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International Journal of Mass Spectrometry 223–224 (2003) 9–19

International Journal of Mass Spectrometry

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Temperature dependencies in dissociative electron attachment to CCl_4, CCl_2F_2, $CHCl_3$ and $CHBr_3$

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Received 13 December 2001; accepted 25 January 2002

Dedicated to the memory of Prof. Werner Lindinger.

Abstract

The studies of dissociative electron attachment to CCl_4, CCl_2F_2, $CHCl_3$, and $CHBr_3$ molecules have been performed in the electron energy range from 0 to 2 eV and in the gas temperature range from 300 to 550 K using a new crossed electron-molecular beams apparatus with a temperature regulated, effusive molecular beam source. In the case of dissociative electron attachment channels $Cl^-/CHCl_3$ and Cl^-/CCl_2F_2 strong enhancements of the negative ion production with the gas temperature at low electron energies has been observed. Activation energies for dissociative electron attachment of 80 ± 20 meV for $CHCl_3$ and 130 ± 20 meV for CF_2Cl_2 have been estimated. For the resonances at 0.27 eV in $CHCl_3$ and 0.7 eV in CF_2Cl_2 no dependence of the cross-sections on gas temperature have been observed. In the case of the dissociative electron attachment to Cl^-/CCl_4 and $Br^-/CHBr_3$ the cross-sections do not depend on T in the whole measured electron energy range from 0 to 2 eV. At the elevated gas temperatures above 400 K, unusual temperature effects have been observed for CCl_4, $CHCl_3$ and $CHBr_3$ molecules. These effects might be most likely attributed to the thermal decomposition of molecules on the surface of the molecular beam source. (Int J Mass Spectrom 223–224 (2003) 9–19)

Keywords: Dissociative electron attachment; Temperature dependencies; Electron–molecule interactions

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1. Introduction

The studies of electron attachment (EA) to molecules are of fundamental importance for understanding of electron–molecule interactions and negative ion formation. Electron attachment reactions to the molecules play important role in various fields of chemistry, physics, and in large number of technological applications [1]. For this reason EA reactions have attracted scientific attention and have been studied in many experiments using both beam and swarm techniques. The present paper is devoted to the study of the gas temperature effect on the dissociative electron attachment (DEA) to some electron attaching molecules. In order to study these reactions a new high-resolution electron-molecular crossed beams apparatus has been constructed. In this paper, meticulous description of this new apparatus is given and the first EA studies are presented.

Previous beam EA studies to a large number of molecules demonstrated that the electron attachment reactions depend on the kinetic energy of electrons

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1387-3806/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII S1387-3806(02)00776-5

[1–3] and in many cases DEA to the molecules is strongly enhanced by heating the attaching gas to higher temperatures [4,5]. The gas temperature dependencies of the dissociative electron attachment reactions have been measured in a large number of swarm [6–9] and beam experiments [4,5,10–12]. Detailed survey of the electron attachment studies to excited molecules can be found in [13].

In the present work the gas temperature dependencies of the DEA have been studied for CCl_4, CF_2Cl_2, $CHCl_3$, and $CHBr_3$ molecules (reactions (R1)–(R4) with exothermicities derived from thermodynamical data in [14]):

$$e^- + CCl_4 \rightleftarrows (CCl_4)^{*-} \rightarrow Cl^- + CCl_3 + 0.43\,eV \tag{R1}$$

$$e^- + CHCl_3 \rightleftarrows (CHCl_3)^{*-} \rightarrow Cl^- + CHCl_2 + 0.16\,eV \tag{R2}$$

$$e^- + CF_2Cl_2 \rightleftarrows (CF_2Cl_2)^{*-} \rightarrow Cl^- + CF_2Cl + 0.4\,eV \tag{R3}$$

$$e^- + CHBr_3 \rightleftarrows (CHBr_3)^{*-} \rightarrow Br^- + CHBr_2 + 0.45\,eV \tag{R4}$$

The gas temperature studies of the DEA (reactions (R1)–(R3)) in beam experiments have already been performed [4,12,15]. The main reason for the present studies of these reactions was to test the quality of the new apparatus and its ability to measure gas temperature dependencies for DEA. For $CHBr_3$ (R4) there are at present time no beam data for DEA.

Dissociative electron attachment reaction is a two-step process. The first step is the formation of a temporary negative ion (TNI) and the second one is dissociation of the TNI. DEA reactions can be either: (i) exothermic, or (ii) endothermic. The reactions (R1)–(R4) are exothermic, therefore we will consider here only exothermic reactions. In the case of exothermic DEA reaction an activation energy (AE) may exist. The presence of the AE can hinder the dissociation of the TNI and the DEA cross-section depends strongly on T at the low electron energies (≈0 eV). The dependence of the ion signal on T at very low electron energies is then described by the Arrhenius equation:

$$I(T) = I_0 \exp\left(-\frac{E_A}{kT}\right) \tag{1}$$

where $I(T)$ is the ion current at very low electron energies (≈0 eV) and k is the Boltzmann constant. In case of AE absence the cross-section for DEA reaction at low electron energies does not depend on the T.

Dissociative electron attachment to CCl_4 (R1) is an example of an exothermic reaction without AE. This reaction does not show any dependence on T [7]. The reactions (R2) and (R3) represent the exothermic DEA reactions with AE. Therefore, the cross-sections for DEA to $CHCl_3$ and CCl_2F_2 molecules at low electron energies (≈0 eV) considerably depend on the temperature T.

