Dissociation of F_2 by electron impact excitation of the lowest $^3\Pi_u$ electronic state

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An *ab initio* theoretical study is reported for dissociation of F_2 via excitation of the lowest $^3\Pi_u$ electronic state by electron impact. Differential and integrated cross sections are given for impact energies from 5 to 40 eV. Our distorted-wave model predicts a resonancelike feature in the integrated cross section near threshold with a maximum value of about 0.4×10^{-16} cm^2. When target polarization effects are included this feature disappears and the maximum cross section is reduced to about 0.15×10^{-16} cm^2.

I. INTRODUCTION

Electronic excitation of F_2 by low-energy electron impact is an important process in fluorine-containing gas discharges and plays a key role in the kinetic modeling of the KrF laser. In particular, since F_2 can be dissociated via excitation of the lowest $^3\Pi_u$ state—the calculated[1] vertical excitation energy to this level is only 3.35 eV—cross sections for this process are crucial in determining the low-energy electron distributions and concentrations of atomic flourine in gas discharges. Also while dissociative electron attachment and vibrational excitation in F_2 have been the subjects of a number of recent experimental and theoretical efforts,[2] there have been no studies as yet of electronic excitation in this molecule.

The calculation of accurate *ab initio* cross sections for singlet-triplet electronic transitions in molecules by low-energy electron impact is a formidable theoretical task. The transition potential for this process is dominated by short-range interactions, and the cross section is sensitive to approximations made in the scattering wave function. Moreover, the complexity of current theoretical methods for electron-molecule scattering, which remain applicable at low impact energies, has generally limited applications to electronically elastic processes.[3] Hence, at this stage the distorted-wave approximation[4]—which expresses the inelastic scattering amplitude in terms of matrix elements of elastic-scattering wave functions—is of considerable practical interest.

In a recent paper[5] we applied a form of the distorted-wave approximation to the calculation of several singlet-triplet excitation processes in molecular nitrogen. Our approach is similar to the prescription for electronically inelastic scattering developed by Rescigno *et al.*[6] As they have shown,[6] this prescription is essentially equivalent to the "first-order many-body theory" (FOMBT) of Taylor and co-workers.[7] We use the discrete-basis-set method of Fliflet and McKoy[8] to obtain the electron-molecule continuum wave functions. Comparison of our results for e^--N_2 scattering with experiment at impact energies less than 50 eV yielded qualitative agreement for the general shape of the differential cross sections, while the integrated cross sections were overestimated by a factor between 2 and 3 at most impact energies. This type of agreement for singlet-triplet transitions has also been obtained in applications of the FOMBT to several processes in e^--He scattering.[9]

This paper reports cross sections for the excitation of the lowest $^3\Pi_u$ state of F_2 by electron impact calculated using our distorted-wave approach. Differential and integrated cross sections are presented for impact energies from 5 to 40 eV. The theoretical treatment of e^--F_2 scattering is complicated by the strong effect of target polarization in this system.[10] We have estimated the importance of this effect on electronic excitation by using two kinds of distorted-wave functions: (i) the usual choice of functions calculated in the static-exchange potential of the F_2 ground state, and (ii) functions calculated in a more attractive potential which includes polarization effects. Differences in the inelastic cross sections obtained with the scattering wave functions of these two potentials will decrease at higher impact energies and, in fact, become unimportant at incident energies above 15 eV.

Section II summarizes our approach to electronically inelastic electron-molecule scattering. More detailed descriptions of our approach are given in Refs. 5 and 11. Section III describes specific features of these calculations and presents our results. Section IV contains a discussion of our results and conclusions drawn from this work. Except as noted, atomic units are as-

sumed throughout.

