

# Dissociation pathways in low energy (0–2 eV) electron attachment to Cl<sub>2</sub>O

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## Abstract

Dissociative electron attachment (DA) to ClOCl is studied in a high resolution crossed beam experiment. Two complementary ion pairs, Cl<sup>−</sup>/ClO<sup>−</sup> and O<sup>−</sup>/Cl<sub>2</sub><sup>−</sup>, are observed. The Cl<sup>−</sup>/ClO<sup>−</sup> pair arises from a simple Cl–OCl bond cleavage with the electron sitting on either of the two fragments. The O<sup>−</sup>/Cl<sub>2</sub><sup>−</sup> pair is formed by a concerted reaction with the expulsion of O<sup>−</sup> (or O) and formation of Cl<sub>2</sub> (or Cl<sub>2</sub><sup>−</sup>). Ab initio calculations indicate that in low energy electron attachment an electronically excited state of the precursor anion (ClOCl<sup>−</sup>\* (<sup>2</sup>B<sub>2</sub>)) is involved. © 2001 Published by Elsevier Science B.V.

## 1. Introduction

The chlorine oxides (Cl<sub>x</sub>O<sub>y</sub>) have been extensively studied in the last few years due to their important role in reactions leading to ozone destruction in the Earth's stratosphere [1,2]. Although dichlorine monoxide, Cl<sub>2</sub>O, plays only a minor role in atmospheric chemistry, studies of its chemical behaviour as well as its characterization (geometry, electronic structure, etc.) is of general interest for comparison with other more relevant atmospheric chlorine oxides. Cl<sub>2</sub>O is also used as a

source of ClO (either through direct photolysis [3] or reactions with oxygen [4] or halogen radicals [5,6]) in laboratory experiments and ClO is central to the catalytic loss processes of ozone in the stratosphere. Dichlorine monoxide in the structure Cl–O–Cl is non-linear with an angle  $\phi(\text{Cl–O–Cl}) = 110.9^\circ$  and has a bond length  $R(\text{Cl–O}) = 169.6 \text{ pm}$  [7].

In this Letter we present results of a study of electron attachment to ClOCl using a high resolution crossed beam experiment with mass spectrometric detection of the ions. The comparatively weak bond dissociation energy  $D(\text{Cl–OCl}) = 1.48 \text{ eV}$  [8] leads to the dissociative attachment (DA) channel Cl<sup>−</sup> + ClO (and also its complement Cl + ClO<sup>−</sup>) being considerably exothermic (see below). It is also interesting to

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compare the present results with the previously studied OClO (chlorine dioxide) [9]. For this compound the corresponding numbers are  $\phi(\text{O}-\text{Cl}-\text{O}) = 117.4^\circ$ ,  $R(\text{O}-\text{Cl}) = 147$  pm [10] and  $D(\text{O}-\text{ClO}) = 2.56$  eV [9]. Both chlorine oxides also exist in their respective isomeric forms ClOO and OCICl. While in chlorine dioxide the two isomers are very close in energy (with ClOO more stable by about 0.013 eV [11]), the compound ClOCl is predicted to be more stable by about 0.75 eV than its isomeric form ClCIO [12] which is not a stable species in the gas phase.

The photo-absorption spectrum of ClOCl in the range  $650 < \lambda < 220$  nm (1.9–5.6 eV) exhibits three broad and unstructured bands [13–15] which are assigned to the excitation of valence electronic states with dissociative character [16]. Additional strong features in the vacuum ultraviolet have been revealed by experiments using synchrotron radiation [17]: a strong continuous band with a peak at 171 nm (7.25 eV) and several vibrationally resolved bands in the energy region being found between 7.5 and 10 eV. The continuous band is interpreted as excitation to a dissociative valence excited state while the higher energy structured bands are classified into several Rydberg states.