2. Experiment

The present study has been carried out using a new high-resolution electron-molecular beam apparatus. A schematic of the apparatus is shown in the Fig. 1. The electron beam formed by a trochoidal electron monochromator (TEM) and accelerated to a selected

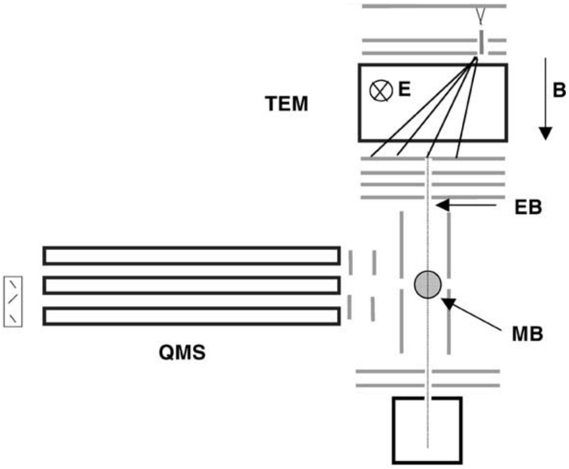

Fig. 1. Schematic view of the electron-molecular beam apparatus, TEM: trochoidal electron monochromator, EB: electron beam, MB: molecular beam, QMS: quadrupole mass spectrometer.

electron energy is crossed by a molecular beam formed by an effusive molecular beam source (EMBS). The negative ions produced in the reaction chamber are extracted by a weak electric field (typically 2–20 V/m) from the interaction region and focused into the entrance of the quadrupole mass spectrometer (QMS). Due to the weak electric field in the reaction chamber, ion kinetic energy discrimination effects can occur in ion yields. The mass selected negative ions are detected as a function of the electron energy in a single-ion counting mode using a secondary electron multiplier (SEM), an ion counting electronics and a PC acquisition system. The entire system is closed in a high vacuum chamber and pumped by 500 L s^{-1} turbo-molecular pump. Two halogen lamps (2×500 W) inside the vacuum chamber are used as internal heaters in order to keep the surfaces clean (base pressure of the apparatus $P < 5 \times 10^{-7}$ Pa). During the measurements, when the gas flow through EMBS into the vacuum chamber is established, the pressure in the main vacuum chamber is usually below 8×10^{-6} Pa.

The TEM (Fig. 2) invented by Stamatovic and Schulz [16] has been used as a source of monoenergetic electrons. The electrons are produced by thermal emission from a hairpin filament directly heated by passing current. The electron beam formed by a system of electrostatic lenses is directed in the x-direction and enters dispersive element of TEM. In the dispersive region of the monochromator, electrons are separated according to their x-component–velocity due to the active role of perpendicularly crossed homogenous electric (y-direction) and magnetic fields (x-direction). Using an aperture with a diameter of 1 mm, only electrons with a narrow energy spread pass through it and are further accelerated or decelerated by a system of the three electrodes. The electrons enter the reaction chamber and react with the molecules in the molecular beam. The kinetic energy of the electrons is defined by the potential difference between the filament and the reaction chamber. The homogenous electric field E of the dispersive region is formed by a system of two planar electrodes (typical values of E about 1 V/cm). The homogenous magnetic field B is produced by a pair of Helmholtz coils mounted outside of the vacuum chamber (typical value of the magnetic field B is about 0.01 T). The electron energy distribution function in the electron beam is characterised by a full-width at half-maximum (FWHM). Adjusting separately the electric and magnetic field of the TEM, the energy distribution function of the electron beam at the exit of the dispersive region is affected. In this way one can vary electron energy distribution function from very broad (FWHM more than 200 meV, high electron current) to very narrow (FWHM of 20 meV low electron current).

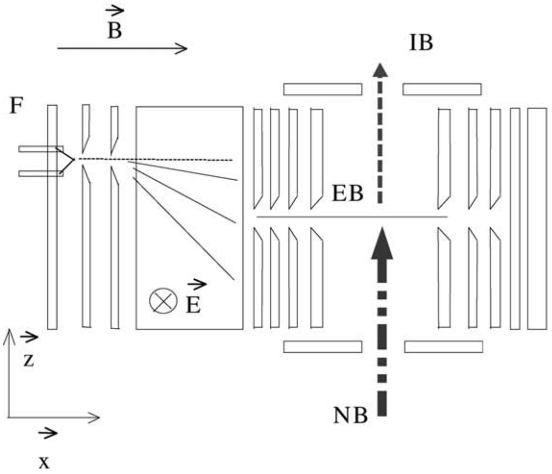

Fig. 2. Schematic view of the trochoidal electron monochromator, F: hot filament, EB: electron beam, NB: molecular beam, IB: ion beam.