II. THEORY

Using the Born-Oppenheimer and Franck-Condon approximations, and treating the target rotational levels as essentially degenerate, the differential cross section for electronic excitation by electron impact may be expressed in the form

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

for impact energy $E=\frac{1}{2}k_0^2$. In Eq. (1) $f_{k_0}(n\leftarrow 0;\vec{R}',\hat{r}')$ is the fixed-nuclei scattering amplitude in the laboratory frame (with z' axis in the direction of the incident electron beam), $\vec{R}'$ denotes the nuclear coordinates of the target, and $\hat{r}'$ denotes the scattering angles. The symbol $q_{v'0}$ is the Franck-Condon factor between the $v=0$ ground-state vibrational level and the v' level of the excited state. The momentum of the outgoing electron is given by

$$k'_{v'} = [k_0^2 - 2(E_{v'} - E_0)]^{1/2}, \tag{2}$$

where E_0 is the energy of the initial target state in the ground vibrational level, and $E_{v'}$ is the energy of the v' level of the final target state. Equation (1) implicitly neglects the dependence of the scattering amplitude on the vibrational level of the final target state. The factor S results from summing over final and averaging over initial spin substates and equals $\frac{3}{2}$ for singlet to triplet excitation of a closed-shell target. For a linear molecule M_n is the orbital angular-momentum projection-degeneracy factor of the final target state (2 in the present case).

In the prescription previously applied to electronic excitation of H_2 and N_2 by electron impact,[5,6,11] the scattering amplitude is treated in a form of the distorted-wave approximation derived from the two-potential formula[4]; the initial target state is the Hartree-Fock ground state, and the final target state is treated in the single-channel Tamm-Dancoff approximation (TDA).[12] The single-channel TDA 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.[13] A simplifying feature of this formulation is that both incident and outgoing electron wave functions are calculated in the static-exchange potential of the ground state.

Since in this formulation the initial and final target states differ by only one orbital, the electronic part of the body-fixed frame (with z axis along the principal symmetry axis) transition matrix element is given by

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

where $\langle ij|v|kl\rangle$ is a Coulomb two-electron matrix element. Note that a singlet-triplet transition involves only an exchange-type matrix element. The initial, final distorted-wave functions $\psi^{(+)}_{\vec{k}_0}$, $\psi^{(-)}_{\vec{k}_n}$ are Hartree-Fock (static-exchange) continuum orbitals satisfying outgoing-wave, incoming-wave boundary conditions; ϕ_α is a Hartree-Fock occupied orbital; $\bar{\phi}_n$ is an orbital of the V^{N-1} potential formed by removing an electron from the target orbital α.

To treat the target-orientation dependence of the scattering analytically, the initial and final continuum orbitals are expanded in the partial-wave series:

$$\psi^{(+)}_{k_0}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{lm} i^l \psi^{(+)}_{k_0 lm}(\vec{r}) Y_{lm}(\hat{k}_0), \tag{4a}$$

$$\psi^{(-)}_{k_n}(\vec{r}) = \left(\frac{2}{\pi}\right)^{1/2} \sum_{lm} i^l \psi^{(-)}_{k_n lm}(\vec{r}) Y_{lm}(\hat{k}_n). \tag{4b}$$

This leads to a single-center expansion of the transition matrix in the body-fixed frame of the form

$$\langle \vec{k}_n, n | T_{el} | \vec{k}_0, 0\rangle = \sum_{ll'mm'} \langle k_n lm, n | T_{el} | k_0 l'm', 0\rangle \times Y_{lm}(\hat{k}_n) Y^*_{l'm'}(\hat{k}_0). \tag{5}$$

This single-center expansion converges rapidly for exchange-type transitions.

