Brief Reports

Exchange in low-energy e-CO_2 collisions

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The validity of three approximate treatments of the exchange interaction in low-energy e-CO_2 scattering is assessed by comparing approximate and exact static-exchange eigenphase sums in the resonant Π_u symmetry and the nonresonant Σ_g and Σ_u symmetries. Of the approximations studied—orthogonalized static, free-electron-gas model potential, and orthogonalized model potential—the latter has yielded results in best agreement with those of the exact treatment of exchange. Newly calculated static-exchange-polarization cross sections for energies from 0.1 to 2.0 eV are presented.

In our initial investigation[1] of e-CO_2 scattering, we used a static-model exchange-polarization (SEP) interaction potential to calculate total integrated, momentum-transfer, and differential cross sections. This model potential has also been employed to study rotational and vibrational excitations.[2-4] Recent experimental measurements of the total integrated cross sections[5] agree very well with our theoretical results. However, the difficulty of measuring absolute e-CO_2 cross sections[5-7] at low energies and the sensitivity of the cross section to the form of the interaction potential, necessitate further study of our model potential. One of the more questionable components of this potential is the exchange contribution, which was derived from a free-electron-gas (FEG) formulation.[8-10] In this paper, we investigate, in more detail, the validity of using an FEG formulation to represent the e-CO_2 exchange interaction by comparing the results of model-potential and exact static-exchange (ESE) calculations.

In the static-model exchange calculations, we implemented three procedures for including exchange: the orthogonalized-static (OS), the Hara free-electron-gas exchange model potential (HFEGE), and orthogonalized model potential (OHFEGE). In each case, we calculated fixed-nuclei eigenphase sums in the resonant Π_u and nonresonant Σ_g and Σ_u e-CO_2 symmetries. These results were compared with ESE eigenphase sums calculated using the linear-algebraic method of Schneider and Collins.[11] The ESE calculations treat exactly the full nonlocal and energy-dependent character of the exchange interaction. Since these three approximate treatments of exchange,[9] theoretical,[1] and computational[12] details of the scattering calculations have been discussed elsewhere, we shall only summarize the salient points of the models here.

In our earlier e-CO_2 calculations,[1-4] exchange effects were incorporated via the (HFEGE) potential,[8,9] which is a local approximation to the two-electron exchange terms in the coupled scattering equations that are obtained in the usual body-frame—fixed-nuclei formulation of electron-molecule collision theory (see, for example, Ref. 13). To obtain the HFEGE potential, two approximations are made *in the exchange terms only:* (1) the molecular electrons are treated as a free-electron gas with a charge density determined from a near-Hartree-Fock target wave function, and (2) distortions of the continuum function are neglected.

In the orthogonalized-static (OS) method,[14] the aforementioned two-electron exchange terms are

TABLE I. Resonance energies (E_r) and width (Γ) for the Π_u shape resonance in e-CO_2 scattering in the static-exchange approximation as determined from a Breit-Wigner fit of the eigenphase sums.

Method	E_r(eV)	Γ(eV)
ESE (Ref. 11)	5.4	0.68
OHFEGE	6.7	0.7
HFEGE	7.2	0.9
OS	~16.0	~5.0

completely neglected, and exchange effects are partially reintroduced by enforcing orthogonality of the scattering function to all bound molecular orbitals (MO's) of the same symmetry. Lagrange undetermined multipliers are used to enforce these orthogonality constraints. Both the HFEGE (Ref. 9) and OS (Ref. 15) approximations have been extensively used in calculations of low-energy electron-molecule cross sections.

The third approximation to the exchange interaction is a composite of the OS and HFEGE schemes. In this orthogonalized-Hara-free-electron-gas (OHFEGE) procedure,[16] the two-electron exchange terms are approximated by the HFEGE potential as described above. The orthogonality conditions on the continuum function, which are *rigorously* satisfied only if exchange is treated exactly, are then imposed using Lagrange multipliers as in the OS method.

In all four sets of SE calculations, the $X^1\Sigma_g^+$ ground electronic state of CO_2 was represented by the near-Hartree-Fock wave function of McLean and Yoshimine[17] at the equilibrium (oxygen-carbon) separation of $2.19440a_0$. This wave function was used to compute the static[18] and HFEGE potentials and to evaluate the exchange integrals in the ESE calculations. In the single-center expansion of the scattering function in spherical har-

monics, partial waves through order $l_{max} = 58 (\Sigma_g)$, $27(\Pi_u)$, and $23 (\Sigma_u)$ were retained. In the OS and OHFEGE calculations, we include Lagrange multipliers for all relevant bound MO's and keep the same order of expansion in the bound and continuum orbitals.

In the SE approximation, there is a shape resonance in the Π_u symmetry below 10.0 eV. At energies near this resonance, the T matrix is quite sensitive to the treatment of exchange, since at these energies the scattering wave function is confined to the short-range region. In Table I we present the resonant energies and widths for the ESE, OS, HFEGE, and OHFEGE cases. Only the OS procedure failed to produce a resonance near ESE position of 5.4 eV, although there are indications of an enhancement in the eigenphase sum near 16.0 eV. Both the HFEGE and OHFEGE appear to give reasonable representations of one exchange interaction in the sensitive region around the resonance. The differences between FEG models and ESE results are comparable to those observed in other systems,[9] with the OHFEGE procedure giving moderately better results.

