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Free electron attachment to the chloromethane $CHCl_3$

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Abstract

Dissociative electron attachment (DEA) to chloroform ($CHCl_3$) is studied in the electron energy range from about 0 up to 25 eV. The measurements are carried out with a two sector field mass spectrometer providing very high mass resolution and sensitivity. The ion yields of anions formed close to 0 eV are also measured utilizing a hemispherical electron monochromator providing an electron energy resolution better than 70 meV. In agreement with previous studies we observe Cl^- as the most abundant anion formed in DEA to $CHCl_3$ with a distinct peak at about 0 eV and the main resonance at about 300 meV. Moreover, due to the high sensitivity of the two sector field instrument we are also able to determine the ion yield of nine other product anions (H^-, C^-, CH^-, CCl^-, $CHCl^-$, $Cl_2{}^-$, $HCl_2{}^-$, $CCl_2{}^-$ and $CHCl_2{}^-$) formed via DEA to chloroform. The present results are compared with previous data of DEA to chloroform in the gas phase and in the condensed phase.

Keywords: Dissociative electron attachment; Chloroform; Negative ion yields; Mass spectra

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1. Introduction

Dissociative Electron Attachment (DEA) processes as illustrated in reaction (1) are known to be of fundamental importance in many diverse fields of chemistry, physics and technical applications such as plasma etching and high voltage power switches [1]. Thus, various crossed beam techniques have been developed to explore the dynamics of such reactions [1,2]

$$e^- + ABC \rightarrow (ABC)^{*-} \rightarrow A^- + BC \qquad (1)$$

The transient negative ion $(ABC)^{*-}$ formed is unstable with respect to dissociation and this leads to the formation of a (stable) fragment anion and at least one neutral fragment. Recently, such reactions have been shown to be common in low energy electron interactions with biomolecules, DEA being considered to be an initial step in strand break formation in DNA induced by ionizing radiation [3]. The molecule studied in the present experiment, chloroform ($CHCl_3$), belongs to the class of halogenated hydrocarbons. Electron attachment studies with such compounds have found practical applications in plasma etching [4] and gas phase dielectrics [5]. In general, chlorination of a molecule can lead to a strong modification of the behaviour in electron attachment, which is caused by the high electron affinity (EA) of the Cl radical (EA = 3.61 eV [6]). Thus, for many chlorinated molecules the dissociative electron attachment process becomes energetically exothermic, i.e., the dissociation limit of the chlorine anion and the neutral fragment is below the ground state of the neutral molecule. Moreover, the molecules can dissociate with very high cross-sections at very low electron energies because of an approximately reciprocal dependence on the electron energy [1,2]. However, an exothermic attachment reaction may require an activation energy (AE). In such a case the DEA cross-section at low electron energy depends strongly on the gas temperature. The study of temperature effects in DEA to chloroform has been the content of several previous investigations [7–10].

The first such study has been carried out by Spence and Schulz [7], who measured the total cross-section for the production of negative ions up to gas temperatures of about 850 °C. At ambient gas temperature the total attachment cross-section of $CHCl_3$ had its maximum in two resonances close to 0 and 0.2 eV. They observed a strong increase of the first peak at higher gas temperatures [7]. More recently Matejcik et al. [8] investigated the temperature effect on the $Cl^-/CHCl_3$ channel in the temperature range between 30 and 160 °C. For this dissociation channel they derived the AE of 110 ± 20 meV. In a more recent study

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using a similar crossed beams setup Matejcik et al. repeated the experiment and obtained an AE = 80 ± 20 meV [9].