To obtain representations of the continuum orbitals $\psi^{(-)}_{k_n lm}$ and $\psi^{(+)}_{k_0 l'm'}$, we use the method of Fliflet and McKoy[8], which is based on the discrete-basis-set approach to nonspherical potential scattering introduced by Rescigno *et al.*[14] In this approach the scattering potential U is approximated by its projection onto a subspace of square-integrable functions

$$U^t = \sum_{\alpha\beta} |\alpha\rangle\langle\alpha|U|\beta\rangle\langle\beta|. \tag{6}$$

For potentials having this separable form the Lippmann-Schwinger equation for the T matrix,

$$T = U + UG_0^+ T, \tag{7}$$

where G_0^+ is the free-particle Green's function, reduces to a finite matrix equation with solution

$$T^t = (1 - U^t G_0^+)^{-1} U^t. \tag{8}$$

The solution T^t corresponds to the wave function

$$\psi_{klm}^{t(+)} = \phi_{klm} + G_0^+ T^t \phi_{klm}, \tag{9}$$

where $\phi_{klm} = j_l(kr) Y_{lm}(\hat{r})$ and $j_l(kr)$ is a spherical Bessel function. The wave function $\psi_{klm}^{t(+)}$ satisfies the Schrödinger equation

$$(-\nabla^2 + U^t - k^2)\psi_{klm}^t = 0 \tag{10}$$

and has the correct asymptotic form for scattering. The discrete-basis-set subspace $\{|\alpha\rangle\}$ is chosen such that the truncated potential U^t is an adequate representation of the full potential U over a limited range of scattering energies. A technique for obtaining numerical representations of the radial functions occurring in the single-center expansion

$$\psi_{klm}^t(r) = \sum_{l'} g_{ll'm}(k,r) Y_{l'm}(\hat{r}) \tag{11}$$

has been given Fliflet and McKoy.[8]

III. CALCULATIONS AND RESULTS

The $X^1\Sigma_g^+$ ground state of F_2 has the electronic configuration $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 \times (1\pi_g)$.[4] To determine the Hartree-Fock wave function for the ground state, we carried out a self-consistent-field (SCF) calculation at the equilibrium internuclear separation of 2.68 a.u. using a $4s3p1d_{zz}1d_{xz}1d_{yz}$ contracted Gaussian basis set on each nucleus. In the single-channel TDA the lowest $^3\Pi_u$ excited state is characterized by the single-electron transition from the ground state: $1\pi_g \rightarrow 3\sigma_u$. The $3\sigma_u$ orbital is an eigenfunction of the V^{N-1} potential formed by removing an electron from the π_g occupied orbital. We solved for the $3\sigma_u$ orbital in the space of the SCF Gaussian basis set using the approach developed by Hunt and Goddard.[15]

To determine the energy of the outgoing electron for a given impact energy, we used the best available theoretical value for the vertical excitation energy between the ground and lowest $^3\Pi_u$ state. This is the 3.35-eV value obtained by Hay and Cartwright in their configuration interaction studies.[1] Our numerical techniques for calculating the distorted-wave-approximation transition matrix element are discussed in Refs. 5 and 11. The Gaussian basis sets used to construct the separable approximation distorted-wave potentials U^t for the Σ, Π, and $\Delta(m=0,1,2)$ scattering symmetries are similar to those used in our calculations for $e^- - N_2$ inelastic scattering.[5] In the present work we have approximated the sum over Franck-Condon factors

$$\sum_{v'} k_{v'} q_{v'0}$$

in Eq. (1) by the quantity $k_n = (k_0^2 - 2\Delta)^{1/2}$, where ΔE is the vertical excitation energy. This approximation tends to overestimate the cross section near threshold. We estimate that the error due to this approximation is less than 20% at 5-eV impact energy and less than 5% at 10 eV and above.

From previous studies of the elastic scattering of electrons by F_2 in the static-exchange approximation, we know there is a broad shape resonance in the Σ_u scattering symmetry at 2.2eV.[10,16] We also know that this resonance is an artifact of the static-exchange model and that a proper treatment of polarization effects would lead to a more attractive interaction potential and a disappearance of the resonance since the F_2^- ion is actually bound at $R = 2.68$ a.u. (Ref. 17). Now since in our model the distorted waves are calculated in the static-exchange potential of the ground state, we may expect a significant enhancement of the inelastic cross sections at impact energies a few eV above threshold. This indeed turns out to be the case, as shown in Fig. 1. The solid curve shows the integrated cross section obtained using the previously described model (the circles indicate calculated values). This model predicts a broad resonancelike feature at about 6-eV impact energy with a maximum cross section of about 0.4×10^{-16} cm.[2] The differential cross section for this model is shown at four impact energies by the solid curves in Fig. 2.

