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A study of dissociative electron attachment to CHBr_3 and CHI_3

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Abstract

Dissociative electron attachment (DEA) has been studied in the systems $\text{Br}^-/\text{CHBr}_3$ and I^-/CHI_3 in a crossed electron/molecular beams experiment in the electron energy range from about 0 to 10 eV. In addition to prominent low-energy resonances (also observed in previous studies), we find a resonance in the system $\text{Br}^-/\text{CHBr}_3$ at 4.65 eV and we find three additional resonant features in the system I^-/CHI_3 at 2.1, 2.9 and 4.1 eV. The absolute partial cross-section for the $\text{Br}^-/\text{CHBr}_3$ DEA reaction was estimated as $(3 \pm 1) \times 10^{-17} \text{ cm}^2$ at 0.5 eV and $(2 \pm 1) \times 10^{-18} \text{ cm}^2$ at 4.65 eV. Analysis of the energy dependence of the I^-/CHI_3 cross-section reveals s-wave attachment near threshold ($\approx 0 \text{ eV}$) and an additional pronounced feature located at 58 meV. We tentatively assign this feature to vibrational Feshbach resonance associated with excitation of the ν_2 vibrational quanta of CHI_3 .

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Dissociative electron attachment (DEA) to molecules is a reaction relevant in many fields of pure and applied science (electrical discharges, plasmas, atmospheric chemistry, interstellar chemistry, radiation chemistry etc). Halogenated hydrocarbons belong to the group of gases showing the best electron attachment. The halogenated methanes have been the subject of extensive swarm and crossed beam studies [1]. The haloforms CHX_3 (where X stands for a halogen atom) constitute a special class of the halo-methanes. While fluoroform (CHF_3) [2–6] and chloroform [7–10] have been studied in a large number of crossed beam and swarm studies,

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Table 1. Resonances observed in DEA to CHBr_3 in the present experiment and in an ETS experiment [11] together with the present estimated values of the DEA cross-section.

Resonances, DEA (eV)	Resonances, ETS [11] (eV)	Cross-section, DEA (cm^2)
0	—	—
0.5	0.85	$(3 \pm 1) \times 10^{-17}$
4.65	—	$(2 \pm 1) \times 10^{-18}$

Table 2. Resonances observed in DEA to CHI_3 in the present experiment and in an ETS experiment [11].

Resonances in DEA, present work (eV)	Resonances in ETS [11] (eV)
0.058	0.2
2.1	2.2
2.9	3.1
4.1	4.7
—	6.2

for the molecule CHI_3 we found only one beam study, performed by Modelli *et al* [11]. CHBr_3 was studied in beam experiments by Modelli *et al* [11] and Matejcik *et al* [12] and also in a swarm experiment by Sunagawa *et al* [13].

Modelli *et al* studied electron attachment (EA) to CHBr_3 and CHI_3 molecules by means of electron transmission spectroscopy (ETS) and DEA spectroscopy in the electron energy range from ≈ 0 to 6 eV. Although they have observed several resonances in the ETS spectra of both molecules, negative ions were detected only in the electron energy range below 1 eV. Matejcik [12] studied CHBr_3 in the energy range from 0 to 2 eV, including the dependence of the DEA cross-section on the gas temperature.

In the present work we study DEA to CHBr_3 and CHI_3 with emphasis on negative ion formation at higher electron energies and an estimation of the absolute partial cross-section. For CHI_3 we additionally examine the cross-section behaviour near threshold (≈ 0 eV).

2. Experiment

The present work was carried out in the crossed electron/molecular beam apparatus recently established in a Bratislava laboratory. The apparatus has been described in detail in [12]; therefore we will give only a brief description. A schematic view of the apparatus is shown in figure 1. The electron beam is formed in a trochoidal electron monochromator with an electron energy resolution of about 90 meV in the case of CHBr_3 and 120 meV in the case of CHI_3 . The calibration of the electron energy scale and the estimation of the electron energy resolution were performed through measurement of the $\text{SF}_6^-/\text{SF}_6$ EA process.

