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Low-energy electron scattering from CH_3Cl

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The complex Kohn variational method is used to study low-energy electron collision processes involving CH_3Cl. The elastic differential and momentum transfer cross sections are studied from low electron energy (0.5 eV) through the resonance region (3.5 eV) to 10 eV. The effects of target correlation and polarization are studied. A comparison is made between the results of this study and experimental results available for this system. [S1050-2947(97)01510-2]

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I. INTRODUCTION

Electron collisions with molecular gases play a key role in a number of industrial plasma remediation processes currently under study [1]. Modeling of these systems have been hampered by the lack of comprehensive electron-impact cross section sets for reactive gases. We have made considerable progress over the past few years in developing accurate theoretical methods for computing low-energy electron-molecule cross sections and are presently engaged in a theoretical research effort to provide electron collision cross sections for a variety of industrially important gases. We have recently reported dissociation cross sections for CH_4 [2], Cl_2 [3], NF_3 [4], and HBr [5]; here we report the results of a theoretical study of low-energy electron-CH_3Cl scattering.

CH_3Cl is the simplest chlorohydrocarbon. The chloromethanes exhibit a range of dissociative attachment cross sections, with the CH_3Cl cross section believed to be almost six orders of magnitude smaller than CCl_4 [6–8]. Calculations of elastic electron scattering will help to quantify the characteristics of the resonant negative ion states that dominate the scattering in this class of molecules and provide a necessary first step towards a fully *ab initio* study of dissociative attachment in these systems. Furthermore, Shi *et al.* have reported differential and momentum transfer cross sections for low-energy electron scattering from CH_3Cl [9] that allow a detailed comparison between theory and experiment. Although model calculations have been performed on dissociative attachment in this system [10], to our knowledge no previous *ab initio* studies of electron-CH_3Cl scattering have been reported.

In this paper we report the results of *ab initio* calculations of $e^- + CH_3Cl$ collisions in the 0–10 eV energy range. We have used the complex Kohn variational technique [12,13] to calculate cross sections for elastic scattering and momentum transfer and have studied the effect of target correlation and polarization. Moreover, an integral technology that allows us to go beyond the primitive separable approximation for including the effects of electron exchange at low energies is applied here to a molecular target. The theoretical method is briefly outlined in the following section. The calculations and results are described in Sec. III. In Sec. IV we discuss our results in the light of previous experimental investigations.

II. THEORY

The complex Kohn method has been fully described in previous publications [11,12], so a lengthy description will not be repeated here. In this method, the fixed-nuclei scattering parameters are obtained from a stationary principle for the T matrix using a trial wave function constructed from both square-integrable (Cartesian Gaussian) and continuum basis functions, the latter used to incorporate physically correct, outgoing-wave boundary conditions. We will highlight those particular technical elements of the complex Kohn variational method that are relevant to the problem at hand.

In all our calculations we used a single-configuration, self-consistent-field (SCF) wave function for the ground state of the target. The scattering calculations were carried out at two different levels of approximation. We carried out static-exchange calculations; in this approximation, dynamic polarization of the target is ignored by using a trial function for the $(N+1)$-electron system that is simply the antisymmetrized product of the ground-state wave function and an additional scattering orbital. We also carried out calculations at the polarized-SCF level. This type of trial function was originally used in our study of low-energy $e^- + CH_4$ scattering [13], as well as in several later studies involving closed-shell polar molecules (H_2O [14], NH_3 [15], NF_3 [4], and H_2S [11]), where it was found to give a consistent treatment of correlation in the N- and $(N+1)$-electron portions of the problem. In this approximation, target distortion and polarization effects are introduced by including closed-channel terms in the trial function. These terms are generated as the direct products of unoccupied orbitals and configurations obtained by singly exciting the SCF target into a compact set of virtual orbitals. Instead of using all the Hartree-Fock virtual orbitals to define a space of singly excited configurations, only a subset of these orbitals, the polarized virtual orbitals, are used. This procedure, which is fully described in Ref. [13], greatly reduces the number of terms in the Kohn trial function by providing a small set of orbitals (generally, three for each occupied orbital that is polarized) while giving a value for the polarizability that is essentially the same as the value that would be obtained by single excitations of the occupied orbitals into the entire virtual space.