Early studies of  $\text{Cl}_2\text{O}$  photolysis [18,19] showed that the Cl–OCl bond fission is the dominant fragmentation pathway. More recent studies using laser excitation of jet cooled  $\text{Cl}_2\text{O}$  molecules and applying fragment translational spectroscopy and ion imaging techniques [8,20,21] revealed a much more detailed picture on the complex photo-dissociation dynamics (kinetic energy release and angular distribution of fragments) including the dissociation pathway leading to  $\text{Cl}_2 + \text{O}$  in addition to the usually dominant Cl–OCl bond breakage.

## 2. Experimental

The DA spectrometer used in these experiments consists of a molecular beam system, a high resolution trochoidal electron monochromator (TEM) and a quadrupole mass filter with a pulse counting system for analyzing and detecting

the ionic products. The modified TEM has recently been described in detail [22] where it has been shown that the very high energy resolution (several meV) at energies close to zero eV reported earlier [23,24] quickly deteriorates to 100 meV with increasing electron energy. Using electron trajectory calculations, a modified version of a TEM has been designed to correct for these deficiencies. With the new monochromator, an energy resolution of 50 meV can routinely be achieved independent of the electron energy. However, for the present experiments, where only small amounts of sample were available, the instrument was operated at an FWHM of  $\approx 90$  meV. In addition, introduction of the reactive dichlorine monoxide causes some shift in the energy scale due to adsorption of ClOCl molecules on spectrometer surfaces. This shift can be stabilized by flowing the gas through the instrument prior to collecting data. A small amount of  $\text{SF}_6$  is added to the sample throughout the experiments to monitor the energy resolution and the shift of the energy scale via the narrow  $\text{SF}_6^-$  feature close to zero energy [25].

The ion draw out field in the collision region is very small ( $< 0.1$  Vcm $^{-1}$ ) which makes the Innsbruck device particularly sensitive for studying processes at very low electron energies. However, the instrument discriminates, to some degree, against ions produced with higher translational energy.

Dichlorine monoxide samples were prepared using the University College mobile ClOCl generator. A stream of chlorine gas passes through a reaction column packed with mercuric oxide at room temperature. Gaseous dichlorine monoxide is formed according to the reaction



The effluent gas shows the presence of a  $\text{Cl}_2$  impurity as can be seen on the  $\text{Cl}^-$  channel in the observed DA spectrum (see discussion below) and from the previous absorption experiments [17]. From a scaling procedure used in these absorption experiments the sample purity was estimated to be 90%. It is well known that this standardized production methodology does not produce any other impurities e.g. OClO.

### 3. Results and discussion

Figs. 1 and 2 show the negative ions formed by electron impact with ClOCl in the energy range up to 2 eV. Above that energy only the  $\text{Cl}^-$  channel revealed a small signal which may arise from the  $\text{Cl}_2$  impurity. In addition, a very weak anion signal of the stoichiometric composition of the parent anion close to zero eV is observed (not shown here).

The present results are in good agreement with those of a previous (unpublished) study of electron attachment to ClOCl using an electron beam with a broader energy width (0.2 eV FWHM) and an ion extraction field of  $2 \text{ V cm}^{-1}$  [26]. The presently obtained relative intensities ( $\text{Cl}^-$ :  $\text{ClO}^-$ :  $\text{Cl}_2^-$ :

$\text{O}^- = 32:100:45:<1$  (peak values)) differ slightly from those reported in the previous work ( $100:25:25:<1$ ) [26]. The higher  $\text{Cl}^-$  intensity can be attributed to the higher detection efficiency of energetic ions in the previous device. An analysis of the kinetic energy release [26] showed a mean kinetic energy of 0.2 eV for  $\text{Cl}^-$  at threshold (0 eV) increasing with electron energy. Although no kinetic energy analysis was performed for the diatomic anions we expect less translational energy due to the smaller exothermicity of those channels (Eqs. (2a)–(2c)) and also from momentum conservation.