The molecular beam was produced in a heatable effusive molecular beam source (EMBS). The beam is formed by the effusion of the gas through a channel (0.5 mm diameter and 4 mm long) and an external aperture. In the case of CHBr_3 the vapour is introduced into the EMBS through a gas inlet system and a precisely regulating valve. The vapour pressure in the EMBS was measured using an absolute pressure gauge. In the case of CHI_3 , which is solid under normal conditions, we placed the powder directly into the stainless steel container of the EMBS.

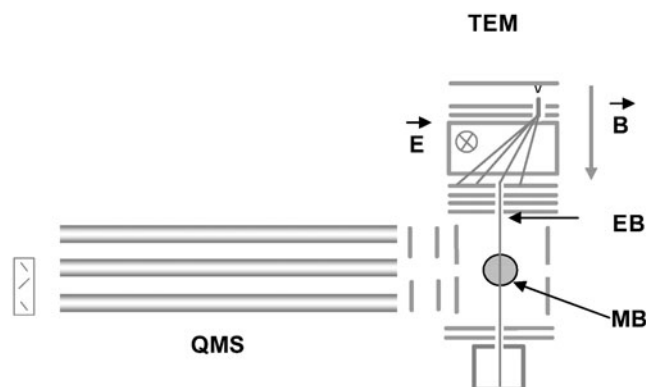


Figure 1. A schematic view of the electron–molecular beam apparatus. TEM: trochoidal electron monochromator; EB: electron beam; MB: molecular beam; QMS: quadrupole mass spectrometer.

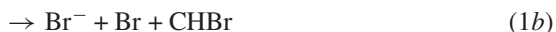
The sublimation pressure of CHI_3 at room temperature was sufficient for providing an intense molecular beam.

The negative ions formed at the intersection between the electron and the molecular beams are extracted by a weak electric field (1 V m^{-1}) into a quadrupole mass spectrometer (QMS). The mass spectroscopically analysed negative ion signal was measured as a function of the electron energy.

3. Results and discussion

3.1. CHBr_3

In the electron energy range from $\approx 0 \text{ eV}$ to about 10 eV , DEA to CHBr_3 may proceed through the following reaction channels:



Whereas reaction (1a) is exothermic by 1.53 eV , the channels (1b), (1c) and (1d) are endothermic by 2.53 eV , ≈ 4 and $\approx 6 \text{ eV}$ respectively. These values were calculated from the available data (standard enthalpies of formation: $\Delta_f H_g^0(\text{CHBr}_3) = 23.8 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{CHBr}_3) = 188.3 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{Br}) = 111.8 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{Br}_2) = 30.9 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{CH}) = 596 \text{ kJ mol}^{-1}$ and the electron affinity of bromine $\text{EA}(\text{Br}) = 3.36 \text{ eV}$ [14]). For the calculation of the appearance energy of the channel (1b) we used the value $\Delta_f H_g^0(\text{CHBr}) = 373 \text{ kJ mol}^{-1}$ from [15].

Modelli *et al* identified in the ETS spectrum of CHBr_3 only one state at 0.85 eV . In the negative ion spectrum for $\text{Br}^-/\text{CHBr}_3$ they observed two peaks, the first one at $\approx 0 \text{ eV}$ and a second at 0.5 eV . The second peak in the negative ion spectra is correlated with the 0.85 eV resonance detected in the ETS spectrum (see table 1). The DEA resonance is shifted to low energies by 0.35 eV due to the competition between autodetachment and dissociation (the survival probability shift). The negative ion yield $\text{Br}^-/\text{CHBr}_3$ observed by Matejcik *et al* [12] is in very good agreement with the data of Modelli *et al* [11] as regards the energies of

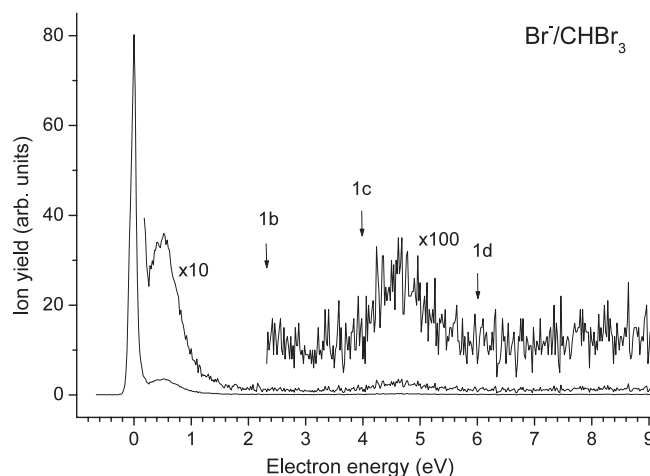


Figure 2. The ion yield curve for the $\text{Br}^-/\text{CHBr}_3$ DEA reaction. The arrows indicate the thermodynamical thresholds for particular DEA channels.

