Elastic electron scattering by ethylene, C_2H_4

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We report first-principles calculations on the elastic scattering of low-energy electrons by ethylene, C_2H_4. We introduce a simple but effective method of representing polarization effects and show that it provides differential cross sections in close agreement with experiment.

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I. INTRODUCTION

As a prototypical polyatomic molecule, ethylene, C_2H_4, has been of interest from the earliest days of electron-molecule collision studies [1] and has continued to attract interest up to the present [2]. Recent careful and detailed measurements [3] of the low-energy elastic differential cross section (DCS) pose a challenge to theory, exhibiting features that have not been reproduced in high-level calculations [4–6], including our own. In particular, the calculated DCS fails to exhibit the local minimum that is observed in small-angle scattering above the energy of the π^* resonance. Buckman and Chadderton [7] and Kitajima and co-workers [8] have noted the ubiquity of similar minima in low-energy electron-molecule scattering and the desirability of improved calculations in this energy range.

The principal limiting approximations in calculations of electron-molecule elastic collision cross sections arise in the treatment of polarization effects—that is, the dynamic response of the target molecule to the presence of the projectile—and in the treatment of nuclear motion. Most calculations have been carried out in the fixed-nuclei approximation, which breaks down when the interaction time is long. An exception is the study of Trevisan and co-workers [5], who included the symmetric stretch vibration in the adiabatic approximation. Vibrational effects proved important in the immediate vicinity of the π^* resonance but were minor at higher or lower energies, and below ~ 8 eV, the results of Trevisan and co-workers, though the best computed values reported to date, do not agree in detail with the measurements, particularly at small scattering angles.

To improve our understanding of what is required to compute accurate electron-molecule cross sections in the low-energy range, we conducted an extensive study of low-energy elastic electron scattering by two small molecules that display low-energy shape resonances, N_2O and C_2H_4. In the course of our study, we examined vibrational effects to some degree, and we also experimented with different one-electron basis sets, but we focused on the representation of polarization as likely the most critical limiting factor. Results for N_2O will be reported separately. In this paper, we present results for C_2H_4 that demonstrate the effectiveness of a straightforward procedure for incorporating polarization effects. As will be seen, the procedure adopted is successful at capturing details of the low-energy DCS, including the small-angle minimum, that were not obtained in previous calculations.

II. COMPUTATIONAL DETAILS

Our electron-molecule collision calculations employ the Schwinger multichannel (SMC) method [9] in its parallel implementation [10,11]. General features of the SMC method may be found in the references; here we concentrate on the treatment of polarization. In the SMC method, as in others, polarization is represented through virtual excitations of the target molecule (closed channels). That is, in building an $(N+1)$-electron variational basis for the scattering calculation, one includes not only configurations of the type $\mathcal{A}\Phi_0\chi_i$, where Φ_0 is the N-electron ground state of the target molecule, χ_i a one-electron function ("scattering orbital"), and $\mathcal{A}$ an antisymmetrizer, but also configurations of the type $\mathcal{A}\Phi_n\chi_i$, built from excited states Φ_n, $n>0$. The Φ_n may be physical states of the target molecule, but they need not be; indeed, a long-standing focus of research has been the selection of Φ_n that provide compact and computationally convenient representations of polarization effects.

In scattering symmetries dominated by shape resonances, the "relaxed SCF" method of Rescigno and co-workers [12–14] has proven effective. This approach consists of employing only single excitations into "particle" virtual orbitals that have the same symmetry as the "hole" occupied orbital from which the excitation is made, while requiring that the scattering orbitals all belong to the shape-resonant symmetry. In our own work, we have used an even more compact description of polarization [15], with the same restrictions on the holes and particles but employing only a single scattering orbital that is constructed to be resonance like. It is noteworthy that both approaches aim to cope with the problem of overcorrelation—that is, to avoid an $(N+1)$-particle variational space that is "too good" relative to the description of the N-particle function Φ_0, which in most work to date is of Hartree-Fock quality, and that would therefore place the resonance energy too low. In nonresonant symmetries, by contrast, the challenge has been to develop representations of polarization that are good enough.