In addition to several studies concerning the total dissociative attachment cross-section of chloroform [7,11–13] three groups have investigated which anions are formed in the DEA process and recorded their production as a function of incident electron energy [14–16]. Dorman [14] utilized a standard mass spectrometer and studied the formation of anions in the electron energy range from about 0.5 up to 8 eV. He observed that Cl^- was by far the most abundant anion and was produced through two resonances, one below 0.5 eV and one at about 6.5 eV [14]. In addition to the Cl^- channel he reported the formation of $HCl_2{}^-$ and $CCl_2{}^-$ [14]. The latter two anions were formed in a single resonance at about 1.6 eV. Johnson et al. [15] carried out time-of-flight mass spectrometry and, in agreement with Dorman, observed two anions produced in a single resonance at about 1.7 eV. However, they assigned these ion yields to $Cl_2{}^-$ and $CHCl_2{}^-$. Scheunemann et al. [16] studied DEA to chloroform using a trochoidal electron monochromator combined with a quadrupole mass spectrometer. Like Dorman [14] and Johnson et al. [15] they reported the formation of three anions (i) Cl^- with resonances at about 0.3 and 6.2 eV and (ii) $HCl_2{}^-$ and $CCl_2{}^-$ with a single resonance at about 1.6 eV. Thynne et al. [17] reported anions formed in the interaction of 30 eV electrons and chloroform. They observed Cl^-, CH^-, CCl^-, $Cl_2{}^-$ and $CHCl_2{}^-$. Resonant electron capture at this electron energy is not likely to occur, instead ion pair formation is the dominant process, where the incoming electron forms an electronically excited neutral intermediate state which decays finally into an anion and the corresponding positive ion like for example:

$$e^- + ABC \rightarrow A^- + BC^+ + e^- \qquad (2)$$

However, at the electron energy of 30 eV used by Thynne et al. [17] also secondary electron reactions are possible [15]. Thus, like stated in [15], it is difficult to compare the results reported in [17] with direct DEA data shown here and in [14–16].

In this paper we present a detailed study of DEA to chloroform in the electron energy range between about 0 and 25 eV. Previous mass resolved DEA studies [14–16] showed some inconsistencies concerning the correct mass assignment of ion yields observed (see above). Moreover, in no previous gas phase measurement has the formation of the dehydrogenated chloroform anion and the complementary anion H^- been observed. The comprehensive knowledge of anion formation upon DEA to molecules in the gas phase is of particular relevance for the interpretation of DEA processes in more complex systems, e.g., clusters. A recent study of DEA to nucleobase (NB) clusters embedded in helium droplets revealed the signature of the H^- anion in the anion efficiency curve of $(NB–H)^-$ [18]. This was explained by an electron transfer process from H^- to the neutral fragment (NB–H) formed in the DEA reaction $e^- + NB \rightarrow H^- + (NB–H)$. Thus, the cross-sections of all low intensity anions and particularly the H^- fragment have to be known to understand DEA to chloroform embedded in He droplets which is planned as a follow up study of the present work. We have, therefore, carried out a detailed DEA study of chloromethane $CHCl_3$ utilizing a mass spectrometer with very high mass resolution and sensitivity. The high sensitivity allows us to present seven new ion yields of fragments anions which have not been reported in previous DEA studies. The ion yields of anions formed close to 0 eV are also measured utilizing a hemispherical electron monochromator providing a high energy resolution.

2. Experimental setup

The present experiments are carried out with a double focusing two sector field mass spectrometer (VG-ZAB2-SEQ) of reversed Nier–Johnson type BE geometry (see also [19]). Chloroform purchased from Sigma–Aldrich (stated purity of >99%) is introduced via an external gas inlet which is connected to a capillary with 1 mm diameter. The latter directly reaches into the collision chamber of ion source where the interaction of the neutral effusive beam and the low energy electrons takes place. The whole ion source is heated to about 190 °C to avoid contamination of the source. The energy resolution of the electron beam amounts approximately to 1 eV at the electron current of 10 μA. The anions formed in the ion source are extracted by a weak electric field and accelerated through a potential drop of 7 kV into the mass spectrometer. They pass then through the first field free region, are momentum-analyzed by a magnetic sector field B, enter a second field-free region, pass through an 81° electric sector field E and finally are detected by a channeltron-type secondary electron multiplier operated in the pulse counting regime. The nominal maximal mass resolution of the mass spectrometer is 125,000 (10% valley definition) and high enough to unambiguously separate isobaric ions with different composition such as $NH_2{}^-$ and O^-. However, in the present experiments the slits are opened completely for high sensitivity, but with reduced mass resolution. Another advantage of a sector field mass spectrometer is the uniform transmission for all ion masses. This allows a more correct determination of the relative cross-section of the fragment anions.

