

Spin-exchange effects in elastic electron-radical collisions

M. M. Fujimoto,¹ S. E. Michelin,² I. Iga,³ and M.-T. Lee³

¹*Departamento de Física, UFPR, 81531-990 Curitiba, PR, Brazil*

²*Departamento de Física, UFSC, 88040-900 Florianópolis, SC, Brazil*

³*Departamento de Química, UFSCar, 13565-905, São Carlos, SP, Brazil*

(Received 8 September 2005; published 20 January 2006)

This work presents a theoretical investigation on the spin-exchange effects in the low-energy elastic electron-C₂O radical collisions. Spin-polarization differential and integral cross sections calculated in the 1–10-eV energy range are reported. Our calculation has shown that the exchange between the scattering and unpaired target electron is strongly influenced by the occurrence of shape resonances. More specifically, our calculated rotationally summed spin-polarization fractions show significant deviation from unity in the resonance region. An analysis of the contributions from individual rotational transitions is also made.

DOI: [10.1103/PhysRevA.73.012714](https://doi.org/10.1103/PhysRevA.73.012714)

PACS number(s): 34.80.Bm

I. INTRODUCTION

Low-energy electron collisions with atoms, molecules, radicals, and surfaces are, in general, strongly influenced by electron-exchange effects. Such effects can be easily characterized in the so-called spin-forbidden excitations (for instance, singlet-to-triplet transitions) by electron impact. Nevertheless, although an exchange mechanism is also important in elastic collisions, it is usually masked since most experimental studies for electron-molecule scattering have been performed with unpolarized electron sources and with no spin analysis of the scattered beam. Therefore, experimental studies with spin-polarized electrons and with spin analysis of the scattered electrons would provide richer information about the role of exchange collisions.

In 1991, spin-flip (SF) differential cross sections (DCSs) for elastic electron scattering by some atoms (Na, Hg) and open-shell molecules (O₂, NO) in the 4–15-eV energy range were reported by Hegemann *et al.* [1]. Significant spin-exchange effects were found in these studies for atomic targets, in agreement with the theoretical predictions [2,3]. In contrast, these effects were found to be much smaller for collisions with O₂ and NO. This observation was confirmed by Ratliff *et al.* [4] in the measurement of average SF cross sections for scattering of electrons from O₂ and NO molecules at thermal energies.

In 1992, da Paixão *et al.* [5] carried out DCS calculations for elastic collisions of polarized and unpolarized electrons with O₂ using the Schwinger multichannel method. Their calculated results provided an explanation for the small spin-exchange effects in elastic e^- -O₂ collisions as observed in the experiments. As a matter of fact, they found that the spin-polarization fractions (P'/P), calculated for a given orientation of target in space, can deviate significantly from unity at some scattering angles. Nevertheless, electron collisions with targets of different orientations exhibit quite different angular behavior of polarization ratios, therefore the calculated P'/P averaged over all orientations became almost isotropic and close to unity. Some other calculations [6–8] for O₂ and NO using different theoretical methods have also confirmed the observation of da Paixão *et al.* [5].

Recently, we reported a theoretical investigation on elastic electron collisions with the C₂O radical [9]. In that study, DCSs and momentum transfer cross sections (MTCSs) in a wide energy range were calculated and reported. Since C₂O is an open-shell radical with the ground-state electronic configuration $X^3\Sigma^-$, two spin-specific scattering schemes, namely the doublet and quartet couplings between the scattering electron and the isolated 2π electrons of the target, were considered. Two sharp resonance features located at 3.0 and 4.4 eV, respectively, were observed in the spin-averaged MTCS's for elastic e^- -C₂O collisions. The resonance centered at around 3.0 eV was identified as due to the $^4\Pi$ scattering channel and that located at 4.4 eV is due to the $^2\Pi$ symmetry. The shift of about 1.4 eV between the resonance features in C₂O is originated by the different exchange potential operator used in the doublet- and quartet-coupling scattering calculations. The shift in the resonance positions due to different spin couplings is somehow expected, since a resonance is a quasibound state and the energy splitting in bound states due to the spin coupling is well known. Meanwhile, this shift due to the different spin couplings clearly indicates the strong influence of the exchange effects and, therefore, significant SF DCSs are expected for elastic e^- -C₂O collisions in this energy region. However, neither calculated SF DCSs nor depolarization ratios were reported in that study.