At long range, the electron-molecule interaction is decomposable into electrostatic multipoles, with the charge-induced-dipole potential being the leading polarization term, and this provides some guidance in the choice of closed-channel space. In particular, one may employ for Φ_n the polarized pseudostates [16], which are equivalent to the first-order wave functions that arise when Φ_0 is perturbed by a weak electric field. The polarized pseudostates provide an extremely (indeed, optimally) compact representation of long-range polarization, with the computational drawback that they can only be represented through extensive mixing of either N-electron configurations or one-electron orbitals. Rescigno and co-workers have developed a related "polarized self-consistent-field" (SCF) procedure [14,17] that employs single-configuration closed-channel states Φ_n. In the polarized SCF method, the virtual orbitals are transformed to bring the perturbative expansion of the polarization energy into as compact a form as possible. This prescription defines a particle space of three "polarized orbitals" for any given hole orbital. Because all but the smallest molecular problems involve multiple hole orbitals and one typically imposes orthogonality on the virtual orbitals, more than three particle orbitals per hole orbital are generally required, but in practice the space of Φ_n is generally expanded still further by using all of the polarized orbitals as particle orbitals for each of the hole orbitals, without regard to dipole coupling [5,14,17–21]. Although good and sometimes excellent cross sections can be obtained this way, the evident need to employ additional closed-channel terms beyond those implied by the procedure used to construct the polarized orbitals suggests that other perspectives may be relevant. Indeed, it should not be surprising if approaches based on the long-range, perturbative form of the electron-molecule interaction do not fully capture polarization, which after all encompasses stronger, short-range interactions as well.

Azevedo and co-workers have suggested [22–24] an alternative procedure in which polarization is represented using "effective configurations," which are actually multiconfigurational ($N+1$)-particle wave functions. These functions are constructed by diagonalizing an ($N+1$)-particle Hamiltonian and selecting its lowest-energy eigenstates for inclusion in the variational basis set used in the scattering calculation. Because some of the low-energy states are very diffuse and essentially noninteracting, and therefore make little contribution to polarization, a localization criterion is applied to ensure that only states having significant density near the molecule are selected. Besides the required diagonalization, the price one pays is, as with polarized pseudostates, the additional computational complexity entailed by multiconfigurational basis functions.

After exploring a number of different approaches to nonresonant polarization in C_2H_4, we tested a straightforward procedure that borrows concepts from both the polarized-orbital and effective-configuration methods and that appears to work quite well. Our starting point was the observation that the polarized orbitals are, by construction, well localized and valence like and that this character alone might be at least as important as their ability to represent the dipole response compactly. Accordingly, we used the modified virtual orbital (MVO) technique [25] to form valence like virtual orbitals localized near the molecule. The MVO technique removes a specified number of electrons from the Hartree-Fock ground state to form a cationic Fock operator and then diagonalizes that operator in the space of Hartree-Fock virtual orbitals to produce a transformed set of virtuals. In the spirit of the effective-configuration method, we then selected the lowest-energy MVO's as our particle space, and we formed the set of Φ_n consisting of all singlet-coupled single excitations from the occupied valence orbitals into that particle space.

To be specific, we used the $6\text{-}311++G(3d,2p)$ basis set as contained in the electronic structure program GAMESS [26], with default exponents for the diffuse functions and default splitting factors for the p and d supplements. All six Cartesian components of the d orbitals were retained. To provide additional flexibility in the scattering calculation, we augmented the basis set with 124 s Gaussians, all with exponent 0.036, arranged on a $5\times5\times5$ cubic grid centered on the molecule, with grid spacing 2.3 bohr units and with the point at the molecular center omitted to reduce linear dependence. The total number of contracted Gaussians in the basis set was 234. The ground state Φ_0 was described at the Hartree-Fock level, and the Hartree-Fock virtuals were transformed into MVO's using a 4+ cation operator. In forming closed-channel terms to describe polarization, the hole space included all six valence occupied orbitals. For the resonant $^2B_{2g}$ symmetry, we included all singlet- and triplet-coupled single excitations from any valence orbital into virtual orbitals of the same symmetry in the presence of a single scattering orbital, the lowest-energy b_{2g} MVO. In the nonresonant symmetries, we included all singlet single excitations from the 6 hole orbitals into a particle space comprising the 30 lowest-energy MVO's, with the entire set of virtuals used as scattering orbitals. The variational spaces for the scattering calculations thus contained 469 doublet configuration state functions (CSF's) for $^2B_{2g}$ symmetry and 5301, 4496, 4556, 5225, 5047, 4981, and 4593 CSF's for ^2A_g, ^2A_u, $^2B_{1g}$, $^2B_{1u}$, $^2B_{2u}$, $^2B_{3g}$, and $^2B_{3u}$, respectively. All calculations were carried out at the equilibrium geometry determined by recent high-level calculations [27].