the resonances. In the gas temperature range from 340 to 420 K the cross-section, via both resonances, was independent of temperature.

The ion yield for the reaction $\text{Br}^-/\text{CHBr}_3$ is presented in figure 2. In the low-electron-energy range it is in very good agreement with previous studies [11, 12]. In addition to findings from previous studies, we observe a resonance peaking at 4.65 eV (at a width of about 1 eV FWHM and an appearance energy of 3.8 ± 0.2 eV). This resonance is most probably core excited, i.e. associated with an electronic excitation in the molecule. Within the electron energy range of this feature, the reaction channels (1a), (1b) and (1c) are energetically accessible. The symmetric shape of the DEA feature indicates that the entire initial resonance is located above the DEA threshold; for this reason we assume that channel (1c) does not significantly contribute to the ion signal. To further reveal the decomposition associated with the 4.65 eV resonance (i.e., the branching ratio for channel (1a) and (1b)) one would need additional information, e.g. via an analysis of the kinetic energy imposed on the fragmentation.

In figure 3, potential energy curves for the ground state of the neutral CHBr_3 molecule ($^1\text{A}_1$) and two anionic states are presented. $^2\text{A}_1$ is assigned as the electronic ground state and $^2\text{E}_1$ as an electronically excited state of the parent anion. These potential energy curves were calculated in the multireference configuration interaction study by Rozsak *et al* [16]. According to these calculations, the lowest anionic state $^2\text{A}_1$ crosses the ground state of the neutral molecule $^1\text{A}_1$ at its minimum. This is supported by the observation that the DEA cross-section at low energy (≈ 0 eV) is temperature independent [12]. In figure 3 we have also schematically included the two hypothetical states associated with the resonant features at 0.5 and 4.65 eV. The lower state (with unknown symmetry and most probably repulsive) is responsible for the 0.5 eV DEA resonance (0.85 eV resonance—ETS); its crossing of the $^1\text{A}_1$ surface may result in the observation of Br^- .

We have estimated the absolute partial cross-section σ for the $\text{Br}^-/\text{CHBr}_3$ DEA process as $\sigma = (3 \pm 1) \times 10^{-17} \text{ cm}^2$ at 0.5 eV and $\sigma = (2 \pm 1) \times 10^{-18} \text{ cm}^2$ at 4.65 eV. The estimation was performed by comparing the ion yield $\text{Br}^-/\text{CHBr}_3$ with that of Cl^-/CCl_4 measured at comparable experimental conditions (absolute pressure, electron current and electron energy distribution). For the latter system the absolute partial cross-section is given with considerable precision, as described by Aflatooni *et al* [17]. For the present estimation we assumed identical

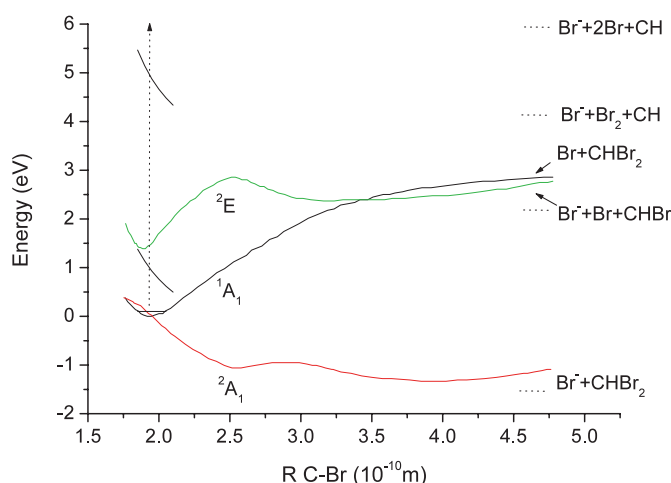


Figure 3. Potential energy curves for the ground electronic state 1A_1 of the neutral CHBr_3 , the ground anionic state 2A_1 , the excited anionic state 2E of CHBr_3^- (*ab initio* calculation [16]) and excited anionic electronic states, which may explain the present results, are indicated. Arrows on the right indicate the thermodynamical thresholds for the particular DEA channels.

discrimination effects, transmission probabilities and detection efficiencies for the Cl^- and Br^- ions.

