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Production of Cl^- via dissociative electron attachment to Cl_2

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Abstract

Dissociative electron attachment (DEA) experiments to Cl_2 are reported for the extended energy range between about 0 and 9 eV using a high-resolution crossed beam apparatus. A hemispherical electron monochromator is used to produce an electron beam with a small energy distribution. Electron currents of 20 nA at an electron energy of 20 eV with an energy resolution in the incident electron beam of about 80–150 meV full-width half-maximum (FWHM) were achieved. Three dissociative attachment processes peaking at slightly above 0, 2.53 and 5.64 eV were observed. (Int J Mass Spectrom 223–224 (2003) 661–667)

Keywords: Chlorine; Electron attachment; Cross-section

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1. Introduction

The dissociative electron attachment (DEA) is one of the fundamental inelastic processes in low-energy collisions of electrons with Cl_2 molecules. This considerably affects properties of electrical plasmas and subsequently the efficiency of technologies utilising the plasma, such as those generated in either pure chlorine or mixtures of chlorine with other gases. For example, the increase in the rate of etching of Si by TM ECR plasma is considered to result from the contribution of negative Cl^- ions, since they can easily be transported to the biased substrate [1]. Moreover, the negative ion flux is thought to suppress plasma induced charge-up damage and notching [2]. In excimer lasers, the DEA represents an important source of Cl^- ions, which efficiently recombine with the rare-gas positive ions and form excited states. The formed molecules such as $XeCl^*$ emit UV radiation very efficiently [3].

Both the application of chlorine in plasma etching technologies as well as in the production of excimer lasers have motivated simulations of processes in plasmas containing chlorine. One well-known problem of modelling is the quality of input data, particularly that regarding elementary physical and chemical processes. The quality of a model is only as good as the quality of the input data. Starting from the 1930s [4], several studies have been conducted to determine the properties of the DEA reaction

$$Cl_2(X^1\Sigma_g^+) + e \rightarrow Cl_2^{*-} \rightarrow Cl^-(^1S_0) + Cl(^2P_{3/2,\,1/2}) \qquad (1)$$

involving the ground state $X^1\Sigma_g^+$ of Cl_2 and four negative ion states $^2\Sigma_u^+$, $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g^+$ of $Cl_2{}^-$.

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Over more than 60 years a considerable body of data for the electron attachment rate constant has become available, at ambient and even at elevated temperatures. Most of them have been discussed in detail by Smith et al. [5] and recently by Christophorou and Olthoff [6]. It can be mentioned, however, that they differ from each other remarkably, as it has been recently concluded [6]. In contrast, only a few experiments have been carried out to determine the cross-section (CS) of process (1).

In the measurements conducted by Tam and Wong [7], the relative electron attachment CS to Cl_2 has been measured using a crossed electron–molecule beam apparatus in the energy range of 0–8 eV. Monoenergetic electrons were produced by a trochoidal monochromator. A quadrupole mass spectrometer was used to analyse the ions generated in the collision chamber. The observed formation of Cl^- showed a sharp peak at zero energy and two broader peaks at the energy of 2.5 and 5.5 eV, respectively.

Experiments performed by Kurepa and Belic [8], which seem to be the only direct measurement of the absolute CSs, also confirmed the existence of a relatively sharp zero energy peak and two additional peaks at higher electron energies. The electron beam produced by a trochoidal electron monochromator was characterised by a full-width half-maximum (FWHM) of 200 meV and an intensity of 0.1 μA. The measured absolute CS determined by Kurepa and Belic [8] exhibited four DA maxima at 0, 2.50, 5.75 and 9.7 eV with CS of 201.6, 2.84, 4.84 and $0.39 \times 10^{-22}\,m^2$, respectively. It is worthy to note that according to Kurepa and Belic [8] the experimentally determined CS at zero electron energy is dependent on the tuning of the trochoidal electron monochromator.

According to Azria et al. [9], there are three CS peaks observed at energies of 0, 2.5 and around 6 eV, respectively. It must be noted, however, that due to strong discrimination in the transmission of zero energy incident electrons the data on the yield of Cl^- ions cannot be used for determination of even the relative CS for attachment processes. The shape and the energy position of DA at an electron energy around 6 eV changes with the angle of observation, whereas for the 2.5 eV peak no changes are observable.