To investigate the sensitivity of our results to the Σ_u shape resonance in the distorted waves, we have obtained results using a more attractive potential which does not support a shape resonance. This was done by constructing a static-exchange potential in which the usual neutral target occupied orbitals were replaced by orbitals taken from an SCF calculation for the F_2^- negative ion. In contrast to the F_2 molecule, the F_2^- ion is well described at the SCF level. Unlike the standard static-exchange potential, this potential supports a bound $(N+1)$ electron state (the F_2^- ion) and does not show resonance behavior. The S-matrix pole which leads to a shape resonance in the standard static-exchange potential has been shifted into the discrete spectrum in the modified potential. The physical effect modeled by using negative-ion orbitals is the rearrangement of the target orbitals due to the presence of the scattered electron. Of course, this approach yields a static approximation to what is clearly a dynamical effect. We only used this potential to calculate the Σ_u distorted-wave functions since this is the only symmetry which shows resonance behavior. These continuum orbitals are not in general orthogonal to the $F_2\sigma_u$ occupied orbitals, and this leads to

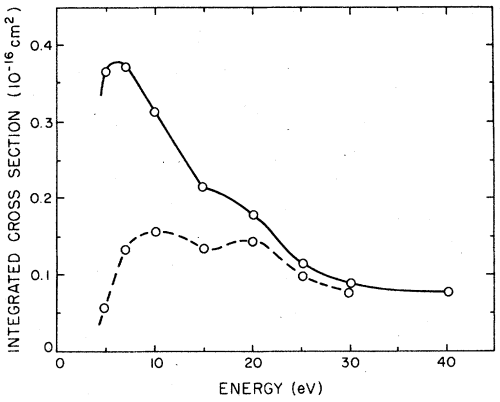

FIG. 1. Integrated cross sections for dissociation of F_2 by electron impact excitation of the lowest $^3\Pi_u$ state. Solid curve: results obtained using neutral F_2 orbitals to construct the static-exchange potential for the distorted waves. Dashed curve: results obtained using F_2^- orbitals to construct potential for the Σ_u component of the distorted waves. Circles indicate calculated values.

additional terms in the expression for the transition matrix element. These additional terms are estimated to be small and have been neglected in the present work. The dashed curve in Fig. 1 shows the integrated cross section obtained using the modified potential for the Σ_u distorted waves. The low-energy enhancement has clearly disappeared. This model predicts a rather flat integrated cross section with a maximum of about 0.15×10^{-16} cm^2. Differential cross sections for this model are indicated by the dashed curves in Fig. 2.

We estimate the uncertainty in our results due to numerical round-off errors and lack of completeness in the discrete basis sets for the distorted-wave potentials to be about 30% for the differential cross sections and about 15% for the integrated cross sections.

IV. DISCUSSION AND CONCLUSIONS

Our standard distorted-wave model predicts a peak electron impact dissociation cross section for F_2 of about 0.4×10^{-16} cm^2 due to excitation of the lowest $^3\Pi_u$ state. When target polarization effects are included the maximum cross section is reduced to about 0.15×10^{-16} cm^2. It is our opinion that the modified distorted-wave results are the more reliable at low energy although including the internuclear separation dependence of the problem could build in some resonance structure near threshold since F_2^- becomes unbound at a value of R slightly less than 2.68 a.u.[17] The choice of negative ion orbitals in the present context is not without precedent; similar procedures have been used in elastic e^--F_2 scattering[11] and in resonant e^--N_2 scattering.[18,19] The differential cross sections for both models (shown in Fig. 2) are typical of what one finds in singlet-triplet transitions: the short-range exchange interaction leads to predominantly large-angle scattering associated classically with small impact parameter collisions. Note that both models give essentially the same result at higher energies where polarization effects are expected to be less important.

