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Temperature dependence of electron attachment to $CHCl_2Br$

A crossed beams study

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Abstract. Dissociative electron attachment (DEA) to $CHCl_2Br$ has been studied in a crossed electron/molecular beams experiment in the electron energy range between 0 and 8 eV and in the gas temperature range from 321 to 478 K. The two negative fragment ions Cl^- and Br^- are formed from a prominent low energy resonant feature close to zero eV and at comparatively weaker resonances at about 0.38 eV, 2.2 eV and 5.5 eV. In contrast to swarm experiments [7], the bihalogen ion Cl_2^- was not detected in our experiment. The absolute partial cross-sections for Br^- and Cl^- reaction channels have been estimated. We find that in the low electron energy range (≈0 eV) the overall DEA cross-section as well as the partial DEA cross-section for Br^- formation slightly decrease with increasing gas temperature whilst the partial cross-section for the Cl^- channel is temperature independent.

PACS. 34.80.Ht Dissociation and dissociative attachment by electron impact

1 Introduction

Dissociative electron attachment (DEA) to molecules is often a very effective reaction and responsible, e.g., for negative ion formation in plasmas [1]. DEA to halogenated hydrocarbons in many cases is exothermic and hence already low energy electrons are able to ionize and dissociate the corresponding molecules. The rate coefficients in many exothermic DEA reactions depend sensitively on both the electron and gas temperature [2]. In most plasmas used for industrial application like material processing low energy electrons in the range of a few eV are abundantly present and the feed gas molecules exist at elevated temperatures. Therefore knowledge of the electron energy dependence of the DEA cross-section as well as its dependence on the gas temperature is essential to describe and model such plasmas.

In this paper we present results of a crossed electron/molecule beams study of DEA to $CHCl_2Br$. The reaction is studied in the electron energy range from about 0 to 8 eV and in the gas temperature range from 321 to 475 K. At low energy, the appearance of the two fragment ions Cl^- and Br^- is due to the following reactions:

$$e(0\text{ eV}) + CHCl_2Br \rightarrow Cl^- + CHClBr \quad (1)$$

$$\rightarrow Br^- + CHCl_2. \quad (2)$$

Both reactions are most probably exothermic with the Br-channel at lower energies (in analogy to CH_2ClBr and $CHClBr_2$). However, the existing thermodynamic data do not allow us calculate the exact enthalpies of these reactions [3,4].

The present study was motivated by our former experiments on DEA to the compounds CH_2ClBr and $CHClBr_2$ [5,6]. In these studies we have measured the total DEA cross-section its temperature dependence and the partitioning of the two exothermic reaction channels Br^- and Cl^-.

The general feature in DEA to chloro-bromo-methanes is the appreciable dominance of Br^- over Cl^-. This is due to the fact, that the Br-channel is energetically more favourable. In addition, the higher polarizability of Br leads to a preferential localization of the excess charge towards the Br site already at the instant of electron attachment. Most remarkable, the temperature dependence of the DEA cross-sections in the low electron energy range (below 0.2 eV) shows a very different behavior in each molecule. In the case of CH_2ClBr both total DEA and the Br^- partial cross-sections increase with increasing gas temperature while the Cl^- channel decreases. On the other hand, in the similar system $CHClBr_2$ both the total DEA and the Br^- partial cross-sections are temperature independent while the Cl^- channel increases with temperature [6,7].

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DEA to $CHCl_2Br$ has been previously studied in a swarm experiment [7]. Using the Flowing Afterglow Langmuir Probe (FALP) technique the overall rate coefficient as a function of the electron and gas temperature was measured. The overall rate coefficient at 300 K was estimated as 4×10^{-8} ($\pm 15\%$) $cm^3\,s^{-1}$. Using a mass-spectrometer the product ions and the partial rate coefficient was obtained. In addition to Br^- and Cl^- a significant fraction of the bihalogen ion Cl_2^- was detected.