In this work, we report a theoretical calculation of SF DCSs and spin-polarization fractions (SPFs) for elastic electron scattering by C₂O in the 1–10-eV energy range. A comparison of our calculated SPFs for the low-lying rotational excitations and those that are rotationally summed (equivalent to the orientation-averaged results of da Paixão *et al.* [5]) would provide insight into the role played by the spin-exchange mechanisms in the collisional dynamics.

The organization of this paper is as follows. In Sec. II, an outline of the theory used is presented, providing a few details of the calculations. In Sec. III, we present our results, and we also present a brief conclusion.

II. THEORY AND CALCULATION

Within the fixed-nuclei framework, the electron-molecule scattering dynamics is represented by a static-exchange-

polarization potential V^{SEP} , composed of the static (V_{st}), the exchange (V_{ex}), and the correlation-polarization contribution (V_{cp}) components. In our calculation, V_{st} and V_{ex} are derived exactly from a restricted open-shell Hartree-Fock self-consistent-field (SCF) target wave function. A parameter-free model potential introduced by Padial and Norcross [10] is used to account for the correlation-polarization contributions. In this model, a short-range correlation potential between the scattering and target electrons is defined in an inner interaction region and a long-range polarization potential in an outer region. The first crossing of the correlation and polarization potential curves defines the inner and outer regions. The short-range correlation potential is derived using the target electronic density according to Eq. (9) of Padial and Norcross. In addition, an asymptotic form of the polarization potential is used for the long-range electron-target interactions. Dipole polarizabilities are needed to generate the asymptotic form of V_{cp} . Since there are no experimental and/or theoretical values available in the literature for the C_2O radical, they were calculated in this work at the single- and double-excitation configuration-interaction level of approximation. No cutoff or other adjusted parameters are needed in the calculation of V_{cp} .

Since C_2O is an open-shell target, the coupling of the incident electron with the two unpaired 2π electrons of the target leads to two spin-specific scattering channels, namely the doublet ($S=1/2$) and quartet ($S=3/2$) couplings. The main difference between the doublet and quartet scattering channels would reflect on the treatment of the electron-exchange term in the potential operator.

Further, the spin-specific Lippmann-Schwinger equation is solved using the iterative Schwinger variational method [11]. The continuum wave functions are single-center expanded as

$$\chi_{\vec{k}}^{\pm}(\vec{r}) = (2/\pi)^{1/2} \sum_{lm} \frac{(i)^l}{k} \chi_{klm}^{\pm}(\vec{r}) Y_{lm}(\hat{k}), \quad (1)$$

where the superscripts (+) and (−) denote the incoming- and outgoing-wave boundary conditions, respectively, \vec{k} is the linear momentum of the scattering electron, and $Y_{lm}(\hat{k})$ are the usual spherical harmonics.

In the present work, we have limited the partial-wave expansion of T -matrix elements up to $l_{\text{max}}=50$ and $m_{\text{max}}=16$. A Born-closure procedure is used to account for the contribution of higher partial-wave dipole components to scattering amplitudes. In order to avoid the divergent behavior of the DCSs in the forward direction, nuclear-rotational dynamics is treated explicitly.

Within the adiabatic-nuclear-rotation framework, the spin-specific rotational scattering amplitude is expressed as

$$f_{jm_j \leftarrow j_0 m_{j_0}}^S = \langle jm_j | f^S | j_0 m_{j_0} \rangle, \quad (2)$$

where $|jm_j\rangle$ are the rigid-rotor wave functions, $f^{(S)}$ is the spin-specific fixed-nuclei electron scattering amplitude in the laboratory-frame (LF), and S is the total spin of the (electron+target) system. Accordingly, the spin-specific DCS

for the rotational excitation from an initial level j_0 to a final level j is given by

$$\left(\frac{d\sigma}{d\Omega}\right)^S(j \leftarrow j_0) = \frac{k_f}{k_0} \frac{1}{(2j_0+1)} \sum_{m_j m_{j_0}} |f_{jm_j \leftarrow j_0 m_{j_0}}^S|^2, \quad (3)$$

where k_f and k_0 are the final and initial linear momenta of the scattering electron, respectively. Moreover, the spin-specific rotationally unresolved DCSs for elastic $e^- - \text{C}_2\text{O}$ scattering are calculated via a summation of rotationally resolved DCSs,

$$\left(\frac{d\sigma}{d\Omega}\right)^S = \sum_{j=0} \left(\frac{d\sigma}{d\Omega}\right)^S(j \leftarrow j_0). \quad (4)$$