The present experiments have been performed at a pressure of  $5 \times 10^{-6}$  mbar (as read on an

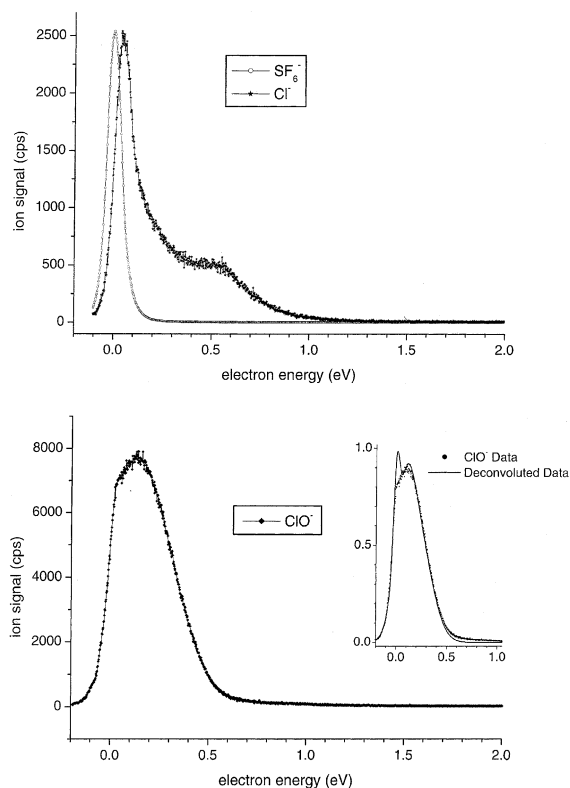


Fig. 1. Formation of the complementary ions  $\text{Cl}^-$  and  $\text{ClO}^-$  from ClOCl as a function of the electron energy. The insert shows the two contributions, i.e., s-wave near zero eV and Gaussian curve at 145 meV (deconvoluted data), from which the experimental data can perfectly be synthesized (see the text). For comparison the  $\text{SF}_6^-$  yield (normalized to the  $\text{Cl}^-$  peak height) from a small admixture of  $\text{SF}_6$  is also shown.

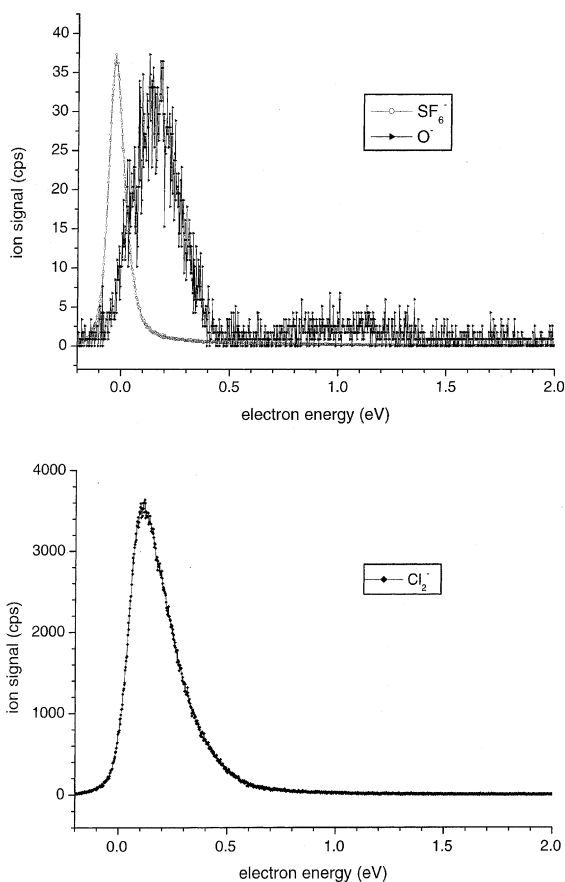


Fig. 2. Formation of the complementary ions  $\text{O}^-$  and  $\text{Cl}_2^-$  from ClOCl as a function of the electron energy. For comparison the  $\text{SF}_6^-$  yield (normalized to the  $\text{O}^-$  peak height) from a small admixture of  $\text{SF}_6$  is also shown.