The first absolute values of scattering CS were recorded for Cl_2 at energies between 20 meV and 9.5 eV. These were determined using electron transmission experiments performed by Gulley et al. [10] with an energy resolution in the incident electron beam between 3 and 4 meV FWHM. According to these authors, the rapid rise in the total scattering CS at very low-electron energy can be attributed to effective DEA.

Two recently published papers have theoretically analysed EA to Cl_2 [11,12]. The electron attachment CS to Cl_2 has been calculated by Fabrikant et al. [11] using a semi-empirical version of the resonance R-matrix theory. The theoretical CS shows a maximum at the energy of 0.05 eV. This is explained by a very sharp variation of the Franck–Condon factor as a function of energy. Golovitskij calculated the CS with the Condon reflection method for various gas temperatures [12]. In contrast to Fabrikant et al., the theoretically calculated attachment CS peaks at zero electron energy, in accordance with the previous experimental data [7–9].

In order to resolve the discrepancies between theoretical and experimental results and even more between two recently published theoretical results, the crossed electron–molecule beam apparatus, having a better resolution than previously, was used for determining the CS particular concerning the zero energy peak.

2. Experimental

The apparatus used for the present experiments has been described earlier [13,14] hence only the details regarding the actual experiment are described here.

A standard home-built hemispherical electron analyser, whose performance has been improved by careful attention to a number of technical details, produces the beam of monoenergetic electrons. The hemispheres, the sample inlet system, and all electron–ion optical elements have been made of a single material (stainless steel) to improve the uniformity of surface potentials. Pumping of the main chamber by a turbomolecular pump and frequent bake-outs are used to reduce contamination of the surfaces by the sample gas. Residual magnetic fields in the whole apparatus are kept low with instrument-size solenoids compensating the Earth's magnetic field. All voltages applied to the electron–ion optical elements are supplied by one specially constructed power supply.

Ions formed in the collision chamber are extracted by a weak electric field of 0–150 mV. These extracted ions are then analysed by a quadrupole mass spectrometer with a nominal mass range of 2000 amu. The mass selected ions are detected by a channeltron multiplier operating in single ion counting mode. The energy scale and energy resolution (for the optimum operating conditions) was determined by measuring the CS of SF_6^- at zero energy. For the present measurements we achieved a nominal electron energy resolution (FWHM) of ~80 meV at electron currents large enough to study the production of anions with low EA CSs.

The present experiments have been carried out using a mixture of Cl_2, SF_6, and Ar with standard purity and no special pre-treatment. A mixing ratio of 1:1:1 up to 1:3:8 has been used. The main reason to mix argon with chlorine was to avoid the deterioration of the monochromator surface due to the intensive corrosion processes involving chlorine. The mixture has been introduced directly into the main chamber of the apparatus using a needle valve to control the gas flow. Experiments have been performed at ambient temperature.

3. Results

Fig. 1 shows the yield of Cl^- ions from Cl_2 in the energy range 0–10 eV. In Fig. 2 the same results are represented with a logarithmic scale. Four attachment maxima can be seen, i.e., at ~0 eV (I), 0.89 eV (II), 2.53 eV (III), and 5.64 eV (IV). The corresponding single peaks are shown in Fig. 3.

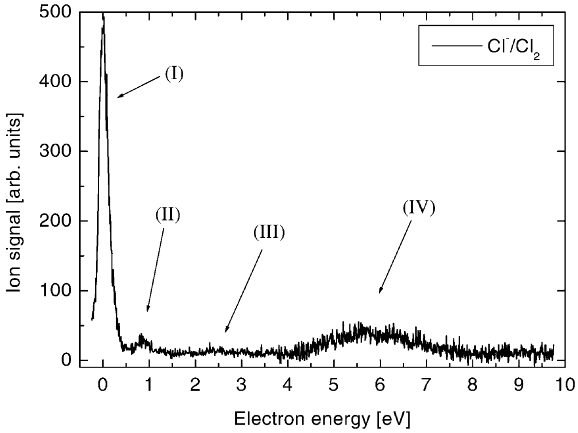

Fig. 1. Ion yield for Cl^- ions from Cl_2.

There exists a reasonable agreement of the energy position, shape, and relative peak intensity for the three Cl^- peaks (I), (III), (IV) with previous results (see Tables 1 and 2).

