Elastic e-NO collisions

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In this paper we use the Schwinger multichannel method (SMC) to calculate several types of cross sections related to the elastic electron scattering by NO. We show through the NO system that the elastic scattering of an electron by an open shell molecule is a much richer process than the corresponding scattering by closed shell targets. We present cross sections for unpolarized electron scattering by (oriented and nonoriented) molecules, spin-flip cross sections (in the form of polarization fractions), and zero-energy electronic excitation cross sections (due to orbital degeneracy of the NO ground state). Our results agree well with published experimental values for elastic unpolarized data as well as recent polarized electron-NO scattering. We also present a detailed study of the dependence of the polarization fraction on molecular orientation. Our results also show a shape resonance which is also seen experimentally around 18 eV, and we suggest its symmetry.

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I. INTRODUCTION

Cross sections for rotational, vibrational, and electronic excitation of NO by low-energy electrons play an important role in modeling the radiative signatures of spacecraft [1] and the catalytic destruction of ozone [2]. Most experimental studies of e-NO collisions have been restricted to measurements of total cross sections and most of these focused on resonance phenomena at energies below 3.0 eV [3–14]. Two exceptions are the measurements of elastic differential cross sections (DCS's) at energies of 5, 10, and 20 eV by Kubo *et al.* [15] and of the angular behavior of the polarization fraction for polarized electron scattering by Hegeman *et al.* [16]. On the theoretical side, Lefebvre-Brion [17] used the stabilization procedure and Tennyson and Noble [18] the R-matrix method to study these low-energy resonance processes. Recently Tao *et al.* [19] have also carried out a calculation of the elastic differential cross sections using the Schwinger variational method for the potential scattering [20].

In this paper we use the Schwinger multichannel method (SMC) [21] to calculate cross sections related to several phenomena present in elastic electron-NO scattering. The spin and orbital degeneracy of an open shell molecule allow new elastic processes not present in a closed shell molecule. The ground-state orbital degeneracy contributes to the elastic process with two channels, one, very strong, corresponding to no state change, and another corresponding to an electronic transition between orthogonal degenerate states. The ground-state spin degeneracy allows the electron spin to flip. DCS experiments made with an unpolarized electron source, a molecule in the gas phase, and without final spin analysis, measure an average between four different processes. The use of a polarized electron source allows the measurement of the spin-flip cross section [16]. This quantity is usually presented in the form of the polarization fraction (P'/P), where P and P' specify the spin polarization of the incident and scattered electrons. Here we present results for three differ-

ent elastic processes present in the e-NO elastic scattering. We calculate the elastic scattering by polarized and unpolarized electrons with NO and the DCS's for transitions between magnetic sublevels ($^2\Pi^+ \rightarrow \,^2\Pi^-$). In opposition to the atomic case [16] P'/P for the molecule shows an almost isotropic angular behavior. This phenomenon was related to the averaging over all molecular orientations inherent in gas phase collision processes [22]. When the molecule was oriented P'/P presents angular behavior similar to those seen in atoms [22]. We present a detailed study of the dependence of the polarization fraction on the molecular orientation. Some of our features are in qualitative agreement with those suggested by Nordbeck *et al.* [23] in a study on O_2. Our results agree well with available measurements of the elastic cross sections for scattering of both unpolarized and polarized electrons by NO.

The outline of our paper is as follows. In Sec. II we present a few essential features of the SMC method [21] and its extension to the case of open shell molecules. In Sec. III we present the results of our calculations and their comparison with available measured data. We close our paper with a few concluding remarks.

II. THEORY

In the SMC method [21] the variational stable expression for the full scattering amplitude is

$$[f_{\vec{k}_f, \vec{k}_i}] = \sum_{m,n} \langle S_{\vec{k}_f} | V | \Psi_m \rangle d_{mn}^{-1} \langle \Psi_n | V | S_{\vec{k}_i} \rangle, \quad (1)$$

where

$$d_{mn} = \langle \Psi_m | A^{(+)} | \Psi_n \rangle, \quad (2)$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{P\hat{H}+\hat{H}P}{2} + \frac{PV+VP}{2} - VG_P^{(+)}V. \quad (3)$$

In these equations $S_{\vec{k}_i}$ is a product of a target state and a plane wave, V is the interaction potential, Ψ_m is an $(N+1)$-electron Slater determinant (or combination of them) in which the variational trial function is expanded, $\hat{H}$ is the total energy minus the full Hamiltonian of the system, N is the total number of electrons in the target, P is a projector onto the open electronic target states, and $G_P^{(+)}$ is the Green's function projected on this P space. Details of the SMC method have been given previously [21,24].