Another feature of the present calculations on CH_3Cl is our use of an effective core potential (ECP) to replace the inner-shell electrons of chlorine. Such potentials lead to significant computational savings by reducing the number of electrons that must be treated explicitly, while the cross sections are completely insensitive to the inner-shell electrons at the low collision energies of interest here. We have previously outlined an efficient numerical procedure for incorporating ECP's into the complex Kohn variational method [16] and applied this technique to electron scattering from HBr [5]. Further details on this procedure can be found in these two references.

One recent development employed here is a different technology for computing bound-free integrals that allows us to go beyond the primitive separable approximation for including the effects of electron exchange at low energies [17]. Since this technology is being applied here to a molecular target, we will give a brief description of the salient features. Our previous calculations have employed a ''primitive'' separable approximation to represent the exchange portions of the electron-target interaction:

$$V_{\mathrm{PS}}^{\mathrm{ex}} = \sum_{\alpha,\beta=1}^{N} |\alpha\rangle\langle\alpha|V^{\mathrm{ex}}|\beta\rangle\langle\beta|, \tag{1}$$

and only short-ranged functions are employed in the sums. As we have previously shown, this construction obviates the need for any free-free or bound-free exchange matrix elements since the continuum functions can be orthogonalized to the bound functions used to represent the exchange operator.

As an alternative to the primitive separable approximation for exchange, we consider a separable expansion of the form

$$V_{SS}^{\mathrm{ex}} = \sum_{\alpha,\beta=1}^{N} V^{\mathrm{ex}}|\alpha\rangle d_{\alpha,\beta}\langle\beta|V^{\mathrm{ex}}, \tag{2}$$

where

$$[d^{-1}]_{\alpha,\beta} = \langle\alpha|V^{\mathrm{ex}}|\beta\rangle. \tag{3}$$

This approximation, which forms the basis of the Schwinger variational method [18], is known to converge more rapidly than the primitive separable form given in Eq. (1) [19]. The use of Eq. (2) does require bound-free exchange matrix elements for its implementation, which in turn leads us to consider integrals of the form

$$\langle \eta_l b \| cd\rangle = \int\int d^3r\, d^3r'\, \eta_l(r)\varphi_b^B(r) \times \frac{1}{|r-r'|}\varphi_c^C(r')\varphi_d^D(r'), \tag{4}$$

where $\varphi_a^A(r)$ is an arbitrary Cartesian Gaussian function centered at A,

$$\varphi_a^A(\mathbf{r}) = (x-A_x)^l (y-A_y)^m (z-A_z)^n e^{-a(\mathbf{r}-\mathbf{A})^2}, \tag{5}$$

and η_l is a continuum basis function. If η_l is defined as the function obtained by operating with the outgoing-wave free-particle Green's function on a Gaussian,

$$\eta_l = N_l G_0^{+}\phi_l, \tag{6}$$

where

$$\phi_l = r^l e^{-ar^2} Y_{l,m}(\hat{\mathbf{r}}) \equiv \sum_{i,j,k=0}^{l} c_{ijk}^{l} x^i y^j z^k e^{-ar^2}, \quad i+j+k=l, \tag{7}$$

and N_l is a normalization constant, then we have shown that these integrals can be expressed as the Fourier transform of Gaussian two-electron integrals, where one of the Gaussians is a spreading wave packet

$$\langle n_l b\|cd\rangle = N_l \frac{1}{i}\int_0^\infty e^{iEt+\gamma_t}dt \sum_{\substack{i,j,k=0\\ i+j+k=l}}^{l} c_{ijk}^{l} \times \left[\int\int d^3\mathbf{r}\, d^3\mathbf{r}'\, x^i y^j z^k e^{-a_t r^2}\varphi_b^B(\mathbf{r}) \times \frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi_c^C(\mathbf{r}')\varphi_d^D(\mathbf{r}')\right], \tag{8}$$

with

$$a_t = a/(1+2iat), \quad \gamma_t = \left[-\frac{2l+3}{2}\right]\ln(1+2iat). \tag{9}$$

These integrals can be evaluated by modifying the algorithms in standard molecular integral codes to allow one Gaussian orbital exponent to be complex and the entire evaluation of bound-free exchange integrals can be reduced to one-dimensional numerical quadrature. For further details, we refer the interested reader to Ref. [17].

