Spin Exchange in Elastic e-O_2 Collisions

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Recent experiments using polarized electron beams have shown that spin-exchange effects for elastic collisions with O_2 and NO are much smaller than for Na atoms. We report calculated spin-flip differential cross sections for elastic collisions of polarized electrons with O_2 in agreement with experiment. In general, we can attribute large variations of the spin-flip differential cross sections to resonances and interference effects. Such features arising from interference, however, may be washed out in the molecular case due to the average over orientations. Calculations with oriented O_2 show strong exchange effects as for Na.

The dynamics of low-energy electron collisions with atoms, molecules, and surfaces is, in general, strongly influenced by exchange collisions. To date most theoretical and experimental studies of such collisions *with molecules* have been for unpolarized electron sources and with no spin analysis of the scattered beam. Although these cross sections may often be strongly influenced by spin-polarization effects, the underlying spin dynamics of the collision is masked in such studies. Studies with spin-polarized sources and with spin analysis of the scattered electrons, however, yield dynamically richer cross sections [1–5] which can directly furnish information about the role of exchange collisions in these processes. Moreover, such cross sections clearly provide a much more stringent test of theoretical models [6].

Recently, Hegeman *et al.* [7] have used polarized electrons to measure the spin-flip differential cross sections (SFDCS) in elastic collisions with Na and Hg atoms and the open-shell molecules O_2 and NO for energies between 4 and 15 eV and scattering angles up to 110°. Whereas significant spin-exchange effects were observed in these studies for elastic and inelastic collisions with Na and Hg atoms, in agreement with previous theoretical predictions [8,9], spin-exchange effects were found to be much smaller for collisions with O_2 and NO. In a recent measurement Ratliff *et al.* [10] have also measured the average spin-flip cross sections for scattering of electrons from O_2 and NO molecules at thermal energies. These energy-averaged cross sections were significantly smaller than those found for scattering from alkali or hydrogen atoms.

In this Letter we report the results of calculations of the cross sections for elastic collisions of polarized and unpolarized electrons with O_2 and provide an explanation for the angular behavior seen in the spin-exchange experiments [7]. Our calculated spin-flip differential cross sections for these oscillations, obtained using a Schwinger multichannel variational principle [11], agree well with the recent measurements of Hegeman *et al.* [7] and confirm their values that are much smaller than those seen for Na atoms. We attribute the large spin-flip cross

sections for elastic collisions with Na atoms to resonances and interference effects in this system. These effects are expected to be seen in general for atoms and molecules. However, the averaging over molecular orientations inherent in gas-phase collision processes may wash out such interference effects in molecules. This is the case for the present e-O_2 study where such averaging leads to an almost flat angular distribution. In what follows we will see, in fact, that strong exchange effects, comparable to those in Na, are seen for certain angles of incidence in collisions with oriented O_2 molecules.

In these studies we used the Schwinger multichannel (SMC) method [11] which was previously formulated as a multichannel extension of Schwinger's variational principle [12]. This multichannel formulation preserves the important feature of the original Schwinger variational principle of allowing a purely L^2 expansion of the scattering wave function. The SMC method is one of several methods which have been recently developed for carrying out *ab initio* studies of electron-molecule collisions. Other approaches include the R-matrix and linear algebraic methods [13,14] and the complex form of the Kohn variational principle [15]. In principle, these methods can account for important physical effects in these collisions which arise from closed and open channels. Previous theoretical studies of electron collisions with O_2 reported cross sections for electronic excitation by unpolarized electrons [16,17].

In the SMC method [11] the variational expression for the scattering amplitude is

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

where

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

and

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

In these equations S_{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) used as a variational trial function, $\hat{H}$ is the total energy minus the full Hamiltonian of the system, N is the total number of electrons on the target, P is a projector onto the open electronic target states, and $G_P^{(\pm)}$ is the Green's function projected on this P space. Details of the SMC method have been given previously [18].

Our calculation included three open channels, the $X\,^3\Sigma_g^-$ ground state and the $a\,^1\Delta_g$ and $b\,^1\Sigma_g^+$ excited states of O_2. The basis set used here is the double-zeta basis of contracted Gaussians of Dunning [19] supplemented by a set of d basis functions on each oxygen (exponent $\alpha = 0.9$) [20]. These X, a, and b states all arise from the ground-state $(1\pi_g)^2$ electron configuration. For the $X\,^3\Sigma_g^-$ ground state we used a Hartree-Fock wave function. Our basis gives a self-consistent-field (SCF) energy of -149.6394 a.u. which can be compared with the Hartree-Fock limit of -149.6659 a.u. [21]. The electronic wave functions for the $a\,^1\Delta g$ and $b\,^1\Sigma_g^+$ states are constructed by a simple recoupling of the ground-state SCF orbitals.