To treat open shell molecules we start from the general expression for the scattering amplitudes for particles with spin (within a nonrelativistic approximation) [25]

$$f_{\vec{k}_f,\vec{k}_i}(M_{S_f}m_f,M_{S_i}m_i) = \sum_{S,M_S} C_{M_{S_f}m_f}^{S_f \ 1/2 \ S}{}_{M_S} C_{M_{S_i}m_i}^{S_i \ 1/2 \ S}{}_{M_S} f_{\vec{k}_f,\vec{k}_i}^{(2S+1)}, \quad (4)$$

where M_{S_i} (M_{S_f}) is the spin component of the initial (final) target state, m_i (m_f) is the spin component of the incident (scattered) electron and the $C_{M_{S_f}m_f}^{S_f \ 1/2 \ S}{}_{M_S}$ is a Clebsch-Gordan coefficient. It is convenient to work with scattering amplitudes for the system (electron + target) with a defined total spin S. In this form the spin-irreducible scattering amplitudes f^{2S+1} can be calculated directly. Computer codes have been developed to provide these spin-irreducible scattering amplitudes f^{2S+1}.

The differential cross section for elastic scattering of unpolarized electrons is given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\{3|f^{(3)}|^2 + |f^{(1)}|^2\}. \quad (5)$$

The polarization ratio is related to the spin-flip and unpolarized elastic cross sections by

$$\frac{P'}{P} = 1 - 2\frac{(d\sigma_{sf}/d\Omega)}{(d\sigma/d\Omega)}, \quad (6)$$

where

$$\frac{d\sigma_{sf}}{d\Omega} = \frac{1}{4}|f^{(3)} - f^{(1)}|^2. \quad (7)$$

III. CALCULATION AND RESULTS

The $X\,^2\Pi$ ground state of NO has spin and orbital degeneracy. Spin degeneracy is taken into account through the calculation of two scattering amplitudes: $f^{(3)}$ and $f^{(1)}$. Orbital degeneracy corresponds to the two possible azimuthal angular momenta $\Lambda = 1$ and -1 of a Π symmetry ground state. These two states (Π^+ and Π^-) are always degenerate by symmetry in a nonrelativistic approximation. The fact that they are degenerate does not mean that these states are un-coupled during the scattering process. The scattering electron can transfer angular momentum to the target without transferring energy in such a way that the $\Lambda = 1$ to -1 (or vice-versa) transition is possible by electron impact. This is a
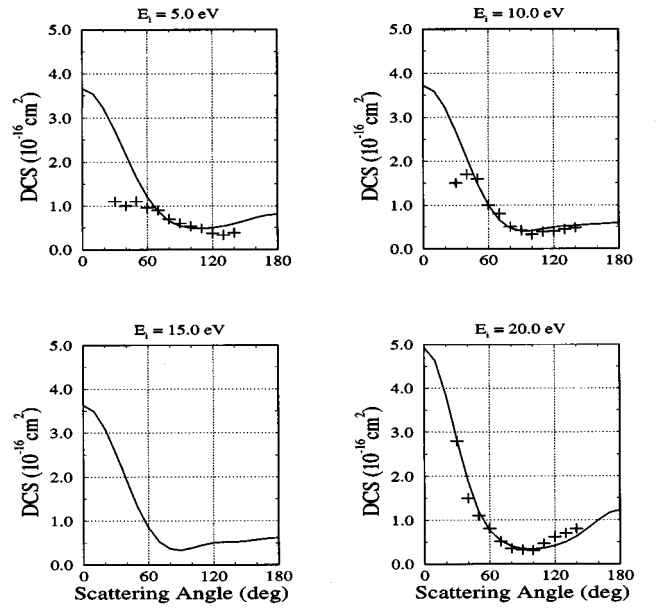

FIG. 1. Elastic differential cross section of electrons by a free NO molecule. Present theoretical result is plotted as a continuous line; $+$ are experimental results from Kubo $et\ al.$ [15].

feature present in the scattering of open shell molecules with orbital degeneracy, and it cannot be described by simple potential scattering theories.