The ion yields are also measured utilizing a crossed electron/neutral beam apparatus equipped with a hemispherical electron monochromator (for more details see [20]). In this setup a neutral effusive beam of chloroform interacts with an energetically well defined electron beam in the collision chamber of the monochomator. The energy resolution of the electron beam from the presently used hemispherical electron monochromator is set to a value of about 70 meV. The anions formed are extracted into a quadrupole mass spectrometer and they are finally detected by a channeltron-type secondary electron multiplier operated in a pulse counting mode.

The present study is carried out applying two different measurement techniques (i) negative ion mass spectra of chloroform are recorded for fixed electron energies and (ii) the mass spectrometer is set to a certain mass and the corresponding ion yield is recorded as a function of the electron energy in the range between about 0 and 17.5 eV (for H^-, C^-, and CH^- up to 25 eV). The energy scale is determined by measuring the ion yield of a calibration gas under identical conditions. The electron energy scale of the electron monochromator is calibrated by the following DEA reaction (s-wave electron attachment reaction to SF_6) [21]:

$$SF_6 + e \rightarrow SF_6^- \tag{3}$$

The ion yield of SF_6^-/SF_6 exhibits a sharp 0 eV peak resulting from s-wave electron attachment to the neutral molecules. The energy scale is calibrated by the position of this peak and its full-width-at-half-maximum is a measure for the energy resolution. The electron energy scale of the sector field mass spectrometer is calibrated with the main resonance of NO_2^- at 4.2 eV [22] formed upon DEA to residual 1,4 dinitrobenzene present in the chamber from previous measurements. Such energy calibration for the sector field instrument is required due to the lack of a sufficient electron current close to 0 eV.

3. Results and discussion

Negative ion mass spectra of chloroform are recorded for three different electron energies (~0, 1 and 9.5 eV) in the mass range between 36 and 120 amu utilizing the two sector field mass spectrometer. The spectra are shown in Fig. 1. As in other halomethanes no stable parent anion is observed in free electron attachment to chloromethane. In present G2(MP2) [23] calculations a non-positive EA close to 0 eV for $CHCl_3$ is observed which is in agreement with the experimental result. We also do not see any sign for formation of the dehydrogenated chloroform anion. In each mass spectrum the (by far) most abundant anion is Cl^-. In order to avoid any damage to the detector by too intense ion currents the mass scans are started above $^{35}Cl^-$ and only the chlorine isotope anion $^{37}Cl^-$ is recorded. The second most abundant anion is formed at mass 82 amu with corresponding isotopomer peaks extending up the following five masses. These peaks can be assigned to CCl_2^-. However, a careful analysis of the isotope pattern shows that also the formation of $CHCl_2^-$ can be observed. Other peaks visible in both low energy spectra above 70 amu can be assigned to HCl_2^- with corresponding isotope peaks. In the mass spectrum recorded at 9.5 eV we ascribe the abundant peaks close to 70 amu to the anions Cl_2^- and HCl_2^-. Also peaks in the mass region from 47 up to 51 amu appear at this energy, ascribed to CCl^- and $CHCl^-$ with the corresponding isotopomer peaks formed via DEA to chloroform. The peak at 46 amu in each mass spectrum cannot be formed upon DEA to chloroform and is ascribed to NO_2^- which is formed via DEA to residual dinitrobenzene. No sign of HCl^- is observed which was assumed to be the main thermal decomposition product of CH_3Cl at elevated gas temperatures [24] thus excluding thermal decomposition from the heating of the ion source.

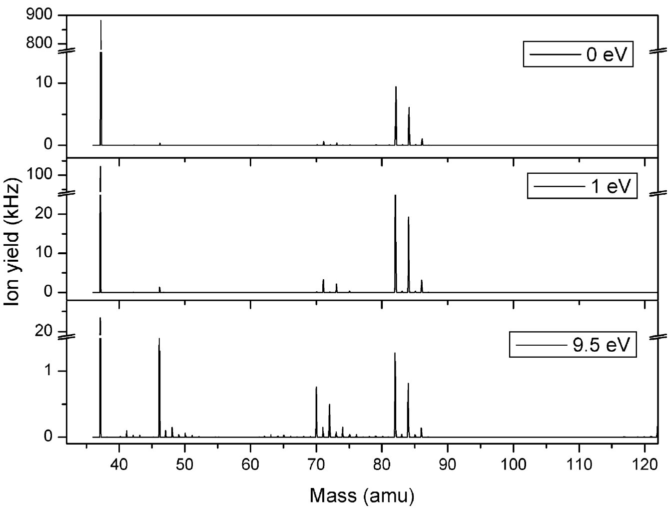

Fig. 1. Negative ion mass spectra of chloroform measured at the electron energy of about 0, 1 and 9.5 eV in the mass range between 36 and 120 amu utilizing the two sector field mass spectrometer.