The existence of peak (II) is very likely due to formation of Cl^- via DEA to HCl, since the position of the peak in the electron energy scale is in good agreement with the previous experimental results shown in Table 3. HCl can be produced by reactions of molecular chlorine with organic compounds or by hydrolysis of chlorine with traces of water in the gas inlet system. This explanation is supported by the temporal behaviour of the ion signal at 0.89 eV. Peak (II) was at its maximum at the start of the experiments, just

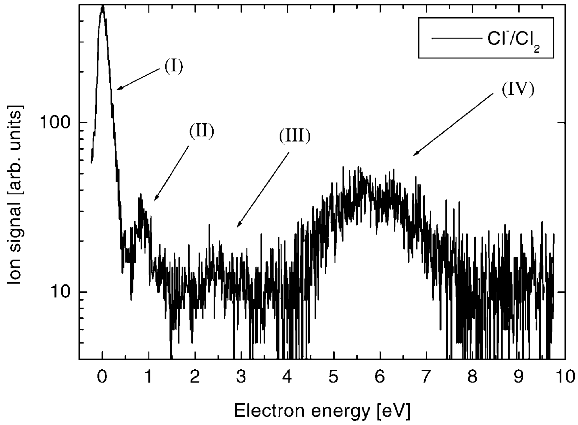

Fig. 2. Ion yield for Cl^- ions from Cl_2 plotted in semi-logarithmic scale.

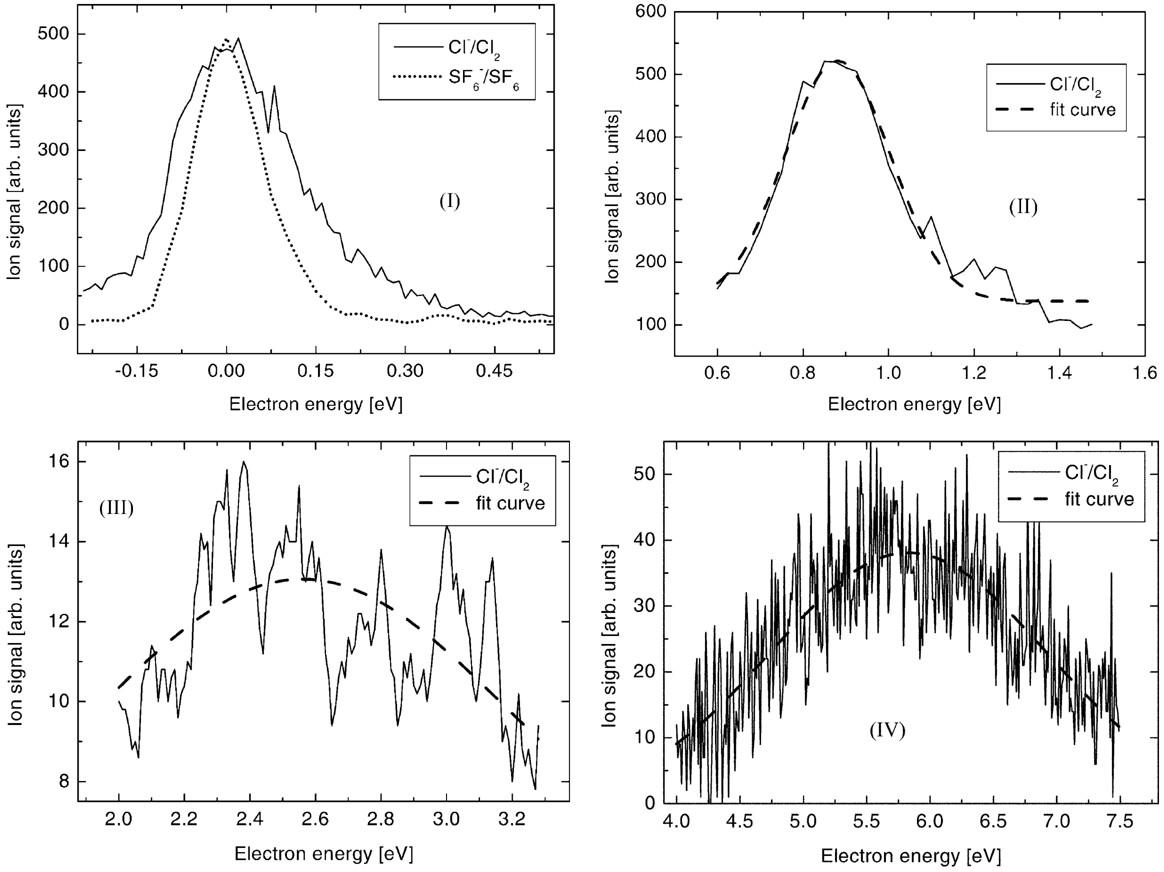

Fig. 3. (I–IV): Single peaks of the Cl^- ion yield curve. The dashed line in (I) is the calibration curve of SF_6^-; in (II), (III), and (IV) it represents a fit curve to the Cl^- data.

after the cleaning of the apparatus, and later became smaller until its intensity became comparable with the intensities of the other three peeks.