III. COMPUTATIONS

Variational calculations of elastic $e^- + CH_3Cl$ scattering were carried out in the fixed-nuclei approximation. All calculations in this study were performed at the equilibrium geometry of the target ($R_{\mathrm{CCl}} = 1.781$ Å, $R_{\mathrm{CH}} = 1.113$ Å, and $\theta_{\mathrm{HCCl}} = 110.5°$ [20]) in the reduced symmetry C_s. The basis set used to construct the target states consisted of Dunning's [21] $4s2p$ contraction of a $9s5p$ basis set for carbon with the addition of one d-type function ($\alpha = 0.75$) and Dunning's $2s$ contraction of a $4s$ basis set for hydrogen. The $1s$, $2s$, and $2p$ core electrons on chlorine were replaced with the *ab initio* effective core potential of Wadt and Hay and their $5s,4p,1d$ set [22] was used uncontracted to describe the remaining electrons. To construct the complex Kohn trial function, the target set was augmented with one diffuse s-type ($\alpha = 0.04$), one diffuse p-type ($\alpha = 0.04$), and one d-type ($\alpha = 0.2$) functions on carbon and one diffuse p-type ($\alpha = 0.06$) and one d-type ($\alpha = 0.25$) functions on chlorine. The computed dipole moment was 0.87 a.u. compared to the experimental value of 0.74 a.u. [23].

The complex Kohn variational calculations were carried out using trial functions built from the square-integrable ba-

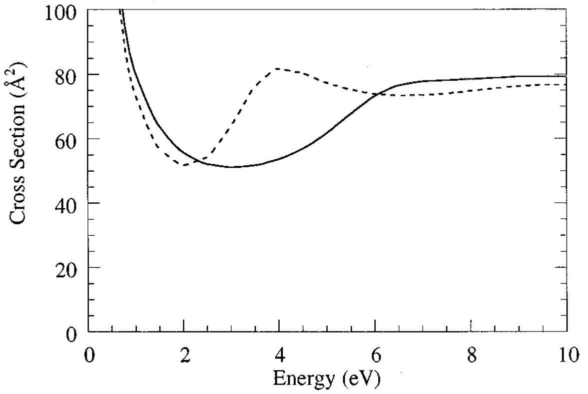

FIG. 1. Momentum transfer cross sections for $e^- + CH_3Cl$. Solid line, static exchange; dashed line, polarized-SCF result.

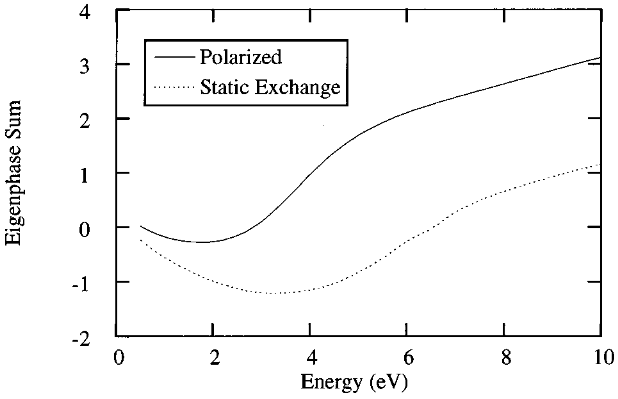

FIG. 2. $^2A_1$ eigenphase sums for $e^- + CH_3Cl$ computed at the polarized-SCF and static-exchange levels.

sis functions specified above along with continuum functions up to and including $l = 5$ and $|m| = 5$. For electronically elastic scattering by a molecule such as CH_3Cl that has a permanent dipole moment, the fixed-nuclei treatment must include the long-range electron-dipole interaction, which dominates the scattering at low energies and small scattering angles. To address this problem, we employed the same procedure we used in previous work on polar molecules: We used a closure formula based on the dipole-Born approximation to include contributions from the higher partial waves not explicitly included in the trial function [15].