After the identification of the anions formed by means of these high resolution mass spectra we subsequently measure the electron energy dependence of the anions formed according to the following reactions:

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow Cl^- + \text{neutral fragments} \tag{4}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow CCl^- + \text{neutral fragments} \tag{5}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow CHCl^- + \text{neutral fragments} \tag{6}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow Cl_2^- + \text{neutral fragments} \tag{7}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow HCl_2^- + \text{neutral fragments} \tag{8}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow CCl_2^- + \text{neutral fragments} \tag{9}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow CHCl_2^- + \text{neutral fragments} \tag{10}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow CH^- + \text{neutral fragments} \tag{11}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow C^- + \text{neutral fragments} \tag{12}$$

$$e^- + CHCl_3 \rightarrow (CHCl_3)^{*-} \rightarrow H^- + \text{neutral fragments} \tag{13}$$

The relative ion yields (presented on a true scale) are shown in Figs. 2–5. In these figures solid lines represent measurements utilizing the two sector field instrument. In addition, in Figs. 2 and 3 the ion yields of Cl^-, HCl_2^- and CCl_2^- (shown in dashed lines) have been measured with the high resolution hemispherical monochromator. The insets in these figures (solid lines

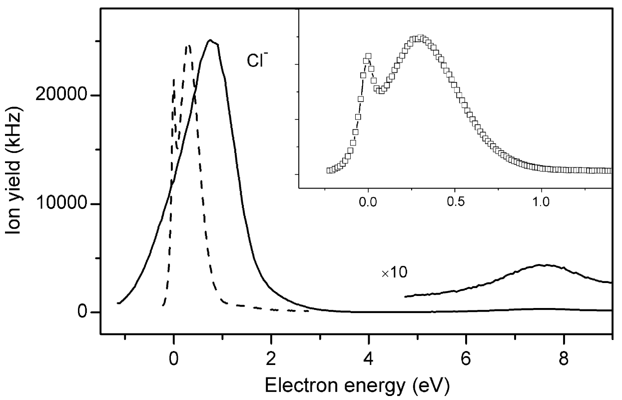

Fig. 2. Ion yield of Cl^- formed via DEA to chloroform in the electron energy range from about 0 up to 9 eV measured with the two sector field mass spectrometer (solid line) and the hemispherical electron monochromator (dashed line), respectively. The inset shows in detail the ion yield of Cl^- below 1.4 eV measured with the electron monochromator (solid line with open squares).

