Reaction and Scattering in Cold Electron Collisions

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Experimental data are presented for the scattering of electrons by CCl_4 between 8 and 200 meV impact energy. These results are used in conjunction with data for the reactive process, yielding Cl^-, to study the low energy behavior of a system which simultaneously displays both reactive and elastic scattering channels. Phase shifts are derived and illustrate how channel competition develops as the energy falls. This behavior and the involvement of vibronic effects at impact energies above ~30 meV pose a challenge to theory.

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The scattering and attachment of low energy electrons by atomic and molecular targets display fundamental quantum phenomena [1–5], such as virtual state scattering [6,7], giant resonances [8], and Feshbach resonances [9]. This field is intimately related to the general field of cold collisions involving heavy particles, since the de Broglie wavelengths of low energy electrons and cold atoms are comparable and interactions tend to be governed by asymptotic long range potentials [10]. We discuss in the present work experimental results which illustrate a qualitatively new aspect of cold collisional phenomena, in which elastic and reactive scattering occur side by side as competing channels.

Data are reported here for low energy collisions of electrons with CCl_4 in the energy range between 8 and 200 meV. Dissociative attachment (DA) of electrons to CCl_4, yielding Cl^- and CCl_3, an exothermic process at all collision energies, has been very extensively studied [2,3]. The present data record the total scattering cross section, involving the sum of both reactive and elastic channels in the cold collision regime, for which there are no data in the literature.

The experimental system has been described in detail elsewhere [1,6,11]. Synchrotron radiation from the ASTRID storage ring at the University of Aarhus is focused into a cell containing Ar. Radiation is tuned to an energy of 15.75 eV, yielding photoelectrons, through threshold photoionization, of 2 to 3 meV in energy. The energy resolution of the photoelectrons is determined by the resolution of the beam line monochromator, set here to be between 0.9 and 1.6 meV at full width half maximum. Electrons are formed into a beam and pass through a room temperature sample of CCl_4 vapor. The intensity of the electron beam, in the presence and absence of target gas, is recorded at a channeltron, as a function of electron energy. This yields the variation of the total integral scattering cross section for both elastic and reactive collisions, $\sigma_{T,I}$, via $\sigma_{T,I} = (Nl)^{-1} \ln(I_0/I_t)$ where N is the target gas number density, l is the path length in the gas, and I_0 and I_t are, respectively, the intensities of the incident and transmitted electron beams. Electron energies are calibrated by comparison with data for N_2 and at low energies are accurate to between ±1 and ±2 meV [1].

In separate measurements, an axial magnetic field of strength $\sim 2 \times 10^{-3}$ T may also be introduced. Under these conditions, those electrons which are elastically scattered into the backward hemisphere are recorded as lost to the incident beam. Those that are forward scattered are guided onto the detector and therefore do not contribute to the measured cross section. Electrons which attach to CCl_4 to form Cl^- are also lost to the beam, as in experiments in the absence of the axial magnetic field. The trajectories of the product ions are not materially affected by the weak magnetic field in the system. The small average solid angles subtended by the apertures in the collision cell ensure that a negligible fraction of negative ions escape from the cell, in the presence or absence of the magnetic field.

Experimental results are shown in Fig. 1, for cross sections obtained both in the absence $\sigma_{T,I}$ and presence $\sigma_{T,B}$ of the magnetic field. Data at energies up to 3 eV are available on request and agree within experimental error with data in [12–14]. Cross sections represent events which lead to loss of current in the incident beam, including elastic scattering and, in principle, both dissociative attachment to form Cl^- and attachment to form CCl_4^-, with subsequent loss of the electron but without dissociation. Orient *et al.* [15] have however shown that once an electron has attached to CCl_4, CCl_4^- always survives for a sufficient time for the species to cross through the neutral molecule potential before autodetachment can occur, up to energies considerably in excess of those considered here [16]. Thus attachment and dissociative attachment are indistinguishable in the reactive channel. With this in mind, cross-section measurement in the absence of the magnetic field records the sum of the integral elastic and the reaction cross section, $\sigma_{T,I} = \sigma_I^{el} + \sigma_I^r$. In the presence of the axial magnetic field the cross-section measurement records the elastic backward

