

Accurate *Ab Initio* Treatment of Low-Energy Electron Collisions with Ethylene

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(Received 19 February 1991)

We report the results of a complex Kohn variational calculation of the low-energy electron scattering from ethylene, C₂H₄. Our calculations are the first to confirm the existence of the Ramsauer-Townsend effect in a molecule which possesses a permanent quadrupole moment and suggest that such minima may be found in electron-scattering cross sections for many nonpolar molecules. The calculations also reveal a low-energy shape resonance in ²B_{2g} symmetry at 1.83 eV, in excellent agreement with both beam and swarm measurements.

PACS numbers: 34.80.Bm

The scattering of low-energy electrons by atoms and molecules can be dominated by effects which depend critically on the balance of direct electrostatic interactions, electron exchange, and electron correlation. It is well known that the proper balance of these effects is needed to theoretically describe the Ramsauer-Townsend effect. Moreover, polarization of the electron cloud of a molecule as simple as H₂ produces an elastic cross section which is qualitatively different from the static-exchange (SE) value below 3 eV.¹ Shape resonances are also profoundly affected by electron correlation.² In most cases that have been investigated, the SE results place the position of shape resonances too high in energy and with too broad a width.³ This in turn causes vibrational excitation cross sections derived from SE calculations to exhibit too little vibrational substructure and to vary incorrectly with initial and/or final vibrational level of the target.⁴ The inclusion of target distortion and polarization, using *ab initio* optical potentials or pseudo-states, has been shown to correct the inadequacies of the SE approximation. This has been demonstrated in mole-

cules as diverse as H₂,¹ N₂,⁴ HCl,⁵ H₂CO,^{6,7} and CH₄.⁸ Recent complex Kohn variational calculations on H₂CO (Refs. 6 and 7) by the authors have produced good agreement with observations on the position and width of the ²B₁ resonant state of H₂CO⁻, as well as on the substructure seen in the available vibrational excitation cross section which is dominated by the C=O stretch vibrational mode.

In this Letter we report the results of an investigation of the collision of low-energy electrons with C₂H₄. The calculations were performed using the complex Kohn method. The complex Kohn method is an algebraic variational technique which characterizes the *T* matrix (scattering amplitude) as the stationary value of a variational functional. In this method, the trial wave function is expanded in terms of a set of square-integrable basis functions, along with regular and outgoing free functions that incorporate the correct asymptotic boundary conditions. Our implementation of the method has been described in detail in a number of earlier publications.⁹⁻¹² Correlation effects were included by using a trial wave function of the following form:

$$\psi(r_1, \dots, r_{n+1}) = A[\chi(r_1, \dots, r_n)F(r_{n+1})] + \sum_i c_i \Theta_i(r_1, \dots, r_{n+1}) \equiv P\psi + Q\psi, \quad (1)$$

where χ is the ground-state Hartree-Fock wave function of C₂H₄. The *Q*-space configurations Θ_i consist of particle-hole excitations of the Hartree-Fock target coupled to a virtual orbital representing the incident electron (two-particle-one-hole excitations). The size of *Q* space depends upon the size of the one-particle basis set used for the calculation and the scattering symmetry under consideration. For these calculations a *Q* space of 2000-3000 configurations may be considered typical. It is not necessary to solve for *Q* ψ explicitly. Rather, we incorporate the *Q*-space configurations into an effective optical potential by using Feshbach partitioning.¹¹

As with H₂CO, C₂H₄ has a low-lying shape resonance whose position and width are dramatically affected by target-distortion effects. The resonance is of ²B_{2g} symmetry and corresponds to the temporary capture of the incident electron into an empty, antibonding, valence orbital quite similar in character to the π_g^* orbital in N₂⁻. The most important *Q*-space configurations in the resonant symmetry are those particle-hole excitations of the *N*-electron-target core which preserve spatial symmetry. This core relaxation effect roughly corresponds to what would be obtained from a self-consistent-field calculation

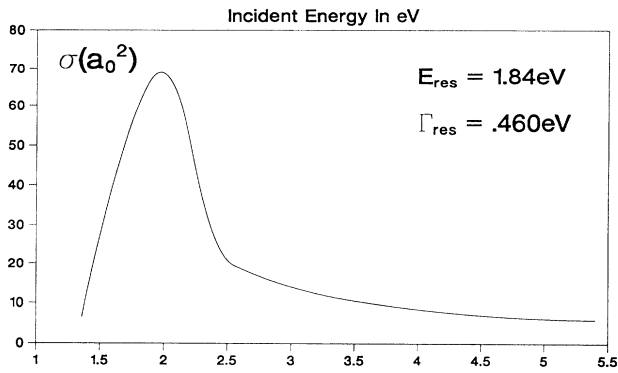


FIG. 1. ${}^2B_{2g}$ partial integrated cross section for e^- - C_2H_4 scattering.

on the $C_2H_4^-$ negative ion. Such a calculation includes the dominant physical effect present in a shape resonance: the distortion of the charge cloud of the target by the incident electron. Again, it is worth emphasizing that this distortion is a charge cloud rearrangement which preserves the symmetry of the N -electron system and should not be confused with the dipolar polarization which gives rise to an interaction potential which varies as a/r^4 at large electron-target distances. This latter interaction has often been modeled by a cutoff polarization potential which is tuned to reproduce the position of the resonance and then used to calculate the cross section at other energies. Using the resonance position to fix the cutoff parameter in a model potential may reproduce the short-range interaction fairly adequately but obviously this has little to do with the choice of the long-range form of the interaction.