The value derived here at 0.5 eV of $(3 \pm 1) \times 10^{-17} \text{ cm}^2$ is lower by nearly one order of magnitude than that reported by Sunagawa from an electron swarm experiment at the same energy ($2 \times 10^{-16} \text{ cm}^2$ [13]). This difference is beyond any reasonable error bars and must be due to the different experimental conditions. While our beam experiment operates under collision-free conditions, a transient negative ion in a swarm experiment is subjected to dissipative collisions. The net effect is a suppression of autodetachment in favour of stable negative ion formation (stabilized parents CHBr_3^- and fragments Br^-). As a general rule, one expects a lower (dissociative) EA cross-section under collision-free conditions. In the swarm experiment, the overall rate coefficient for EA to CHBr_3 was estimated from the temporal decrease of the electron density. The experiment was performed at high pressures (≈ 70 Torr) and therefore collisional stabilization of the transient negative ion $\text{CHBr}_3^{\#-}$ may substantially increase the overall EA rate coefficient with respect to the present experiment performed under collision-free conditions (present experiment). There is also some difference in shape of the cross-sections. The cross-section presented by Sunagawa *et al* [13] shows a monotonic decrease over the entire electron energy range from about 0 up to 2 eV. The 0.5 eV resonance observed in the present experiment and also by Modelli *et al* [11] is not visible.

3.2. CHI_3

DEA to CHI_3 was measured in the electron energy range from ≈ 0 to 6 eV. In this energy range the following reaction channels are energetically accessible:



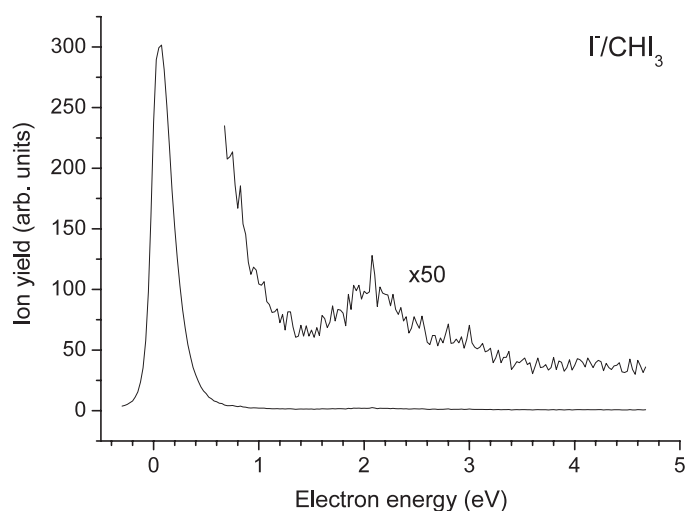


Figure 4. The ion yield curve for the I^-/CHI_3 DEA reaction.

According to the thermodynamical data available in [14] (standard enthalpies of formation: $\Delta_f H_g^0(\text{CHI}_3) = 251 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{CHI}_2) = 333.9 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{I}) = 106.8 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{I}_2) = 62.4 \text{ kJ mol}^{-1}$, $\Delta_f H_g^0(\text{CH}) = 596 \text{ kJ mol}^{-1}$ and the electron affinity of iodine $\text{EA}(\text{I}) = 3.05 \text{ eV}$), the reaction channel (2a) is exothermic by $\sim 1 \text{ eV}$ and the channels (2c) and (2d) are endothermic by 2.28 and 3.83 eV respectively.