III. RESULTS AND DISCUSSION

Our differential cross sections for elastic electron scattering by C_2H_4 are compared in Figs. 1 and 2 to measured values [3] and to the results of recent calculations [4,5]. We can note immediately that the present results do not agree with experiment in the vicinity of the π^* resonance (~1.5–2.5 eV), where the fixed-nuclei calculation makes the resonance too sharp and fails to distinguish vibrationally elastic and vibrationally inelastic channels. At both lower and higher energies, however, agreement with experiment is satisfactory. In particular, our calculated DCS at 1 eV, the lowest energy for which experimental values are available, agrees with the measurements within the quoted error bars, while at ~3–5 eV, our DCS displays the minimum or plateau evident in the small-angle experimental DCS. The calculation also reproduces well the shape of the measured DCS at larger scattering angles, including the location of the glo-
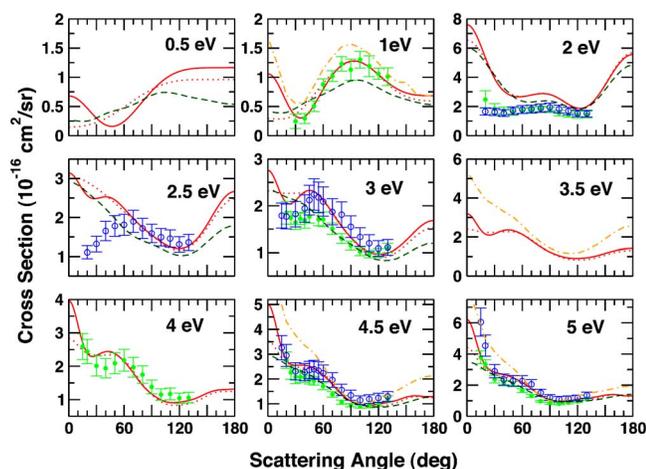
FIG. 1. (Color online) Differential cross sections for elastic scattering of low-energy electrons by C$_2$H$_4$. Calculated values are present work (solid line), results of Ref. [4] (dot-dashed line), and fixed-nuclei results of Ref. [5] (dashed line). The results shown at 3.5 and 4.5 eV for Ref. [4] were computed at 3.3 and 4.3 eV, respectively. Experimental values (solid and open circles) are from Ref. [3]; the open circles shown at 3, 4, and 5 eV were measured at 3.1, 4.1, and 5.1 eV, respectively. The dotted curve shows the effect of truncating the basis set in five symmetries (see text for discussion).

bal minimum, from 2.5 to 10 eV. The results of Trevisan and co-workers [5] also agree quite well with the measurements at most energies and angles, and near the resonance their results including vibrational motion (not shown in Figs. 1 and 2) are in much better agreement with experiment than the other calculations; however, they do not see the small-angle minimum above resonance, though there is perhaps some suggestion of a plateau in their results at 4.5 eV. The calculation of Brescansin and co-workers [4] appears to yield good results at 1 eV but may overestimate the forward scattering at higher energies.

Because the present calculation differs from previous work both in its treatment of polarization and in using a distributed basis set of s Gaussians, it is natural to wonder which factor accounts for the improvement in results. To address this question, we recomputed the ^2A_g, $^2B_{1u}$, $^2B_{2u}$, $^2B_{3u}$, and $^2B_{3g}$ scattering amplitudes using the same treatment of polarization but without the 124 distributed s functions in the one-electron basis set, and those results are also shown in Figs. 1 and 2. The greatest differences are seen at the lowest energies and smallest scattering angles, suggesting that the distributed basis is useful in improving the description of the long-range electron-molecule interaction. However, a minimum or plateau near 30° is still observed above resonance even without the distributed s functions, and indeed the agreement with the results from the larger basis set, and with experiment, is quite good in general. We therefore conclude that, although adding the s functions does improve the results, an adequate treatment of polarization is the most critical factor in obtaining qualitatively correct differential cross sections.

Integral cross sections for each symmetry component are shown in Fig. 3. The Ramsauer minimum originally reported
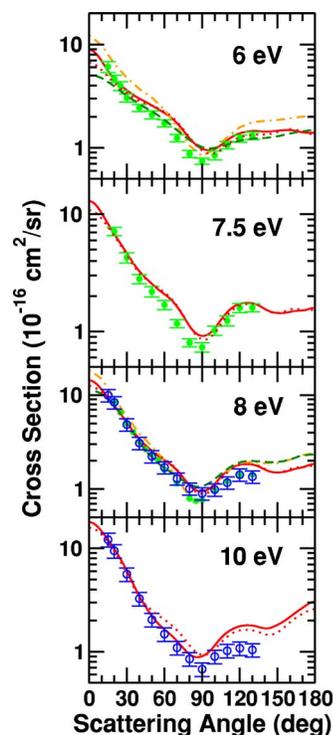

FIG. 2. (Color online) As in Fig. 1, at higher energies. The open circles shown at 8 and 10 eV were measured at 8.1 and 10.1 eV, respectively; the result from Ref. [4] shown at 6 eV was calculated at 6.1 eV.