The measured ion yield shown in Fig. 1 was converted to an absolute CS curve by normalisation with a known attachment rate constant. The procedure described recently was applied for normalisation [20]. A rate constant value of $1.93 \times 10^{-9}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$, recommended by Christophorou and Olthoff [6] was used in this procedure. The obtained CS data as a function of electron energy are displayed in Fig. 4.

Table 1
Energy position of peak (III) and (IV)

Peak (III) energy (eV)	Peak (IV) energy (eV)	Authors
2.53 ± 0.03	5.64 ± 0.12	This work
2.5 ± 0.08	5.75 ± 0.08	Kurepa and Belic [8]
2.4 ± 0.1	–	Frost and McDowell [15]
2.5 ± 0.15	5.5 ± 0.15	Tam and Wong [7]

The present data are a mean value of several repeated measurements of DEA to chlorine.

Table 2
Relative peak heights for peak (I), (III), and (IV) setting peak (I) to 1

Authors	Relative peak heights		
	Peak (I)	Peak (III)	Peak (IV)
This work	1	0.022	0.031
Kurepa and Belic [8]	1	0.014	0.024
Tam and Wong [7]	1	0.016	0.035

Table 3
Ion peak position for Cl^- from HCl and the present peak (II)

Peak energy (eV)	Authors
0.89 ± 0.02	This work peak (II)
0.84 ± 0.05	Ziesel et al. [16]
0.77 ± 0.10	Frost and McDowell [17]
0.82	Christophorou et al. [18]
0.81	Fox [19]

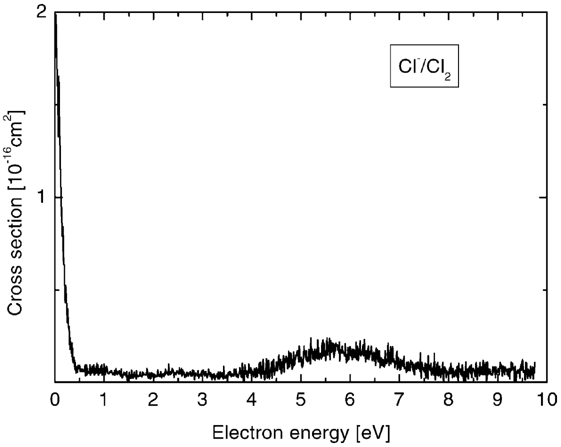

Fig. 4. Absolute attachment CS data for process (1) (calibration see the text; artefact peak (II) has been subtracted accordingly).

4. Discussion

The Cl_2^- negative ion consisting of Cl^- ($^1S_0$) and Cl ($^2P_{3/2,\,1/2}$) has four electronic states. These states are in order of increasing energy: $^2\Sigma_u^+$, $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g$. The Cl^- resonances at ∼0, 2.5, and 5.5 eV were ascribed due to production via the $^2\Sigma_u^+$, $^2\Pi_g$, and $^2\Pi_u$ resonant states of Cl_2^-, respectively. The ground state, $^2\Sigma_u^+$, of Cl_2^- is formed by the addition of an extra electron to the lowest unfilled Cl_2 orbital. The core-excited $^2\Pi_g$ and $^2\Pi_u$ states of Cl_2^- are formed by exciting one electron of the $^2\Sigma_u^+$ shape resonance. The participation of these states in DEA of Cl_2 depends on the way their potential energy curves cross the ground-state potential energy curve, $X^1\Sigma_g^+$, of the neutral Cl_2 molecule.