In Fig. 1 we compare our calculated SFDCS, expressed as a ratio (known as the polarization fraction P'/P) of the polarization P' after the collision and the initial polarization P, with the measured values of Ref. [7] at 10 and 15 eV, respectively.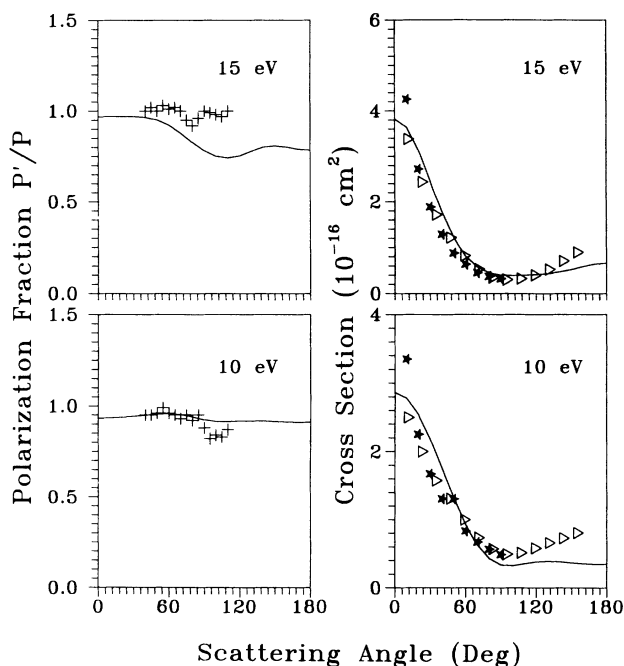 This figure also shows calculated differ-ential cross sections for elastic scattering of an unpolar-ized electron beam by O_2 for electron impact energies of 10 and 15 eV along with the measured values of Trajmar, Cartwright, and Williams [22] and Shyn and Sharp [23]. The differential cross section for elastic scattering of an unpolarized electron beam is given by

$$\frac{d\sigma}{d\Omega} = \tfrac{1}{3}\,\{2|f^{(4)}|^2 + |f^{(2)}|^2\}\,, \tag{4}$$

where $f^{(2S+1)}$ are spin-irreducible scattering amplitudes for a total spin (molecule plus electron) $S = S_i \mp \tfrac{1}{2}$. The agreement between the calculated and measured cross sections at 10 and 15 eV is quite good.

The ratio of P' to P is related to the spin-flip and unpo-larized elastic cross sections by

$$\frac{P'}{P} = 1 - 2\frac{d\sigma_{\mathrm{sf}}/d\Omega}{d\sigma/d\Omega}\,. \tag{5}$$

In terms of the amplitudes $f^{(4)}$ and $f^{(2)}$ of Eq. (4) the spin-flip elastic differential cross section is given by

$$\frac{d\sigma_{\mathrm{sf}}}{d\Omega} = \tfrac{4}{27}\,|f^{(4)} - f^{(2)}|^2\,, \tag{6}$$

showing that the spin-flip process is sensitive to the rela-tive phase between the $f^{(4)}$ and $f^{(2)}$ and hence to in-terference phenomena. In fact, it can be shown that spin-flip cross sections always arise from the difference between the $f^{(2S_i+2)}$ and $f^{(2S_i)}$ amplitudes, where S_i is the total electronic spin of the target [24]. The exchange interaction of the scattered electron with the unpaired electrons of the target is the essential mechanism for this spin-flip process. The exchange potential and possible resonances govern the magnitude of these cross sections since they may both affect $f^{(4)}$ and $f^{(2)}$ asymmetrically. Our calculated spin polarizations (P'/P) agree quite well with the measured values [7]. Recent measurements by Ratliff et al. [10] have also shown that the averaged spin-flip cross sections for scattering of electrons by O_2 and NO molecules at thermal energies are much smaller than those for scattering by alkali or hydrogen atoms. It is worth noting that the calculated spin-flip elastic cross sections are of the same order of magnitude as the cross sections for electron impact excitation of the $a\,^1\Delta_g$ and $b\,^1\Sigma_g^+$ states of O_2 which are also pure exchange process-es.