Calculation of the thermodynamical threshold for the channel (2b) is not straightforward, since no value for $\Delta_f H_g^0(\text{CHI})$ is available. However, it is possible to calculate this quantity from the known values $\Delta_f H_g^0(\text{CHI}^-) = 266 \text{ kJ mol}^{-1}$ and $\text{EA}(\text{CHI}) = 1.68 \text{ eV}$ [18]. This leads to $\Delta_f H_g^0(\text{CHI}) = 428 \text{ kJ mol}^{-1}$; hence the thermodynamical threshold for (2b) is $\sim 1 \text{ eV}$.

Modelli *et al* [11] observed five resonances (see table 2) in the ETS spectrum of CHI_3 located at 0.2, 2.2, 3.1, 4.7 and 6.2 eV. In the negative ion yield they only detected one resonance, peaking at 0.04 eV. In the present experiment we extended the study of negative ion formation with enhanced sensitivity to higher energy (figure 4). We observed the dominant low-energy resonance at about 0.058 eV and an additional contribution in the electron energy range from about 1.4–4.5 eV. A detailed data analysis of the signal reveals three resonances located at 2.1, 2.9 and 4.1 eV (figure 5). These resonances correspond to the ETS resonances of [11] and are shifted towards low electron energies by 0.1, 0.2 and 0.6 eV, respectively, due to the competition of autodetachment during dissociation of the transient negative ion (TNI). In figure 5 the arrows indicate the thermodynamic thresholds of the DEA channels.

3.3. DEA to CHI_3 at low electron energies

For exothermic DEA processes, the associated peak in the ion yield is usually observed directly at threshold ($\approx 0 \text{ eV}$; see the DEA to CCl_4 , CH_3I [19]). In the present system, the DEA process is also exothermic; in this case, however, the peak in the ion yield is at about 50 meV. Figure 6 shows a comparison with the $\text{SF}_6^-/\text{SF}_6$ yield which was used for calibration. The width of the SF_6^- resonance indicates an electron energy resolution of 120 meV FWHM. We have carried out an extensive analysis of the experimental data, in order to extract the true cross-section behaviour in the system I^-/CHI_3 .

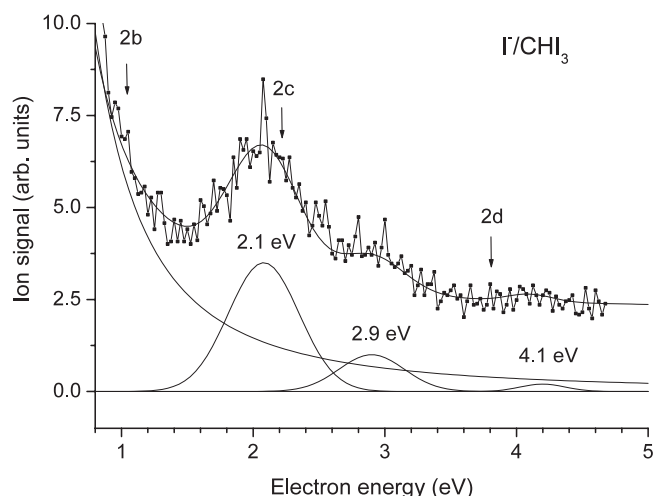


Figure 5. An expanded view of the ion yield curve for I^-/CHI_3 DEA in the electron energy range from 0.8 to 6 eV. Using a Gaussian fitting procedure, the positions of the resonances were estimated; the numbers above the Gaussians indicate the peak positions. The arrows indicate the thermodynamical thresholds for particular DEA channels.

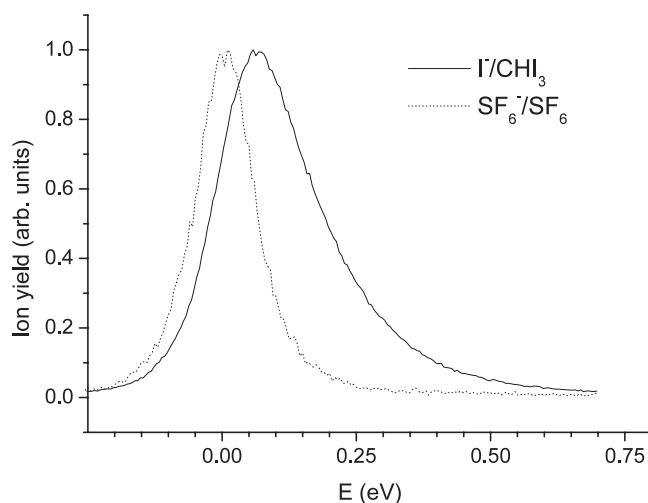


Figure 6. Ion yields curves for I^-/CHI_3 DEA and for $\text{SF}_6^-/\text{SF}_6$ EA, measured under identical experimental conditions.