The spin-averaged DCS for elastic $e^- - \text{C}_2\text{O}$ scattering is calculated using the statistical weight for doublet (2/6) and quartet (4/6) scattering channels, as

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{6} \left[4 \left(\frac{d\sigma}{d\Omega}\right)^{3/2} + 2 \left(\frac{d\sigma}{d\Omega}\right)^{1/2} \right]. \quad (5)$$

Moreover, the SF DCS for elastic $e^- - \text{C}_2\text{O}$ collisions can be defined in terms of the spin-specific electron scattering amplitudes by

$$\left(\frac{d\sigma_{\text{sf}}}{d\Omega}\right) = \frac{4}{27} |f^{3/2} - f^{1/2}|^2. \quad (6)$$

Finally, the SPF is given by

$$\frac{P'}{P} = 1 - 2 \frac{d\sigma_{\text{sf}}/d\Omega}{d\sigma/d\Omega}. \quad (7)$$

In the same way, one can also define the rotational-dependent SF DCSs from an initial level j_0 to a final level j as

$$\frac{d\sigma_{\text{sf}}}{d\Omega}(j \leftarrow j_0) = \frac{4}{27} \frac{k_f}{k_0} \frac{1}{(2j_0+1)} \sum_{m_j m_{j_0}} |f_{jm_j \leftarrow j_0 m_{j_0}}^{3/2} - f_{jm_j \leftarrow j_0 m_{j_0}}^{1/2}|^2 \quad (8)$$

and the spin-averaged rotational excitation DCS as

$$\left(\frac{d\sigma}{d\Omega}\right)_{(j \leftarrow j_0)} = \frac{1}{6} \left[4 \left(\frac{d\sigma}{d\Omega}\right)_{(j \leftarrow j_0)}^{3/2} + 2 \left(\frac{d\sigma}{d\Omega}\right)_{(j \leftarrow j_0)}^{1/2} \right]. \quad (9)$$

Consequently, the rotational-dependent SPF is defined as

$$\frac{P'}{P}(j \leftarrow j_0) = 1 - 2 \frac{(d\sigma_{\text{sf}}/d\Omega)_{(j \leftarrow j_0)}}{(d\sigma/d\Omega)_{(j \leftarrow j_0)}}. \quad (10)$$

In the present study, a standard triple-zeta-valence basis set [12] augmented by one s ($\alpha=0.0438$), one p ($\alpha=0.0438$), and three d ($\alpha=2.88, 0.72$, and 0.18) uncontracted functions for carbon atom and one s ($\alpha=0.0845$), one p ($\alpha=0.0845$), and three d ($\alpha=5.12, 1.28$, and 0.32) for oxygen atom is used for the calculation of the SCF wave function of the target. The results of some calculated properties are summarized in Table I, where the SCF results of Brown *et al.* [13] are also shown for comparison.

TABLE I. Calculated properties of C_2O .

	Present	Brown <i>et al.</i> [13]
Energy (Hartree)	-150.512058	-150.510065
r_{CC} (bohr)	2.5908	2.5772
r_{CO} (bohr)	2.1448	2.1205
dipole moment (D)	1.381	1.380
α_0 (a.u.)	27.3512	
α_2 (a.u.)	13.2130	
IP (eV)	12.0	

III. RESULTS AND DISCUSSION

In Fig. 1, we present the calculated SF DCSs for elastic electron collisions with C_2O radical in the 1–10-eV energy range. It is clearly seen that the SF DCSs in the 3–5-eV energy region are about two orders of magnitude larger than the corresponding data elsewhere. In Fig. 2, the calculated SF integral cross sections (ICSs) in the 1–10-eV energy range are also shown. Two resonance features located at 3.0 eV and at around 4.4 eV, respectively, are evident. Out of the resonance region, the calculated SF ICSs are significantly smaller. In our previous study [9], we have identified that the sharp resonances located in this energy region are due to the $^4\Pi$ (at 3.0 eV) and $^2\Pi$ (at 4.4 eV) scattering channels. Therefore, the present calculation seems to indicate that the spin-exchange effects between the scattered electron and

