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Very low energy electron collisions with molecular chlorine

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Abstract. Electron transmission experiments are reported involving the measurement of absolute total cross-sections for scattering of electrons by Cl_2 for energies between 20 meV and 9.5 eV, with an energy resolution in the incident electron beam of between 3 and 4 meV full-width half-maximum. These data represent the first absolute values of scattering cross-sections recorded for Cl_2. Results are also reported for scattering in the presence of an axial magnetic field of 20 G over an energy range which extends from 16 meV to 250 meV.

Strong evidence is found for electron attachment at very low impact energies, in agreement with the results of other groups. Data suggest that attachment occurs through the p-partial wave. A resonance in the form of a doublet in the total scattering cross-section has been found between 70 and 200 meV. This structure is absent in the spectrum obtained in the presence of an axial magnetic field.

A qualitative mechanism is suggested for the formation of the observed structure involving virtual excitation of the first vibrational quantum of Cl_2. The doublet nature of the resonance is attributed to the intervention of the excited Π-states of Cl_2^-. The plausibility of the proposed mechanism could be checked by accurate calculations of excited state potentials for Cl_2^- and by measurement of the yield of Cl^- ions as a function both of the electron energy and the temperature of the target gas.

1. Introduction

The study of low energy electron scattering from molecular chlorine has attracted very limited experimental and theoretical attention in recent years, despite its wide use in the plasma etching of semiconductors and its importance in the perturbed chemistry of the polar stratosphere (Wayne 1991). The present work reports the first measurements of absolute cross-sections for the scattering of electrons from molecular chlorine. However, cross-sections for dissociative electron attachment have been measured by Cener and Mandl (1972), Kurepa and Belić (1977, 1978), Tam and Wong (1978), Kurepa *et al* (1981) and Azria *et al* (1982). Spence (1974) also located the energetically lowest-lying Feshbach resonances around 7.5–8.0 eV using an electron transmission spectrometer. Momentum transfer cross-sections have been derived from Boltzmann analysis and early swarm measurements, by Rogoff *et al* (1986). To our knowledge, the only theoretical study of the scattering of electrons from Cl_2 is by Rescigno (1994). The calculated cross-sections of Rescigno (1994) are compared with our data in section 3.

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The present work concerns electron transmission studies in the range of electron energy between a few meV and ∼10 eV, concentrating upon the very low energy regime below a few hundred meV. Absolute scattering cross-sections are reported both in the presence and absence of an axial magnetic field. The apparatus is briefly described in section 2. Experimental results are presented and discussed in section 3.

2. Apparatus

The apparatus is described in detail in Gulley *et al* (1998) and is based upon that described by Field *et al* (1991). Briefly, the system consists of a photoionization source for the production of low energy monochromatic electrons, electrostatic optics to form a beam of variable energy, a collision cell containing the target gas and a channel electron multiplier for recording the electron current. The whole system can be immersed in an axial magnetic field, which is typically set to 20 G. The primary electrons are formed by photoionization of argon, close to threshold, using monochromatized synchrotron radiation from the Daresbury Synchrotron Radiation Source (SRS, Daresbury Laboratory, UK), at 78.65 nm (Radler and Berkowitz 1979), using the 5 m McPherson normal-incidence monochromator on the VUV3.2 beamline. The energy resolution of the electrons is determined by the photon bandwidth of the ionizing radiation, in this case ∼ 0.2 Å, yielding an effective electron energy resolution of 3.5 meV FWHM (Field *et al* 1988). The electrons are formed into a beam using a weak DC draw-out field across the photoionization chamber and focused into a field-free collision chamber in which the target gas is contained.

Absolute cross-sections are measured through attenuation of the incident beam and evaluated using the Beer–Lambert law:

$$I(t) = I(0)\exp(-\sigma n l) \tag{1}$$

where $I(0)$ and $I(t)$ are the unattenuated and attenuated electron currents, respectively, σ is the scattering cross-section (see below), n is the target gas number density and l is the effective electron path length. The pressure in the target cell was measured with an Edwards 655 capacitance manometer. Pressures were chosen such that multiple scattering did not make an appreciable contribution. The measured cross-sections are placed on an absolute scale by calibrating the apparatus against the theoretical helium cross-sections of Saha (1993), using a procedure described in detail in Randell *et al* (1994). The absolute uncertainty (one standard deviation) in the measurements is estimated to be ±8%, taking into account the uncertainties in the pressure measurement, small random fluctuations in the measured electron beam intensities, and the uncertainty associated with absolute calibration to the helium cross-section.