The effusive molecular beam source (Fig. 3) consists of a heated stainless steel gas container (volume $\approx 10\,cm^3$, inner surface $\approx 20\,cm^2$) with a single 4 mm long cylindrical channel 0.5 mm diameter. The pressure inside the EMBS is measured with an absolute pressure sensor (MKS Barratron, pressure range 0–7 Pa). A well defined molecular beam with a narrow angular distribution function is formed by effusion of the molecules through this channel. An aperture with a diameter of 3 mm in a shielding is placed between the EMBS and the reaction chamber of the TEM in order to reduce the flow of the gas in the reaction chamber and the TEM. The EMBS is resistively heated (temperature range 300–650 K) using six heaters made from ceramic tubes and tungsten

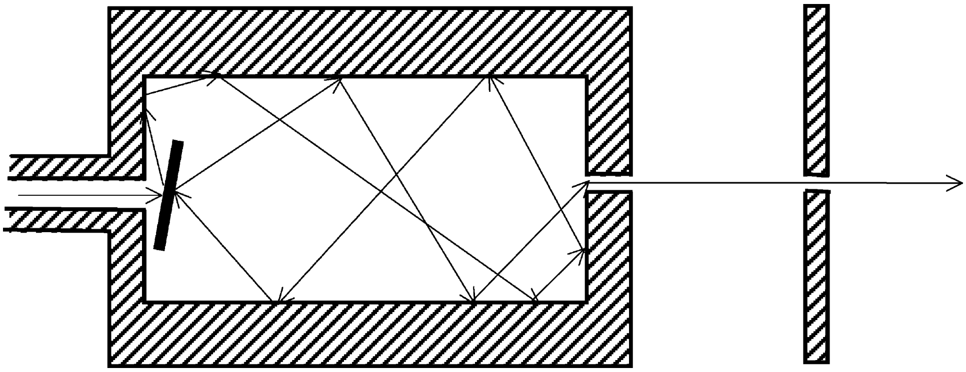

Fig. 3. Schematic view of the effusive molecular beam source.

wire (diameter of 0.25 mm). The temperature of the EMBS is measured at two various positions by a pair of thermocouples (chromel–alumel). The gas inlet system of EMBS is working at higher pressure (typically 100–10^5 Pa) and the gas is introduced to the EMBS through a precise diaphragm regulating valve, reducing the gas pressure to 0.1–7 Pa. At these pressures the mean free path of the molecules in the EMBS is much longer than the typical dimension of the EMBS and thus the collisions of the molecules with the walls are dominant ($\approx 10^4$ collisions). We assume that the molecules are in thermal equilibrium with the walls of the EMBS and thus the temperature of the molecules is equal to the temperature of the walls measured by the thermocouples. If the gas flow through the EMBS is constant, the density of the gas in the molecular beam n_0 varies with the temperature of EMBS (hence T) according to following expression:

$$n_0 \sim T^{-0.5} \tag{2}$$

If a cross-section for DEA does not depend on T, the ion current will follow this dependence.

Calibration of the electron energy scale and estimation of the electron energy distribution function of the electrons have been performed using the EA reaction:

$$e^- + SF_6 \rightleftarrows (SF_6)^{*-} \tag{R5}$$

This molecule possesses in the threshold region ($\approx$0 eV) a very high attachment cross-sections. Transient negative ions $(SF_6)^{*-}$ can be detected in a mass spectroscopic experiment due to its very long lifetime. The cross-section of the reaction (R5) has been measured with sub-millivolt energy resolutions by Klar et al. [17] using the laser photo-ionisation technique. The threshold behaviour of the EA cross-section has been measured and strong decrease in the cross-section with increasing electron energy has been observed ($E^{-1/2}$ at nearly 0 electron energy). For that reason SF_6 molecule is frequently used for the calibration of an electron energy scale as well as for the estimation of the spread of the electron energy distribution function in crossed beams experiments [12]. Fig. 4 shows a typical dependence of the SF_6^- ion current measured as a function of the electron energy. The shape of the low electron energy peak is due to the convolution of the attachment cross-section and the

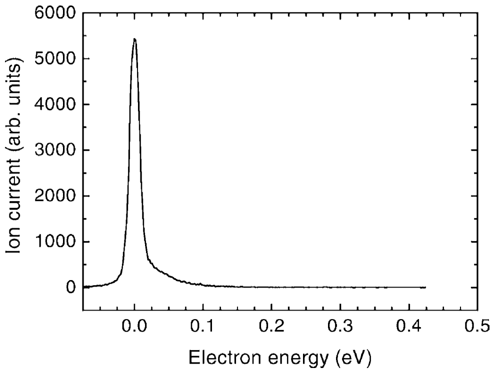

Fig. 4. Ion yield curve for the non-dissociative electron attachment SF_6^-/SF_6 at room temperature.

electron energy distribution function. The maximum of the peak indicates zero electron energy and the width of the peak at the half maximum is a measure of the electron energy distribution.

3. Results

3.1. CCl_4

The dissociative electron attachment to the CCl_4 molecule (R1) proceeds through two steps: (i) formation of the TNI and (ii) dissociation of the TNI. The lifetime of TNI has been observed by Kalamandris et al. to be short [18] ($\tau \approx 30$ ps) and therefore no parent molecular ions can be detected in a crossed-beams experiment at low electron energies (below 2 eV). The only product of DEA reaction in the low electron energy range observed in crossed beams experiments is Cl^- ion. The cross-section for DEA to CCl_4 has two well distinguished peaks, the first one at very low energies due to DEA induced by a capture of slow s-wave electrons to the ground ion state of $^2A_1$, and the second one at around 0.8 eV due to the DEA process to the excited state of the negative ion state $^2T_2$ [19].