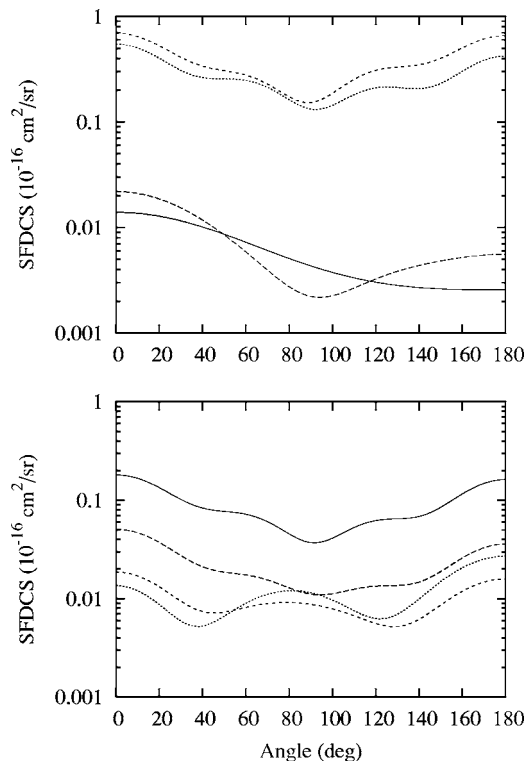


FIG. 1. Calculated SF DCSs for elastic e^-C_2O collisions. Top: solid line, at 1 eV; dashed line, at 2 eV; short-dashed line, at 3 eV; and dotted line, at 4 eV. Bottom: solid line, at 5 eV; dashed line, at 6 eV; short-dashed line, at 8 eV; and dotted line, at 10 eV.

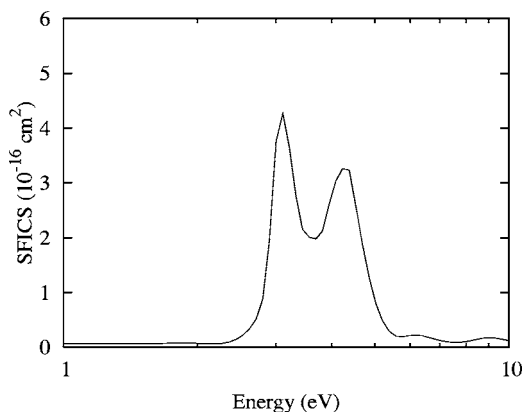


FIG. 2. Calculated SF ICSs for elastic e^-C_2O collisions in the 1–10-eV range.

the unpaired electrons of the target are significantly enhanced by the occurrence of the shape resonances. Particularly, the shift of the energy positions (1.4 eV) between the shape resonances associated to the doublet and quartet couplings has contributed to the large SF DCSs in the resonance region. In contrast, out of this region the calculated SF DCSs are insignificant, showing the contribution of the exchange effects are similar for both spin couplings.

In Fig. 3, we present the angular distribution of the SPFs, calculated in the 1–10-eV energy range. The present polarization fractions are calculated according to Eq. (7) using the rotationally summed DCSs and SF DCSs. Actually, the summation over rotational transitions is mathematically equiva-

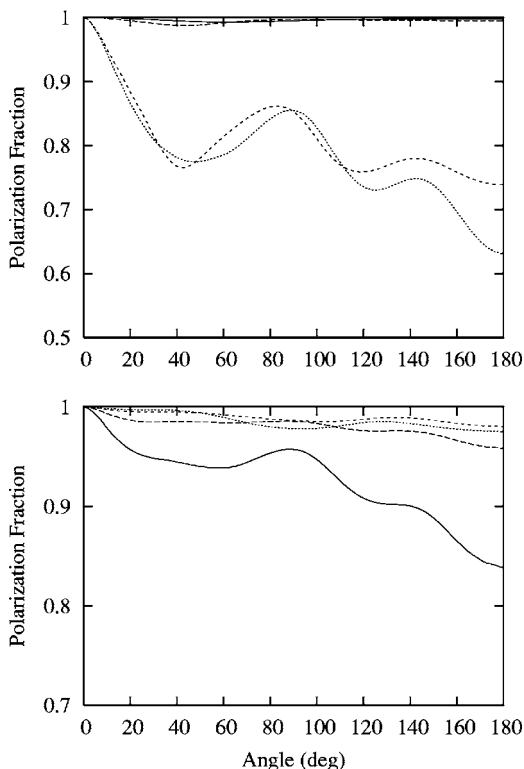


FIG. 3. Angular distribution of the SPFs for elastic e^-C_2O collisions. The symbols used are the same as those in Fig. 1.