According to earlier data, reviewed by Christophorou and Olthoff [6], the potential energy curve corresponding to the ground state of the molecular negative ion $Cl_2^-(^2\Sigma_u^+)$ is crossing the potential energy curve of Cl_2 ($^1\Sigma_g^+$) at its minimum. From this one would expect formation of Cl^- ions from $Cl_2^-(^2\Sigma_u^+)$ ions at zero electron energy. This interpretation is difficult to reconcile with theory, since according to theory, process (1) is dominated by p-wave CS and should exhibit a maximum at low but not zero energy [11]. It is evident from a comparison of the shape of normalised Cl^- CSs of Cl_2 and CCl_4, obtained here at nearly the same value of FWHM, that the CS for a typical s-wave process in CCl_4 decreases much more steeply than that of Cl_2 (see Fig. 5 in the range of energy from 10 to 100 meV), indicating then the presence of another mechanism (i.e. p-wave attachment acting above 0 eV electron energy). This fact lead us to consider that the real CS data for Cl_2 should exhibit a maximum that is similar to the CS shape recently predicted theoretically by Fabrikant et al. [11]. Moreover, this is also in accordance with the predicted crossing of the potential curves of the $Cl_2(^1\Sigma_g^+)$ and $Cl_2^-(^2\Sigma_u^+)$ state, recently calculated

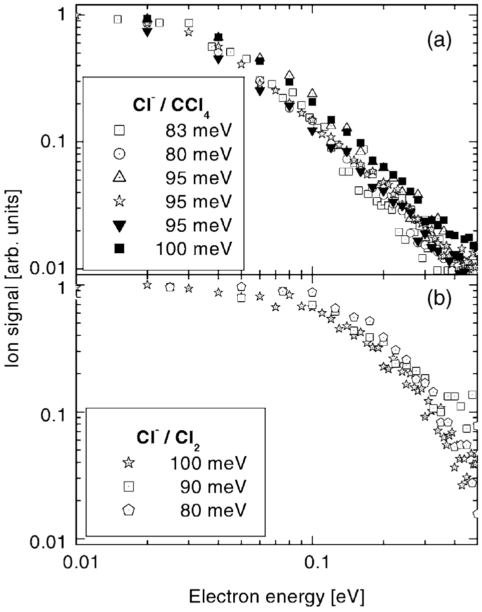

Fig. 5. (a and b): Normalised yields of Cl^- from CCl_4 and Cl_2 obtained with different electron energy resolutions between 80 and 100 meV.

by an ab initio method [21]. The maximum in the CS predicted by Fabricant et al. to occur at about 50 meV electron energy, however, cannot be observed directly in the measured ion yield, due to the insufficient resolution in the energy of the electron beam used here and in the experiments performed by Kurepa and Belic [8].

To verify this hypothesis two procedures have been performed. In the first one, an apparent ion signal I was calculated by convoluting the theoretical CS of Fabrikant et al. [11] with a Gaussian distribution function.

The calculated values of the ion yield I, normalised to maximum value, are shown in Fig. 6 together with normalised CS data measured by Kurepa and Belic [8], theoretical data by Fabrikant et al. [11], theoretical data by Golovitskij [12], and normalised data from the present experiment. Three different resolutions 10, 80, and 200 meV were selected to illustrate the effect of resolution on the shape of the measured ion yield. It is clear that at a resolution of 200 meV the maximum in the apparent CSs cannot be seen any longer.

In the second procedure the theoretically calculated CS [11] was convoluted with a more realistic electron energy distribution function. It is known that a determination of the resolution of the electron energy distribution function, which characterises an electron monochromator used, is in most cases carried out by using a calibration gas with s-wave attachment CS around zero electron energy [22]. Hence, we have assumed that the shape of real electron distribution function is very close to the shape of the ion yield measured in SF_6 gas used for calibration in our experiments. In Fig. 7, the result of this procedure, normalised to maximum value is plotted together with the theoretical and experimental data.

It is interesting to note that in this case by using a more realistic electron energy distribution function for the convolution procedure an excellent agreement is apparent between the present experimental data (designated by stars connected by line) and the normalised ion yield (designated by full dots connected by a line) obtained by convolution of theoretical values of CS predicted by Fabrikant et al. [11] with the electron energy distribution function derived from ex-