The first gas temperature DEA study to CCl_4 in a crossed beam experiment has been performed by Hickam and Berg [20]. They observed two peaks in the DEA ion yield curves, at about 0 and 0.6 eV. In this experiment a decrease of the intensity of the first peak with the gas temperature was observed in the temperature range 353–523 °C. The second peak showed only small changes with the gas temperature. Spence and Schulz studied the gas temperature effects in the DEA to CCl_4 [4] (up to 1050 K) and reported temperature effects only at the highest temperature (increase of the second peak). At lower gas temperatures no effects have been observed, this was probably due to usage of an iridium oven in contrast to the present stainless steel one. In another crossed beam experiment, no dependence of the cross-section for DEA to CCl_4 in T has been observed [12]. Several gas temperature dependent studies of DEA to CCl_4 have been performed in the swarm experiments. These studies demonstrated that the DEA to CCl_4 was not enhanced by increasing the temperature and indicating that no AE for DEA to CCl_4 exists [7,21,22,23].

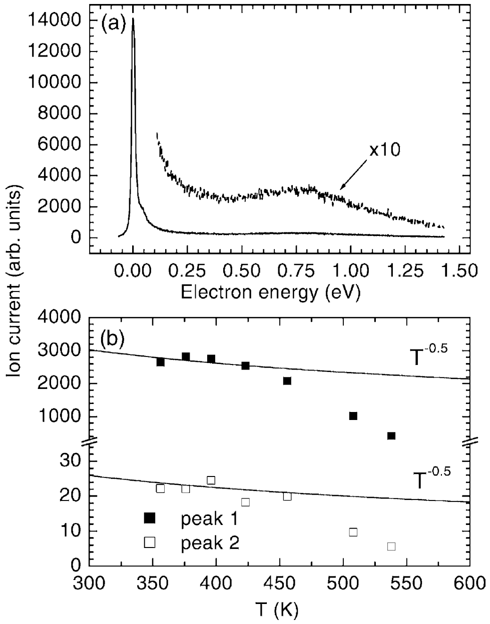

Fig. 5. (a) Ion yield curve for DEA reaction Cl^-/CCl_4 as a function of electron energy and gas temperature. (b) The intensities of the ≈0 and 0.8 eV peaks for DEA to CCl_4 as a function of T. The $T^{-0.5}$ dependence of the ion signal is indicated by the solid line.

In the present study Cl^- ion yield has been measured as a function of the electron energy for DEA reaction to CCl_4 (Fig. 5a) at an electron energy resolution 17 meV (FWHM). The shape of the ion yield as a function of electron energy is in very good agreement with previous beam studies [5,12,19]. The first, most intense peak has been located at 0 electron energy and the second, broad peak at about 0.8 eV. The gas temperature dependent studies of DEA to CCl_4 showed slow decrease of the zero peak intensity with T in the range 340–450 K (Fig. 5b). At the gas temperatures above 470 K more pronounced decrease of the Cl^- signal with T has been observed; very similar dependence of the ion intensity on T has been observed for the 0.8 eV peak. The slow decrease of the Cl^- signal with T for both peaks is only due to the decrease in the gas number density of the molecular beam with T and thus follows the $T^{-0.5}$ law (2). For this reason it can be concluded, that the cross-section for the DEA does not depend on T in the temperature range 340–450 K.

A considerable decrease in the ion intensity at temperatures above 470 K is most probably due to thermal decomposition of CCl_4 in the EMBS. Analogous effects have been observed in the DEA studies to CH_3Cl, C_2H_5Cl and C_3H_7Cl by Pearl and Burrow [24]. In that work HCl as a product of the thermal decomposition of these molecules on the surfaces has been clearly identify. Thermal decomposition of CCl_4 on iron has been observed by Lara et al. [25] in the temperature range from 500 to 700 K. As a main decomposition product was identified iron chloride in form of surface film. In the EMBS the collisions of the molecules with the hot walls prevail. Due to the collisions of the molecules with the walls a catalytic-enhanced thermal decomposition of molecules may take place and therefore already at a relatively low gas temperature 470 K the decrease in the number density of CCl_4 in the molecular beam is observed. The thermal decomposition of the molecules in the gas phase requires much higher temperature [26]. After finishing these gas temperature studies the EMBS has been opened and the surfaces of the EMBS have been covered with a black film. This film contained most probably thermal decomposition products as observed in [25].

3.2. $CHCl_3$

The first measurement of the gas temperature dependence of DEA to $CHCl_3$ (R2) in a crossed-beams experiments has been carried out by Spence and Schulz [4]. The measured DEA cross-section as a function of electron energy to $CHCl_3$ (chloroform) exhibited two peaks, the first one at about 0 electron energy and the second one at about 200 meV. An increase of the intensity of the first peak with T has been observed. From this increase of the cross-section at electron energy ≈0 eV an activation energy for DEA to $CHCl_3$ of about 25 meV can be derived. Chu and Burrow [19] measured the DEA cross-section to $CHCl_3$ at the room temperature and found the position of the first peak at the zero electron energy and the position of the second peak at about 270 meV. Matejčik et al. [12] measured DEA cross-section to $CHCl_3$ as a function of T in the gas temperature range 310–436 K. The position of the two peaks was in agreement with the foregoing experiment in [19]. The intensity of the second peak was less pronounced, probably due to discrimination effects in the reaction chamber for high energetic ions. An activation energy of 110 meV has been derived from the gas temperature dependence of the zero energy peaks. In a large number of DEA studies to $CHCl_3$ in swarm experiments, the activation energy between 95 [7] and 120 meV [8] has been obtained. Recently, Sunagawa and Shimamori published gas temperature studies of DEA to $CHCl_3$ using a pulsed-radiolysis microwave technique [27]. Using this technique the activation energy of 130 meV has been determined.