In the absence of the magnetic field, the cross-section obtained using expression (1) is the total cross-section, σ_t, involving all elastic and inelastic events so far as the geometry and potentials in the system allow. In this connection, a retarding lens element beyond the collision chamber is used to reject any electrons that have lost energy through inelastic scattering in the collision chamber but are forward scattered into a small solid angle and pass through the exit hole of the collision chamber (Johnston and Burrow 1982, Gulley *et al* 1998). In the presence of the axial magnetic field, any electrons scattered into the forward hemisphere by the target gas are realigned to perform forward moving helical trajectories around the axis of the field and are detected as unscattered. The apparatus then determines cross-sections for scattering between 90° and 180°, which are termed total backward scattering cross-sections, σ_b, the term ‘total’ implying that all types of events that lead to backward scattering are included in the cross-section. Above a certain energy, electrons scattered at close to 90° will have transverse energies giving a spiral path with a diameter such they cannot pass through the exit hole of the target gas cell. For electrons on axis, this energy is ~800 meV, but the energy is lower for off-axis incident electrons. The energy to which absolute backward scattering cross-sections are reliable has been determined experimentally to be ~650 meV, by comparison of our observed values of scattering cross-section with differential cross-sections given in Sun *et al* (1995) integrated between 90° and 180°.

An additional problem arises in the current work, since electron attachment takes place when very low energy electrons encounter chlorine. The cross-sections derived from equation (1) in the presence of a magnetic field cannot then be associated with scattering into the angular range 90°–180°, as discussed in section 3. Nevertheless, for simplicity we continue to refer to cross-sections measured in the presence of the magnetic field as backward scattering cross-sections, even in the very low energy regime in which electron attachment may dominate the scattering.

The absolute electron energy scale is calibrated by observing the peak in the N_2^- $^2\Pi_g$ resonance at 2.442 eV (Kennerly 1980). The energy of this resonance peak is known not to depend on scattering angle and is therefore a good calibrator for experiments with and without the magnetic field present.

3. Results and discussion

Experimental results are displayed in figures 1–4. Figure 1 shows an overview of the total scattering cross-section up to 9.5 eV, illustrating the rapid rise in cross-section at very low energy, a double-peaked resonance around 100 meV and a maximum in the higher energy scattering around 7.55 eV in the region of the Feshbach resonances recorded in Spence (1974). Since there is relatively little contribution to the total scattering cross-section from inelastic events in the energy range between 200 meV and 9.5 eV, our data may be compared

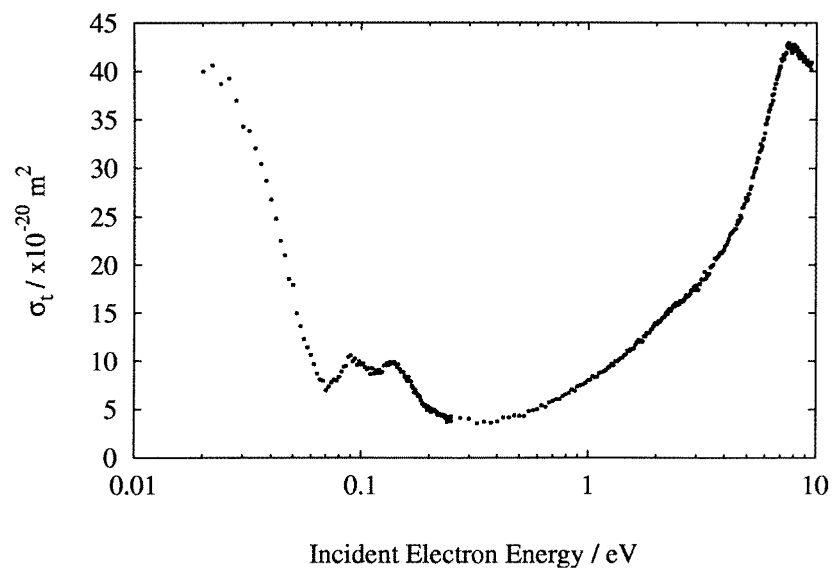

Figure 1. An overview of the variation of the total scattering cross-section for Cl_2 with electron kinetic energy between 20 meV and 9.5 eV.