- (i) Using a deconvolution procedure, we have derived the electron energy distribution function (EEDF) of the electrons in the electron beam from the measured SF_6^- -ion yield. For the deconvolution we have used the cross-section for SF_6 [19]. The calculated EEDF is presented in figure 7(a). In figure 7(b) we show a comparison between the measured and the calculated SF_6^- -ion yields. The latter was obtained by convolution of the cross-section for SF_6 with the EEDF. There is obviously very good agreement, indicating that the EEDF extracted is of reasonable quality.
- (ii) We have applied the deconvolution to the measured I^- -ion yield, using the calculated EEDF. The result of this procedure is the relative partial cross-section for DEA to CHI_3

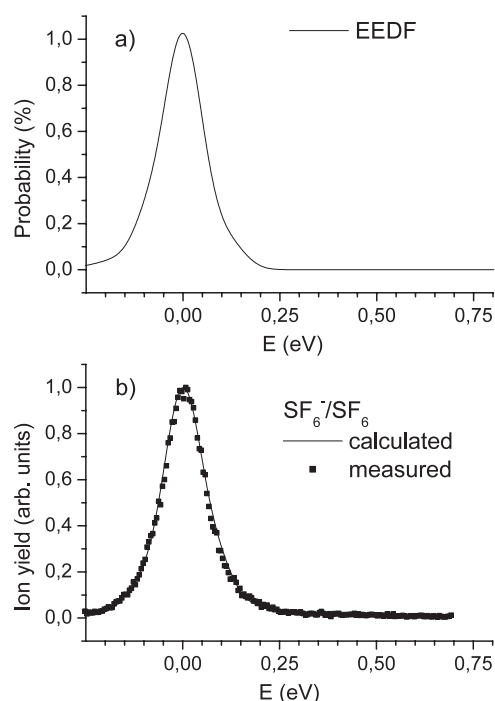


Figure 7. (a) The electron energy distribution function (EEDF) of the electron beam derived from the measured SF_6^- -ion yield (deconvolution with a cross-section for the $\text{SF}_6^-/\text{SF}_6$ EA [19]). (b) Comparison of the ‘calculated’ ion yield of $\text{SF}_6^-/\text{SF}_6$ (convolution of the EEDF and a cross-section for $\text{SF}_6^-/\text{SF}_6$ EA [19]) with the measured one.

presented in figure 8(a). In figure 8(b) a comparison of a ‘calculated’ I^- -ion yield (convolution of the EEDF with the calculated cross-section) with the measured one is presented. A satisfactory agreement between the calculated and measured data is found.

The derived relative cross-section for DEA to CHI_3 (figure 8(a)) indicates a peak at the threshold and a second peak at about 58 meV. The first peak can be interpreted as s-wave attachment, while the origin of the second feature is *a priori* not clear. We tentatively assign it as a vibrational Feshbach resonance, i.e. a negative ion state located, in energy, slightly below the associated vibrational excited neutral state. Such states have been identified in ultrahigh-resolution EA experiments on CH_3I [19] molecules. In the present case the CI symmetric stretching mode ($\nu_2 = 425 \text{ cm}^{-1}$ ($\sim 53 \text{ meV}$)) [20] of CHI_3 could be responsible for this resonance. While the present tentative assignment is based on deconvolution of the experimental spectrum, it would be desirable to verify the present tentative observation with a meV resolution experiment.

The potential energy curves for the molecule CHI_3 in the ground electronic state $^1\text{A}_1$ and for the anionic states $^2\text{A}_1$ and ^2E (as calculated by Rozsak *et al* [16] in the multireference configuration interaction study) are presented in figure 9. The observed resonances at 2.1, 2.9 and 4.1 eV cannot be explained in terms of these calculated potential energy curves. On the basis of the present experimental data, the existence of additional negative ion states is proposed. The energies of these negative ion states are indicated in figure 9 at the equilibrium C–I distance of the neutral molecules.