For the target state we used a self-consistent field (SCF) wave function. The basis set is the $(9s5p1d/5s5p)$ basis of Gaussians of Dunning [26] on each nuclear center with no contractions for the p functions and supplemented with a $2s1p1d$ set (exponents 2.1 and 0.0533 for s, 0.041 35 for p, and 0.8 for d on N and 2.8194 and 0.071 15 for s, 0.053 42 for p, and 0.85 for d on O) at the internuclear distance of 2.1743 a.u. For the scattering calculation we supplemented the basis with a set of $1s1p$ functions on each atom (exponents 0.0067 for s and 0.0052 for p on N and 0.0089 for s and 0.0067 for p on O). This approach gives a SCF energy of -129.272 a.u. and a permanent dipole moment of 0.310 D which can be compared with the near-Hartree-Fock limit -129.295 a.u. which generates a dipole moment of 0.260 D [27].

Figure 1 shows our calculated elastic DCS's for e-NO scattering at energies of 5, 10, 15, and 20 eV along with the measured values of Kubo $et\ al.$ [15]. Our calculated cross sections agree well with values for scattering angles greater than 80°. At the higher impact energy of 20 eV agreement is still quite good at angles below 80°. However, the disagreement between the calculated and measured DCS's for lower angles at 5 and 10 eV reflects the importance of polarization effects, which are not included in the present studies, at these lower energies. These results are very close to those published by Tao $et\ al.$ [19]. We also present our calculated DCS at 15 eV since spin-polarized measurements are available at this energy.

In Fig. 2 we show calculated differential cross sections for transitions between magnetic sublevels ($^2\Pi^+ \rightarrow {}^2\Pi^-$) of NO molecules due to collisions with an unpolarized electron beam. This value of the DCS decreases when the energy increases at a rate faster than the elastic cross section. This
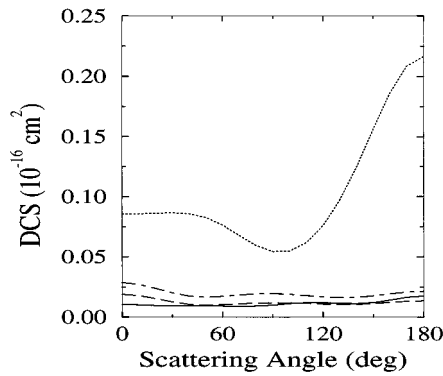
FIG. 2. Π^+ to Π^- elastic differential cross section of electrons by a free NO molecule. Dotted line is 5 eV, dot-dashed is 10 eV, long-dashed is 15 eV, and solid line is 20 eV.

behavior is similar to that of the excitation cross section. Such transitions would lead to a depolarization of polarized NO molecules. Although measurements of such cross sections are, in principle, difficult to make, our results show that they are of the same order of magnitude as those for electron impact excitation processes. In other words, these two degenerate states give rise to two energetically open channels for any positive energy of the incoming electron. Since they are coupled in the e^--molecule scattering process, the elastic scattering calculation of NO is indeed a two-channel problem. Although such coupling is not expected to greatly affect the elastic cross sections, methods developed to describe accurately the electron-molecule scattering phenomena should not neglect this process. To our knowledge, this is the first time these zero-energy excitation cross sections have been reported.

In Fig. 3 we present our calculated results for the polarization fraction P'/P for electron energies of 2.5, 5.0, 10, and 15 eV along with the measured values of Hanne and
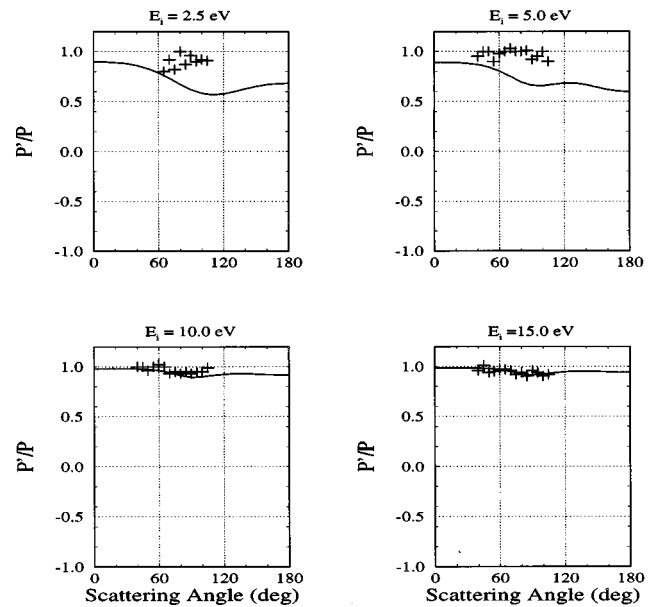