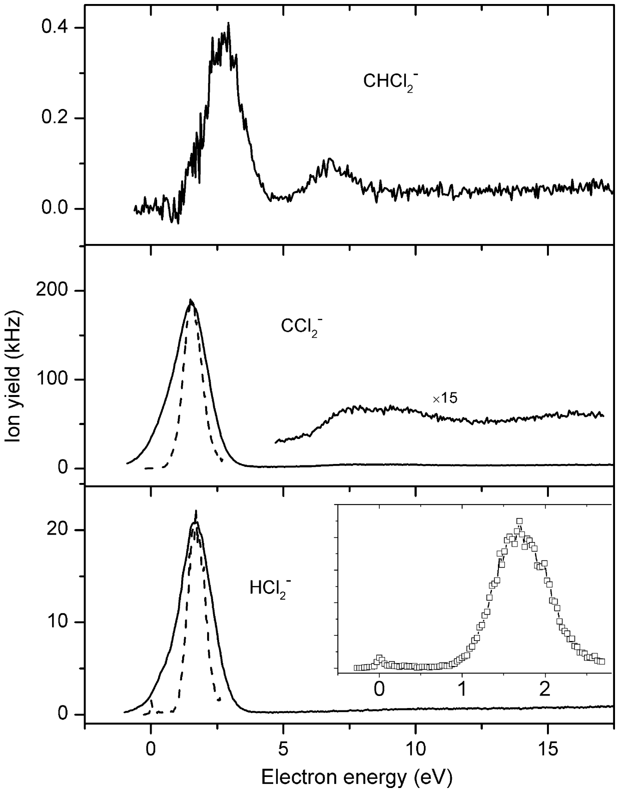

Fig. 3. Ion yield of $CHCl_2^-$, CCl_2^- and HCl_2^- formed via DEA to chloroform in the electron energy range from about 0 up to 17.5 eV measured with the two sector field mass spectrometer (solid lines). The ion yield of CCl_2^- and HCl_2^- measured with the hemispherical electron monochromator are shown in dashed lines. The inset in the bottom panel shows in detail the ion yield of HCl_2^- below 2.8 eV measured with the electron monochromator (solid line with open squares).

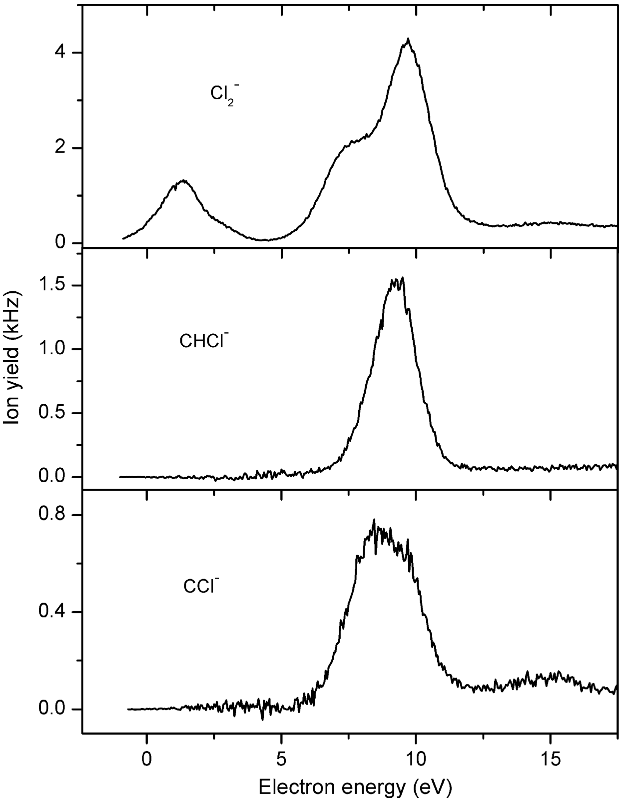

Fig. 4. Ion yield of Cl_2^-, $CHCl^-$ and CCl^- formed via DEA to chloroform in the electron energy range from about 0 up to 17.5 eV measured with the two sector field mass spectrometer.

with open squares) show a detailed view of the high resolution measurements near 0 eV. The peak positions of all resonances observed are summarized in Table 1. From the comparison of the peak positions in figures and in table we can conclude that many anions have resonances at similar electron energies, which indicates that these resonances are formed via the decay of a common precursor state of the temporary negative anion.

3.1. Cl^-

The anion Cl^-, formed via reaction (4), shows a distinct peak at about 0 eV which is followed by the main resonance at about 0.3 eV. Moreover, Cl^- is formed in a much weaker resonance at about 7.7 eV with a weak shoulder at about 9.3 eV. The bond dissociation energy (BDE) of $CHCl_2$–Cl has been calculated previously by Lazarou et al. [25] (BDE = 3.22 eV). Using this value the threshold energy (E_{Th}) for anion formation via reaction (4) can be calculated by BDE ($CHCl_2$–Cl) − EA(Cl) = −0.39 eV which is in accordance with the observation of a 0 eV peak. The present Cl^- ion yield is in good agreement with the previous data recorded with an energy resolution below 100 meV, e.g., in the measurement of $Cl^-/CHCl_3$ of Matejcik et al. [8] and in the total dissociative attachment (DA) cross-section measurements by Chu and Burrow [11] and Aflatooni and Burrow [13], where