For elastic $e^- + CH_3Cl$ scattering, we carried out complex Kohn calculations at both the static-exchange and polarized-SCF levels. In the polarized-SCF calculations, the three inner-shell orbitals, corresponding roughly to the carbon $1s$ and $2s$ and Cl $3s$ orbitals, were held doubly occupied and 13 polarized orbitals were generated from the outer five occupied orbitals. The value of the polarizability obtained from a single-excitation, configuration-interaction calculation using only the polarized orbitals was 4.38 Å^3, which is roughly 90% of the experimental value [24]. The differential and momentum transfer cross sections were obtained from the first-order Born-corrected T matrix, as outlined above.

Figure 1 shows the calculated momentum transfer cross sections at the static-exchange and polarized-SCF levels. The calculated cross sections at the more extensive polarized-SCF level show the presence of a broad $^2A_1$ shape resonance that appears near 3.5 eV. At the static-exchange level, the resonance behavior is much less pronounced, appearing only as a gradual rise in the cross section around 6.25 eV. This behavior is clearly seen from a comparison of the $^2A_1$ eigenphase sums in Fig. 2. The behavior of the resonance is further illustrated in Fig. 3, which shows the energy dependence of the elastic differential cross section at two fixed angles. For this figure, the polarized-SCF results are compared with the experimental values of Shi *et al.* [9]. At 100° the resonance peak is clearly evident, while at 30° the cross section is dominated by the contribution of the dipole scattering, which masks the resonance peak.

Figure 4 shows a composite of the elastic differential cross section from 5° to 180° for a series of energies. For comparison, we show both calculated polarized-SCF and simple dipole-Born results along with experimental values. The cross section shows the characteristic forward peaking that is typical of a polar molecule. However, in the resonance region, the polarized-SCF calculations as well as experiment show that the differential cross section develop a weak secondary shoulder at higher angles.

Although the agreement between theory and experiment is reasonable, there is a noticeable deviation in absolute magnitude at the two lowest energies shown in Fig. 4, where the dipole-Born result actually agrees better with experiment than the variational results. This is a little disturbing since the scattering at these energies is insensitive to the inclusion of target polarization, being dominated by the long-range dipole. As a further test of the accuracy of our procedures, we therefore repeated the calculations at these two energies using the more accurate treatment of exchange outlined in Sec. II. (Calculations at the higher energies using the Schwinger form gave results virtually identical to the primitive separable exchange results.) The McMurchie-Davidson algorithm [25] was modified to evaluate the complex bound-free integrals required in Eq. (8) and the Schwinger form of the exchange operator [Eq. (2)] was used in computing the free-free exchange integrals. Figure 5 compares the results of these calculations with the primitive separable results. Evi-

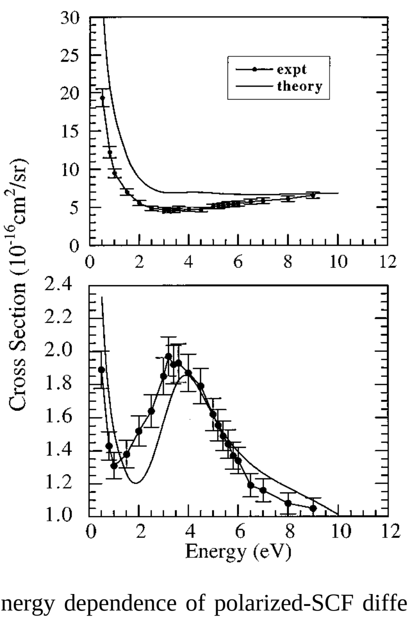

FIG. 3. Energy dependence of polarized-SCF differential cross sections for elastic $e^- + CH_3Cl$ scattering at fixed angles. Upper panel, 30°; lower panel, 100°.