At energies below the 5.4-eV resonance, the principal contributions to e-CO_2 scattering come from the Σ_g and Σ_u symmetries, with the former dominating the cross sections at very low energies (≤ 0.1 eV). Exchange effects are also important in these nonresonant symmetries. To assess the various approximations, we calculated eigenphase sums in the Σ_u and Σ_g symmetries, which are presented in Tables II and III (Ref. 19), respectively. For the Σ_u symmetry, all three approximations to exchange produce eigenphase sums within roughly 15% of the ESE results. The HFEGE model demonstrates a comparable degree of accuracy for Σ_g scattering. Thus, it appears that the HFEGE potential provides an adequate representation of the exchange interaction for low-energy electron-

TABLE II. Eigenphase sums (modulo π) for e-CO_2 scattering in the nonresonant Σ_u symmetry in the static-exchange approximation using four treatments of exchange, as described in the text.

Energy (eV)	OS	HFEGE	OHFEGE	ESE (Ref. 11)
0.5	−0.2161	−0.2434	−0.2022	−0.1640
2.0	−0.6050	−0.6856	−0.5436	−0.5680
4.0	−0.9974	−1.0865	−0.8890	−0.9467
6.0	−1.3045	−1.3756	−1.1567	−1.2244
8.0	−1.5565	−1.5974	−1.3709	−1.4404
10.0	−1.7710	−1.7753	−1.5478	−1.6115

TABLE III. Comparison of the eigenphase sums for e-CO_2 collisions in Σ_g symmetry.

Energy (eV)	HFEGE	ESE (Ref. 11)
0.5	−0.3670	−0.3263
2.0	−0.7016	−0.6264
4.0	−0.9706	−0.8788
6.0	−1.1786	−1.1025
8.0	−1.3162	−1.2536
10.0	−1.3488	−1.3244

CO_2 collisions.

In all of these calculations, the polarization interaction has been ignored on the grounds that in many instances its inclusion can obscure the very exchange effects we set out to study. This interaction, however, is of great importance in determining low-energy electron-scattering cross sections for comparison to experimental data or for applied needs. Therefore we conclude this study by presenting in Table IV *newly determined* SEP cross sections (and eigenphase sums) for e-CO_2 scattering at energies from 0.1 to 2.0 eV. These results differ from those in our earlier paper in several respects. First, the same CO_2 wave function[17] was used in the present SE *and* SEP calculations. Second, the semiempirical polarization component, the form of which is given in Eqs. (2.14) and (2.15) of Ref. 1, has been retuned to the Π_u resonance at the experimentally determined energy of 3.8 eV, giving a cutoff radius r_c of $2.615a_0$. Finally, more strin-

gent convergence criteria have been imposed on calculating the results of Table IV than were used in our earlier calculations.

The quality of agreement of the static-exchange HFEGE and exact results for e-CO_2 scattering indicates that this model is a rather accurate representation of the exchange interaction for this system. This assertion is further supported by the comparatively minor improvement to the HFEGE results brought about by orthogonalization. Therefore the principal uncertainties remaining in the SEP results of Table IV are in the polarization potential and, for near-resonant energies, in the neglect of the vibrational motion of the nuclei in the body-frame—fixed-nuclei scattering theory.

Considered in the context provided by our previous examination[9] of the utility of exchange models for low-energy electron collisions with polar and nonpolar *diatomic* molecules, the present investigation contains encouraging indications that the reliability of the simple, easily calculated HFEGE potential, without additional orthogonalization or tuning, increases with the number of electrons comprising the collision system. If confirmed by further research, this conclusion augers well for the determination to within a few percent accuracy of cross sections for the vast array of electron-molecule systems for which ESE calculations are prohibitive even with present day techniques and computers. Moreover, the HFEGE potential offers an appealingly simple conceptual picture of the elusive, acutely nonclassical exchange interaction.

TABLE IV. Total integrated cross sections (in a_0^2) and eigenphase sums (in parentheses) for e-CO_2 scattering in the SEP approximation as described in the present text and in Ref. 1. The results are shown for the four dominant e-CO_2 symmetries and include elastic and rotational-excitation contributions. To obtain cross sections for comparison to experiment, these results should be summed across each row.

Energy (eV)	Σ_g	Σ_u	Π_u	Π_g
0.2	102.535	2.827	12.596	0.141
	(0.327)	(−0.068)	(0.075)	(−0.095)
0.5	37.309	2.932	12.918	0.111
	(0.295)	(−0.107)	(0.124)	(−0.007)
0.6	29.503	3.136	12.377	0.112
	(0.280)	(−0.120)	(0.133)	(−0.006)
1.0	14.743	4.258	9.563	0.126
	(0.222)	(−0.174)	(0.153)	(−0.001)
1.5	8.884	5.889	6.540	0.126
	(0.157)	(−0.242)	(0.157)	(0.003)
2.0	6.681	7.494	4.691	0.109
	(0.096)	(−0.310)	(0.155)	(0.003)

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