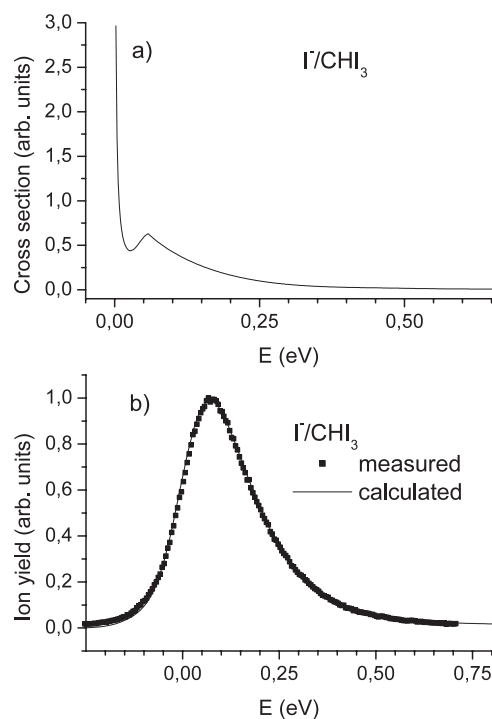


Figure 8. (a) The relative partial cross-section for I^-/CHI_3 DEA derived from the measured ion yield (deconvolution with the EEDF—figure 7(a)). (b) Comparison of the calculated ion yield of I^-/CHI_3 (convolution of the EEDF and the calculated partial cross-section—figure 8(a)) with the measured one.

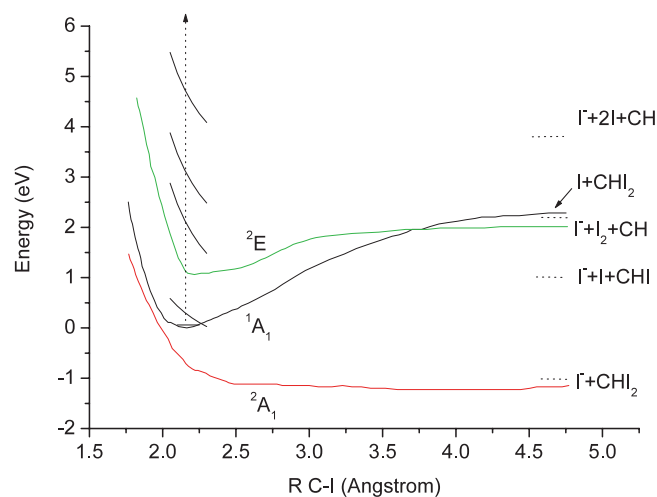


Figure 9. Potential energy curves for the ground electronic state $^1\text{A}_1$ of the neutral CHI_3 and the ground anionic state $^2\text{A}_1$ and excited anionic state ^2E of CHI_3^- according to *ab initio* calculation [16]. Additional anionic electronic states, which may explain the present results, are indicated. Arrows on the right indicate the thermodynamical thresholds for the particular DEA channels.

4. Conclusions

We have measured $\text{Br}^-/\text{CHBr}_3$ and I^-/CHI_3 DEA in the electron energy range from 0 to 10 eV. In the case of DEA to CHBr_3 we have observed, extending the previous studies, a new resonance at 4.65 eV. The absolute partial cross-sections for $\text{Br}^-/\text{CHBr}_3$ DEA of $(3 \pm 1) \times 10^{-17} \text{ cm}^2$ at 0.5 eV and $(2 \pm 1) \times 10^{-18} \text{ cm}^2$ at 4.65 eV were estimated. In the I^-/CHI_3 DEA spectra we have observed three new resonances, at 2.1, 2.9 and 4.1 eV. These resonances correspond to the resonances observed by Modelli *et al* [11] in the ETS spectra. For the low-electron-energy range we have performed a deconvolution of the measured I^- -ion yield. In the deconvoluted cross-section an s-wave EA at the threshold and a resonance at 58 meV were observed. This resonance was assigned to a vibrational Feshbach resonance associated with excitation of the ν_2 vibrational quanta of CHI_3 .

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