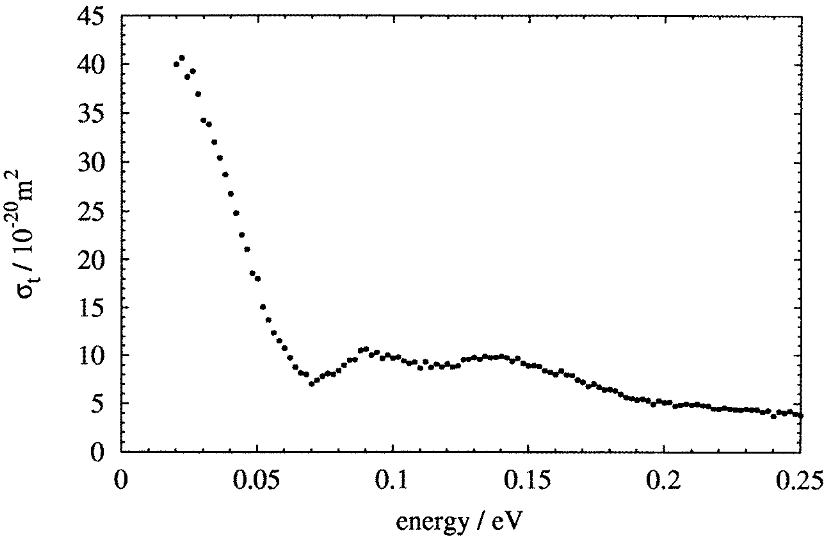

Figure 2. The variation of the total scattering cross-section for Cl_2 with electron kinetic energy in the low energy regime.

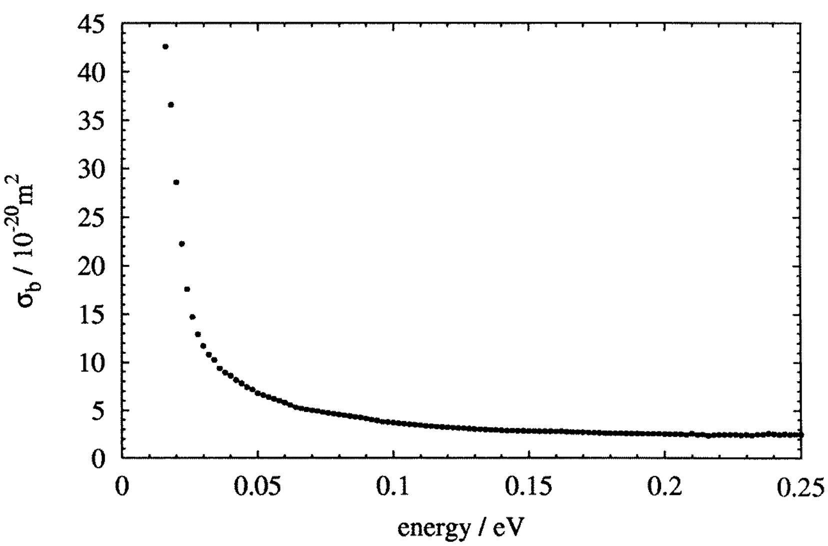

Figure 3. The variation of the backward scattering cross-section for Cl_2 with electron kinetic energy in the low energy regime obtained in the presence of a 20 G axial magnetic field. Note the absence of the resonance seen in figures 1 and 2.