ionization gauge on one of the chamber flanges) and the count rates are given in absolute numbers. The pressure in the reaction volume is 2–3 orders of magnitude higher as can be estimated from the pumping speed and the diameter of the capillary forming the effusive molecular beam. The *absolute* value for the attachment rate  $k_a$  of *thermal* electrons to ClOCl is available from a previous electron cyclotron resonance (ECR) study as  $k_a = 1.5 \pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  [27]. The rate constant,  $k_a$ , and cross-section,  $\sigma$ , are connected by

$$k_a = \int f(v) v \sigma(v) dv,$$

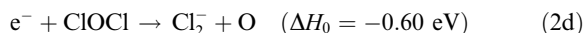
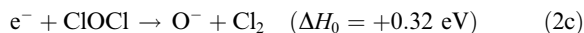
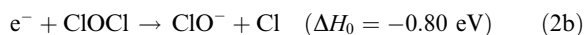
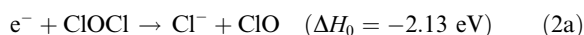
where  $f(v)$  is the normalized velocity distribution of the electrons at the correct gas temperature. As a simple approximation we can use the averaged quantities yielding

$$k_a = \langle \sigma \rangle \langle v \rangle$$

and assume an average velocity from a standard Maxwell–Boltzmann distribution ( $\langle v \rangle \approx 10^7 \text{ cm s}^{-1}$  at 300 K). We then derive a mean cross-section of  $\langle \sigma \rangle \approx 1.5 \times 10^{-17} \text{ cm}^2$  for the attachment of thermal electrons at 300 K. An estimate of the absolute cross-section from the present experiment by comparing with the  $\text{SF}_6^-$  intensity was not possible since the mixing ratio between ClOCl and  $\text{SF}_6$  could not be determined under the flow conditions of ClOCl production.

As is evident from Figs. 1 and 2 electron attachment to ClOCl is almost exclusively a dissociative process producing fragment ions at low energies. We can therefore conclude that in the energy range below  $\approx 0.3 \text{ eV}$  the DA cross-section (under single collision conditions) is in the range of  $10^{-17} \text{ cm}^2$ . This is more than one-order of magnitude larger than the cross-section for photolysis in the visible and UV: the total absorption cross-section (which can be viewed as an upper limit for the cross-section of photo-dissociation) being in the range between  $10^{-20}$  and  $10^{-18} \text{ cm}^2$  for photon energies between 2 and 6.5 eV [16].

At low energies ( $< 0.5 \text{ eV}$ ) the fragment ions observed ( $\text{Cl}^-$ ,  $\text{ClO}^-$ ,  $\text{O}^-$  and  $\text{Cl}_2^-$ ) can be assigned to one of the four following DA reactions:



with the thermodynamic thresholds ( $\Delta H_0$ ) being calculated from the relevant electron affinities ( $\text{EA}(\text{ClO}) = 2.28 \text{ eV}$ ,  $\text{EA}(\text{Cl}_2) = 2.38 \text{ eV}$ ,  $\text{EA}(\text{O}) = 1.46 \text{ eV}$  and  $\text{EA}(\text{Cl}) = 3.61 \text{ eV}$  [28]) and bond dissociation energies ( $D(\text{Cl–OCl}) = 1.48 \text{ eV}$  [8],  $D(\text{Cl–Cl}) = 2.52 \text{ eV}$ ,  $D(\text{Cl–O}) = 2.82 \text{ eV}$  [28]). The EA values are known with spectroscopic accuracy but are given here to only two digits. Note that the two reaction pairs (2a)/(2b) and (2c)/(2d) are complementary with respect to the negative charge with the first pair corresponding to a simple Cl–OCl bond cleavage and the second to the expulsion of  $\text{O}^-$  (or O) and formation of  $\text{Cl}_2$  (or  $\text{Cl}_2^-$ ). The cross-section for the expulsion of neutral O and formation of  $\text{Cl}_2^-$  is of the same order of magnitude as the simple Cl–OCl bond cleavage, i.e., formation of  $\text{Cl}^-$  or  $\text{ClO}^-$ . This is in contrast to photo-dissociation studies [20] which showed that the formation of  $\text{O} + \text{Cl}_2$  was only observed at 193 nm although the energetic threshold is close to 700 nm. Excitation at 193 nm creates highly excited  $\text{Cl}_2$  fragments with the majority undergoing spontaneous dissociation into atomic Cl fragments.