Present studies of DEA to $CHCl_3$ (Fig. 6a) are in the agreement with the previous crossed beam studies [12,19,28] concerning positions of the apparent peaks. The ion yields for DEA to chloroform have two

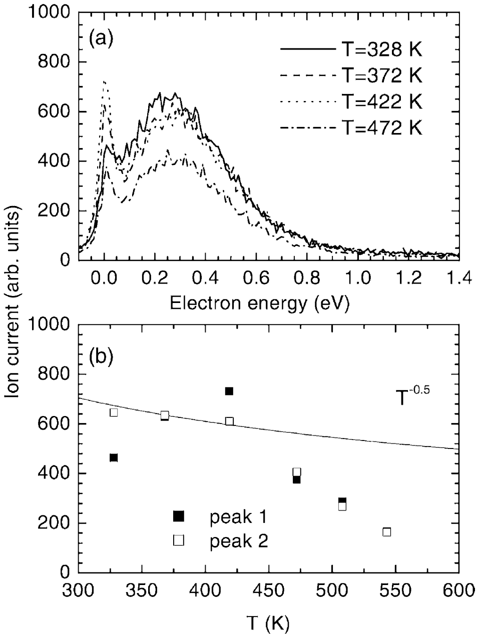

Fig. 6. (a) Ion yield for DEA reaction $Cl^-/CHCl_3$ as the functions of the electron energy and the gas temperature. (b) Cl^- intensitiy of the ≈0 and 0.27 eV peaks in $CHCl_3$ as the functions of T. The $T^{-0.5}$ dependence of the ion signal is indicated by a solid line.

well-resolved peaks, the first one at about 0 electron energy and the second one at 270 meV. Both peaks result from the electron capture to the ground anionic state $^2A_1$ of the chloroform [19]. At electron energies above 1 eV contribution of the ^2E anionic state to the DEA has been observed [28]. The ion yields have been measured in the gas temperature range 328–520 K and with an electron energy distribution of about 50 meV FWHM. The variations of the intensities of the first and the second peak with T are plotted in the Fig. 6b. The first peak increases with T in the temperature range 328–419 K. At higher gas temperatures a decrease of the signal is observed. This effect is attributed to the thermal decomposition of $CHCl_3$ in the molecular beam source, similarly as in the case of CCl_4 and in [24]. The intensity of the second peak decreases with T according to $T^{-0.5}$ law (in the temperature range 328–422 K). Therefore, one can surmise that the second peak of DEA cross-section to $CHCl_3$ does not depend on T in this temperature range. An Arrhenius plot for the zero energy peak of the $CHCl_3$ molecule is presented in Fig. 9. From the slope of the Arrhenius plot, an activation energy for DEA to $CHCl_3$ of 80 ± 20 meV has been estimated. The value of the activation energy is close to the value of 95 meV measured by Wentworth et al. [29], but in most swarm experiments the activation energies for $CHCl_3$ close to 130 meV has been found [27]. The lower value of AE in the present experiment is probably due to the thermal decomposition of $CHCl_3$ in the molecular beam source. Due to the thermal decomposition of the $CHCl_3$ in the EMBS at higher temperatures, number density of $CHCl_3$ in the molecular beam drastically decreases and this decrease affects the apparent reduction in the intensity of the Cl^- signal at electron energy ≈0 eV.

In order to obtain the absolute partial cross-section at the gas temperatures 328 and 422 K (Fig. 7.), the present ion yield (for $T = 328$ and 422 K) has been calibrated using the cross-section estimated for DEA to $CHCl_3$ in [28] (9.63×10^{-16} cm^2 at 0.27 eV). The second peak does not depend on the gas temperature, therefore can be used for calibration purposes. For comparison the cross-section from [28] is presented. There exists very good agreement between the present data and earlier data [28] within the electron energy range 0.15–0.9 eV. The second peak has been located in both experiments at 0.27 eV. The differences observed at electron energies below 0.15 eV are most likely due to rapid changes of the electron current in this region, which is difficult to take into account and also due to the different electron distribution functions. The shoulder within the electron energy interval of 1–2 eV, due to DEA process via ^2E anionic state has been observed in present experiment with relatively higher intensity than in [28]. In the present experiment, the contribution of the $CHCl_2^-$ ion to this shoulder can be excluded. The cross-section for DEA to $CHCl_3$ has been derived from the electron temperature dependence of the DEA rate coefficient [27] by using a deconvolution procedure. Those for the gas temperature 300 and 450 K, respectively, are shown in Fig. 7 together with the present cross-section data obtained at the gas temperature of 328 and 419 K. The cross-sections have a similar shape at electron energies above 100 meV, however the second peak found in [27] is slightly shifted towards the higher electron energy (330 meV). At electron energies below 0.1 eV the increase of the cross-sections with decreasing electron energy has been found in the present study and also in earlier experiments [27]. The increase in this part of the cross-section with T is evident from Fig. 7.

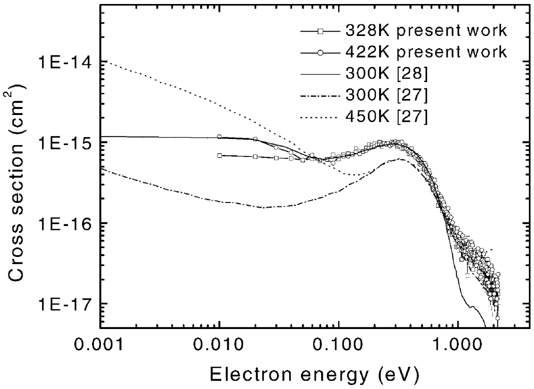

Fig. 7. Cross-section for the DEA reaction $Cl^-/CHCl_3$ as a function of the electron energy at 328 and 419 K.