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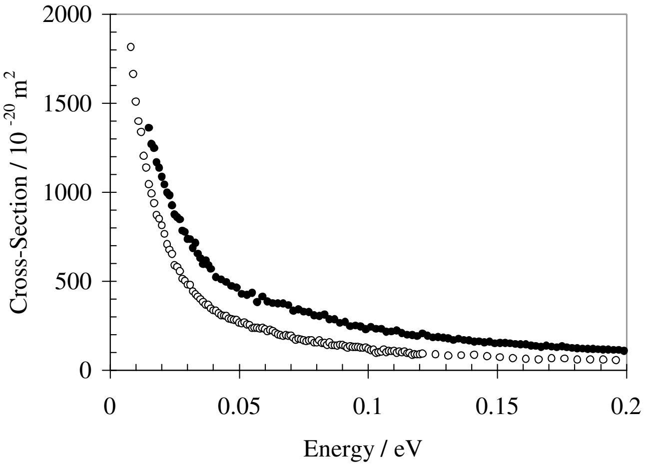

FIG. 1. Total integral $\sigma_{T,I}$ (upper set) and backward $\sigma_{T,B}$ cross sections (lower set) for scattering of electrons by CCl_4 as a function of electron impact energy. Errors in the cross sections are ±8% at the lowest energies, falling to ±5% at energies above ~20 meV.

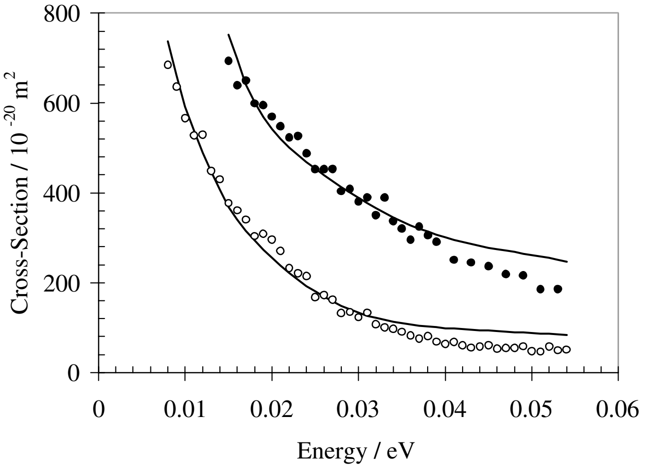

FIG. 2. Elastic integral σ_I^{el} (upper set) and backward σ_B^{el} scattering cross sections (lower set) for scattering of electrons by CCl_4 as a function of electron impact energy. Errors in the cross sections are ±8% at the lowest energies, falling to ±5% at energies above ~20 meV. The curves show the result of fitting using Eqs. (3) and (4), as described in the text.

scattering cross section, into the backward 2π steradians, plus the integral cross section in the reaction channel, $\sigma_{T,B} = \sigma_B^{\mathrm{el}} + \sigma_I^r$.

In recent work [3], accurate estimates have been made of the variation of the cross section for the reactive (DA) channel in CCl_4, with an energy resolution very comparable to that of our scattering data. Thus by subtracting data in [3] from our data in Fig. 1, we obtain the elastic contribution to the integral σ_I^{el} and backward σ_B^{el} scattering cross sections for collisions of electrons with CCl_4. Resulting elastic cross sections up to ~55 meV (see below) are shown in Fig. 2.

We set out to extract the s- and p-wave phase shifts from the experimental data in Fig. 2. The theory of collisions exhibiting both reaction and scattering has been treated, for example, in [17,18] in terms of scattering by complex potentials. The system is treated for elastic scattering and reaction in a complex central force field, in other words without reference to structure in the target. Thus the target is viewed as pointlike to the incoming long wavelength de Broglie wave. We neglect vibration in the target, to which we return below. In addition, in the case of CCl_4 the intermediate bound state is of ${}^2A_1$ symmetry (see [3] and references therein) and we consider scattering only involving this symmetry. The absence of other spin surfaces implies that all significant exchange effects are included in the formalism below.

We use the standard expression for the scattering amplitude [19], and write the S matrix, S^l, for the lth partial wave in the form

$$S^l = \epsilon_l \exp(2i\eta_l), \tag{1}$$

where η_l is the partial wave phase shift and ϵ_l describes the inelastic attachment channel in the angular momentum representation [20,21]; thus ϵ_0^2 may be identified with $|S_0|^2$ of Eq. (7) in [20] [see also Eq. (5) below]. ϵ_l essentially dictate the relative importance of reaction and scattering as a function of energy. The cross section for elastic scattering, for s and p waves, may then be shown to be

$$\sigma^{\mathrm{el}}(\theta) = \frac{\pi}{2k^2}\{1 + \epsilon_0^2 - 2\epsilon_0\cos 2\eta_0 + 6\cos\theta[\epsilon_0\epsilon_1\cos 2(\eta_0 - \eta_1) - \epsilon_0\cos\eta_0 - \epsilon_1\cos\eta_1 + 1] + 9\cos^2\theta(1 + \epsilon_1^2 - 2\epsilon_1\cos 2\eta_1)\}, \tag{2}$$