It can be seen in Figs. 1 and 2 that the width of the peaks and also the peak shapes differ between the fragment ions; the  $\text{Cl}^-$  and  $\text{ClO}^-$  ion yields seem to have some specific structure. To discuss and interpret the shape of these anion resonances and their origin we need to recall how DA proceeds in a polyatomic molecule.

In the simplest case of DA to a *diatomic* molecule via a single repulsive potential energy curve without exciting any internal degrees of freedom in the product fragments and with the dissociation asymptote below the Franck–Condon region (e.g., as in the oxygen system  $\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^* \rightarrow \text{O}^- + \text{O}$ ) the ion yield has a simple Gaussian shape (reflection principle). The peak is eventually modified and red-shifted by an energy dependent autodetachment rate (survival probability shift) which is the competing channel to dissociation. Consequently the DA cross-section,  $\sigma_{\text{DA}}$ , is the result of a two-step process characterized by the

electron capture cross-section,  $\sigma_0$ , and the dissociation probability, viz,

$$\sigma_{\text{DA}} = \sigma_0 \times P, \quad (3)$$

where  $P$  expresses the probability that the ionic system survives dissociation with respect to autodetachment ( $0 < P < 1$ ). In a *polyatomic* molecule we can still describe the cross-section by Eq. (3) but the situation becomes more complex with respect to both steps: (i) the increasing density of electronic states can result in energetically overlapping resonances accessible via Franck–Condon transitions and (ii)  $P$  represents (in addition to the competitive channel of autodetachment) the probability of decomposing into the particular channel under observation (with respect to the other energetically available channels) including multiple fragmentation.  $P$  also contains the probability for creating the fragments in internally excited states. Thus structures in the ion yield curve can arise from different overlapping precursor states and by the opening of additional dissociation channels.

We have carried out *ab initio* coupled cluster (CCSD(T)) calculations [29] with the aug-cc-pVTZ basis set [30] on both the neutral and anionic compound in an attempt to gain some information on the structure and stability of the anion and on the character of the lowest unoccupied molecular orbitals (LUMOs) involved in electron capture. For the neutral molecule the calculation reproduces the experimental bond length and Cl–OCl angle within 1%. In the relaxed anion the bond length is increased by about 13% to 193.3 pm and the angle by 18% to  $\phi(\text{Cl–O–Cl}) = 131^\circ$ . The energy difference between the neutral and the relaxed anion (by definition the adiabatic electron affinity) is predicted as  $\text{EA}(\text{ClOCl}) = 2.07 \text{ eV}$ . At this level of calculation the energy of the lowest dissociation channel  $\text{Cl}^- + \text{ClO}$  is at  $-2.04 \text{ eV}$  indicating a very shallow potential minimum (30 meV) for the ground-state anion, see Fig. 3 (the asymptotic energy obtained from the literature thermochemical data is at  $-2.13 \text{ eV}$ ). The vertical attachment energy (VAE) is calculated to be  $-1.14 \text{ eV}$ , i.e., the energy of the anion at the geometry of the neutral ( $R_0$  in Fig. 3) is  $1.14 \text{ eV}$  below that of the neutral

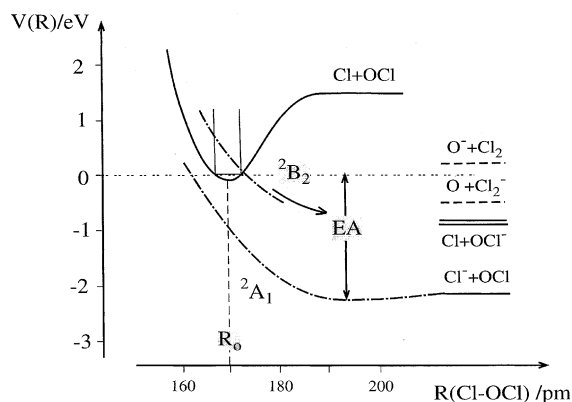


Fig. 3. Schematic two dimensional potential energy curve illustrating dissociative electron attachment to ClOCl. The dotted curves represent the two low lying states of the anion (see the text). The distance refers to the simple Cl–OCl bond fission (channels (2a) and (2b)). The thermodynamic limits of the concerted reaction (channels  $\text{O} + \text{Cl}_2^-$  and  $\text{O}^- + \text{Cl}_2$ ) is also shown.