FIG. 3. Elastic polarization fraction P'/P for scattering of polarized electrons by a NO molecule. Present theoretical result is plotted as a continuous line; + are experimental results from Hegeman *et al.* [16].

collaborators [16]. Calculated and measured polarization fractions P'/P show in the molecular case very limited structure with angle. For 10 and 15 eV, experiments and theory present a value of P'/P very close to 1. At larger angles the polarization fraction has a slightly higher deviation from 1, and it reflects the importance of exchange. The same behavior was seen in the case of O_2 [22].

In our paper about the O_2 molecule we were able to show that the almost constant value of P'/P over a wide angular region was due to the orientational averaging inherent in
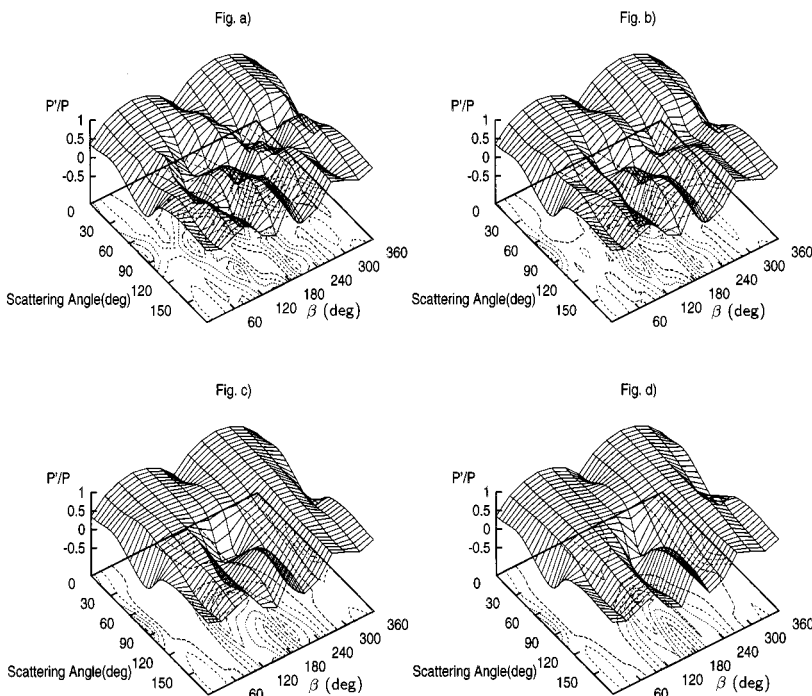

FIG. 4. Elastic polarization fraction P'/P for scattering of polarized electrons with incident energy E = 5.0 eV against oriented NO molecule at orientation angle α. (a) $\alpha=0°$; (b) $\alpha=30°$; (c) $\alpha=60°$; (d) $\alpha=90°$.
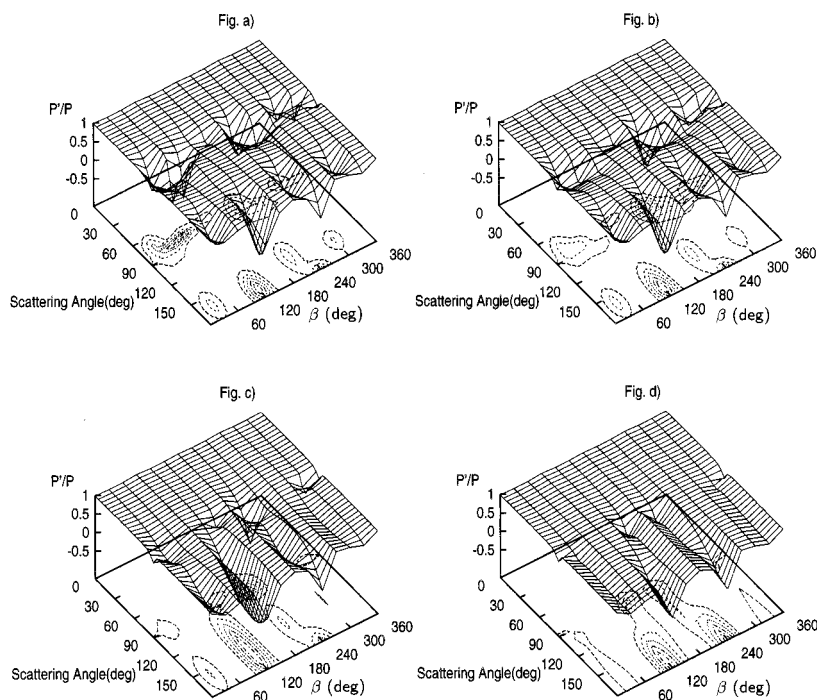
FIG. 5. Elastic polarization fraction P'/P as in Fig. 4 but for incident energy $E = 10.0$ eV.

