunctions		56
VI. CONCLUSIONS		59
REFERENCES		61

FIGURES

1.	The Potential Energy Curves for the Ground and Seven Lowest Triplet States of N_2 as Functions of the Internuclear Distance . . .	31
2.	Total Cross Sections (σ_{00}^n), as Defined by Eq (24), for Excitation of the Seven lowest Triplet Electronic States of N_2	34
3.	Total Cross Section for Excitation of the $C^3\Pi_u$ State From $X^1\Sigma_g^+(v'' = 0)$ as a Function of the Incident Electron Energy	37
4.	Total Cross Section for Excitation of the $B^3\Pi_g(v' = 0, \dots, 18)$ State From $X^1\Sigma_g^+(v'' = 0)$ as a Function of Incident Electron Energy	41
5.	Total Cross Section for Excitation of the $A^3\Sigma_u^+(v' = 0, \dots, 20)$ State from $X^1\Sigma_g^+(v'' = 0)$ as a Function of Incident Electron Energy	44
6.	Total Cross Section for Excitation of the $E^3\Sigma_g^+(v' = 0, 1)$ State From $X^1\Sigma_g^+(v'' = 0)$ as a Function of Incident Electron Energy	48
7.	Total Cross Section for Excitation of the $D^3\Sigma_u^+(v' = 0, 1)$ State From $X^1\Sigma_g^+(v'' = 0)$ as a Function of Incident Electron Energy	49
8a.	Synthetic Energy Loss Spectrum	52
8b.	Smoothed Experimental Energy Loss Spectrum	53

TABLES

I.	The Electronic Configurations of the Ground and Excited Triplet States of Molecular Nitrogen	18
II.	The Screening Constants and Coefficients of the Primitive Symmetry Orbitals for Rydberg MO's of the $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$ States of N_2	21
III.	Transformed Coefficients of the Ransil (BL) Primitive Symmetry MO's for the $B\leftarrow X$ and $G\leftarrow X$ Transitions in N_2	23
IV.	Excitation Energies and Franck-Condon Factors for the Transition $A^3\Sigma_u^+ (v' = 0 \dots 20) \leftarrow X^1\Sigma_g^+ (v' = 0)$	26
V.	The Spectroscopic Constants Used to Calculate the Potential Energy Curves for the $W^3\Delta_u$, $E^3\Sigma_g^+$, and $D^3\Sigma_u^+$ States	28
VI.	Excitation Energies and Franck-Condon Factors for the $W^3\Delta_u (v' = 0, \dots, 12)$, $E^3\Sigma_g^+ (v' = 0, 1)$, $D^3\Sigma_u^+ (v' = 0, 1)$, $\leftarrow X^1\Sigma_g^+ (v'' = 0)$ Transitions in N_2	30

I. INTRODUCTION

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

In this paper total cross sections for the electron impact excitation of the seven lowest triplet states of molecular nitrogen from the lowest vibrational level of the ground electronic state are reported.⁴ The calculations were done in the framework of a modified first order perturbation approximation (Ochkur-Rudge) which has been successful in describing similar processes in molecular hydrogen. The calculated cross section for excitation of the $B^3\Pi_g$ state agrees well with that implied by recent data on the excitation of the second positive system by electron impact. The calculated excitation cross section for the $C^3\Pi_u$ state agrees well with two experimental determinations but is larger than

another set of measurements for the same process. The cross sections for excitation to the $W^3\Delta_u$, $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$ states, for which little or no data exists, are found to be large enough to play an important role in the population of the lower electronic states in the triplet system of N_2 .

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

II. THEORY

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

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

where $S1$ and $S2$ denote the quantum state of the incident and target particle respectively, including spin. The function Ψ_{S2} , denoting the target particle, is assumed to be the correctly antisymmetrized solution of the N_0 -electron problem and ζ_{S1} is the free electron wavefunction. The complete antisymmetrized wavefunction for the $N_0 + 1$ electron system is then given by⁵

$$\mathcal{A}(a) \equiv \mathcal{A}\chi_a = \frac{\sqrt{N_0 + 1}}{(N_0 + 1)!} \sum_Q \epsilon_Q \hat{Q} \zeta_{S1}(\xi_0) \Psi_{S2}(\xi_1 \dots \xi_{N_0}), \quad (2)$$

where \hat{Q} is one of the $N!$ permutations of the N particles and ϵ_Q is the parity of the permutation. When the number of identical particles (N) is the same in both the incident and final channels, the T -matrix for the collision process can be written as⁵

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

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

$$\chi_b = \zeta_{S_1}(\xi_0) \Psi_{S_2}(\xi_1 \dots \xi_{N_0}). \quad (4)$$

When Eq (4) is inserted into Eq (3) and use is made of the fact that Ψ_{S_2} is antisymmetric with respect to its N_0 particles, Eq (3) can be rewritten in the form

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

In Eq (5) the symbol \hat{Q}_{oj} denotes interchange of the incident electron and the j^{th} bound electron.

A. Pure Exchange Excitation

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

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

Since the interactions producing the exchange excitation are taken to be independent of spin and only the lowest order term in the exchange transition amplitude is to be treated, the integration over spin variables

can be performed in a number of equivalent ways. One may reduce the general expressions for the N electron problem derived from the symmetric group to those terms of lowest order in the exchange interaction. The correct factors from the spin integration then appear as coefficients of these first order terms, expressed as functions of the tableaux shape.⁶ As a good approximation, one may also assume that the complete wavefunction for both the target and the incident electron can be explicitly factored into a product of two terms, one involving only spatial variables and the other the spin eigenfunction of the particle. Then since channel spin⁷ is conserved, the spin integration can be performed with the aid of vector coupling techniques and without having to manipulate explicit spin wavefunctions. This is particularly straight forward when the initial spin state of the bound state is a singlet for then the incident channel spin state, $|S, S_z\rangle$, in terms of the two particle spin states, $|\uparrow, \uparrow_z\rangle_i$, $i=b$ or e , is

$$|1/2 \ 1/2\rangle_{\text{initial}} = |00\rangle_b |1/2 \ 1/2\rangle_e. \quad (6)$$

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

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

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

$$\langle 1/2 \ 1/2 | 1/2 \ 1/2 \rangle_e \langle 10 | 00 \rangle_b = -\sqrt{3} \quad , \quad (8)$$

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

$$\begin{aligned} T_{\epsilon x}^{(1)} &= -N_0 \langle \hat{Q}_{0\lambda} \chi_b | T^{(1)} | \chi_a \rangle \\ &= \sqrt{3} \sum_{\lambda=1}^{N_0} \langle \hat{Q}_{0\lambda} \phi_f(\vec{r}_0) \psi_f(\vec{r}_1 \dots \vec{r}_{N_0}) | T^{(1)} | \phi_i(\vec{r}_0) \psi_i(\vec{r}_1 \dots \vec{r}_{N_0}) \rangle, \end{aligned} \quad (9)$$

where the permutation $\hat{Q}_{0\lambda}$ now involves only the spatial variables and the superscript (1) means only the first order term in the exchange interaction is retained. In Eq (9), ϕ and ψ are used to denote the spatial portions of the free (plane wave) and bound particle wavefunctions and the subscripts i and f denote initial and final states respectively. As a third equivalent procedure for treatment of the spin variables, one may form the differential cross section in terms of the spatial portions of the transition amplitude and merely sum this cross section over the spin projections of the final bound particle (triplet) and average over the initial spin projections of the bound particle.⁷ One then obtains a cross section which is proportional to the square of (9). The normal experimental

situation of an unpolarized beam yields the same result as given in Eq (9) since the two possible free electron spin states are weighted equally.⁷

The complete \mathcal{T} operator for the (e, N_2) system is⁵

$$\mathcal{T} = V + V \hat{Q}_{o\lambda} \frac{1}{E - i\eta - H} V, \quad (10)$$

where H and E respectively are the Hamiltonian and total energy of the system and V is (in atomic units)

$$V = -\frac{7}{r_{Ao}} - \frac{7}{r_{Bo}} + \sum_{i=1}^{14} \frac{1}{|\vec{r}_i - \vec{r}_o|}. \quad (11)$$

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

B. The Ochkur-Rudge Modification

The Born-Oppenheimer (BO) scattering amplitude as given in Eq (9) possesses well known difficulties⁸ in describing the scattering process for low energy electrons. Modifications of the (BO) amplitude by Ochkur⁹ and Rudge¹⁰ have removed the major difficulties while still maintaining the first order simplicity. The Ochkur-Rudge (OR) approximation to the exchange amplitude has been shown to predict reliable total cross sections for exchange scattering processes involving H_2^{11a} , He, and H^{11b} and therefore has been used with some confidence in this study of the

(e, N₂) system. The (OR) approximation is obtained as follows. The nuclear and electronic motion are separated by writing the bound state wavefunction as

$$\begin{aligned}\Psi_i &\equiv \Psi_{n''v''J''M''} = \psi_i(\vec{r}_1 \dots \vec{r}_{N_0}; R) \xi_{n''v''}(R) Y_{J''M''}(\Theta, \phi) \\ \Psi_f &\equiv \Psi_{n'v'J'M'} = \psi_f(\vec{r}_1 \dots \vec{r}_{N_0}; R) \xi_{n'v'}(R) Y_{J'M'}(\Theta, \phi) \quad , \quad (12)\end{aligned}$$

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

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

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

$$T_{fi} \equiv \sum_{\lambda=1}^{N_0} \sqrt{3} \langle \hat{Q}_{\lambda} \phi_f(\vec{r}_0) \psi_f(\vec{r}_1 \dots \vec{r}_{N_0}) | V | \phi_i(\vec{r}_0) \psi_i(\vec{r}_1 \dots \vec{r}_{N_0}) \rangle \quad . \quad (14)$$