lent to the molecular orientations averaging procedure used by da Paixão *et al.* [5]. It is interesting to see in Fig. 3 that our calculated rotationally summed SPFs show strong interference-like features in the resonance region and their magnitudes are far from 1. This observation is quite different from that seen by da Paixão *et al.* [5,6] for elastic electron scattering from open-shell targets O_2 and NO. In those studies [5,6], the angular behavior of the orientation-averaged SPFs is almost isotropic and with the values close to unity. On the other hand, their calculated P'/P fractions for oriented targets have shown significant interference features such as dips and bumps, and with magnitudes that are comparable to those seen in elastic electron scattering with alkali atoms. They also observed that such structures are sensitive to the molecular orientation and thus are washed out by orientation averaging. It is well known that the exchange interaction between the scattered electron and the unpaired electrons of the target is the mechanism that makes $f^{3/2}$ different from $f^{1/2}$. Therefore, P'/P close to 1 implies that both the magnitudes and the phases of $f^{3/2}$ and $f^{1/2}$ are almost the same. However, for elastic e^- - C_2O collisions the exchange interaction is enhanced by the occurrence of shape resonances. The fact that the resonances of different spin couplings are located at different positions is fundamental for the significant deviation of the rotationally summed SPFs from unity.

In order to understand the contribution of SF DCSs from an individual rotational transition to the rotationally summed quantities, in Fig. 4 we present the SPFs for the $0 \rightarrow 0$, 1, and 2 rotational transitions for e^- - C_2O collisions at incident energies of 4.4 and 10 eV. At 4.4 eV, where the center of the $^2\Pi$ resonance is located, strong interference-like features are seen for all rotational transitions. These features are originated from the angular behavior of some particular partial-wave components. According to Eq. (8), the rotational SF DCSs depend exclusively on the magnitude of the difference of the partial-wave spin-specific scattering amplitudes. Near the resonance region, the differences between few partial-wave components become dominant, and therefore the structures shown in Fig. 4 reflect the angular behavior and interference of those components. For each rotational transition, different partial waves contribute to the SF DCSs. For instance, only the diagonal elements ($\Delta l=0$) of the T matrix contribute to the $0 \rightarrow 0$ transition. Particularly for this case, the element $T_{ll'm}$ for $l=l'=3$ and $m=1$ is predominant, followed by T_{221} and T_{442} . Therefore, the number and the positions of the dips and bumps are different for each transition. Also, it is seen that the values of SPFs at the dips for the $0 \rightarrow 0$ transition deviate strongly from unity. Such strong deviation is interesting, but is somehow expected. It is well known that for this rotational transition, only the spherical part of the interaction potential is accounted for during the collision, similar to what happens in the electron-alkali atom scattering. Therefore, similar results are also expected. The contributions of higher rotational transitions can wash out only partly the strong interference-like features, and therefore structures remain in the rotationally summed SPFs. In contrast, although some structures are also present in the rotational SPFs at 10 eV, they are in general very weak and lead the rotationally summed SPFs to nearly 1 at the entire angular range.

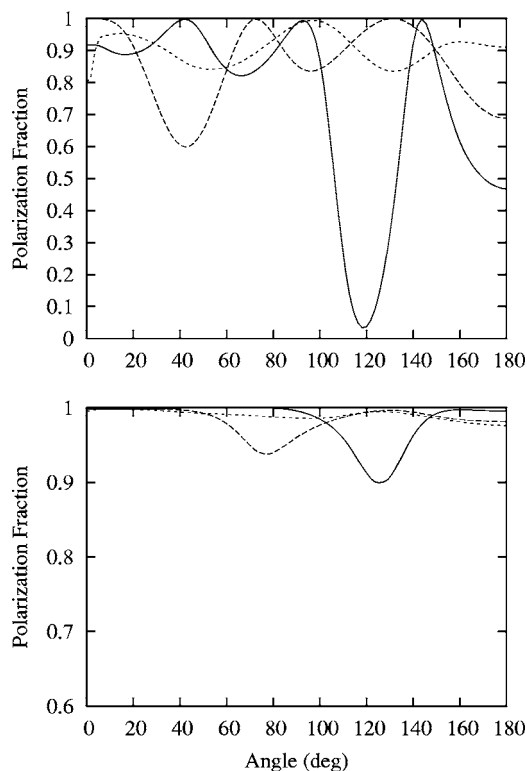


FIG. 4. Rotationally resolved SPFs for elastic e^- - C_2O collisions at 4.4 eV (top) and 10 eV (bottom). Solid line, for the $0 \rightarrow 0$ transition; dashed line, for the $0 \rightarrow 1$ transition; and short-dashed line, for the $0 \rightarrow 2$ transition.