molecular gas-phase collisions [22]. When we studied the case of an oriented molecule, the angular behavior for some directions was highly anisotropic, similar to the Na case [16]. Here we will present a detailed study for oriented NO. These results may serve as a motivation to the experimentalists to measure spin-flip cross sections of oriented molecules. Experiments with oriented molecules have recently shown strong changes in the angular distribution for photoionization between free and space oriented for the CH_3I molecule by Kaesdorf *et al.* [28] and N_2 by Shigemasa *et al.* [29]. Cross sections for electron scattering by oriented CH_3I molecule

obtained by Böwering *et al.* [30] show significant differences from those obtained with a randomly oriented molecule.

Figures 4, 5, 6, and 7 show tridimensional plots for the polarization fraction against the scattering angle θ and orientation angle β. In these figures NO is taken originally oriented along the z axis (N on the positive side), and then rotated by Euler angles α and β. α is a Euler angle of rotation around the original z axis. β is a rotation angle around the new y axis and it varies over 360° to allow a complete loop of NO in a plane. θ is scattering angle defined by the incident and scattered beams in the original xz plane.
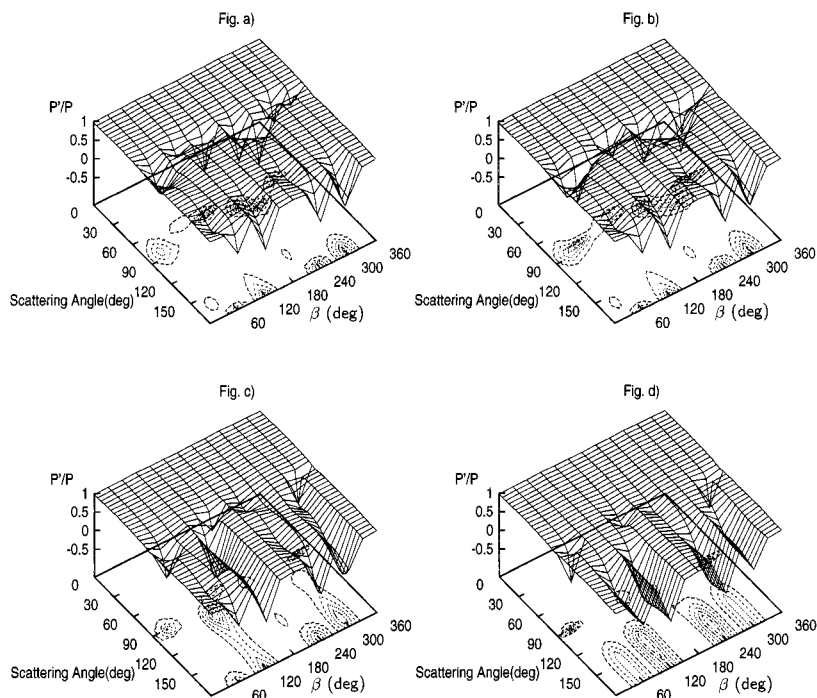