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

$$T_{fi}^{OR} = \sqrt{3} \langle \psi_f(\vec{r}_1 \dots \vec{r}_{N_o}) \left| \sum_{j=1}^{N_o} \frac{4\pi e^{i\vec{q} \cdot \vec{r}_j}}{[k' - i I_{n', n''}]^{1/2}} \right| \psi_i(\vec{r}_1 \dots \vec{r}_{N_o}) \rangle, \quad (15)$$

where the wavenumber k' is related to the incident electron energy, k_o^2 , and the energy difference between the molecular states by

$$k' = \left[k_o^2 - 2(E_f - E_i) \right]^{1/2}, \quad (16)$$

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

Additional simplifications of Eq (15) can be made when specific configurations are chosen for the initial and final electronic states and their respective electronic wavefunctions are expressed as single Slater determinants. Then if the orbitals used for the initial and final electronic states, customarily obtained by energy minimization, are transformed by unitary transformations such that the overlap matrix between the two sets of orbitals used in the wavefunctions is diagonal,¹² Eq (15) reduces to

$$T_{fi}^{OR} = \frac{\sqrt{3} 4\pi}{[k' - i I_{l''}]^{1/2}} \langle \varphi_l(\vec{r}) | e^{i\vec{q} \cdot \vec{r}} | \varphi_{l''}(\vec{r}) \rangle D_{ll''}^{1/2}. \quad (17)$$

The symbol $\varphi_{l''}$ (φ_l) has been used to denote the initial (final) non-degenerate "corresponding orbital"¹² involved in the excitation process for the chosen pair of configurations and $I_{n''}$ has been replaced by the theoretical orbital eigenvalue of the $\varphi_{l''}$ orbital, denoted as $I_{l''}$. The multiplicative factor

$D_{l'l''}^{1/2}$ results from the diagonalization of the overlap matrix between the initial and final electronic states.¹² In writing Eq (17) the additional phase factors of the electronic transition amplitude introduced by the unitary transformation of the orbitals have been omitted since they are not important for a pure exchange process. It should be noted that the simplification of the summation in Eq (15) to the single term in Eq (17) is a result of the orthogonality of the "corresponding orbitals", the choice of specific single configurations for the initial and final electronic states and the fact that the transition operator ($e^{i\hat{q}\cdot\vec{r}}$) is a single-particle operator. This simplification is the usual Slater-Condon rule except for the factor $D_{l'l''}^{1/2}$ and the fact that the orbitals $\phi_{l''}$ and $\phi_{l'}$ are "corresponding" orbitals. These two modifications are necessary whenever the MO sets used to describe the ground and excited electronic states are non-orthogonal. The extension to multiconfigurational wavefunctions can be made without difficulty.

C. Rotationally Averaged Cross Sections

The differential cross section (in units of πa_0^2) for the excitation process, I_i^f , is related to the transition amplitude, Eq (13) by⁵

$$I_i^f(k_0, \theta, \varphi) = \frac{1}{4\pi^3} \frac{k'}{k_0} |\mathcal{T}_{\epsilon x}^{(1)}(T_{fi})|^2, \quad (18)$$

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

$$I_{n''v''}^{n'v'}(k_0, \theta, \varphi) = \frac{1}{4\pi^3} \frac{k''}{k_0} |\langle \xi_{n'v'} | T_{n''v''}^{n'v'} | \xi_{n''v''} \rangle |_{AVE}^2 \quad (19)$$

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

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

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

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

$$I_i^f(k_0, \theta, \varphi) = \frac{1}{4\pi^3} \frac{k''}{k_0} \omega_f |\langle \xi_{n'v'} | T_{n''v''}^{n'v'} | \xi_{n''v''} \rangle |_{AVE}^2 \quad (20)$$

It should be pointed out that no additional factor need be introduced for the case of the four equivalent π_u electrons in the ground state. This

equivalence and any similar equivalence in the excited states, is accounted for when the symmetry of the final state is specified.

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

1. The R-centroid Approximation

This approximation consists of replacing

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

where $\bar{R}_{v'v''}$ is called the R-centroid¹³ of the (v', v'') transition and is defined by $\bar{R}_{v'v''} = \langle \xi_{n'v'} | R | \xi_{n''v''} \rangle$. Eq (20) then reduces to

$$I_{n''v''}^{n'v'}(k_0, \theta, \varphi) = \frac{1}{4\pi^3} \frac{k''}{k_0} \omega_f | T_{n''v''}^{n'v'}(k_0, \theta, \varphi; \bar{R}_{v'v''}) |_{AVE}^2 q_{v'v''} \quad (21)$$

where $q_{v'v''}$, called the Franck-Condon factor, is defined by $q_{v'v''} = \langle \xi_{n'v'} | \xi_{n''v''} \rangle$. This R-centroid approximation has been quite useful in the analysis of molecular spectra but has recently been criticized¹⁴ as to its validity for certain molecular transitions, and in particular for transitions in N_2 . It would have been interesting to test this approximation for the transitions of interest here but unfortunately not enough molecular information is known. That is, while the R-centroids and Franck-Condon factors are readily available, the necessary excited state wavefunctions optimized at various values of the internuclear distance have not yet been published. Consequently the R-centroid approximation could not be applied in this work.

2. The Franck-Condon Approximation

The Franck-Condon approximation¹³ is based on the assumption that the electronic transition amplitude, Eq (14), is a slowly varying function of the internuclear distance over the normal range of the variable and consequently can be replaced by a constant, $T_{n''v''}^{n'v'}(R_e)$, in the integration over R. Equation (20) then takes the form

$$I_{n''v''}^{n'v'}(k_0, \theta, \varphi) = \frac{1}{4\pi^3} \frac{k''}{k_0} \omega_f |T_{n''v''}^{n'v'}(k_0, \theta, \varphi; R_e)|_{AVE}^2 q_{v'v''} \quad (22)$$

Except for those transitions from $v'' = 0$ or to $v' = 0$, the choice of R_e is not obvious and as might be expected, the Franck-Condon approximation is not always reliable for all (v', v'') transitions. However, for processes originating from $v'' = 0$, the Franck-Condon approximation has been shown to be quite good,¹⁵ in most cases accurate to within 10%. This result is due to the fact that the initial vibrational wavefunction ($\xi_{n'', v''=0}$) is gaussian in character centered at the R_e of the initial electronic state and consequently the major contribution to $\mathcal{J}_{\epsilon x}^{(1)}$, Eq (13), must occur at this same R_e . Since the processes of interest in this study originate from $v'' = 0$, the Franck-Condon approximation has been employed and is expected to be a reliable approximation to the more complicated expression, Eq (20).

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

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

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

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

III. WAVEFUNCTIONS

There have been a number of accurate extended and/or fully optimized basis set calculations reported for the $X^1\Sigma_g^+$ state of N_2 .¹⁶ However these results did not include wavefunctions for the various excited states of N_2 of interest in this work. In addition, the programs employed in the present calculations for the evaluation of the multicenter terms which appear in the transition amplitude were not able to include atomic orbitals with principle quantum numbers ≥ 3 . Consequently an elaborate ground state wavefunction could not be used and to be consistent, the present calculations were limited whenever possible to wavefunctions for the ground and excited states which were formed from atomic orbitals with principle quantum number equal to 1 and 2.

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

For $B^3\Pi_g$ and $C^3\Pi_u$ electronic states, the SCF-MO set of wavefunctions constructed from minimum basis set Slater type atomic orbitals by Sahni and De Lorenzo¹⁷ (SDL) were used. Since the B and C excited states are open shell states, the wavefunctions for these states were determined within the framework of a "restricted" SCF treatment¹⁷ in

TABLE I

The electronic configurations of the ground
and excited triplet states of molecular nitrogen.*

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

*The occupancy of each MO is indicated by giving the spin
projection of each electron in the MO.

order to issue a pure spin state. The resulting wavefunctions used were in the form of single Slater determinants in which the spin degrees of freedom in the calculation of the transition amplitude were treated separately as outlined in Section II. In the (SDL) wavefunctions, the values used for the screening constants were those given by Slater's Rules¹⁸ and all the wavefunctions were calculated at one internuclear distance, that of the ground electronic state. A detailed discussion of the symmetry structure of the N₂ MO's can be found in work of Scherr.¹⁸ For the excitation of the B and C state, the wavefunction used for the X¹Σ_g⁺ ground electronic state was the exponent-optimized minimum-basis wavefunction of Ransil¹⁹ constructed of orthogonal AO's.

For excitation of the A³Σ_u⁺ and W³Δ_u²⁰ states from the X¹Σ_g⁺ ground state the double minimum-basis set SCF-MO wavefunctions of Richardson²¹ were used. Richardson's calculations are similar to those carried out by (SDL) except that the number of basis functions centered on each nucleus was doubled. The screening constants employed in the Richardson wavefunctions were determined from calculations on the N atom for the 1s atomic orbital and by a slight modification of the customary Slater Rules for the 2s and 2p atomic orbitals. As for the (SDL) and Ransil wavefunctions, the calculations were done only at the equilibrium internuclear separation of the X¹Σ_g⁺ state. Based on the energy criteria for the quality of a wavefunction, the Richardson results should be as good as any single zeta set of wavefunctions in which the screening constants were independently optimized.²¹

Sahni et al,¹⁷ (SDL) also reported wavefunctions for the $X^1\Sigma_g^+$ ground and $A^3\Sigma_u^+$ excited state so the effect of improved wavefunctions on the calculated cross section could be determined in this case by comparing the excitation cross section to the $A^3\Sigma_u^+$ state obtained from the (SDL) set with that obtained using the Richardson double-zeta wavefunctions. The results obtained from this comparison are discussed in Section V.

For excitation to the two Rydberg states, $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$, the wavefunctions calculated by Lefebvre-Brion and Moser²² (LBM) were used. The E and D Rydberg states converge to the $X^2\Sigma_g^+$ state of N_2^+ and were represented by a single configuration in which the core was assumed to be the same for all the Rydberg states. The screening constants for the orbitals were chosen by Slater's Rules and the calculations were carried out at the internuclear separation of the $X^1\Sigma_g^+$ state of N_2 . The coefficients of each Rydberg orbital were found by minimizing the energy of the Rydberg orbital in the field of the fixed core. Of the three nearly equivalent wavefunctions reported by (LBM) for each Rydberg state, the wavefunction corresponding to set B was used in these calculations to describe the E and D Rydberg states. The coefficients and screening constants of the atomic orbitals comprising the Rydberg MO's for these two states are given in Table II.

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

As discussed in Section II, the simplification of Eq (15) to the form of Eq (17) requires orthonormality between the orbital sets used

TABLE II

The screening constants and coefficients of the primitive symmetry orbitals for the Rydberg MO's of the $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$ states of N_2 .²² The E and D state MO's are abbreviated g and u respectively.