and hence this anion state is not accessible by free electrons.

We note that a very recent theoretical treatment of electron collisions with ClOCl using the  $R$  matrix method [31] yielded a vertical detachment energy of  $-0.443 \text{ eV}$  in qualitative agreement with the present results but apparently found no bound ground-state anion.

In terms of molecular orbitals (MOs) the ground-state anion can be approximately described by the addition of the extra electron into the LUMO 1. Since this state is not accessible via a Franck–Condon transition by *free* electrons the higher lying unoccupied MOs must be involved in electron attachment.

Our calculations indicate a series of relatively closely spaced (1 eV or less) virtual MOs which are plotted in Fig. 4. LUMO 1 ( $a_1$  symmetry; Fig. 4a) and LUMO 2 ( $b_2$  symmetry; Fig. 4b) ( $C_{2v}$ ) are both Cl–O antibonding with considerable density toward the Cl atoms while LUMO 3 (Fig. 4c) is extended and has no specific valence character.

On the basis of the one electron picture and our *ab initio* calculations we conclude that the first virtual MO cannot be involved in electron attachment and interpret the experimental observations in the following way:

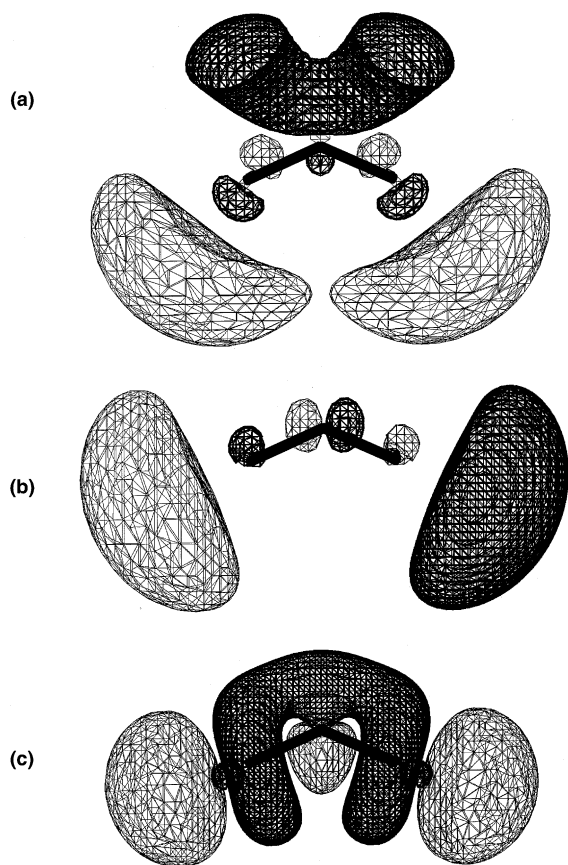


Fig. 4. Isodensity plot of the lowest three (a–c) unoccupied MOs in ClOCl. Isosurfaces are plotted at values of  $+0.02 \text{ bohr}^{-3}$  (dark shading) and of  $-0.02 \text{ bohr}^{-3}$  (light shading).

Dissociative electron attachment proceeds through a single precursor state characterized by accommodation of the electron into the second virtual MO representing the  $^2B_2$  shape resonance located between 0 and  $\approx 0.7 \text{ eV}$  in the Franck–Condon region. This resonance dissociates into the observed DA channels (indicated in Fig. 3 by the arrow).