An interesting question now arises: Why do Na atoms have such a large spin-flip elastic cross section? Spin-flip processes arise from the exchange interaction which should be a small part of the total scattering potential. The corresponding cross sections are, in fact, essentially due to the asymmetric way in which this interaction affects each scattering amplitude $f^{(2S+1)}$. Generally, these spin-flip cross sections can hence be expected to be small. This simple picture can fail if resonances occur or interference effects become significant. A resonance occurs in a specific symmetry and spin S and, hence, will affect just one of the scattering amplitudes $f^{(2S+1)}$ for a

FIG. 1. Polarization fraction P'/P and unpolarized dif-ferential cross section for elastic electron scattering by the $X\,^3\Sigma_g^-$ ground state of O_2: ——, present results averaged over all orientations; +, experimental results of Ref. [7]; *, experi-mental results of Ref. [22]; △, experimental results of Ref. [23].

given collision energy. If the contribution of a particular partial wave (or group of these waves) in the resonance symmetry is large compared to others, the resonant feature will dominate both the direct and spin-flip cross sections and the resulting spin-polarization ratio can deviate significantly from unity. Interference effects may also give rise to large spin-flip cross sections in certain situations. For example, if one of the scattering amplitudes has a minimum in its absolute value at a given angle, the other component will dominate and lead to large exchange effects. Such behavior should be limited to a small angular region. Interference effects may also lead to large spin-flip cross sections if the scattering amplitudes $f^{(2S+1)}$ have a phase difference close to π. This behavior should again be expected in a localized angular region. A large depolarization due to interference is analogous to the spin-polarization effect of Kessler [25]. There, the small spin-orbit potential becomes important at those angles where the unpolarized differential cross section has a minimum. This makes the potential different for each spin component and produces an angularly localized spin polarization.

With these considerations, the significant depolarization seen around 50° at 12.1 eV for elastic collisions with Na atoms [7] should probably be attributed to interference. At this energy the region around 50° shows strong depolarization while elsewhere the polarization ratio is close to unity. On the other hand, at 4 eV depolarization occurs over a wide angular region [7] and, hence, probably arises from resonances. Such resonant behavior should be apparent in the energy dependence of the partial wave contributions to the elastic cross sections for Na.

It is well known that the O_2 molecule does not have resonances at these energies so we do not expect a broad angular feature like that seen at 4 eV for Na. However, interference phenomena like those seen at 12.1 eV for Na can arise. Why are they not seen? The reason is the orientational averaging inherent in molecular targets in gas-phase collisions. Figure 2 shows the polarization fractions for 10 eV at three different orientations defined by Euler's angles $(\alpha=27, \beta=15)$, $(\alpha=130, \beta=45)$, and $(\alpha=130, \beta=130)$. Our results clearly show strong interference phenomena. These features (dips and bumps) in the SFD cross sections are very sensitive (rapid change in shape and angular position) to the molecular orientation and are washed out by orientational averaging. This explains the unexpected behavior seen in the experiments [7]. This strong dependence of the differential cross sections with respect to the orientation of the molecule may be useful in studies of adsorbate orientation using polarized electron beams on molecules adsorbed on surfaces.
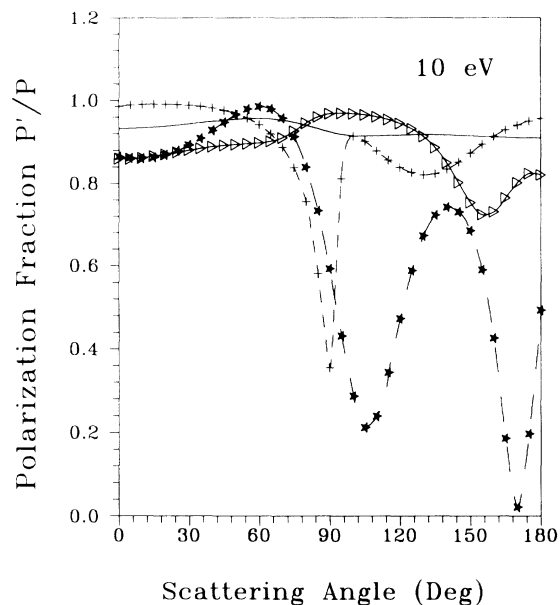
FIG. 2. Polarization fraction P'/P for elastic electron scattering by the $X\,^3\Sigma_g^-$ ground state of O_2: ———, present results averaged over all orientations; +, orientation 1 $(\alpha=27, \beta=15)$; *, orientation 2 $(\alpha=130, \beta=45)$; △, orientation 3 $(\alpha=130, \beta=130)$.

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