3.3. CF_2Cl_2

The molecule CF_2Cl_2 (Freon 12) is of great importance for the atmospheric chemistry. The role of this molecule in destruction of the stratospheric ozone has been recognised. For this reason the study of reactivity of such molecule has attracted high attention over the last three decades. In beam experiments Illenberger et al. [30] have measured DEA to CF_2Cl_2 (R3) at room temperature. At low electron energies only one peak for production of Cl^- at around 0.8 eV has been observed. Chen and Chantry have measured DEA of low-energy electrons to this molecule in the temperature range from 300 to 1000 K, using a retarding potential cross-beam technique [31]. The activation energy of 130 meV has been estimated from the measured zero energy peak. Kiendler et al. [15] experimentally investigated the effect of the gas temperature on the relative cross-section for DEA to CF_2Cl_2. At low electron energies ($\approx$0 eV) a strong peak in attachment cross-section has been observed followed by a shoulder up to 0.8 eV. From the temperature dependence of the ion signal at low electron energies ($\approx$0 eV) an activation energy of 120 meV has been estimated. Recently, Aflatooni and Burrow [32] published absolute cross-section for DEA to CF_2Cl_2. In the electron energy range below 2 eV two resonances have been observed, the first one at $\approx$0 eV and the second one at 0.71 eV. For the second resonance the absolute cross-section has value of 5.44×10^{-17} cm^2. A large number of swarm experiments has been performed to study the process (R3). The temperature dependence of the rate coefficient for DEA to this molecule has been measured by Smith et al. [8] in the temperature range 200–600 K and an activation energy of 150 meV has been derived from these measurements. Using an electron cyclotron resonance technique Schumacher et al. [33] derived an activation energy of 190 meV and Wentworth et al. [29] a value of 150 meV.

In the present work ion yields for DEA to CF_2Cl_2 (R2) have been measured as a function of T in the gas temperature range 402–515 K (Fig. 8a). The electron energy distribution of the electron beam was 56 meV FWHM. The ion signal, as a function of the electron energy at the lowest gas temperature $T = 402$ K, exhibits two peaks, the first one at $\approx$0 eV and the second one at 0.7 eV. The positions of two peaks agree well with those in recently published by Hahndorf and Illenberger [10] and Aflatooni and Burrow [32].

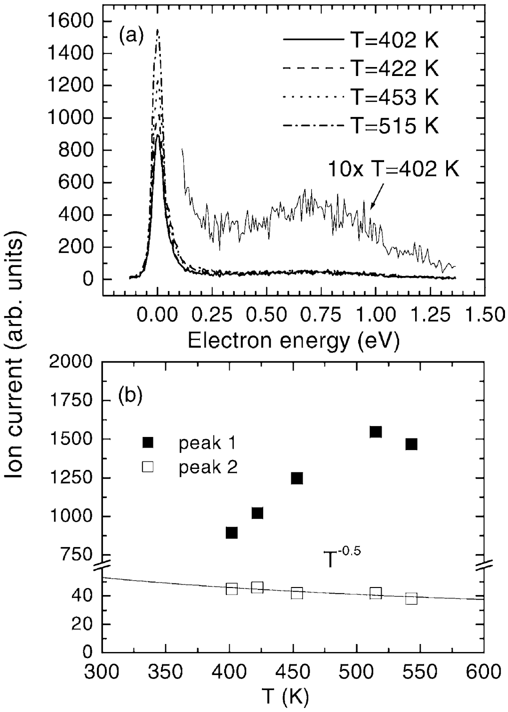

Fig. 8. (a) Ion yield curve for DEA reaction Cl^-/CF_2Cl_2 as a function of the gas temperature. (b) Cl^-/CF_2Cl_2 intensity of the $\approx$0 and 0.7 eV peaks as a function of T. The $T^{-0.5}$ dependence of the ion signal is indicated by a solid line.

Strong temperature dependence of the zero energy peak is evident from Fig. 10b. In the previous temperature-dependent beam experiments [10,15] similar effects have been observed. From the slope of the Arrhenius plot (see Fig. 9) an activation energy of 130 meV can be estimated for. The intensity of the second peak (0.7 eV) decreases with T as $T^{-0.5}$ (Fig. 8b). It hence can be concluded that the cross-section at electron energy of 0.7 eV is independent on gas temperature.

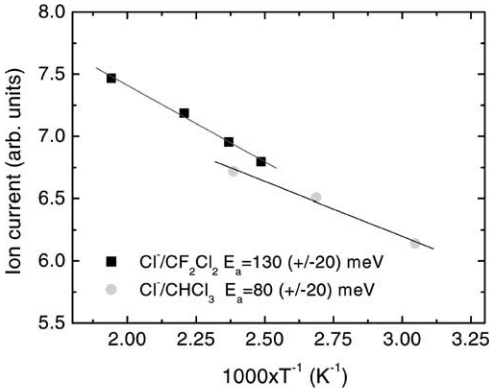

Fig. 9. Arrhenius plots for the DEA Cl^-/CF_2Cl_2 and $Cl^-/CHCl_3$.