Previous applications have shown that our distorted-wave model often overestimates singlet-triplet excitation cross sections by a factor of 2 or 3. Part of this discrepancy is due to the property of the distorted-wave method that all of

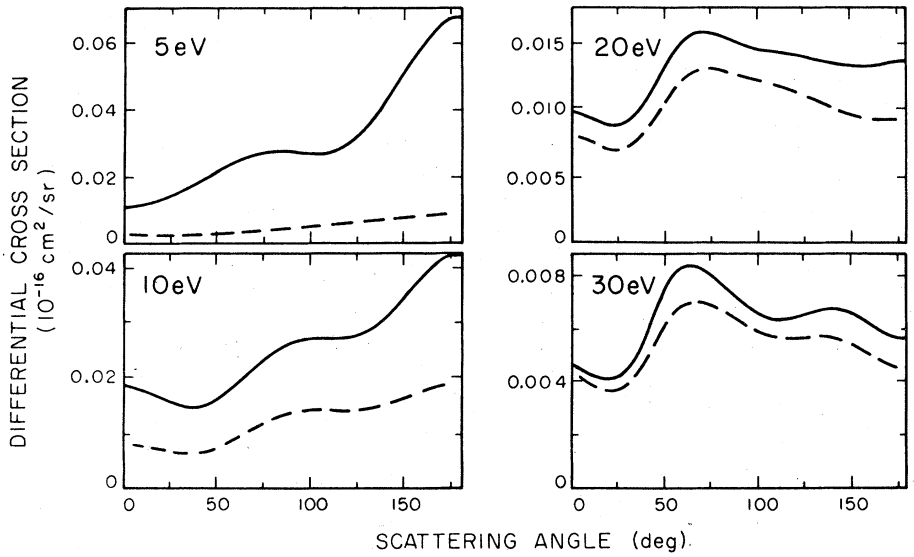

FIG. 2. As in Fig. 1, for differential cross sections.

the scattered flux is restricted to one excitation channel. As discussed by Taylor and co-workers,[9] this effect is most significant when several excited target states are strongly coupled. The lowest $^3\Pi_u$ state of F_2 may be sufficiently separated in energy from other triplet excited states that this coupling effect is relatively small in the present case.[1] On the other hand, coupling between the initial and final channels may be strong due to the low excitation energy. A two-state close-coupling calculation is needed to test this effect. However, the recent measurements of the electron energy-loss spectra in F_2 by Nishimura *et al.*[20] are in reasonable quantitative agreement with our calculated cross sections for the excitation of this triplet state.[20,21] For example, for an incident energy of 30 eV, a scattering angle of 90°, and with a rough estimate of the finite width of their elastic peak, the $^3\Pi_u$ inelastic cross section is about 100 times weaker than the elastic cross section. Assuming a value of 0.2 to 0.3 Å^2 for the elastic differential cross section at 90°, their measurements imply a value in the range of 0.002–0.003 Å^2 for the inelastic differential cross section at 90° for the $^3\Pi_u$ state. Our calculated value is about 0.006 Å^2. This type of agreement is quite consistent with results of similar calculations for other systems.[6,9,11]

Our approach to target polarization effects is appropriate for resonant scattering processes. However, there may be other polarization effects which are important near threshold. In addition, core-excited resonance processes have not been included. Another limitation on the accuracy of our results is the simple single-excitation model for the final target state wave function. The relatively low excitation energy of the $1\pi_g \rightarrow 3\sigma_u$ transition in F_2 suggests that configuration interaction effects may be important.

To summarize, we have reported the first *ab initio* results for electronic excitation of F_2 by electron impact. These results are probably accurate to about a factor of 3. Further theoretical effort will be needed to provide more definitive results.

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