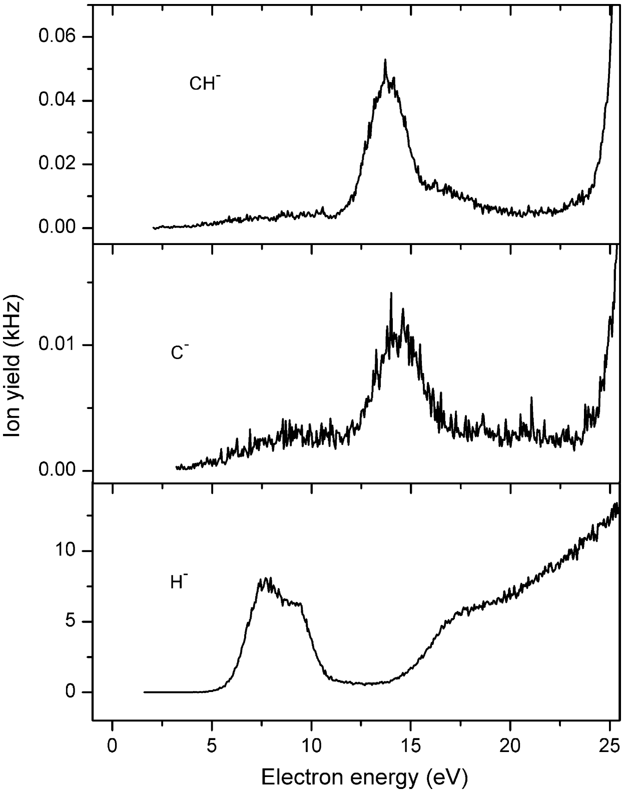

Fig. 5. Ion yield of CH^-, C^- and H^- formed via DEA to chloroform in the electron energy range from about 1 up to 25 eV measured with the two sector field mass spectrometer.

Table 1
Empirical formula, mass of the anions and the peak positions of all observed negative ions formed via DEA to chloroform

Anion	Mass (amu)	Peak energies (eV)
Cl^-	35	0^* 0.3^* 7.7
CCl^-	47	8.8 14.9
$CHCl^-$	48	9.3
Cl_2^-	70	1.3 7.3 9.7 15.1
HCl_2^-	71	0^* 1.71^*
CCl_2^-	82	1.56^* 7.6 9.4
$CHCl_2^-$	83	2.7 6.8
CH^-	13	13.8 16.9
C^-	12	8.9 14.3
H^-	1	7.7 9.1 ~17.4

The peak energies derived from the measurements utilizing the high resolution electron monochromator are indicated by asterisks (*).

two distinct peaks at about 0 and 0.27 eV have been resolved close to the onset. For the second peak the authors in [13] estimated an absolute total DA cross-section of 9.63×10^{-20} m^2. The present and previous [14–16] mass spectrometric investigations of anions show that Cl^- has the strongest contribution to the total DA cross-section. In electron transmission spectroscopy (ETS) experiments the formation of transient negative ion states has been observed at 0.42 and 1.8 eV [26,27]. Thus, there is good agreement between the ETS data [26,27] and the total DA cross-section measurements [13] which shows a resonance at 0.27 eV and a weakly one at about 1.4 eV. The lower lying resonance has been assigned to the formation of a $^2A_1$ temporary negative ion state arising from the σ^* (C–Cl) orbitals [26]. This assignment to the $^2A_1$ state has been questioned by Benitez et al. [28] based on a comparison of ETS and inner-shell excitation spectra. They predicted the lowest temporary anion state at about 1 eV. However, the assignment by Burrow et al. was later fully supported by independent calculations of Guerra et al. [29] and Falcetta and Jordan [30]. In the present Cl^- ion yield we can also observe a weak resonance at about 7.7 eV. In previous ETS experiments with chloroform a transient negative ion state was found at about 7.7 eV.[1] An assignment of the resonance to a temporary negative ion state of chloroform is not available in the literature. Resonances at these electron energies represent core excited resonances, where the incident electron induces electronic excitation of the molecule.