In summary, the present work reports a theoretical investigation on the spin-exchange processes in the low-energy elastic electron- C_2O radical collisions. Our calculation has shown that the exchange between the scattering and unpaired target electrons can be strongly enhanced by the occurrence of shape resonances. In this sense, calculated rotationally summed SPFs, which are equivalent to the molecular orientation averaged results [5], deviate significantly from unity in the resonance region. Probably, the small spin-exchange effects observed in the previous theoretical and experimental elastic electron scattering by NO and O_2 are mainly because there is no manifestation of strong resonances at the incident energies where the studies were carried out. Moreover, in the elastic e^- - C_2O collisions, the fact that the resonances from the doublet and quartet couplings are located at different energies can certainly contribute to the significant differences in the magnitudes of the spin-specific scattering amplitudes. However, the SF DCSs are also sensitive to the relative phases between the $f^{3/2}$ and $f^{1/2}$. Therefore, significant spin-exchange effects may happen even for systems with spin-specific resonances lying at about the same incident energies. Due to the chemical instability, no experimental investigation on electron- C_2O scattering has been carried out yet and probably will not happen in the near future. Fortunately, in the XXIV ICPEAC held recently in Rosario, Argentina, several experimentalists have demonstrated their interest in studying e^- -free radical interactions. Indeed, a few of these studies have appeared recently in the literature [14]. Thus,

we expect that experimental confirmation of spin-exchange effects for elastic electron scattering by open shell molecules might occur in the next few years. However, it is important to discover adequate targets for such experimental studies since the manifestation of relevant spin-exchange effects would depend essentially on the existence of strong resonances during the collision. Intense theoretical studies on electron-radical collisions are needed in order to search those

targets for such studies. Investigation in this direction is now underway.

ACKNOWLEDGMENTS

This research was partially supported by the Brazilian Agencies CNPq, FUNPAR, Fundação Araucária, and FAPESP.

-
- [1] T. Hegemann, M. Oberste-Vorth, R. Vogts, and G. F. Hanne, *Phys. Rev. Lett.* **66**, 2968 (1991).
[2] D. L. Moores, *Comput. Phys. Commun.* **2**, 360 (1971).
[3] K. Bartschat and D. H. Madison, *J. Phys. B* **21**, 1609 (1987).
[4] J. M. Ratliff, G. H. Rutherford, F. B. Dunning, and G. K. Walters, *Phys. Rev. A* **39**, 5584 (1989).
[5] F. J. da Paixão, M. A. P. Lima, and V. McKoy, *Phys. Rev. Lett.* **68**, 1698 (1992).
[6] F. J. da Paixão, M. A. P. Lima, and V. McKoy, *Phys. Rev. A* **53**, 1400 (1996).
[7] G. Woste, K. Higgins, P. Duddy, C. M. Fullerton, and D. G. Thompson, *J. Phys. B* **29**, 2553 (1996).
[8] L. E. Machado, E. M. S. Ribeiro, M.-T. Lee, M. M. Fujimoto, and L. M. Brescansin, *Phys. Rev. A* **60**, 1199 (1999).
[9] M. M. Fujimoto, M.-T. Lee, and S. E. Michelin, *Phys. Rev. A* **69**, 052706 (2004).
[10] N. T. Padial and D. W. Norcross, *Phys. Rev. A* **29**, 1742 (1984).
[11] R. R. Lucchese, G. Raseev, and V. McKoy, *Phys. Rev. A* **25**, 2572 (1982).
[12] T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).
[13] S. T. Brown, Y. Yamaguchi, and H. F. Schaefer III, *J. Phys. Chem. A* **104**, 3603 (2000).
[14] T. A. Field, A. E. Slattery, D. J. Adams, and D. D. Morrison, *J. Phys. B* **38**, 255 (2005).