MO	1s σ	2s σ	3s σ	4s σ	2p σ	3p σ	4p σ	3d σ	4d σ
z	6.70	1.95	0.70	0.35	1.95	0.70	0.35	0.70	0.35
g	-.05770	.315661	-.557553	-.075635	-.181345	-.074023	-1.342060	.125241	-.153941
u	-.046697	.276244	-.282549	5.43409	-.029711	.184171	.684517	-.648868	.173989

to construct the initial and final electronic states. Since the MO sets of (SDL), Ransil, and Richardson were not published in the required orthogonal form, it was necessary to transform certain of the MO sets to the required form. This was performed numerically²³ by employing the unitary transformation of King et al.¹² which is based on the diagonalization of the Hermitian product of the overlap matrix between the ground and excited MO sets. For those transitions for which the initial and final orbitals were π MO's (W, A \leftarrow X), or in which the core was the same for the ground and excited states (D, E \leftarrow X), only the $D_{l'l''}^{1/2}$ factor had to be calculated. This is because that portion of the overlap matrix involving the initial orbitals for these transitions is already diagonal. However, for the wavefunctions used in the B, C \leftarrow X transitions, the transformation of MO's themselves was also important because the initial orbitals for these transitions are σ_g (or σ_u) symmetry and this portion of the overlap matrix is not diagonal. The diagonalization procedure in this case causes the σ_g (and σ_u) orbitals to mix among themselves. The coefficients of the transformed Ransil (BL) initial orbitals are given in Table III for the B \leftarrow X and C \leftarrow X transitions. Included in Table III are the appropriate $D_{l'l''}^{1/2}$ factors used in the calculation of the transition amplitude Eq (17) for all the excitation processes discussed here.

Configuration interaction (CI) may be important in certain of the excited electronic states²⁴ and hence a single Slater determinant may not be an adequate representation of the true state. Of the excited states considered in this work, CI appears to be most important for the A $^3\Sigma_u^+$ state. An approximate test of the A state wavefunctions to determine the importance of CI is discussed in Section V.

TABLE III

Transformed coefficients of the Ransil (BL) primitive symmetry MO's for the B \leftrightarrow X and C \leftrightarrow X transitions in N₂ using the (SDL) excited states. The $D_{I''}^{1/2}$ values, those used in Eq. (17), are also given for these transitions as well as the W, A \leftrightarrow X transitions calculated using the Richardson wavefunctions and the D, E \leftrightarrow X transitions using the (SDL) and (LB) wavefunctions.

Transition	Transformed Coefficients		$D_{I''}^{1/2}$
B($1\pi_g$) \leftrightarrow X($3\sigma_g$)	+ 0.03050 ($\sigma_g 1s$)	+ 0.48415 ($\sigma_g 2s$) - 0.84799 ($\sigma_g 2p$)	0.91842
C($1\pi_g$) \leftrightarrow X($2\sigma_u$)	+ 0.02777 ($\sigma_g 1s$)	+ 1.10999 ($\sigma_g 2s$) - 0.32873 ($\sigma_g 2p$)	0.98153
W,A($1\pi_g$) \leftrightarrow X($1\pi_u$)	None		0.97365
D,E \leftrightarrow X($3\sigma_g$)	None		1.00000

IV. NUMERICAL TECHNIQUES

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

A. Potential Energy Curves and FC Factors

The potential energy curves and vibrational level spacings used for the $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $B^3\Pi_g$ and $C^3\Pi_u$ electronic states were those determined from spectroscopic constants by Benesch et al.²⁵ and Gilmore²⁶ from which the $v'' = 0, v'$ energy separations were calculated. Benesch et al.²⁷ have reported Franck-Condon arrays for transitions from the X state to all v' levels of importance in the B and C states. However it was necessary to extend their published arrays for the $A \leftarrow X$ transition to higher v' -levels even though the extended portion of the array may be of somewhat lower accuracy. The Franck-Condon factors for these high v' -levels of the A state were determined by using spectroscopic constants²⁵ to determine RKR potential energy curves for the X and A states followed by numerical integration of the resulting nuclear wavefunctions to obtain the Franck-Condon²⁸ factors. The calculated energy levels and Franck-Condon factors for transitions to all v' -levels of the A state from $v'' = 0$ of the X state are given in Table IV. The Franck-Condon factors for the lower v' -levels are seen to agree well with those reported by Benesch et al.²⁷

TABLE IV

Excitation energies and Franck-Condon factors
 for the transition $A^3\Sigma_u^+(v' = 0 \dots 20) \leftarrow X^1\Sigma_g^+(v' = 0)$
 as calculated from the spectroscopic data tab-
 ulated by Benesch et al.²⁵

v'	$\Delta E(\text{eV})$	$q_{v'0}$	v'	$\Delta E(\text{eV})$	$q_{v'0}$
0	6.169	.00098	11	7.931	.07562
1	6.346	.00521	12	8.070	.06525
2	6.521	.01482	13	8.205	.05459
3	6.691	.03008	14	8.335	.04452
4	6.859	.04863	15	8.462	.03566
5	7.023	.06722	16	8.585	.02806
6	7.183	.08175	17	8.704	.02173
7	7.340	.09145	18	8.819	.01659
8	7.493	.09457	19	8.930	.01249
9	7.643	.09180	20	9.036	.00927
10	7.789	.08509			

The potential energy curves for the W, E, and D electronic states were calculated by a RKR method from spectroscopic constants determined as follows. The vibrational constants and T_e for the W state have recently been measured by Wu and Benesch.²⁰ The rotational constants used for the W state were taken from the theoretical work of Fraga and Ransil.²⁹ The spectroscopic constants used for the E state were taken from Lofthus²⁴ and ground state ($X^2\Sigma_g^+$) N_2^+ data.³⁰ For the D state, the data of Lofthus²⁴ was combined with that for the $p' \ ^1\Sigma_u^+$ state.³¹ The spectroscopic data used for the RKR ground state was that given by Benesch et al..²⁵ The spectroscopic constants used in the potential energy curve calculations on the W, E, and D states are summarized in Table V.

Freund has recently reported³² measurements on the radiation emitted from the E state and from an analysis of the relative intensities in the various bands he estimated the R_e and B_e values for this state to be $1.16 \pm 0.02 \text{ \AA}$ and $1.77 \pm .06 \text{ cm}^{-1}$ respectively. A potential energy curve for the E state using these values and the corresponding Franck-Condon factors connecting this state with the ground electronic state were calculated but rejected in favor of those obtained from the constants given in Table V. The latter set of constants was determined to better represent the E state because the corresponding Franck-Condon factors for transitions from $v'' = 0$ of the ground state agree much better with those determined from recent energy loss spectra.³³

TABLE V

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

	$W^3\Delta_u$	$E^3\Sigma_g^+$	$D^3\Sigma_u^+$
T_e (cm ⁻¹)	59738.00 ^a	95859.46 ^c	103652.22 ^c
ω_e (cm ⁻¹)	1539.00 ^a	2185.00 ^c	2217.00 ^e
$\omega_e x_e$ (cm ⁻¹)	-17.00 ^a	16.136 ^d	19.00 ^e
$\omega_e y_e$ (cm ⁻¹)		-0.04 ^d	
B_e (cm ⁻¹)	1.546 ^b	1.9322 ^d	1.961 ^c
α_e (cm ⁻¹)	0.01163 ^b	0.0202 ^d	0.00002 ^c
R_e (Å)	1.248 ^a	1.1162 ^d	1.108 ^c

- a) Taken from ref. 20
- b) Taken from ref. 29
- c) Taken from ref. 24
- d) Taken from ref. 30
- e) Taken from ref. 31

The Franck-Condon factors for the E \leftarrow X and D \leftarrow X transitions were calculated in the same manner as described above to extend the A \leftarrow X array. The excitation energies (eV) and Franck-Condon factors for transitions from $v'' = 0$ of the X state to the W, E and D states are given in Table VI and all the potential energy curves are shown in Fig. 1.

B. Evaluation of the Multicenter Terms

When Slater-type-orbitals centered on the nuclei are used to represent the MO's, single center and multicenter terms appear in the evaluation of the transition amplitude Eq (17).^{11a} The single center terms could be done analytically and the methods used to evaluate the multicenter terms have been discussed in detail elsewhere.^{11a, 34} To facilitate the averaging over orientations of the diatomic axis with respect to the incident electron beam, the atomic orbitals on each nucleus were expanded about the center of mass of the diatomic molecule using the zeta function expansion. Multicenter terms composed of atomic orbitals of principle quantum number $n \leq 2$ could be evaluated for any value of the momentum transfer q and internuclear distance R . Since the numerical methods used to evaluate the multicenter terms were not able to treat atomic orbitals of $n \geq 3$, not all the multicenter terms appearing in the scattering amplitude describing excitation to the E and D states could be evaluated. Therefore, in order to be consistent in calculating the E and D state transition amplitudes, none of the multicenter terms appearing in the transition amplitude for excitation of the E and D states were evaluated. Because of the neglect

TABLE VI

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

v'	$W^3\Delta_u$	$E^3\Sigma_g^+$	$D^3\Sigma_u^+$
0	7.355 .0129	11.877 .9278	12.841 .9819
1	7.542 .0522	12.139 .0625	13.097 .0176
2	7.724 .1100		
3	7.902 .1609		
4	8.076 .1820		
5	8.246 .1686		
6	8.412 .1320		
7	8.573 .0887		
8	8.730 .0515		
9	8.883 .0257		
10	9.031 .0108		
11	9.176 .0036		
12	9.316 .0009		