The formation of Cl^- has been also studied in electron attachment to deuterated chloroform $CDCl_3$ desorbed onto a platinum surface and in the bulk of solid krypton [31]. The electron stimulated Cl^- desorption yield had an onset at the electron energy of about 6 eV leading to a broad resonance at about 8 eV with a shoulder at about 9.2 eV. Thus, the resonance at about 7.7 eV of Cl^- seems to be conserved going from the gas phase to the condensed phase. However, the resonance position can be altered due to polarization of the surface and, moreover, pre and post DEA processes, like inelastic electron scattering on the film prior to the attachment and inelastic scattering events of the anions formed with other film constituents. A detailed discussion of such phenomena in DEA to molecules in the condensed phase can be found in [31–33]. Such effects also lead to the absence of the low energy resonances closer to 0 eV, because anions formed at very low electron energies possess too low kinetic energies for the desorption from the thin film. This is also the case for heavier fragment anions and no desorption of polyatomic fragment anions from thin films of chloroform was observed. Such discrimination effects can be identified by the measurement of the charge trapping cross-section, where, similar to the ETS technique in the gas phase, the transmission of electrons through a film is investigated as a function of the electron energy. Anions remaining in the film cause charging of the film and incoming electrons are repelled. Indeed, the charge trapping cross-section for condensed chloroform showed a resonance at about 0 eV (where essentially Cl^- is formed) and a very weak one at about 6 eV [34].

3.2. Polyatomic fragment anions and C^-

The only polyatomic fragment anions reported in [14,16] are HCl_2^- and CCl_2^-, both formed in a single resonance at about 1.6 ± 0.1 eV and 1.45 ± 0.1 eV, respectively. These resonances have been ascribed to the dissociation of the ^2E state of the temporary negative ion, which was observed in ETS at the energy of 1.8 eV [27] and in the total DA cross-section at about 1.4 eV [13]. In contrast Johnson et al. [15] reported in addition to Cl^- the exclusive formation of Cl_2^- and $CHCl_2^-$ at about 1.7 and 1.8 eV. The presently utilized mass spectrometer with very high sensitivity allows the observation of Cl_2^-, HCl_2^-,

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[1] P.D. Burrow, private communication.

CCl_2^- and $CHCl_2^-$. However, HCl_2^- and CCl_2^- are formed most abundantly at about 1.71 and 1.56 eV, respectively, thus the present study supports the mass assignment by Dorman [14] and Scheunemann et al. [16]. In addition, HCl_2^- shows a weak contribution at about 0 eV which was not reported previously. An analysis of the energetics of reaction (8) is possible by means of quantum chemical calculations using the G2(MP2) [23] method. The EA of (HCl_2) is determined to be 5.06 eV and the BDE of $HCl_2^- = 5.55$ eV ($HCl_2^- \rightarrow Cl + Cl^- + H$) assuming a symmetric configuration $(Cl–H–Cl)^-$ with optimized bond length of 1.57 Å. Taking the BDEs from [25] for CCl_3–H = 4.13 eV and $CHCl_2$–Cl = 3.22 eV, reaction (8) is almost thermo-neutral which agrees with the observation of the low intensity peak at 0 eV. The Cl_2^- ion yield is more complex consisting of a low lying resonance at about 1.3 eV and a very broad structure consisting of two overlapping resonances at about 7.3 and 9.7 eV. Cl_2^- is also formed like CCl^- very weakly in a resonance close to 15 eV. However, CCl^- and also $CHCl^-$ are formed much more efficiently in a single resonance close to 9 eV. Both ion yields are measured with presence of chloroform in the ion source and without the presence of chloroform when the gas inlet is closed. This procedure is performed to remove background signal of the isotope anions of NO_2^- peaking at about 4 eV. The resulting CCl^- and $CHCl^-$ ion yields are then obtained by subtraction of the background signal.

Previously Dorman [14] and Scheunemann et al. [16] also determined the ratios of the energy integrated intensities of Cl^-:HCl_2^-:CCl_2^-. They observed a ratio of 1000:1:3 [14] and 1000:2:0.7 [16], respectively. Johnson et al. [15] derived a ratio of Cl^-:Cl_2^-:$CHCl_2^-$ = 1000:0.15:1 which, keeping in mind their wrong mass assignment, corresponds to the ratio of Cl^-:HCl_2^-:CCl_2. In the present study we can observe a ratio of Cl^-:HCl_2^-:CCl_2^- = 1000:0.9:8.6 which is closer to ones of Johnson et al. [15] and Dorman [14].