FIG. 6. Elastic polarization fraction P'/P as in Fig. 4 but for incident energy $E = 15.0$ eV.
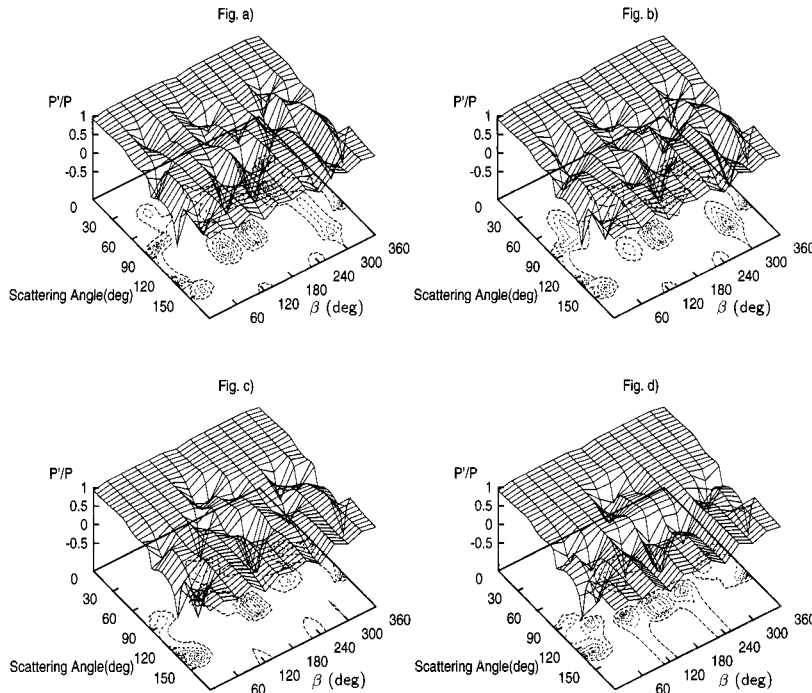
FIG. 7. Elastic polarization fraction P'/P as in Fig. 4 but for incident energy $E = 20.0$ eV.

Our calculated results for the polarization fraction P'/P are shown in these figures for electron energies of 5, 10, 15, and 20 eV, respectively. The general angular behavior of the polarization fraction P'/P is similar to those seen with O_2. It displays an angular behavior with a strong dependence on the orientation of the molecular axis with respect to the incident electron beam.

To understand this phenomenon we recall that the spin-flip process depends on the square modulus of the diference between $f^{(3)}$ and $f^{(1)}$ and the DCS in a weighted square sum of f's. In Fig. 8 we represent $f^{(3)}$, $f^{(1)}$, and $f^{(SF)}$ as a triangle in the complex plane, with $f^{(3)}$ chosen real. The exchange interaction between the scattered and the unpaired electron is the mechanism which makes $f^{(3)}$ different from $f^{(1)}$. This interaction is in general weaker than all other interactions present in the scattering description. As a result the spin-flip cross sections and any other excitation cross sections between states with different spins are usually one or two orders of magnitude smaller than the elastic cross section. The polarization fraction represents a direct comparison between elastic and spin flip, so we should expect the result to be in general very close to 1. P'/P close to 1 implies that $f^{(3)}$ and $f^{(1)}$ are close in magnitude and that the angle χ, the phase difference between them, is very small. However, this is not always true. There are experimental [16] and theoretical [22,25,31] results for the angular distribution which show P'/P far from 1, meaning that at these angles the exchange interaction is very important. What we are saying is very similar to the explanation given by Kessler [32] to the phenomenon of polarizing electrons in an unpolarized electron-atom impact experiment. In this phenomenon the spin-orbit potential is also weak compared with all other interactions. However, when the DCS has a minimum the relative importance of the spin-orbit potential increases and then it allows electrons to be preferentialy scattered in one of its magnetic components. In our case the exchange interation between the

scattered and the unpaired electron plays the role of the spin-orbit potential. It is well known from scattering theory that a minimum in the DCS occurs due to inteference phenomena between partial waves. What the exchange interaction will do is to prevent $f^{(3)}$ and $f^{(1)}$ having minima exactly at the same angles. At these angles we will have $f^{(3)}$ much greater or much smaller than $f^{(1)}$ or the phase χ large. However, due to the interference nature of the process these regions are in general strongly localized in angle. When the molecule is in a gas phase the rotational average smooths this dependence.