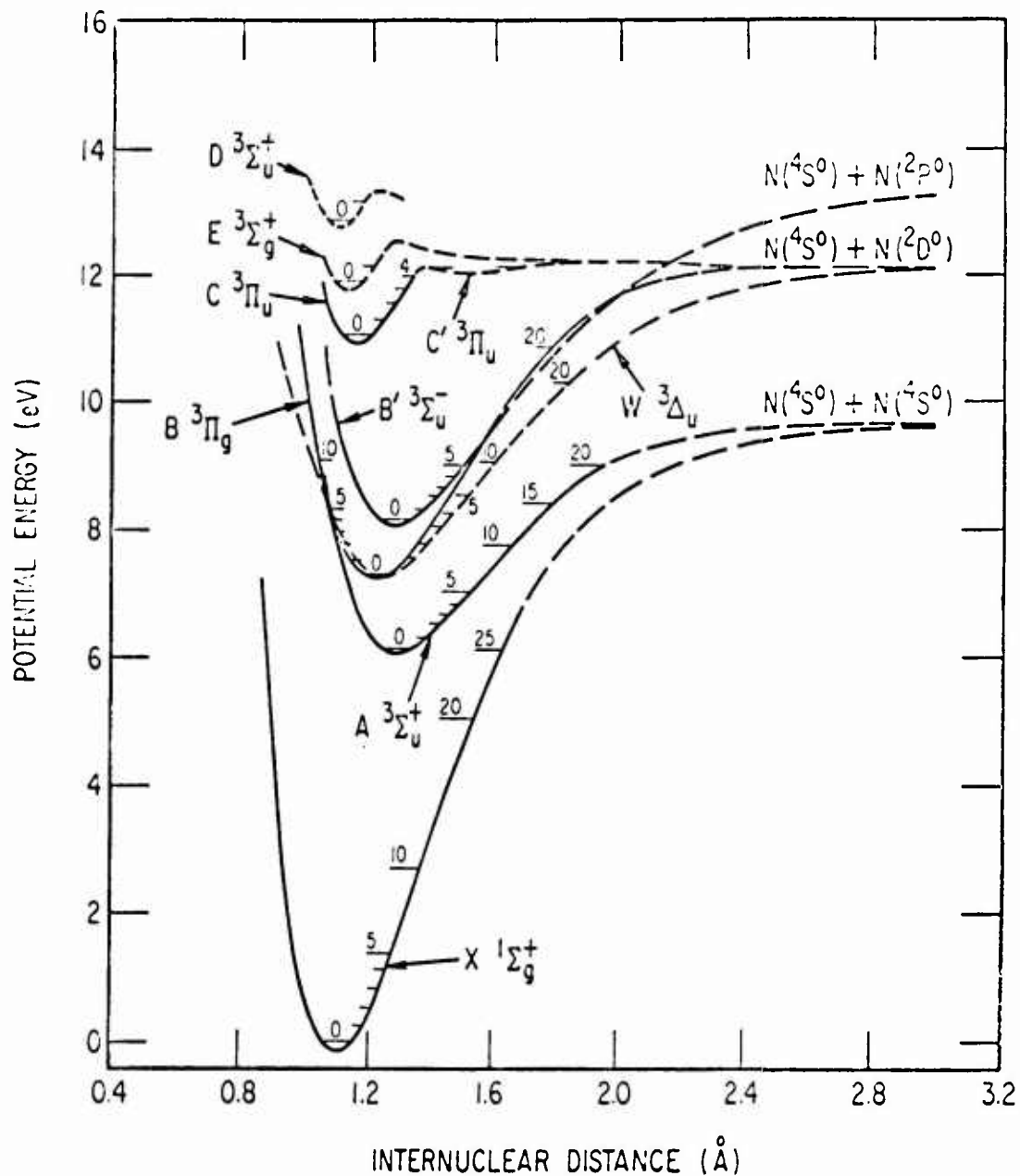


FIG. 1. The potential energy curves for the ground and seven lowest triplet states of N_2 as functions of the internuclear distance. The curves for the $W \ 3\Delta_u$ and $D \ 3\Sigma_u^+$ were calculated as outlined in Section IV, the others were taken from Gilmore.²⁶

of these multicenter terms, the cross sections corresponding to these excitations are of lower accuracy relative to the calculated cross sections for excitations of the A, B, W, and C electronic states. From previous work on the excitation of H_2 , ^{11a} the error in the E←X, D←X cross sections due to the omission of the multicenter terms is not believed to exceed 60%.

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

V. RESULTS

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

In Fig. 2 are shown the total cross sections ($\sigma_{00}^{n'}$) for excitation of the A, B, W, C, E and D triplet states of N_2 from $X^1\Sigma_g^+$ ($v'' = 0$). These total cross sections all exhibit the steep rise to a maximum near threshold followed by the rapid k_0^{-6} fall-off characteristic of pure exchange excitation except that for the W state. The total cross section for excitation of the $B^3\Sigma_u^-$ state from $X^1\Sigma_g^+$ is identically zero in the model used here to describe the scattering process³⁵ and consequently doesn't appear in Fig. 2.

No experimental determination of the W-X excitation cross section has been reported. Peaks corresponding to excitation of the W state will not easily be seen in conventional electron impact spectra because the W state vibrational levels are nearly degenerate in energy with v' -levels of the $B^3\Pi_g$ and $A^3\Sigma_u^+$ states (see Fig. 1) whose cross sections are five to

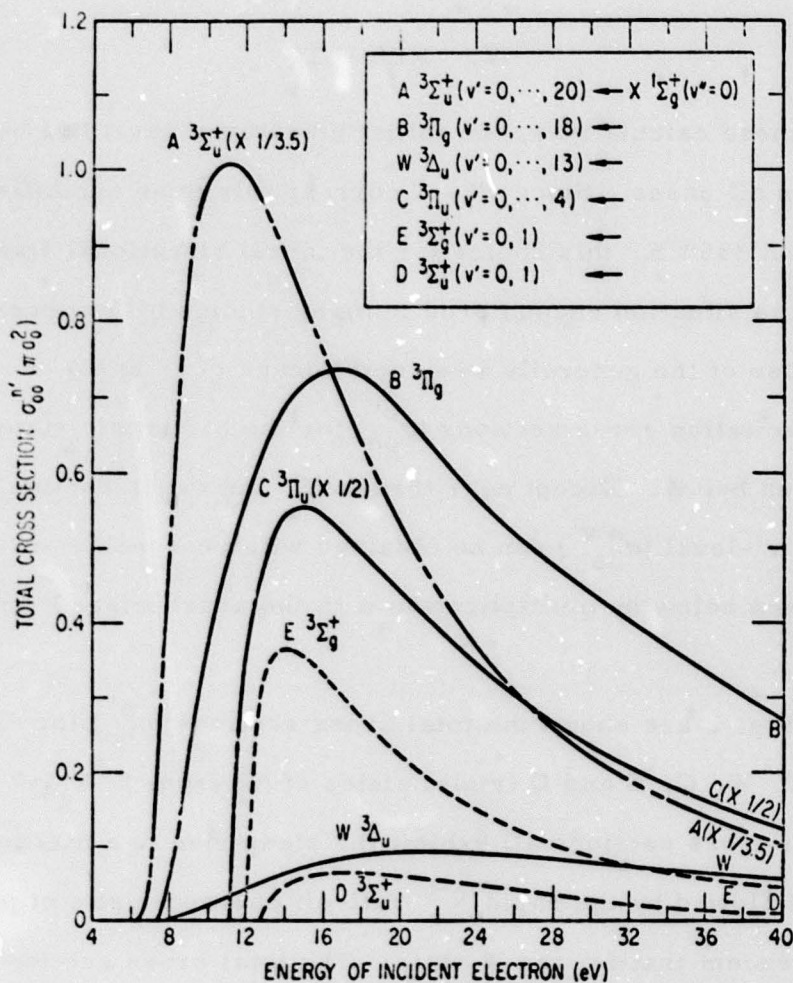
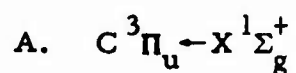


FIG. 2. Total cross sections ($\sigma_{00}^{n'}$), as defined by eq (24), for excitation of the seven lowest triplet electronic states of N_2 from $v'' = 0$ of the ground state as a function of the incident electron energy. The cross section for excitation of the $B'{}^3\Sigma_u^-$ state is zero in this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

ten times larger than that for the W state at all incident electron energies. However, knowledge of the $W \leftarrow X$ total cross section is useful in the analysis of radiation from electron impact excited N_2 . That is, since $W^3\Delta_u \rightarrow B^3\Pi_g$ is dipole allowed and the W state excitation cross section is fairly large and broad in shape, the $W \rightarrow B$ radiation (in the $3.6 \rightarrow 5.3\mu$ region) should be relatively strong in processes such as the aurora. A detailed analysis of the effect of the $W \rightarrow B$ transitions in the population of the A and B states under auroral conditions is the subject of a future publication.

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



The excitation processes of the $C^3\Pi_u$ state have been the most extensively studied of any excited state of the N_2 triplet system. This can be attributed to (a) the fact that the radiation in the Second Positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$) is in a region of the electromagnetic spectrum which is easily measured and; (b) there is little or no cascade population of the C state from higher electronic states and therefore when electrons of

known energy are passed through N_2 gas the resulting radiation in the second positive system can be used to estimate the corresponding C state excitation cross section. The technique which is usually employed is one of calibrating the photon detection system against a standard lamp and/or some other radiation from electron impact excited N_2 for which the cross section is assumed known (such as the 3914 Å band from N_2^+). However, there are a good many experimental difficulties in determining the excitation cross sections from optical data and, as will be discussed below, the cross sections obtained by different investigators using essentially the same technique are not in accord with each other.

The results to which the theoretical $C^3\Pi_u$ excitation cross section can be compared³⁶ are those of Jobe, Sharpton and St. John (JSSJ);^{37a} Burns, Simpson and McConkey (BSM);^{37b} Skubenich and Zapesochny (SZ)^{37c} and Legler(L).^{37d} These investigators used the intensity of the Second Positive system for known incident electron energy as a measure of the excitation cross section. There is also a determination of this cross section by Engelhardt et al.³⁸ based on an analysis of electron transport coefficient data.