The results of our optical-potential calculation are in excellent agreement with available experimental data. The position of the resonance given by the fixed-nuclei calculation is 1.83 eV with a width of 460 meV. Experiments by Burrow and Jordan,¹³ which are vibrationally resolved, give a vertical electron affinity of 1.78 eV. Although Burrow and Jordan did not give any estimate of the resonance width in their work, the vibrational peaks in the experiments suggest that $C_2H_4^-$ is shorter lived than N_2^- , which is also consistent with our calculated results.

In Fig. 1 we present the total cross section for ${}^2B_{2g}$ symmetry. This clearly shows the presence of the shape resonance and gives an indication of the size of the cross section around the resonance energy and its width. Although these calculations will surely be modified by the contribution of other symmetries to the cross section not shown in Fig. 1 and by vibrational effects due to nuclear motion, the qualitative features should still remain.

Of perhaps more interest are our findings in the totally symmetric 2A_g symmetry, which dominates the very low-energy electron-scattering cross section for C_2H_4 . In contrast to the resonant symmetry, the 2A_g -symmetry

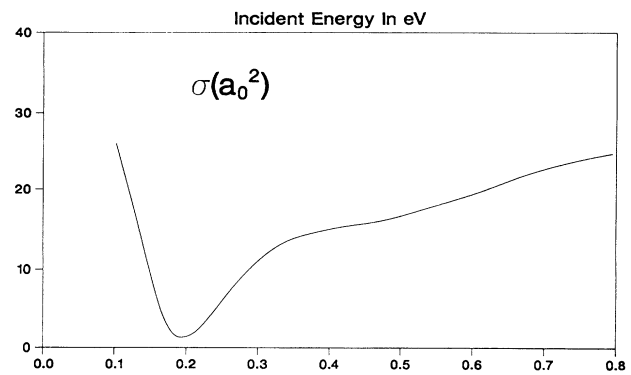


FIG. 2. 2A_g partial integrated cross section for e^- - C_2H_4 scattering.

cross section is profoundly affected by the dipolar distortion of the charge cloud of the neutral molecule by the incident electron. Calculations in this symmetry at the SE level do not show a Ramsauer-Townsend minimum, in accord with *ab initio* theoretical studies of electron scattering by other atoms and molecules. Results for the 2A_g cross section, including polarization, shown in Fig. 2, reveal the presence of a deep minimum in the cross section near 200 meV. This is characteristic of the Ramsauer-Townsend effect seen in many atoms and molecules. This is the first time such a Ramsauer-Townsend minimum has been theoretically predicted in a molecule with a permanent quadrupole moment. Indeed, there is some experimental evidence of a Ramsauer-Townsend minimum in C_2H_4 and in many other hydrocarbons as well.¹⁴

Boness *et al.*¹⁵ have carried out swarm experiments on C_2H_4 . Their data show a maximum in the transmission function for electrons through C_2H_4 near 200 meV, pro-

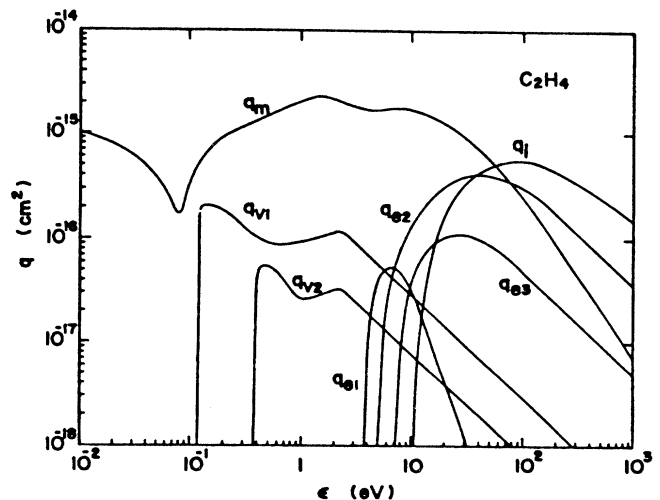


FIG. 3. Scattering cross sections for electrons in C_2H_4 from Ref. 16.

viding strong evidence for the presence of a Ramsauer-Townsend minimum in the total scattering cross section at or near this energy. Figure 3, taken from the recent work of Hayashi,¹⁶ reveals the presence of a deep minimum in the momentum-transfer cross section for C₂H₄ gas near 100 meV. Hayashi's work does not represent an independent experimental investigation of electron-scattering cross sections in molecular gases, but an analysis and "best estimate" of cross sections based on the data of other researchers. Both articles provide additional evidence for the existence of the Ramsauer-Townsend effect in C₂H₄.

The molecular dipole polarizabilities we have computed using the coupled Hartree-Fock method ($\alpha_x=3.09$, $\alpha_y=3.30$, $\alpha_z=5.92$) are in reasonable accord with available experimental data¹⁷ ($\alpha_x=3.78$, $\alpha_y=4.30$, $\alpha_z=6.00$) and other calculations.¹⁸ The variational scattering calculations have been repeated with a number of different basis sets. The presence of a Ramsauer-Townsend minimum was seen in all of the calculations, although the magnitude of the cross section and the exact position of the minimum depended weakly on the basis set used in the computation. Calculations of cross-section contributions from total symmetries other than 2A_g and $^2B_{2g}$ are currently underway. These contributions will be needed to evaluate accurate total and differential scattering cross sections. The results will be presented in a later publication, along with further details of the calculation.

This work was performed under the auspices of the U.S. Department of Energy by the Los Alamos and Lawrence Livermore National Laboratories under Contracts No. W-7405-ENG-36 and No. W-7405-ENG-48. The work at Ohio State University was supported by National Science Foundation Grant No. CHE-8922836

and the Ohio Supercomputer Center.

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