Thynne et al. [17] reported the formation of CH^- in the interaction of 30 eV electrons and chloroform. We measured the ion yield of CH^- and in addition of C^- up to 25 eV (see Fig. 5). Both ion yields show a common resonance close to 14 eV and moreover, C^- is formed in a weak resonance at about 7.7 eV while CH^- has a shoulder at about 16.9 eV not present in C^-. Both anions show, relative to the DEA resonance, very intensive ion pair formation with an onset at about 22.7 eV.

3.3. H^-

The ion yield at mass 1 amu, i.e., H^-, is shown in Fig. 5. The measurement of this anion for isolated chloroform in the gas phase has not been reported previously. Due to the high sensitivity of the present apparatus this mass is always contaminated with ion yields from residual compounds present in the chamber (mostly water). Thus, as for CCl^- and $CHCl^-$, the resulting $H^-/CHCl_3$ ion yield is obtained by subtraction of the background signal at mass 1. A careful check shows if the H^- signal is formed via DEA to H_2O contaminating the gas inlet. However, this we can definitely exclude by the measurement of O^-/H_2O ion yield because no significant increase of the ion yield is observed when the gas inlet is opend. Thus, we can safely assume that the ion yield shown in Fig. 5 corresponds to H^- formed via DEA to chloroform. The ion yield shows an onset at about 4.5 eV with a first broad resonance at about 7.7 eV and a distinct shoulder at about 9.1 eV. Using the EA(H) = 0.75 eV [6] and the BDE (CCl_3–H) = 4.13 eV [25] one obtains a E_{Th} of 3.38 eV for $H^-/CHCl_3$ in fair agreement with the experiment. Moreover, a nearly monotonous increase of the ion yield above electron energies of about 12.5 eV can be observed. This signal can be ascribed to an ion pair formation process as shown in reaction (2), i.e., simultaneous formation of H^- and CCl_3^+. However, in the present case we can also observe an additional resonance at about 17.4 eV in the monotonous increase of the ion signal. It is interesting to note in this context that in addition to the low energy electron stimulated desorption of Cl^-, the formation of D^- was also observed in DEA in thin films of deuterated chloroform, $CDCl_3$, adsorbed on a platinum substrate [31]. In the condensed phase D^- was formed in two distinct resonances at about 7.3 and 9.3 eV [31]. The D^- desorption yields from the $CDCl_3$ species adsorbed on multilayer Kr substrates showed no substantial modification of the first resonance, however the peak position and the relative height of the second resonance was altered. This shows, at least in the case of the second resonance, that the anionic desorption of D^- was affected by other processes like, e.g., inelastic or reactive scattering with adjacent constituents [31]. In line with this, the position of the first resonance in the condensed phase experiment is in good agreement with the present result of H^- formed upon DEA to the gas phase chloroform. The second resonance seems to be a specific feature for DEA to small (chlorinated) hydrocarbons in condensed phase, as also for a CH_4 film the H^- desorption yield shows two resonances while for the isolated molecule in the gas phase only one peak was observed [31]. In [31] results were reported only in the electron energy range from about 0 to 12 eV. Thus, it remains unclear, if ion pair formation plays a role for the $(D^-)H^-$ formation above 12 eV in the condensed phase.

In conclusion electron attachment to chloroform leads to dissociation of the transient anion with Cl^- by far the most abundant anion. The presently recorded energy scans of fragment anions are in good agreement with previously reported measurements with good energy resolution. By utilizing a double focusing sector field machine with high sensitivity we are able to determine the ion yields of seven anions (H^-, C^-, CH^-, CCl^-, $CHCl^-$, Cl_2^- and $CHCl_2^-$) formed via direct DEA to chloroform which have not been measured before. The high mass resolution ensures also a correct mass assignment of the ion yields observed. We also report for the first time the ion yield of H^- formed via DEA to chloroform in the gas phase. The presently obtained results agree well with DEA to $CHCl_3$ in the condensed phase except for anions that are formed with insufficient kinetic energies to desorb from the films. The present study of DEA to isolated molecules in the gas phase provides a comprehensive data set that is required to assign reactions upon DEA to chloroform in more complex environments, e.g., in clusters, thin films or superfluid He droplets, the latter currently being studied in our laboratory.

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