directly with calculated values for elastic scattering in Rescigno (1994). Results given in figure 5 of Rescigno (1994) show a cross-section rising from $\sim$1.5 Å^2 at 200 meV, the lowest energy for which calculations were performed, to a little over 30 Å^2 at 10 eV, representing general agreement with our experimental data. Feshbach resonances are absent in the calculations presumably because, according to Spence (1974), the electronic state(s)

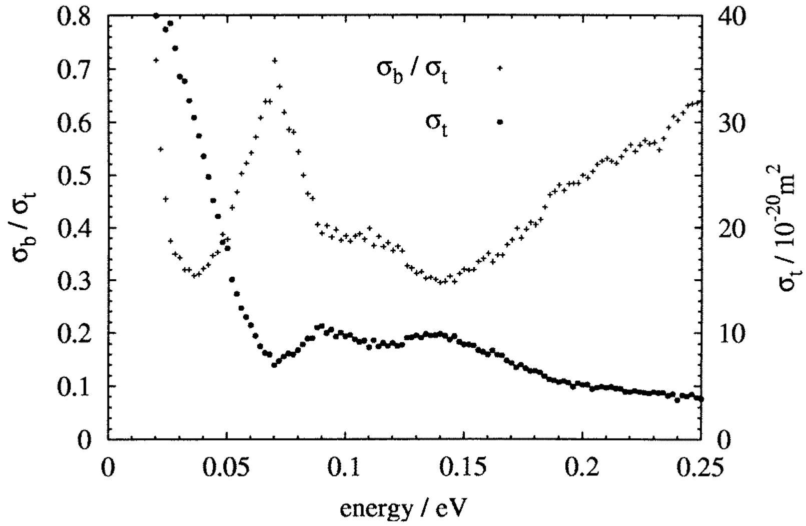

Figure 4. The ratio, σ_b/σ_t ($\equiv R$), of the backward to the total scattering cross-sections, from data in figures 2 and 3, as a function of electron kinetic energy. The total scattering cross-section, σ_t, is also shown for reference.

involved require a double electronic excitation, whereas Rescigno (1994) uses a CI basis set of target states which is too limited to represent this.

Figure 2 shows the variation of the total scattering cross-section from 20 to 250 meV. Figure 3 shows the cross-section recorded in the presence of a 20 G axial magnetic field. The discussion below concerns the rapid rise in cross-section at very low energy and the resonance around 100 meV in the total scattering cross-section.

In figure 4 we show the ratio, σ_b/σ_t ($\equiv R$), of scattering cross-sections measured in the presence and absence of the magnetic field. As discussed in Gulley *et al* (1998), the ratio of the backward to the total scattering cross-section for elastic scattering should lie below 0.5 at low energy and should tend to 0.5 at zero energy. However, at 20 meV, σ_b/σ_t has the value of ~ 0.7, rising to a similar value at an electron energy of 70 meV. Values of σ_b/σ_t greater than 0.5 at low energy are diagnostic of a contribution to the electron scattering cross-section from electron attachment, to form either a long-lived parent ion or, as in this case, a product negative ion through dissociative attachment (DA). The product Cl^- does not in general escape through the exit aperture of the collision chamber, since its trajectory is negligibly affected by the magnetic field. Thus cross-sections recorded in the presence and absence of the magnetic field should tend to assume increasingly similar values as DA becomes the dominant scattering channel, for example at low electron impact energies, as illustrated in figure 4.

We first consider the rapid rise in scattering cross-section in the very low energy regime, below the 100 meV resonance. Dojahn *et al* (1996) have constructed Morse potential curves for Cl_2^-, showing both ground and excited states of Cl_2^- superposed upon the potential curve for the ground state of Cl_2. The ground state of Cl_2^- has also been investigated in configuration-interaction calculations by Peyerimhoff and Buenker (1981), who show a potential curve similar to that of Dojahn *et al* (1996). The ground state of Cl_2^- has the symmetry $^2\Sigma_u^+$ and that of Cl_2 $^1\Sigma_g^+$. The leading electron partial wave involved in the attachment process must be a p-wave, coupling g and u states, as discussed originally in

O'Malley and Taylor (1968), and also in Tronc *et al* (1977) and Azria *et al* (1982), the latter specifically for the case of chlorine. Chlorine presents a classic example of DA in which the negative molecular ion curve crosses the neutral curve close to the equilibrium nuclear distance, within ~ 0.06 Å according to Dojahn *et al* (1996). The chlorine atomic nuclei then move on the negative ion potential surface, whose minimum lies ~ 2.5 eV below the neutral potential. Thus for electron collision energies below a few tens of meV, the system enters a regime in which negligible flux returns to the neutral ground state of the molecule.