Figure 3 shows the comparison between the calculated total excitation cross section, the experimentally determined values for the cross section, and the semi-empirical results of Bauer and Bartky³⁹ (BB) and Stolarski et al.⁴⁰ (SDWG). (For purposes of clarity the experimental results of (BSM) and(SZ), respectively 15% and a factor of 2 smaller than the (JSSJ) curve at 15 eV, are not shown in Fig. 3). From the figure one notes

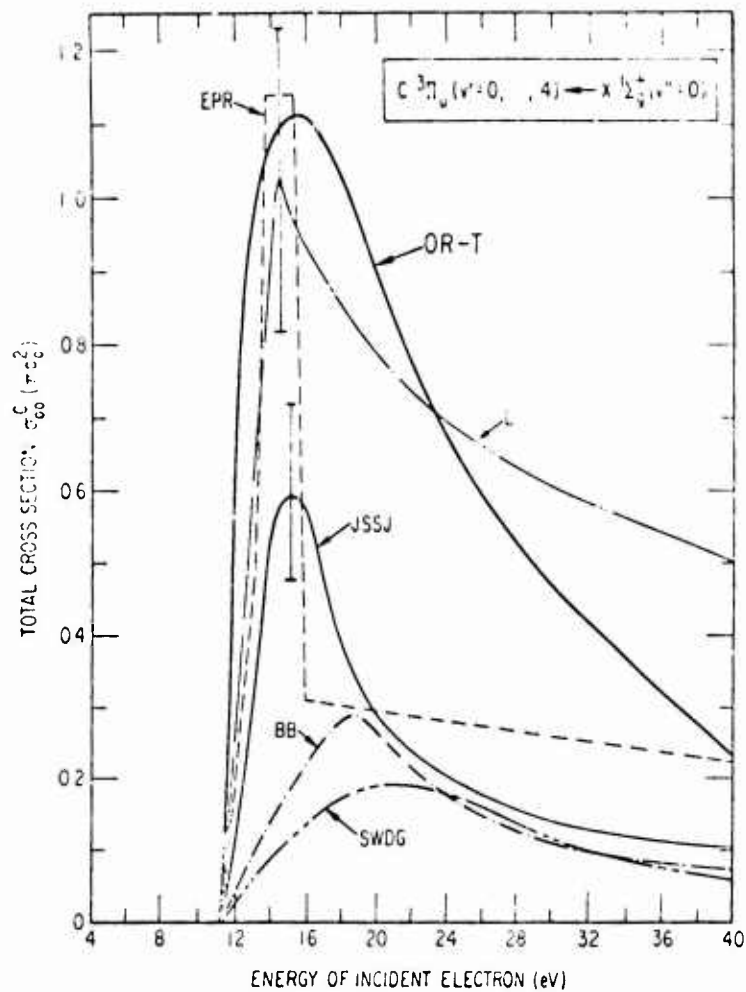
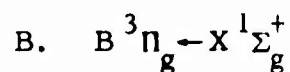


FIG. 3. Total cross section for excitation of the $C^3\Pi_u$ state from $X^1\Sigma_g^+$ ($v'' = 0$) as a function of the incident electron energy. The present results are labeled OR-T and the other cross sections are Engelhardt et al. (EPR)³⁸; Legler (L)^{37d}; Jobe et al. (JSSJ)^{37a}; Bauer and Bartky (BB)³⁹; and Stolarski et al. (SDWG)⁴⁰. The experimental cross sections of Burns et al.^{37b} and Skubenich and Zapesochny^{37c} have been omitted for clarity but are discussed in the text. The vertical bar drawn on the (L) and (JSSJ) curves represent the quoted experimental uncertainty.

that the maximum of the excitation cross section determined in the various experiments falls into one of two groups for which the quoted error bars don't overlap. The maximum value as determined by (EPR) and by (L), is greater than $1.0\pi a_0^2$ and in good agreement with the calculated cross section. The more recent experimental determinations of the cross section by (SZ), (BSM) and (JSSJ) are a factor of two or more smaller and have maxima less than $0.6\pi a_0^2$. However, there is disagreement within this latter group of experimental data in that the (SZ) cross section (not shown in Fig. 3) is about a factor of two smaller at maximum than that obtained by (JSSJ) and (BSM) although the same experimental technique was employed. This discrepancy coupled with the fact that the cross section determination by Legler was also based on photon collection of the second positive bands makes a meaningful comparison between theory and experiment difficult.

Approximations which could lead to a theoretical total cross section which is too large are the relatively simple wave function representations used to describe the ground and excited states (see Section V - F) and/or the scattering model used to describe the excitation process. However, previous calculations involving similar processes in H, He and H₂ employing comparably accurate wavefunctions and the same scattering model have generally been in good agreement with the corresponding experimental measurements. Apparently all that can be concluded from the above comparison is that the theoretical excitation cross section for

the $C^3\Pi_u$ state shown in Fig. 3 is probably larger than the true cross section but most likely accurate to within a factor of two. The resolution of the differences between the various experimental determinations must await the results of further experimental work or a more elaborate theoretical study.



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

In Fig. 4 the calculated total cross section for excitation of the $B^3\Pi_g$ state from $X^1\Sigma_g^+$ ($v''=0$) is compared with the "apparent" excitation cross section as measured by Stanton and St. John^{41a} (SSJ) and Skubenich and Zapesochny^{37c} (SZ). The "apparent" excitation cross section measured by McConkey and Simpson^{41b} (MS) agrees well with the (SSJ) results and have been omitted from Fig. 4 for the sake of clarity. Even though the "apparent" excitation cross sections contain a variety of cascade contributions, the following comparison can be made with the calculated cross section. The first peak in the "apparent" cross sections for excitation of the lower ($v' \leq 5$) v' -levels of the B state has been interpreted by (MS) as being due to direct excitation of these v' -levels from the ground electronic state and the second peak (at about 15 eV) as due to cascading from the $C^3\Pi_u$ state. However preliminary calculations using a reasonable value for the $A^3\Sigma_u^+$ state excitation cross section (see Section V-C) and the known transition moment for the First Positive system⁴² indicate that the first peak at 10 eV in the "apparent" excitation cross section may be due to cascade from the higher vibrational levels of the A state to the particular v' -level of interest in the B state rather than direct excitation from the ground state. This results from the fact that the A state excitation cross section has its maximum near 10 eV incident energy, and has Franck-Condon factors such that its higher vibrational levels ($v' \geq 12$) are appreciably populated by direct excitation from the ground state (see Table IV). Since the second peak in the measured cross section (at

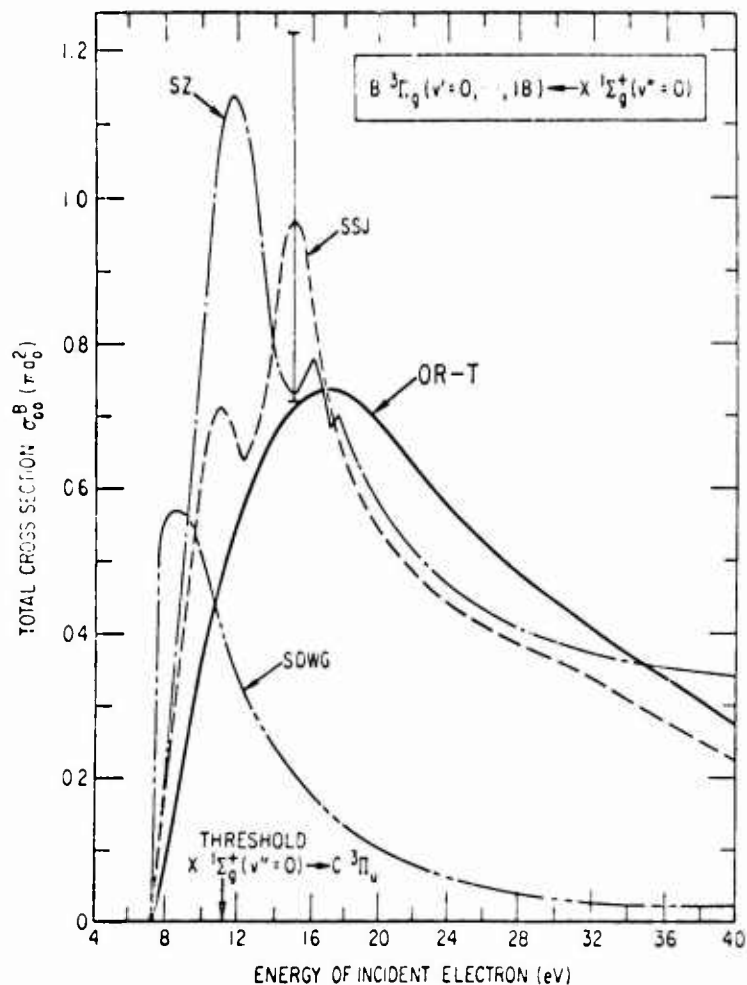
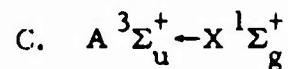


FIG. 4. Total cross section for excitation of the $B^3\Pi_g$ ($v' = 0, \dots, 18$) state from $X^1\Sigma_g^+$ ($v'' = 0$) as a function of incident electron energy. (The present results are labeled OR-T and the other cross sections are Stanton and St. John (SSJ);^{41a} Skubenich and Zapesochny (SZ);^{37c} and Stolarski, et al. (SDWG).⁴⁰ The apparent cross section measured by McConkey and Simpson^{41b} agrees well with the (SSJ) results and is not shown. The vertical bar on the (SSJ) curve represents the $\pm 25\%$ uncertainty in the measured "apparent" excitation section estimated by (MS) for the case of the strongest first positive bands. The cross sections reported by (SSJ), (SZ), and (MS) are "apparent" cross sections, containing cascade effects, and therefore represent experimental upper bounds on the true excitation cross section.)

about 15 eV) is probably due in part to cascade from the C state, the maximum of the "true" B state excitation cross section most likely occurs near the feature observed by (MS) for incident energies between 15 and 16.5 eV. Similar calculations using the theoretical cross section for excitation of the $W^3\Delta_u$ state shown in Fig. 2 and a theoretical transition moment calculated by the author indicate that the shoulder at about 30 eV incident energy observed by (SSJ) and (MS) is due to the W state cascading into the B states. The details of these calculations will be reported in a subsequent publication.

With the cascade effects in mind, the comparison in Fig. 4 indicates that the calculated cross section will agree reasonably well with the "true" B state excitation cross section although the theoretical curve may peak at slightly too large an incident energy and be somewhat too broad. The cause of the discrepancy in the relative magnitudes of the first two peaks in the measured "apparent" excitation function of the B state as determined by (SSJ) and (MS) and that observed by (SZ) may be due to the fact that (SZ) used an extrapolation method to obtain the "apparent" cross section of the entire B state from the cross section for excitation of a few specific v' -levels of the B state. Included in Fig. 4 for purposes of comparison is the semi-empirical cross section estimated by Stolarski et al.⁴⁰ based on relative cross section data obtained by Schulz⁴³ using the trapped electron method.