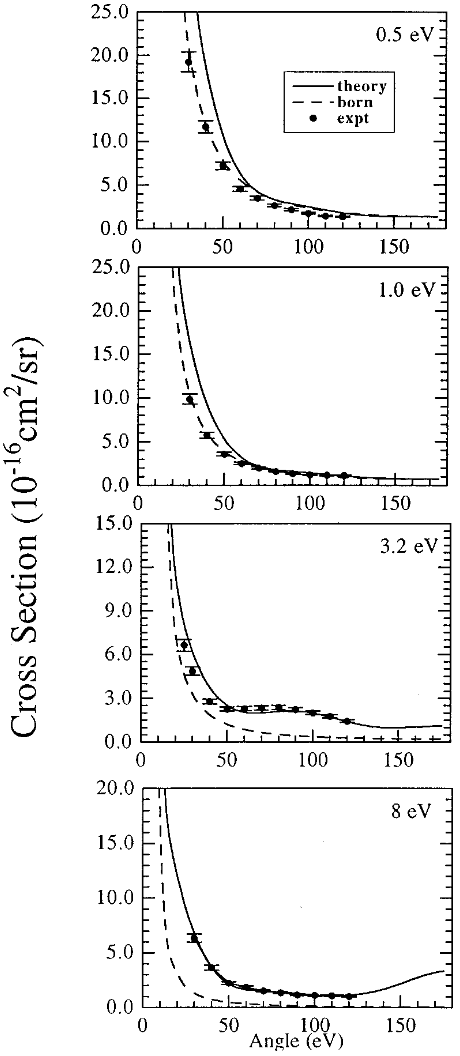

FIG. 4. Differential cross sections for elastic $e^- + CH_3Cl$ scattering at several energies. Solid lines, polarized-SCF results; dashed lines, dipole Born approximation; dots, experiment [9].

dently, the results are quite close. We conclude that the good agreement between the dipole-Born approximation and experiment at these energies is fortuitous and that we have to improve our description of the target ground-state wave function beyond the SCF level to achieve a more accurate result.

IV. CONCLUSION

In summary, we have carried out *ab initio* calculations of low-energy electron-CH_3Cl scattering using the complex Kohn variational technique. Calculations were carried out at the static-exchange and polarized-SCF levels using a Hartree-Fock description of the target wave function. Electron exchange effects were described using both primitive separable and more elaborate Schwinger separable forms of the exchange operator and, in this case, the two different approximations gave very similar results. The momentum-transfer cross section we obtained shows a broad shape resonance near 3.5 eV, which is associated with dissociative electron attachment. Future calculations will address the geometry dependence of the resonance parameters as well as the determination of dissociative attachment cross sections.

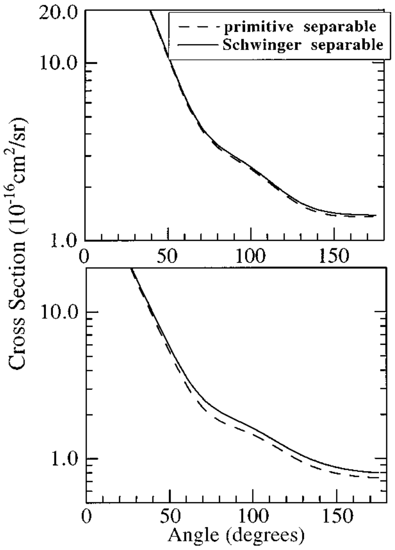

FIG. 5. Comparison of polarized-SCF differential cross sections for $e^- + CH_3Cl$ scattering calculated using the primitive separable exchange approximation (dashed lines) and the Schwinger approximation for exchange (solid lines). Upper panel, 0.5 eV; lower panel, 1.0 eV.

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