The problem with this scenario is that the cross-section for p-wave attachment near threshold (and subsequent DA) should vary as (electron energy)$^{1/2}$. In fact, a log–log plot of the total scattering cross-section versus energy shows that the data do not obey any simple power law in the energy range between 20 and 60 meV. In particular, data do not follow (electron energy)$^{-1/2}$, the behaviour associated with threshold s-wave scattering. At all events, threshold p-wave attachment requires that the cross-section for DA tends to zero at zero electron energy. The same problem is thus encountered here as is encountered for DA in F_2 (Chutjian and Alajajian 1987) in which a rapidly rising cross-section for DA is also observed at energies similar to those in the present data. Various proposals were set out by Chutjian that could in principle give some gerade character to the ground state of F_2^-, which would allow s-wave attachment to take place. Chutjian also suggested that the data (for F_2) may not be sufficiently low in energy for threshold laws to apply, pointing out that threshold laws do not specify the energy at which threshold behaviour is attained. For two reasons we would favour the latter interpretation of our data, that is, that we are observing p-wave attachment but that we remain above the threshold energy range. The first reason is that the absolute cross-sections for scattering, of which attachment is some unknown proportion, are low compared with other known values for low energy attachment or DA for halogen-containing compounds, recognizing that cross-sections are sensitive to the precise disposition of the negative ion and parent potentials. For example, for SF_6, the attachment cross-section at 20 meV electron energy is ~ 300 Å^2 (Klar *et al* 1992) and similar values or greater are encountered for CCl_4 and CCl_3F (Randell *et al* 1992 and references therein). The measured scattering cross-sections for Cl_2 may also be compared with the predictions of an expression known to give reliable estimates for pure s-wave attachment in a single-centre r^{-4} potential (Klots 1976 and references therein, Dunning 1987, Klar *et al* 1992, Randell *et al* 1992, Gulley *et al* 1998). The attachment cross-section, σ_a, may be approximated by

$$\sigma_a = \frac{h^2}{8\pi m_e E}\left[1 - \exp(-4\zeta\alpha E)^{1/2}\right] \tag{2}$$

where all quantities are expressed in SI units, m_e is the mass of the electron, E is the electron energy, α is the target polarizability ($= 4.61 \times 10^{-30}$ m^3) and $\zeta = 1.238\,28 \times 10^{49}$ m^3 J^{-1}. Equation (2) predicts that the s-wave attachment cross-section for Cl_2 should be 344 Å^2 at an electron energy of 20 meV, almost an order of magnitude higher than the observed cross-section. The second reason in support of p-wave attachment is that values of the total cross-section versus electron energy show a tendency to curvature with respect to energy at energies below 30 meV (figures 1 and 2). Data may be entering the regime of energy in which threshold p-wave character becomes apparent.

We now seek to elucidate the qualitative nature of the processes which lead to the resonant structure around 100 meV. Questions that arise are: (i) why the resonance occurs at the observed energy; (ii) why the resonance shows an apparent doublet structure; (iii) why the resonance is isolated, without other companion structures, in contrast, for example, to electron scattering in O_2 (see, for example, Field *et al* 1988, Land and Raith 1974) and

(iv) why the structure is strong in the total scattering cross-section, but, within the limits of our sensitivity, absent in the backward scattering cross-section.

The following assumptions are made.

(i) The ground state potential $^2\Sigma_u^+$ of Cl_2^- and its position relative to the ground state potential of Cl_2 is well established (Peyerimhoff and Buenker 1981, Dojahn *et al* 1996).