To date there have been no published measurements of the absolute cross section for excitation of the $A^3\Sigma_u^+$ state. The long lifetime of the A state together with the fact that the emissions from the A state ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$; Vegard-Kaplan bands) are in the UV makes the determination of the cross section by optical methods difficult. In Fig. 5 the theoretical cross section for excitation of the A state is compared with the semi-classical cross section of Bauer and Bartky (BB),³⁹ and the semi-empirical estimate of Stolarski et al. (SDWG).⁴⁰ The cross section deduced by Engelhardt et al.³⁸ from the trapped electron experiments of Schulz⁴³ is not included in Fig. 5 because the cross section measured by Schulz in the energy region 6-9 eV contained contributions from the excitation of the A, B and W states. One notes from the figure that the A state excitation cross section reported here is considerably larger than previously believed.

There are some recent energy loss spectra to which these calculations can be compared to determine if the theoretical A state cross section is of the correct magnitude relative to that of the B and C states. This comparison, which is discussed in more detail in Section IV-E, indicates that the calculated A, B and C state cross sections are of the correct relative magnitudes at 35 eV and that the A state cross section may well be the largest of the triplet excitation cross sections in the energy range below 35 eV. The cross section obtain-

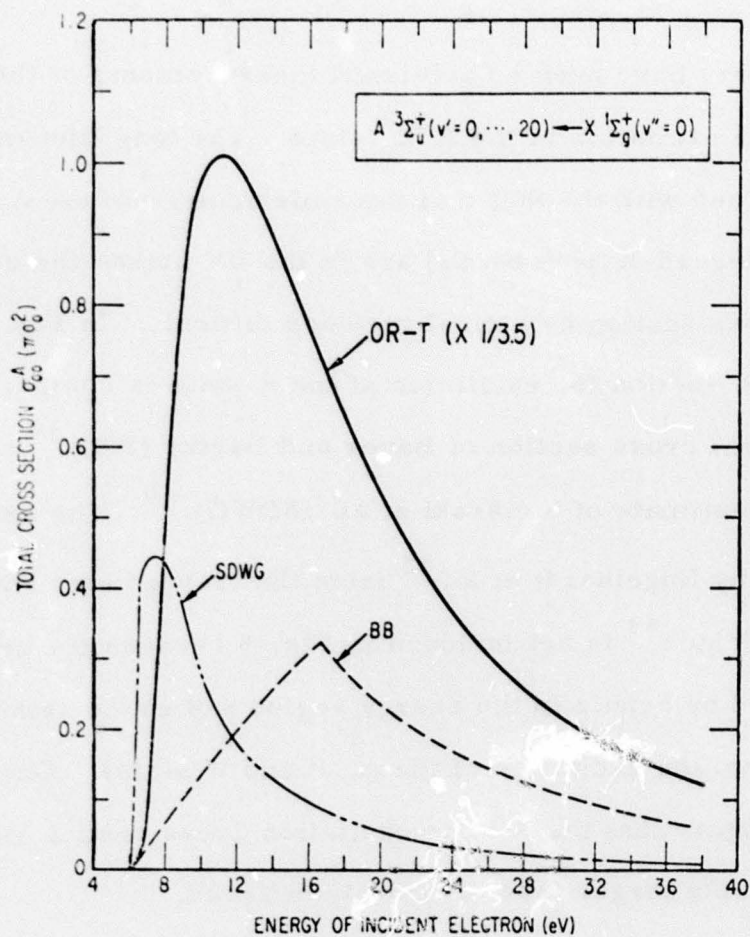


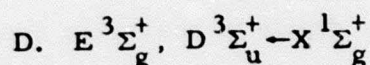
FIG. 5 Total cross section for excitation of the $A^3\Sigma_u^+$ ($v' = 0, \dots, 20$) state from $X^1\Sigma_g^+$ ($v'' = 0$) as a function of incident electron energy. The present result is labeled OR-T and has been reduced by a factor of 3.5. The other curves are Bauer and Bartky (BB)³⁹ and Stolarski et al. (SDWG).⁴⁰

ed in the OR approximation is much larger than that predicted by (SDWG) and (BB) not only for the A state but also for the B and C states. Because of the good agreement between the calculated and measured B state cross section, the A state cross section reported here is probably the most reliable estimate presently available.

The approximate wave functions used for the A state were examined to determine if they are a particularly poor representation of the A state. As mentioned in Section III, the $A^3\Sigma_u^+$ state is not a pure state but contains a mixture of other configurations (mainly $^1\Sigma$ and $^1\Pi$) due to the electron spin-orbit interaction.⁴⁴ This is evidenced by the fact that the radiation in the Vegard-Kaplan bands is electric dipole in character even though the transition is spin forbidden.⁴⁵ Therefore, to properly describe the excitation of the A state, it may be necessary to include the mixing-in of the other configurations in the A state wavefunction. The modification of the available wavefunctions to include such configuration interaction was beyond the scope of this work so the effect of the configuration mixing was estimated as follows. The square of the transition moment (D_{BA}^2) for the first positive system ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) was calculated at an R-centroid value of $R = 1.0941 \text{ \AA}$ using the (SDL) wavefunctions and compared with the measurements of Jeunehomme^{42a} and Turner and Nicholls.^{42b} If the B state wavefunction employed is assumed to be "pure", which appears valid for the B state v' -levels of importance here,²⁴ then any discrepancy between the calculated and observed (D_{BA}^2) could be attributed to the inadequacy of the single configuration A state wavefunction. However, the

calculated transition moment differed from the experimental value by less than 30% and therefore no correction based on this comparison was believed to be justified.

The effect on the cross section of improving the wavefunctions was also determined in the case of the A state excitation by calculating the excitation cross section using the (SDL) X and A state wavefunction pair.¹⁷ The cross section obtained using the (SDL) wavefunctions was found to be only 18% larger than that obtained with the Richardson wavefunctions. Thus for the A←X excitation, this significant improvement in the set of wavefunction used does not produce a significant change in the excitation cross section.



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

Clampitt and Newton have reported⁴⁶ detection of the $E^3\Sigma_g^+$ state in a crossed electron - N_2 beams experiment but gave no quantitative estimate as to the magnitude or energy dependence of the excitation cross section. Freund (F) has given³² a relative "excitation function" for the excitation of the E state over the energy range from threshold to 23 eV based on measurements of the delayed emission spectra observed from a beam of excited N_2 molecules. Figure 6 is a comparison between the theoretical $E^3\Sigma_g^+$ excitation cross section, calculated without the multicenter terms (see Section IV-B), and the "excitation function" measured by Freund. The latter has been normalized to the theoretical

curve at its maximum. Ehrhardt and Willmann (EW) have also reported⁴⁷ a relative cross section for excitation of the E state for incident electron energies from 11 to 17 eV, based on the collection of those electrons which had lost 11.87 eV energy and been scattered into an angle of 20° or less. An energy loss of 11.87 eV corresponds to excitation of $v'=0$ of the E state which is about 93% of the complete cross section σ_{00}^E (see Table VI). The (EW) cross section is quite narrow, with a full width at half maximum of less than 0.5 eV, and for that reason it is not shown in Fig. 6. The theoretical cross section is seen to be considerably broader than both the (F) and (EW) cross sections. This disagreement between the calculated and measured shape of the E state cross section is not expected to be removed by the inclusion of the multicenter terms in the theoretical cross section. The extreme narrowness of the measured E state excitation cross section relative to the cross sections for excitation of the other nitrogen triplet states implies that the E state may be excited by a resonant type process rather than the simple exchange process used in these calculations.

Skubenich and Zapesochny (SZ) have reported^{37c} an "apparent" excitation cross section for the $D^3\Sigma_u^+$ and McConkey and Simpson^{41b}(MS) have estimated the maximum in the D state cross section by assuming certain cascade contributions to the "apparent" cross section which they measure for the $B^3\Pi_g$ state. These experimental values are shown along with the theoretical excitation cross section for the $D^3\Sigma_u^+$ state in Fig. 7. As expected, because the multicenter terms were not included in the evaluation of the D state transition amplitude, the cal-

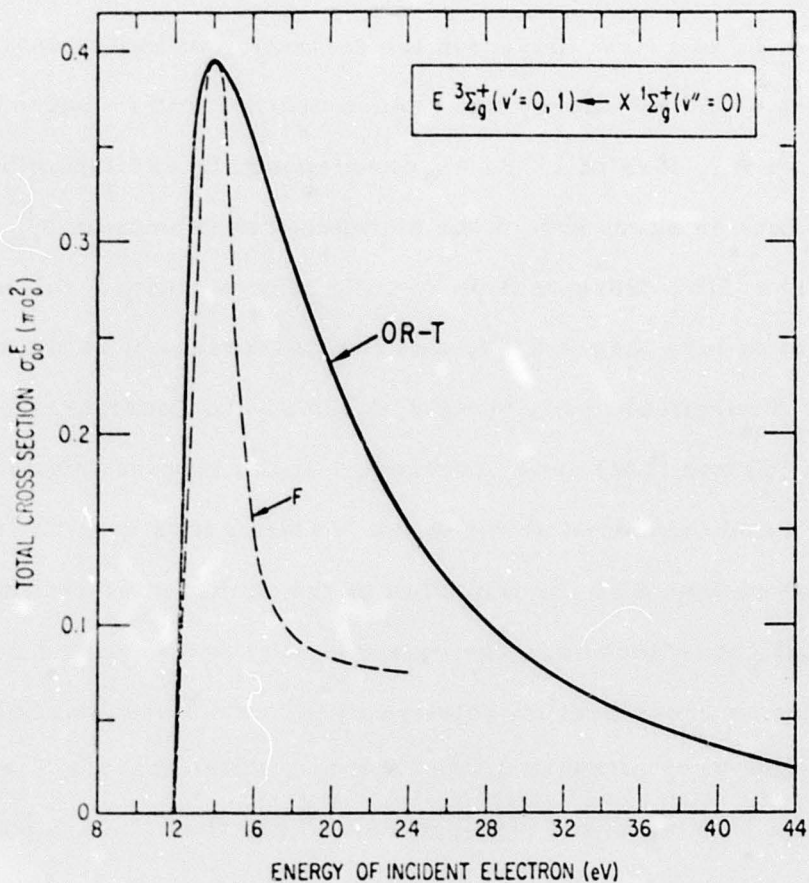


FIG. 6 Total cross section for excitation of the $E \ ^3\Sigma_g^+$ ($v' = 0, 1$) state from $X \ ^1\Sigma_g^+$ ($v'' = 0$) as a function of incident electron energy. The present results are labeled OR-T and the relative cross section measured by Freund³² (F) has been normalized to the theoretical curve at its maximum. See the text for a discussion of the cross section measured by Ehrhardt and Willmann.⁴⁷