The structure observed near  $0.6 \text{ eV}$  in the  $\text{Cl}^-$  ion yield can be interpreted by the opening of the multiple fragmentation channel  $\text{Cl}^- + \text{O} + \text{Cl}$ . Available thermodynamical data indicates an energetic threshold for this channel at  $0.69 \text{ eV}$  which is somewhat above the observed structure (see also discussion on the  $\text{O}^-$  ion below).

The unresolved structures (separated by about  $110 \text{ meV}$ ) in the comparatively broad  $\text{ClO}^-$  ion yield curve may arise from dissociation into the two spin–orbit states of  $\text{Cl}(^2P_{3/2})$  and  $\text{Cl}(^2P_{1/2})$  which are separated by  $109 \text{ meV}$ . Although this reaction is considerably exothermic, different probabilities  $P$  for the dissociation into the different spin–orbit states may result in some structure in the overall DA cross-section. From the shape of the ion yield curve one would then expect a larger population of the spin–orbit ground state. In photo-dissociation at  $235 \text{ nm}$  ( $5.3 \text{ eV}$ ), 90% of the total Cl intensity consists of ground-state Cl ( $J = 3/2$ ) [8]. An alternative explanation for the structures is a contribution from s-wave attachment close to zero eV (having an  $E^{-1/2}$  and  $E^{-1}$  energy dependence [25,32]). Convolution of a cross-section containing a low energy s-wave contribution (peak at zero eV) and a Gaussian curve (maximum at  $145 \text{ meV}$ ) with the  $\text{SF}_6^-$  curve (the monochromator function) in fact perfectly reproduces the experimental distribution (see insert of Fig. 1). Such s-wave contributions producing peaks at zero energy can also arise from transitions involving vibrationally excited states [33]. They can even arise in the case of very poor Franck–Condon overlap where substantial attractive long-range electron–molecule interactions are present [34].

It is interesting to note that the two channels (2a) and (2b) associated with a simple bond cleavage have their peak maximum at some distinct energy above the maximum of the  $\text{SF}_6^-$  ion yield, i.e., above zero. In terms of potential energy curves this is due to a curve crossing at some position to the right of the minimum of the neutral configuration (Fig. 3) which in turn indicates some activation energy. A small activation energy ( $0.02 \text{ eV}$ ) for the attachment of thermal electrons in fact was observed in the early ECR work [27]. Hence we have a situation of direct bond breaking of considerable exothermicity, albeit with a small activation energy.

The complementary channels (2c) and (2d) correspond to the expulsion of the  $\text{O}^-$  ion or neutral O and the formation of a new Cl–Cl bond

in the neutral and ionic compound, respectively. The  $O^-$  ion yield curve peaks at 0.15 eV while the thermodynamic limit for reaction (2d) is at 0.32 eV. We note that in the previous unpublished work [26], the  $O^-$  resonance maximum was also located at 0.15 eV which may be an indication that the Cl–O and Cl–OCl bond dissociation energies used to calculate the threshold are somewhat too high. This would also place the limit for the three particle dissociation (see above) at a lower energy in accordance with the experimental observation. The low intensity of the  $O^-$  channel not only arises from its comparatively unfavourable energy (it is the only endothermic DA channel), but also from the fact that in the initial step of electron attachment to the parent molecule ClOCl the additional charge is largely localized towards the Cl atoms which makes dissociation into  $O^-$  unlikely.

Finally, at higher electron energies the  $Cl^-$  yield shows additional weak features near 3 and 5.5 eV which were also observed in the earlier work [26]. Since the  $Cl^-$  signal from  $Cl_2$  also exhibits features in that energy region [26,35] the question remains open whether this signal originates from  $Cl_2$  impurities or from ClOCl.

We finally mention the observation of a very weak signal due to the stoichiometric composition of  $Cl_2O^-$  near zero eV, also previously observed [26]. This compound is most likely the result of a secondary reaction. If it has the structure of the target molecule, ClOCl $^-$ , it possesses a very weak binding energy (Fig. 3). An alternative possibility is an ion–molecule complex of the form  $O \cdot Cl_2^-$ .

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