(ii) The lowest-lying Π-states of Cl_2^-, $^2\Pi_g$ and $^2\Pi_u$, cut the Cl_2 potential at an internuclear distance a few tenths of an Å greater than the equilibrium distance of Cl_2, and at an energy a few tens to a few hundred meV above the ground vibrational state of Cl_2. The lack of precision here reflects the fact that the form and energy of the excited Π-state potential curves of Cl_2^- are poorly known. Estimates of the energy, above that of the ground vibrational state of Cl_2, at which the Π-states cross the Cl_2 potential curve, vary between close to zero to more than 1 eV for $^2\Pi_g$ (e.g. Tam and Wong 1978, Lee *et al* 1979, Kurepa and Belić 1977, Dojahn *et al* 1996). The $^2\Pi_g$ state is believed to be the lower lying of the two states.

(iii) The strict assignment of u- and g-symmetry to the two lowest-lying excited Π-states may be inappropriate and we tend to refer below to these Π-states without reference to their u- or g-symmetry. In this connection, the configurations associated with the $^2\Pi_g$ state, $\sigma_g^2\pi_u^4\pi_g^3\sigma_u^2$, and with the $^2\Pi_u$ state, $\sigma_g^2\pi_u^3\pi_g^4\sigma_u^2$, are likely to interact strongly. Configuration interaction is known to be important in Cl_2 and Cl_2^- (Rescigno 1994, Peyerimhoff and Buenker 1981).

(iv) The spin–orbit splitting in the Π-states lies between 50 and 100 meV. The splitting for the isoelectronic rare-gas positive ion is $\sim$60 meV (Dojahn *et al* 1996) and the splitting between Cl_2^- $^2\Pi_{g\,1/2}$ and $^2\Pi_{g\,3/2}$ is quoted as 73 meV (without further comment) in Lee *et al* (1979).

We also note that the $v = 1$–0 vibrational quantum lies at 69.4 meV in Cl_2 (Huber and Herzberg 1978). In addition, a plot of the square of the (harmonic) $v = 1$ wavefunction of Cl_2 shows that the maximum of the inner turning point lies at almost precisely the bond length at which the Cl_2^- potential crosses the Cl_2 potential, according to results in Dojahn *et al* (1996).

The resonance has an onset at 70 meV, a maximum cross-section at electron impact energies between 88 and 90 meV and a second maximum between 138 and 140 meV. The structure of this resonance is reminiscent of the doublets seen in scattering in O_2 (Field *et al* 1988). Structures in the O_2 cross-section arise through energetically accessible bound states of $^2\Pi_g$ O_2^-. The situation in Cl_2 is, however, somewhat different, since the Π-states of Cl_2^- do not support bound states in the vicinity of the Cl_2 potential. We also draw attention to the structure in the ratio, R, of the backward to the total scattering cross-section, in figure 4. Assuming that σ_b/σ_t may crudely be used as a measure of the efficiency of DA, these data suggest that DA is enhanced from $\sim$40 meV reaching a peak at 70 meV, dropping thereafter, with a further very weak peak around 110 meV. The cross-section for DA is thus a mirror image of the resonance structure, that is, where the one is weak, the other is strong and vice versa. Beyond 150 meV, DA apparently increases again in cross-section, a phenomenon which is not discussed further here.

We suggest the following mechanism for the 100 meV resonance. The incoming electron with an energy starting below that of the $v = 0$–1 transition (at 69 meV), attaches to Cl_2 via a mechanism involving virtual and true vibrational excitation of Cl_2, with enhancement of the attachment process at the inner turning point of the $v = 1$ vibration. The Cl_2^- temporary negative ion (TNI) achieves the longest lifetime, and therefore the largest probability of DA, at the threshold energy of 70 meV, since at higher energies σ_b/σ_t drops sharply. Above the

$v = 1$–0 threshold, the short-lived Cl_2^- TNI possesses an essentially non-resonant nuclear wavefunction. The diffuse character of this state allows the TNI to couple successively to the two spin–orbit components of the ${}^2\Pi$ Cl_2^- state. This coupling gives rise to the observed doublet structure. The spacing of the peaks in the doublet structure is ~ 50 meV, at the lower end of the range assumed acceptable (see assumption (iv) above).