where the azimuthal angle has been integrated out, and where the cross section is evaluated at the scattering angle θ. k is the magnitude of the wave vector where $k = \sqrt{2E}$ (atomic units, $\hbar = m = e = 1$, are used throughout unless indicated otherwise). It follows that the integral scattering cross section is

$$\sigma_I^{\mathrm{el}} = \frac{\pi}{k^2}(4 + \epsilon_0^2 + 3\epsilon_1^2 - 2\epsilon_0\cos 2\eta_0 - 6\epsilon_1\cos 2\eta_1), \tag{3}$$

and the backward scattering cross section

$$\sigma_B^{\mathrm{el}} = \frac{\pi}{2k^2}\{1 + \epsilon_0^2 + \epsilon_0\cos 2\eta_0 + 3[\epsilon_1^2 - \epsilon_1\cos 2\eta_1 - \epsilon_0\epsilon_1\cos 2(\eta_0 - \eta_1)]\}. \tag{4}$$

At very low energy, below 15 meV, it turns out that the p-wave phase shift is very close to zero and Eqs. (3)

and (4) may be used to obtain s-wave phase shifts directly.

The integral reaction cross section is given by

$$\sigma_I^r = \frac{\pi}{k^2}[4 - \epsilon_0^2 - 3\epsilon_1^2]. \quad (5)$$

In the absence of vibronic phenomena, only s-wave attachment is allowed in CCl_4, since only the s wave has the A_1 symmetry of the lowest unoccupied molecular orbital (LUMO) under the operations of the tetrahedral (T_d) point group. Thus $\epsilon_1 = 1$ in Eqs. (1)–(5) and values of ϵ_0 may be trivially derived, using Eq. (5), from experimental values of the attachment cross section [3].

Equations (3) and (4) are now used to derive phase shifts for s and p waves for the combined DA and elastic scattering processes, thus fully characterizing the collision process. We seek to fit simultaneously the integral and backward elastic scattering cross sections in Fig. 2, by choosing a suitable set of s- and p-wave phase shifts, η_0 and η_1, vs electron collision energy. This is done by expressing the phase shifts as polynomial expansions in k and varying the coefficients of this expansion, as described in [6]. Fits were performed up to energies associated with the Raman active mode at 56.9 meV. This limit was chosen because, at around this energy, the cross section for the reactive channel shows structure associated with this vibration. Results are shown in Fig. 2, which demonstrates that a good fit may be achieved with Eqs. (3) and (4) and experiment up to an energy of ~30 meV.

s- and p-wave phase shifts corresponding to the fits in Fig. 2 are shown in Fig. 3 and demonstrate, for example, that the p wave is strongly excluded at low energy. Values of phase shifts are given modulus π and, from our analysis, we are only able to determine that the signs of the s-wave and p-wave phase shifts are the same. A positive sign is adopted as required by theory [22].

The s-wave phase shifts in Fig. 3 reflect the combined character of scattering and reaction. The phase shift rises as energy falls, as required for a system possessing a bound state in the potential governing the collision [22]. The derived phase shifts do not discriminate between scattering and reaction, because these channels are not independent. This can be seen through the presence of ϵ_0 and ϵ_1, the former derived from attachment cross sections, in Eqs. (3) and (4) for elastic scattering. This interdependence of reactive and scattering channels, introduced at the scattering amplitude level through the S matrix, arises despite the fact that the two channels are very different in aspect, in the one case with the output channel characterized by a free scattered electron and in the other with the electron attached to a Cl atom with a CCl_3 fragment. We also note that the ratio of scattering to reaction cross section is a governing factor in the detailed behavior of the s-wave phase shift with energy. This ratio becomes constant within experimental error at our lowest energies and, as seen in Fig. 3, this causes η_0 also to remain approximately constant in this energy range. This again exemplifies how the variation of η_0 reflects both scattering and reaction.