by Schneider and co-workers [12] is clearly visible in the ^2A_g cross section. The prominent π^* resonance in $^2B_{2g}$ is centered at 2.0 eV, consistent with the recent measurements [3] but slightly higher than the 1.8 eV position obtained in earlier measurements [28,29], and in the calculation of
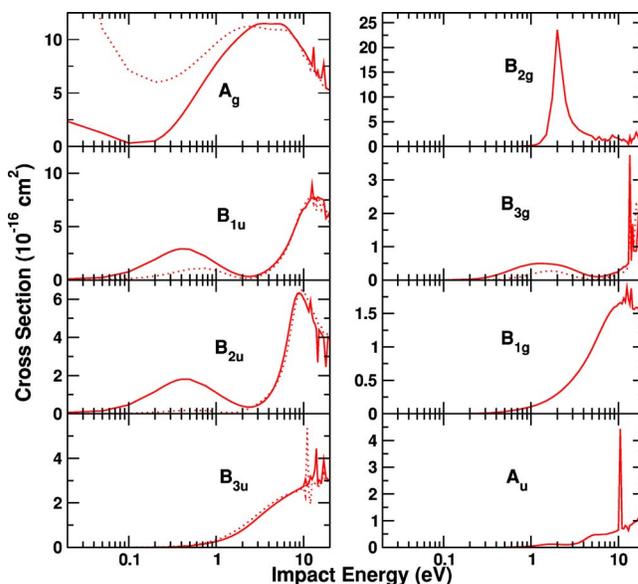

FIG. 3. (Color online) Symmetry components of the integral elastic cross section for electron scattering by C$_2$H$_4$. Solid line: present results. Dotted line: present results after truncating the one-electron basis set (see text for discussion).
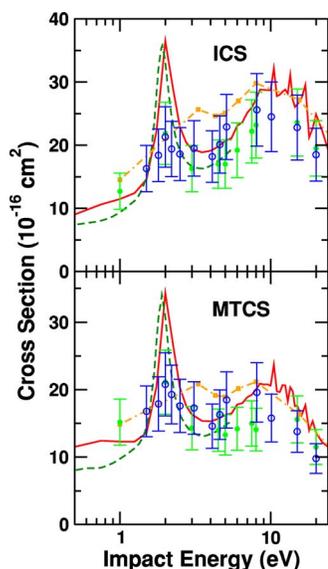
FIG. 4. (Color online) Integral elastic cross section (ICS) and momentum-transfer cross section (MTCS) for low-energy electron scattering by C_2H_4. Calculated results shown are present work (solid line), results of Ref. [4] (dot-dashed line with squares), and fixed-nuclei results of Ref. [5] (dashed line). Experimental points (solid and open circles) are from Ref. [3]. The estimated experimental uncertainty is 20%–25%; the error bars shown are ±22.5%.

Schneider and co-workers [12]. Trevisan and co-workers [5] obtain 1.85 eV with the nuclei fixed at the equilibrium geometry and 2.0 eV after vibrational averaging. The maxima in $^2B_{1u}$ and $^2B_{2u}$ at very low energy are noteworthy. These strong contributions by odd partial waves appear to be responsible for the anisotropy of the low-energy DCS seen in Fig. 1. By contrast, in the static-exchange approximation (omitting polarization), low-energy scattering is completely dominated by the s wave, and all symmetry components except ^2A_g go smoothly to zero at zero energy.

The integral elastic and momentum-transfer cross sections obtained from our calculation are compared to experimental [3] and calculated [4,5] values in Fig. 4. As expected on the basis of the DCS already presented, agreement is quite good up to 10 eV, except at the π^* resonance energy. The results of Ref. [5] also agree well with the experimental values. Above 10 eV, our cross sections are influenced by pseu-

doresonances, as already seen in Fig. 3, and it becomes more difficult to compare them to experiment. Such pseudoresonances arise because we are including excited electronic states in the calculation to describe polarization and are treating all excitation channels as closed, even above the lowest electronic-excitation thresholds. Pseudoresonance effects can be reduced by opening appropriate channels in the calculation; in ethylene, for example, we would expect $(\pi \rightarrow \pi^*)^1B_{1u}$ to be important, because of its large oscillator strength, and perhaps also $(\pi \rightarrow \pi^*)^3B_{1u}$. On the other hand, above 10 eV, the static-exchange approximation begins to be quite successful at predicting elastic cross sections, at least away from narrow resonances, and is very easy to apply.

IV. CONCLUSION

We have examined polarization effects in the computational treatment of low-energy electron scattering by the prototypical polyatomic molecule C_2H_4. Using the lowest-energy modified virtual orbitals as the particle orbitals proves to be a straightforward and effective way of constructing a compact particle space. The fact that the MVO's are ordered by energy provides a systematic way of varying the size of the closed-channel configuration space. Supplementing a standard molecular one-electron basis set with a distributed set of Gaussians appears to improve the computed results at near-forward-scattering angles and, at very low collision energies, has a large effect at all angles. However, obtaining the minimum near 30° in the DCS from ~ 3–5 eV proves to depend primarily on a thorough treatment of polarization rather than on extension of the one-electron basis set.

ACKNOWLEDGMENTS

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