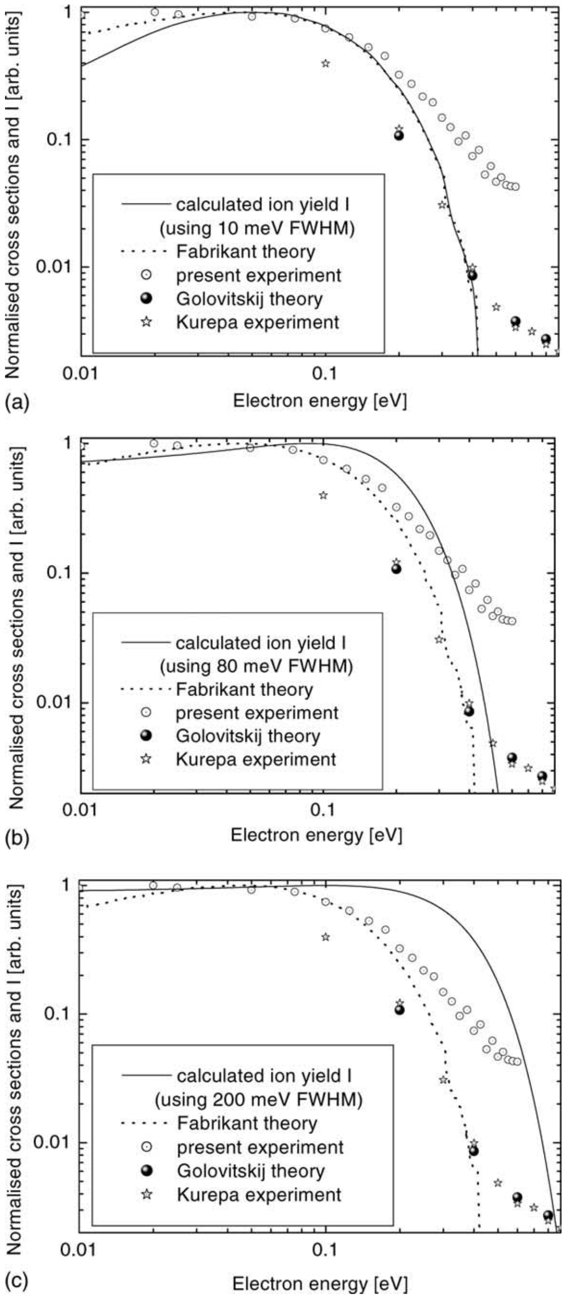

Fig. 6. (a–c): Comparison of normalised theoretical CSs (Fabrikant et al. [11], Golovitskij [12]), with (i) a normalised negative ion signal obtained by convoluting the Fabrikant et al. [11] CS and Gaussian electron energy distribution function (FWHM of 10, 80, and 200 meV), and (ii) with normalised CSs measured here (FWHM 90 meV) and (iii) measured by Kurepa and Belic [8] (FWHM 200 meV).

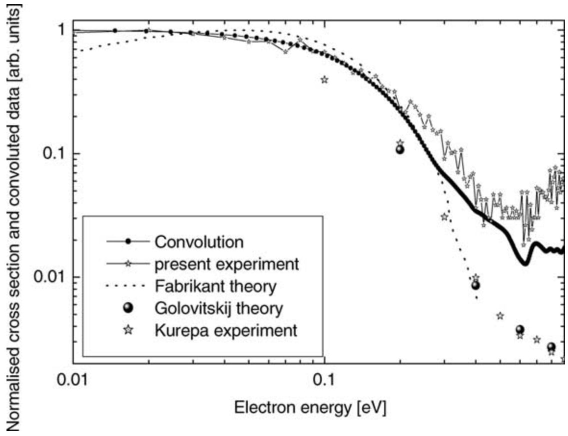

Fig. 7. Comparison of normalised theoretical CSs (Fabrikant et al. [11], Golovitskij [12]), with (i) a normalised negative ion signal obtained by convoluting the Fabrikant et al. [11] CS with the electron energy distribution function derived from experimental measurements of the relative CS for electron attachment to SF_6, and (ii) with normalised CSs measured here (FWHM 90 meV) and (iii) measured by Kurepa and Belic [8] (FWHM 200 meV).

perimental measurements of the relative CS for electron attachment to SF_6. It is clear that therefore, the present results are in accordance with the theoretical predictions of Fabrikant et al. [11]and thus in support of the occurrence of a p-wave dominated Cl^- CS with a maximum slightly above (∼50 meV) zero electron energy.

It is interesting to note that Muigg et al. [23] came to a similar conclusion based on a high-resolution DEA study to Cl_2. Moreover, during the revision stage of this manuscript the authors were informed that the group of Hotop [24] has recently performed a high-resolution experiment in Cl_2 also confirming of this p-wave resonance.

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