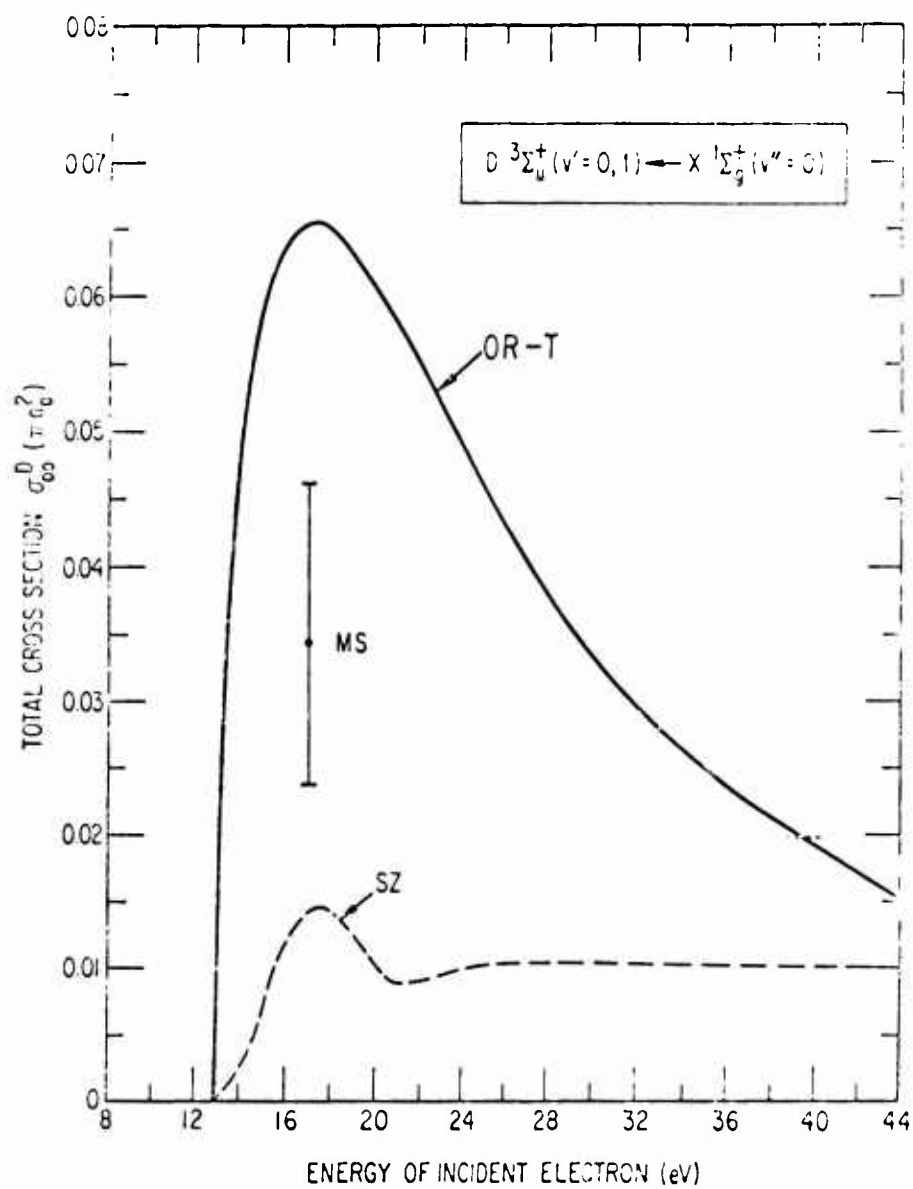


FIG. 7 Total cross section for excitation of the $D^3\Sigma_u^+$ ($v' = 0, 1$) state from $X^1\Sigma_g^+$ ($v'' = 0$) as a function of incident electron energy. The present results are labeled OR-T and the experimental results of McConkey and Simpson^{41b} and Skubenich and Zapesochny^{37c} are labeled MS and SZ respectively.

culated cross section is larger than the experimental values. Previous experience with the effect of the multicenter terms for a Σ_g^+ to Σ_u^+ transition indicates that omission of these terms from the scattering amplitude results in a cross section which is too large by about a factor of two. When the multicenter terms are included in the calculation of the D state transition amplitude, the resulting cross section is expected to agree well with the estimate of (MS) but perhaps still be slightly larger than the (SZ) result.

E. The Relative Magnitudes of the Triplet Excitation Cross Sections

The experimental determination of the magnitude of the total cross section for excitation of the $A^3\Sigma_u^+$ state has a large uncertainty and that for the $W^3\Delta_u$ and $E^3\Sigma_g^+$ states has not yet been made. In this section a comparison is made between a calculated energy-loss spectra, based on the theoretical differential cross sections, and recent experimental energy-loss spectra. The purpose of this comparison is to show that the relative magnitudes of the theoretical cross sections, particularly those for the A, B, W, and C states, are consistent with those determined experimentally and therefore reliable within the accuracy provided by this comparison.

The energy-loss spectrum chosen for this comparison is that obtained by Rice⁴⁸ for an incident electron energy of 35 eV. Since the objective of this comparison is to show that the calculated total cross sections for excitation of the A, B, W and C electronic states

are of the correct relative magnitudes, the comparison with experimental energy-loss spectra is made for a scattering angle (θ) as close as possible to 90° . There are two other reasons for making this comparison at large scattering angles. The first is that for small scattering angles the differential cross sections for singlet-singlet transitions are larger than those for singlet-triplet transitions by an order of magnitude or more. As a result, it is difficult to resolve the singlet-triplet processes at small scattering angles. On the other hand, at larger scattering angles ($\theta \geq 60^\circ$) the singlet-triplet transitions have magnitudes comparable to or larger than the singlet-singlet ones and therefore more easily studied. The second reason is that the (OR) scattering approximation is usually more reliable for scattering angles greater than 40° than it is in the range $0-40^\circ$, the actual range of validity depending on the nature of the scatterer.^{11b, 49} The choice of 35 eV incident energy, calculated from the theoretical differential cross sections assuming a resolution⁵⁰ of 0.080 eV, is shown in Fig. 8a and is to be compared with the experimental spectrum⁴⁸ shown in Fig. 8b. In the experimental spectrum, for energy loss above 8.5 eV, peaks corresponding to excitation of the v' -levels of the $a^1\Pi_g$ singlet state appear. Since only triplet excited states were treated in the calculations reported here, the corresponding peaks are absent in the synthetic spectrum. The energy loss region from 7.35 to 9.0 eV is composed of overlapping peaks due to excitation of the A ($v' \geq 7$), B, and W state vibrational levels and the experimental resolution was not sufficient to resolve the individual excitation processes. Since the experimental

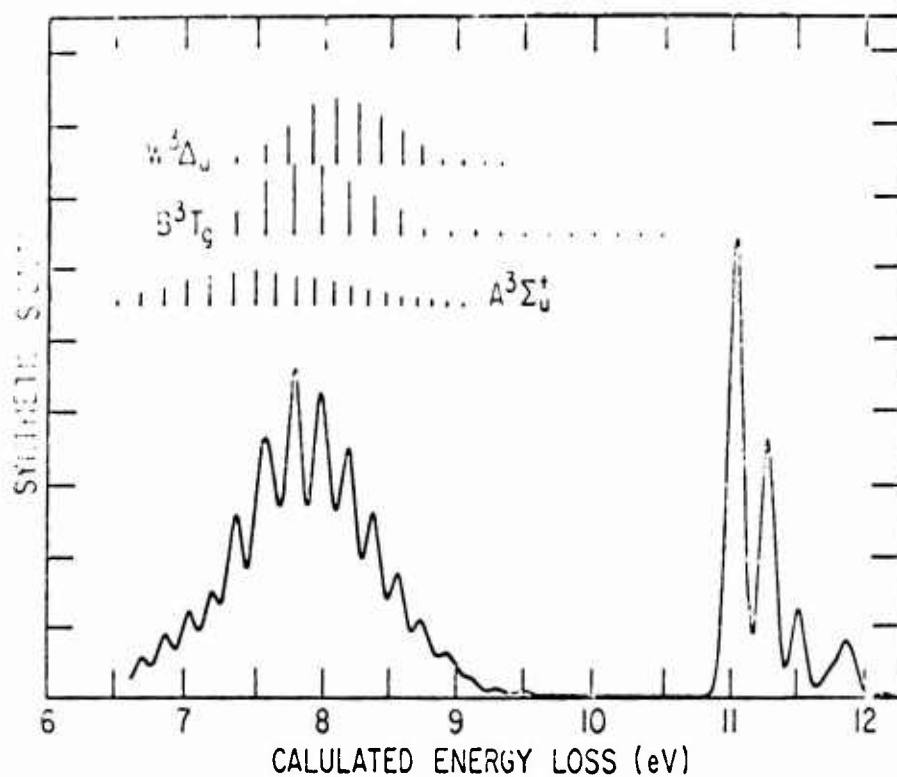


FIG. 8a Synthetic energy loss spectrum based on the theoretical differential cross sections for excitation of the lowest seven triplet states as calculated by the methods described in the text. The incident energy was taken as 35 eV, the scattering angle is 80° and the resolution assumed to be 0.080 eV.⁵⁰ Note that no peaks corresponding to excitation of the singlet states appear in the spectrum since these states were not included in the calculations. The energy-loss locations and Franck-Condon factors of the various vibrational levels of the A, B and W states are indicated by the vertical lines in the figure. All the Franck-Condon factors are relative to that for $v' = 2$ of the B-state and the dots represent v' -levels whose Franck-Condon factors are zero on this scale.