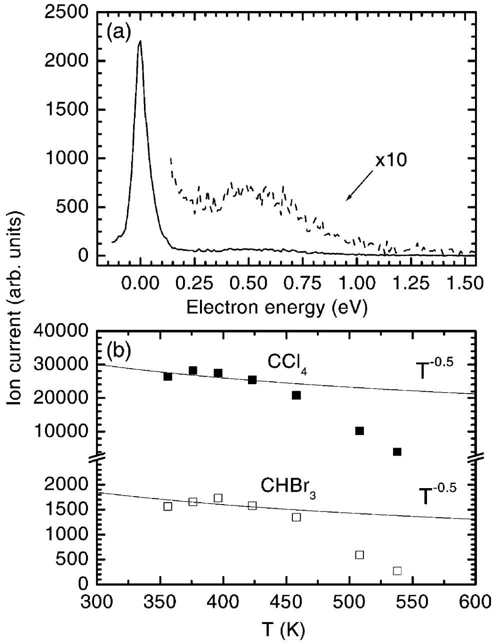

Fig. 10. (a) Ion yield curve for the DEA reaction $Br^-/CHBr_3$. (b) $Br^-/CHBr_3$ intensity of the 0 eV peak as a function of T. For a comparison the gas temperature dependence of the first peak in the DEA to CCl_4 is presented. The $T^{-0.5}$ dependence of the ion signal is indicated by a solid line.

3.4. *CHBr₃*

DEA to bromoform (R4) has been measured as a function of the electron energy and the gas temperature at an FWHM of 70 meV. The Br^- ion yield as a function of electron energy (Fig. 10a) exhibits two peaks, at ≈0 and at 0.5 eV. Sunagawa and Shimamori [34] measured the total rate coefficient for electron attachment to $CHBr_3$ as a function of the electron temperature at $T = 300$ K using pulsed-radiolysis microwave method. Using the rate coefficients and a deconvolution procedure the cross-section for electron attachment to $CHBr_3$ has been derived and is compared with the present data (Fig. 11). The relative data was calibrated by the value $\sigma = 1 \times 10^{-15}$ cm^2 at an electron energy of 200 meV. There are two substantial differences between present data and data published by Sunagawa and Shimamori [34] (i) at electron energies below 100 meV and (ii) above 300 meV. In the low electron energy range (below 100 meV) the shape of present data is apparative, due to the finite electron energy distribution function of the electron beam (FWHM = 70 meV). At the electron energies above 300 meV, clear broad structure appears in the present data, with the maximum at about 500 meV, which is not observed by Sunagawa and Shimamori [34].

The gas temperature dependence of the first peak in the temperature range 356–538 K is shown in the Fig. 10b. In the temperature range 356–458 K the intensity of the first peak varies with the gas temperature as $T^{-0.5}$. It can be surmised that in this temperature range the cross-section for DEA to $CHBr_3$ does not depend on T. The decrease of the ion signal at gas temperatures above 458 K is due to thermal decom-

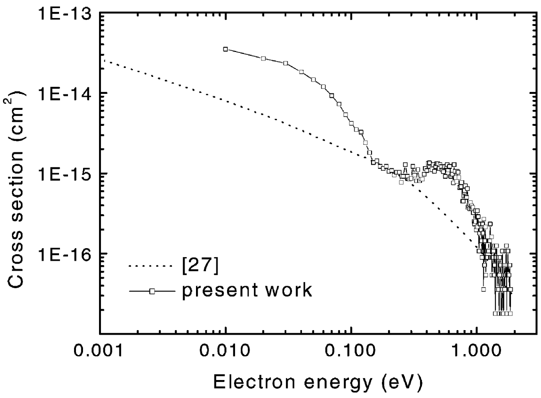

Fig. 11. DEA cross-section $Br^-/CHBr_3$ as a function of the electron energy at room temperature.

position of the $CHBr_3$ in the EMBS. A similar effect has been observed in the case of CCl_4, $CHCl_3$ in present work and in case of CH_3Cl in [24]. In Fig. 10b for comparison, the gas temperature dependence of the zero electron energy peak in DEA CCl_4 is presented. The DEA studies to $CHBr_3$ have been performed in a mixture of $CHBr_3$ and CCl_4, hence both signals have been measured simultaneously. The gas temperature dependencies of the first peaks of $CHBr_3$ and CCl_4 are identical. This fact indicates that both the cross-section for DEA to $CHBr_3$ and to CCl_4 is not affected by gas temperature T and that surface assisted thermal decomposition of $CHBr_3$ on walls of the EMBS has similar character as the thermal decomposition of CCl_4.

4. Conclusions

In the present paper the study of dissociative electron attachment to several halocarbon molecules in the gas phase have been carried out using a new high-resolution electron-molecular beam apparatus. Using a heated effusive molecular beam source the temperature dependencies of dissociative electron attachment to CCl_4, $CHCl_3$, CF_2Cl_2, and $CHBr_3$ have been measured within the gas temperature range 300–550 K and the electron energy range 0–2 eV. DEA to CCl_4 and $CHBr_3$ have been measured in the gas temperature range 376–538 K. In the gas temperature range 376–460 K, and the entire electron energy range the cross-section for DEA does not vary with T. At the gas temperatures above 460 K a strong decrease of the ion signal has been observed for both molecules due to surface assisted thermal decomposition of molecules in the molecular beam source. The DEA attachment reactions to $CHCl_3$ and CF_2Cl_2 showed a different behaviour with increasing temperature T. A substantial increase of the low electron energy peaks has been observed for $CHCl_3$ within the temperature range 328–422 K and for CF_2Cl_2 in the gas temperature range from 402 to 543 K. An activation energy of 80 ± 20 meV for $CHCl_3$ and 130 ± 20 meV for CF_2Cl_2 have been derived from the corresponding Arrhenius plots. The DEA reaction via the second peaks (0.27 eV for $CHCl_3$ and 0.7 eV for CF_2Cl_2) are in this temperature range independent on T. The decrease of the $Cl^-/CHCl_3$ signal at gas temperatures above 422 K is assigned to the surface-assisted thermal decomposition. In the case of CF_2Cl_2 the thermal decomposition has not been observed over the entire measured temperature range.