The resonant structure in the total scattering cross-section is therefore interpreted as arising from a coupled-channel process involving both the ${}^2\Sigma_u^+$ ground state and excited Π-states of Cl_2^-. The relative involvement of these channels is a strong function of the internuclear separation and the electron kinetic energy. Coupling into the ${}^2\Sigma_u^+$ state of Cl_2^- occurs preferentially at an internuclear separation around the inner turning point of the $v = 1$ vibration of Cl_2. Coupling into the two spin–orbit components of the ${}^2\Pi$ state of Cl_2^- occurs with increasing strength at larger internuclear separation, accessed by the diffuse nuclear wavefunction of the short-lived Cl_2^- moiety formed above the vibrational threshold. The wavefunction for the system may be seen as a superposition represented by $a(r, E)\psi^\Sigma + b(r, E)\psi^\Pi$ where the coefficients are functions of both internuclear separation, r, and electron kinetic energy, E, and ψ^Σ refers to Cl_2^- in the ${}^2\Sigma_u^+$ state and ψ^Π in the Π-state. The coefficient $a(r, E)$ dominates strongly below the vibrational threshold at 69 meV. Above 69 meV, $b(r, E)$ begins to grow as the lifetime of the Cl_2^- moiety falls.

The proposed mechanism is consistent with the resonance onset at 70 meV, gives an explanation for the doublet structure and is again consistent with the magnitude of the Π-state splitting. The resonance may be isolated because only $v = 1$ Cl_2 is active in the process as outlined. Since the mechanism relies upon p-wave scattering, there will be a tendency for the process to have strong axial forward–backward asymmetry. This may serve to explain the absence of the resonance in the spectrum obtained in the presence of the magnetic field.

An alternative mechanism for formation of the 100 meV structure might be a purely nuclear-excited Feshbach resonance, involving only the ${}^2\Sigma_u^+$ state of Cl_2^-. Nuclear-excited Feshbach resonances in the hydrogen halides form structures which start at energies below the vibrational threshold. Spectra show a sharp peak and may show additional structure beyond this peak (Rohr and Linder 1976, Gauyacq and Herzenberg 1982, Fandreyer *et al* 1993 and references therein). Whilst this mechanism may have the virtue of greater simplicity than the coupled-channel mechanism proposed above, there are two objections to it. In the first place, the inelastically scattered wave would be dominated by an s-wave, with an isotropic distribution, as measured in Rohr and Linder (1976), for example, and as set out in the theoretical description of Gauyacq and Herzenberg (1982). This conflicts with our observations. In addition, a progression of peaks with decreasing intensity associated with $v = 1, 2, 3, \ldots$ would be expected (Ziesel *et al* 1975, Rohr and Linder 1976, Ziesel and Field 1985, Knoth *et al* 1987, 1989, Radle *et al* 1989), again in conflict with observations. This simpler model therefore appears unattractive on the basis of presently available data.

4. Conclusion

Our results may be summarized as follows. Low energy electron attachment to chlorine takes place most probably through p-wave attachment. The cross-section for attachment is lower, by approximately an order of magnitude at 20 meV impact energy, than for s-wave attachment in other species such as SF_6. A low energy resonance in the form of a doublet has been observed straddling an energy of 100 meV. This resonance has the remarkable property of possessing a cross-section of up to 10 Å^2 in the total scattering cross-section, while being absent within experimental sensitivity in the backward scattering cross-section, measured in the presence of a magnetic field.

A mechanism has been suggested involving a coupled-channel p-wave resonance involving both the ground Σ- and excited Π-states of Cl_2^-. This mechanism broadly accounts for the onset, splitting and angular behaviour of the resonance. An important test of the viability of the proposed mechanism would be the construction of accurate excited state potentials for Cl_2^-, to discover the precise relationship of the Π-states both with respect to each other and with respect to the potential curve for Cl_2^-. In addition, experiments are planned to observe the formation of Cl^- as a function of electron kinetic energy. The proposed mechanism predicts that the cross-section for DA should show a marked temperature dependence, through the influence of thermal populations of $v = 1$ Cl_2. Experiments as a function of target gas temperature are therefore also planned.

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