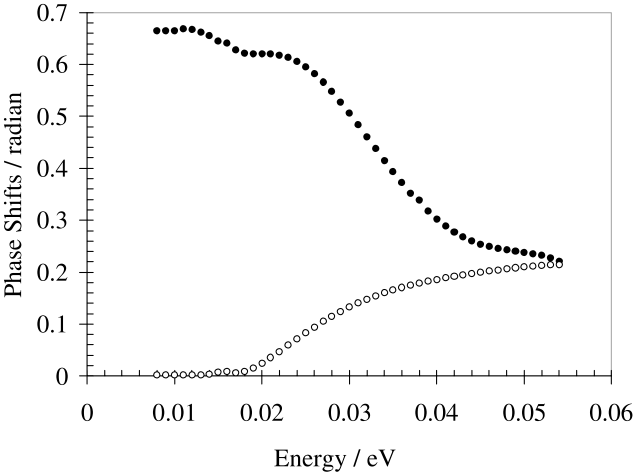

FIG. 3. s-wave (solid circles) and p-wave (open circles) phase shifts for $e^- + CCl_4$ reactive and elastic scattering derived from fitting procedures described in the text. Errors associated with the phase shifts are ±5%.

The behavior of the s-wave phase shift in Fig. 3 may be compared with that encountered in electron scattering by CO_2 [7]. In the case of CO_2, virtual state scattering takes place, and the s-wave phase shift drops rapidly at low energy, falling from 0.29 rad (modulus π) at 50 meV impact energy to 0.16 rad at 10 meV, in qualitative contrast to the present case.

Referring to Fig. 2, we have found that it is not possible to achieve a consistent fit between backward and integral data above ~30 meV. We now consider possible sources of this discrepancy. In this dynamical system, the presence of the incipient s-wave attachment must virtually lower the symmetry of CCl_4 from T_d to C_{3v} in the dissociation channel. In other words, the target becomes a superposition of structures which are both T_d and C_{3v}. As the symmetry of this virtual scattering state assumes some C_{3v} character, the p_z wave comes to possess A_1 character, since p_z transforms as A_1 under the symmetry operations of C_{3v}. Therefore the p_z wave may interact with the residual A_1 contribution to the LUMO of CCl_4. This is analogous to the reverse behavior in CO_2 [7] and CS_2 [8] in which p-wave attachment is allowed, thereby virtually letting in the s wave through virtual excitation of bent states of the target, in virtual state scattering [7]. The phenomenon here of "p-wave leakage" will tend to occur at higher energies, where the p wave has a more powerful interaction with the target. The inclusion of p-wave attachment would cause the value of ϵ_1 to differ from unity. This has the result that our values of ϵ_0 may be increasingly in error at higher energies.

Remaining within the T_d description, we may also consider vibronically allowed processes. CCl_4 possesses an A_1 symmetric stretch at 56.9 meV, a C-Cl bending mode of E symmetry at 26.9 meV, and T_2 asymmetric stretch and deformation modes, respectively, at 92.2 and 38.9 meV [23]. The doubly degenerate Raman active vibration at 26.9 meV possesses one unit of angular momentum [24]. Under the action of the T_d point group, p waves (of T_2 symmetry) could therefore interact with CCl_4 to yield d waves attached to CCl_4, since $d_{xy,xz,yz}$ are also of T_2 symmetry. The direct product of T_2 with T_2 has an irreducible representation E, which therefore overall yields an irreducible representation A_1 for the vibrationally excited CCl_4^- intermediate. Attachment of p waves therefore becomes vibronically allowed. These processes are not included in our analysis and may be a further cause of departure between experiment and theory at energies above 30 meV. In addition, at 300 K, 11% of the population is in the first excited state of the Raman 26.9 meV vibration. The vibronic symmetry of these excited molecules is $A_1 \times E$, that is, E. Thus d waves, $d_{x^2-y^2}$, also of E symmetry under T_d, could attach at higher energies. There is also a 10% thermal population of the T_2 vibration at 38.9 meV. Both p and d waves can interact with this population in the reaction channel. We recognize that these arguments are purely qualitative, since it is not clear to what extent T_d symmetry contributes to the target wave function in the presence of E and T_2 distorting vibrations. These considerations suggest however that if experiments were performed with target gas at low temperature, higher cross sections might be encountered than those recorded in [3]. With respect to very low energy vibrationally inelastic (superelastic) collisions with excited state populations, processes are of too low a cross section to influence our data significantly.

In conclusion, our data show, through a simple partial wave analysis, the strong competition between reaction and scattering in a cold collision, in a manner which has not previously been possible. The analysis is limited in that only electronic effects have been included. Derived phase shifts nevertheless provide valuable data for comparison with future theory. However the present results also point the way to a wealth of vibronic phenomena, such as the proposed p-wave leakage and vibronic attachment. Theory should now aim to assess the importance of these channels. Our present symmetry-based analysis shows only that these mechanisms are plausibly involved in the reaction channel, not that they necessarily make a significant contribution to the cross section.

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