Acknowledgements

This work was supported by the Volkswagen-Stiftung (I/73593) (Germany) and by the Slovak Grant agency VEGA project No. 1/8313/01.

References

[1] L.G. Christophorou (Ed.), Electron–Molecules Interactions and Their Applications, Academic Press, Orlando, 1984.

[2] E. Illenberger, J. Momigny, Gaseous Molecular Ions, Springer-Verlag, New York, 1992.

[3] E. Illenberger, Chem. Rev. 92 (1992) 3369.

[4] D. Spence, G.J. Schulz, J. Chem. Phys. 58 (1973) 1800.

[5] C.L. Chen, P.J. Chantry, J. Chem. Phys. 71 (1979) 3897.

[6] F.C. Fehsenfeld, J. Chem. Phys. 53 (1970) 2000.

[7] L.M. Warman, M.C. Sauer, Int. J. Radiat. Phys. Chem. 3 (1971) 273.

[8] D. Smith, N.G. Adams, E. Alge, J. Phys. B: Atom. Mol. Opt. Phys. 17 (1984) 461.

[9] T.M. Miller, A.E. Stevens Miller, J.F. Paulson, J. Chem. Phys. 100 (1994) 8841.

[10] I. Hahndorf, E. Illenberger, Int. J. Mass Spectrom. Ion Process. 167/168 (1997) 87.

[11] D.M. Pearl, P.D. Burrow, I.I. Fabrikant, G.A. Gallup, J. Chem. Phys. 102 (1995) 2737.

[12] Š. Matejčik, G. Senn, P. Scheier, A. Kiendler, A. Stamatovic, T.D. Märk, J. Phys. Chem 107 (1997) 8955.

[13] L.G. Christophorou, J.K. Olthoff, Adv. Atom. Mol. Opt. Phys. 44 (1999) 155.

[14] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 78th Edition, CRC Press, Boca Raton, New York, 1997–1998.

[15] A. Kiendler, Š. Matejčík, J.D. Skalný, A. Stamatovic, T.D. Märk, J. Phys. B 29 (1996) 6217.

[16] A. Stamatovic, G. Schulz, Rev. Sci. Instrum. 39 (1968) 1752.

[17] D. Klar, M.-W. Ruf, H. Hotop, Chem. Phys. Lett. 189 (1992) 448.

[18] A. Kalamandrisdes, R.W. Marawar, M.A. Durham, B.G. Lindsay, K.A. Smith, F.B. Dunning, J. Chem. Phys. 93 (1990) 4043.

[19] S.C. Chu, P.D. Burrow, Chem. Phys. Lett. 172 (1990) 17.

[20] W.M. Hickam, D. Berg, J. Chem. Phys. 29 (1958) 517.
[21] P. Spanel, Š. Matejčik, D. Smith, J. Phys. B: Atom. Mol. Opt. Phys. 28 (1995) 2941.
[22] L.G. Christophorou, D.L. McCorkle, J.G. Carter, J. Chem. Phys. 54 (1971) 253.
[23] H. Shimamori, Y. Tatsumi, Y. Ogawa, T. Sunagawa, J. Chem. Phys. 97 (1992) 6335.
[24] D.M. Pearl, P.D. Burrow, Chem. Phys. Lett. 206 (1993) 483.
[25] J. Lara, H. Molero, A. Ramirez-Cuesta, W.T. Tysoe, Langmuir 12 (1999) 2488.
[26] S.S. Kumaran, M.C. Su, K.P. Lim, J.V. Michael, S.J. Klippenstein, J. DiFelice, P.S. Mudipalli, J.H. Kiefer, D.A. Dixo, K.A. Peterson, J. Phys. Chem. A 101 (1997) 8653.
[27] T. Sunagawa, H. Shimamori, Int. J. Mass. Spectrom. 205 (2001) 285.
[28] K. Aflatooni, P. Burrow, J. Chem. Phys. 113 (2000) 1455.
[29] W.E. Wentworth, R. George, H. Keith, J. Chem. Phys. 51 (1969) 1791.
[30] E. Illenberger, H.U. Scheunemann, H. Baumgärtel, Chem. Phys. 37 (1979) 21.
[31] C.L. Chen, P.J. Chantry, Bull. Am. Phys. Soc. 17 (1972) 1133.
[32] K. Aflatooni, P.D. Burrow, Int. J. Mass Spectrom. 205 (2001) 149.
[33] R. Schumacher, H.R. Sprinke, A.A. Christodoulides, E.N. Schindler, J. Chem. Phys. 82 (1978) 2248.
[34] T. Sunagawa, H. Shimamori, J. Chem. Phys. 107 (1997) 7876.