Recently Nordbeck *et al.* [23] made a detailed study of the dependence of the polarization fraction P'/P for O_2. Through the properties of the reduced rotation matrices $d_{mn}^j(\beta)$ [33], at certain values of the angle β, they were able to derive conditions for which the unpolarized electron-oriented molecule DCS may be small. Under these conditions they found strong deviation of P'/P from 1. The scattering amplitude for an oriented diatomic molecule is [34]
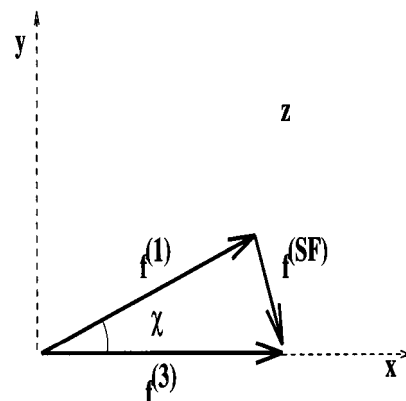

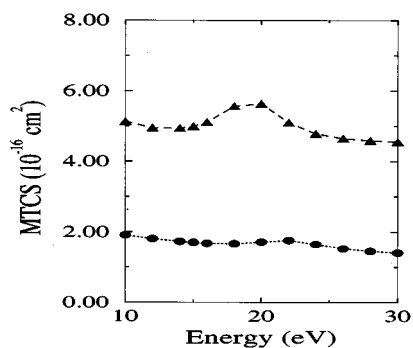FIG. 8. Scattering amplitudes in the complex plane.

FIG. 9. Momentum transfer cross section as a function of impact energy: $\triangle$ is the triplet component and $\bigcirc$ is the singlet component.

$$
f^{(2S+1)}_{\lambda_f \vec{k}_f, \lambda_i \vec{k}_i,}(\Omega) = \frac{i\sqrt{\pi}}{\sqrt{k_f k_i}} \sum_{\Lambda, l_i, l_f, m_{l_f}} i^{l_i - l_f} \sqrt{2l_i + 1} D^{l_i *}_{0, \Lambda - \lambda_i}(\Omega)
$$
$$
\times D^{l_f}_{m_{l_f}, \Lambda - \lambda_f}(\Omega) T^{\Lambda S}_{l_i \Lambda - \lambda_i, l_f \Lambda - \lambda_f} Y_{l_f m_{l_f}}(\hat{r}).
$$

(8)

For example, $\beta = 0$ implies $d^j_{mn}(0) = \delta(m,n)$ and then only Σ symmetry contributes to the sum. When you restrict the partial waves included in the expansion, it increases the possibility of having a minimum in the DCS at that particular orientation and then strong deviation of P'/P from 1. Our results shows similar phenomena for NO. Several features in our data correspond to $\beta = 0$, 90, 180, and 270 where d^j_{mn} imposes some restriction.

For NO the interference usually occurs at angles greater than $60°$; NO has a permanent dipole so it dominates the small angle scattering. As a result the effect of exchange is not seen at small angles. The angular behavior becomes less pronounced as the energy increases because the exchange interaction should reduce its relative effect. As a result $f^{(3)}$ and $f^{(1)}$ become close to each other producing values of P'/P close to 1. This can be seen from our theoretical data by looking at the reduction of the anisotropy as the energy increases. This is true starting from 5 and 10 up to 15 eV, but

for 20 eV there is clearly some enhancement of the anisotropy. We attribute this behavior to a shape resonance present in our calculation and seen also experimentally by Szmytkowski and Maciag [14]. When a resonance occurs it affects both scattering amplitudes asymmetrically. As a consequence the difference between $f^{(3)}$ and $f^{(1)}$ increases, influencing directly the spin-flip process. The resonance is not strong enought to be seen in gas phase measurements of P'/P but its influence is clearly seen when the molecule is oriented. In Fig. 9 we present the momentum transfer cross section for each spin amplitude. There is a clear enhancement of the triplet cross sections at around 20 eV. Althought not shown, our partial cross section indicates a resonance in the overall $^3\Pi$ symmetry.

IV. CONCLUSIONS

Our results for elastic scattering data have in general good agreement with experiments; early SMC studies on polar molecules have shown similar agreement. The agreement becomes poorer with decreasing energy and scattering angles. Under these conditions polarization effects become important and they are not included in the present calculation. The orbital degeneracy of NO molecule allows a *zero-energy* excitation process corresponding to a jump between the states belonging to the Π ground state. Their values have the same order of magnitude as those corresponding to an excitation process.

Our results for the polarization fraction P'/P have good agreement with experiments. It shows the same flat angular behavior already seen in O_2. A detailed study of the variation of this polarization fraction with respect to the orientation of the molecular axis shows an angular behavior with many structures.

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