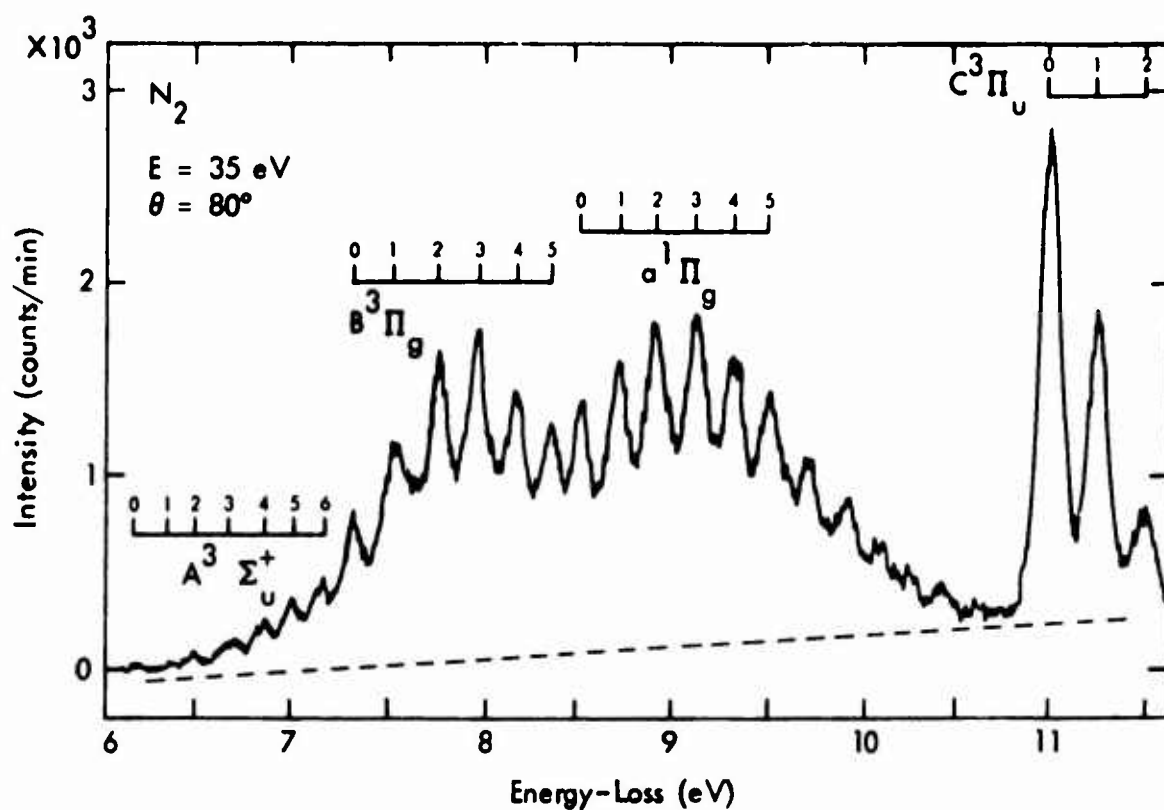


FIG. 8b The smoothed experimental energy loss spectrum obtained by Rice⁴⁸ for an incident energy of 35 eV, scattering angle of 80° and unknown resolution. The identification of some of the vibrational levels is indicated above certain peaks although all of the peaks between 7 and 9 eV consist of more than one unresolved feature.

spectrum is relative, the peaks in this region of the spectrum, some corresponding to the overlap of two or more v' -levels, should be compared to a standard peak. The $C^3\Pi_u (v' = 0, 1)$ peaks at 11.03 and 11.28 eV energy loss are the logical choices for reference peaks since they are the best resolved in the experimental spectrum. The essence of this comparison between theory and experiment is that for the synthetic spectra, the series of peaks between 6.6 and 8.5 eV energy loss have magnitudes relative to the $v'=0$ and $v'=1$ peaks of the C state which agree well with corresponding magnitudes in the measured spectrum when the background is subtracted from the latter.

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

1) Due to the Franck-Condon factors for excitation from the ground state, many more levels of the A state are excited with approximately equal intensity than in the B or W states. Consequently, the low peaks corresponding to excitation of the A state for energy loss ≤ 7.34 eV actually result in a total cross section (summed over v' -levels; σ_{00}^A) which is comparable to that for the B state at 35 eV (see Fig. 2).

2) By varying the magnitude of the A state cross section, it was found that a change of about $\pm 50\%$ in the value of the theoretical A state differential cross section at 35 eV results in poorer agreement between the calculated and measured spectrum. Con-

sequently, assuming that the (OR) scattering model properly predicts the differential cross sections at 35 eV and 80° , this comparison implies that the total cross sections for excitation of the A state is significantly larger than the estimates of Bauer and Bartky³⁹ and of Stolarski et al.⁴⁰

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

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

F. The Effect of Approximate Wavefunctions

As mentioned in Section III, there are a variety of ground state wavefunctions available for the description of the nitrogen molecule ranging in complexity from the minimum basis set Scherr¹⁸ wavefunction to the Hartree-Fock SCF-MO calculations of Nesbet and of Cade et al.¹⁶ The characteristics of the electron charge distribution and of the individual MO's themselves has been shown by Smith and Richardson⁵¹ (SR) to be sensitive to the degree of approximation used in constructing the wavefunction. In the case of the $2\sigma_u$ MO, the initial state MO involved in the excitation of the $C^3\Pi_u$ state, the hybridization⁵¹ and spatial extent were found to vary considerably from one approximation to the other. It has been shown earlier^{11a} that the OR cross section may, for certain symmetry combinations of ground and excited states, be sensitive to the quality of the wavefunctions employed as measured by the spatial electron distribution it predicts. Consequently the B and C state excitation cross sections were calculated with the (SDL) excited state wavefunctions and with the ground state wavefunction of (SDL) and of Ransil in an effort to determine the effect on the calculated cross section of an improvement in the ground state wavefunction. Use of the Ransil rather than the (SDL) ground state wavefunction (with the appropriate transformations to allow use of the Slater-Condon rule) resulted in a 20% reduction in the maximum of the B state cross section and a 5% increase in that for the C state. This indicates that the cross section calculated with the different wavefunctions is not as sensitive

to the "quality" of the MO's as are other properties such as hybridization. Coupled with the comparison between the (SDL) and Richardson ground state wavefunctions made in Section V-C for excitation of the $A^3\Sigma_u^+$ state it can be concluded that although the theoretical cross sections are somewhat sensitive to the quality of the wavefunctions used, the magnitude and direction of the effect does not appear easily predictable.

VI. CONCLUSIONS

A consistent set of total exchange excitation cross sections have been calculated for excitation of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$, $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$ triplet electronic states of molecular nitrogen from the ground $X^1\Sigma_g^+$ ($v''=0$) state. The calculated total cross section for excitation of the $B^3\Pi_g$ state is expected to agree well with the available experimental data when the cascade effects from the higher electronic states to the measured B state cross section are removed. The theoretical cross section for excitation of the C state is found to agree well with one group of measurements but is a factor of 2 larger than another group of results. Unfortunately, the peculiarities found in the $2\sigma_u$ MO of the various approximate ground state wavefunctions means that the agreement between the theoretical C state excitation cross section and the larger experimental cross section value may be fortuitous. When the multicenter terms are included in the calculation of the $D^3\Sigma_u^+$ excitation cross section, the theoretical results are expected to agree well with the recent experimental estimates of the cross section. A comparison between a synthetic energy loss spectrum calculated from theoretical differential cross sections and the available experimental spectra at 35 eV and a scattering angle of 80° indicates that the relative magnitudes of the total cross sections are consistent among themselves and with the experimentally determined relative magnitudes. The results of this comparison indicate that the cross section for excitation of the $A^3\Sigma_u^+$ state is comparable to that for the $B^3\Pi_g$ state at 35 eV. However for lower incident electron

energy, the theoretical A state excitation cross section may be too large due to the approximate nature of the A state wavefunctions used in which configuration interaction was neglected. No previous results for excitation of the $W^3\Delta_u$ state have been reported. The comparison between the calculated cross section for excitation of the $E^3\Sigma_g^+$ state with the available experimental data indicates that the theoretical curve is considerably broader than that which is measured. Although the (OR) scattering model appears generally to predict a total cross section which is slightly broader than that measured, the very large discrepancy in this case implies that the $E^3\Sigma_g^+$ state is excited by some other process than is described by the theory employed here.

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

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DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) The Aerospace Corporation El Segundo, California		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE Total Cross Sections for the Excitation of the Triplet States in Molecular Nitrogen		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (First name, middle initial, last name) David C. Cartwright		
6. REPORT DATE 70 Aug 05	7a. TOTAL NO. OF PAGES 77	7b. NO. OF REFS 51
8a. CONTRACT OR GRANT NO. F04701-70-C-0059	9a. ORIGINATOR'S REPORT NUMBER(S) TR-0059(9260-01)-6	
b. PROJECT NO.		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-70-263	
d.		
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Space and Missile Systems Organization Air Force Systems Command Los Angeles, California
13. ABSTRACT A consistent set of total cross sections for electron impact excitation of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B^1\Sigma_u^-$, $C^3\Pi_u$, $E^3\Sigma_g^+$ and $D^3\Sigma_u^+$ triplet states of molecular nitrogen from the $X^1\Sigma_g^+$ state has been calculated quantum mechanically for incident electron energies from threshold to 80 eV. The Ochkur-Rudge exchange scattering and Franck-Condon approximations were employed to obtain these cross sections. Minimum and double-minimum basis set LCAO-MO wavefunctions centered on the nuclei were used and the multicenter terms in the scattering amplitude were evaluated using a zeta function expansion. Rotationally averaged cross sections were calculated for excitation from $v'' = 0$ to individual v' - levels of the excited electronic states. The calculated total cross section for excitation of the $B^3\Pi_g$ state is in good agreement with that deduced from recent experimental data for the process. The cross section for excitation of the $C^3\Pi_u$ state agrees well with one pair of experimental measurements, is a factor of 2 larger than another pair of measurements, and about a factor of four larger than a fifth experimental determination and the previous calculations. The calculated cross section for excitation of the $A^3\Sigma_u^+$ state is a good deal larger than previous theoretical and experimental estimates. However, a		

KEY WORDS

Electron impact excitation
Molecular nitrogen
Scattering theory

Distribution Statement (Continued)

Abstract (Continued)

comparison with recent experimental differential cross section data indicates that the theoretical $A \ ^3\Sigma_u^+$ total cross section is correct for incident energies greater than about 35 eV. The relative magnitudes of these excitation cross sections lead to interesting predictions concerning N_2 processes in the upper atmosphere.