2 Experimental

The present experiments were performed on the crossed electron/molecular beam apparatus in Bratislava. The experimental set-up has previously been described in detail [8] and only a brief description will be given here. The electron beam is formed by means of a *trochoidal electron monochromator* (TEM). In the course of the present experiments the instrument was operated at an electron energy resolution of about 60 meV. Calibration of the electron energy scale, cross-section and estimation of the electron energy resolution was established using the well-known electron attachment process SF_6^-/SF_6.

The molecular beam was produced in an *effusive molecular beam source* (EMBS) which is temperature controlled. The beam is formed by effusing the gas through a channel (0.5 mm diameter and 4 mm long) and an external aperture. The vapour of $CHClBr_2$ is introduced into the EMBS via a precision leak valve. The vapour pressure inside the EMBS (typically 1 Pa) is measured by an absolute pressure gauge. For this molecular beam source the variation of the gas density in the beam with the gas temperature [8] can be expressed by

$$n \sim T^{-0.5} \tag{3}$$

and the temperature dependencies of the cross-section have to be corrected accordingly. The profile of the molecular beam does not change with the temperature in the present experiment.

Negative ions formed within the intersection between the electron beam and the molecular beam are extracted by a weak electric field (less then 1 $V\,m^{-1}$) and focused onto a Quadrupole Mass Spectrometer (QMS). Working with low extraction fields in the reaction chamber means that there is practically no discrimination of the ions in the reaction chamber due to initial kinetic energy and mass of the ions. The mass analysed negative ion signal is then detected as a function of the electron energy at different target gas temperatures. According to our experiences we may neglect the mass discrimination of the ions in the mass spectrometer in our experiment. Due to large mass difference (45 atomic mass units) between the Cl^- and Br^- negative ions the quadrupole mass spectrometer is tuned to low resolution (thus high transition efficiency), but still good enough to separate the ions. Under these conditions, there are negligible differences in the transmission of the ions. The detection efficiency of the electron multiplier in given mass range is high and constant. For this reason we do not expect discrimination effects concerning the Cl^-/Br^- ratio.

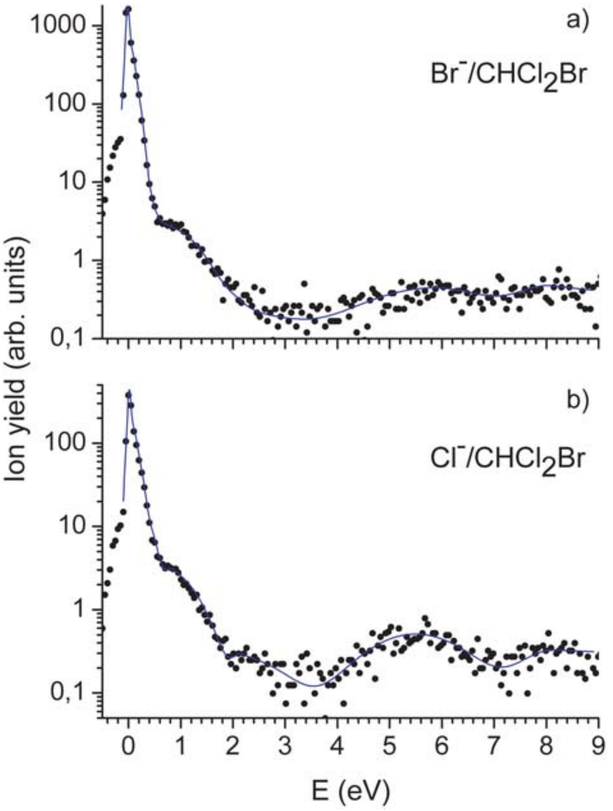

Fig. 1. The Br^- (a) and Cl^- (b) ion yields for DEA to $CHCl_2Br$ measured at $T = 321$ K.

3 Results and discussions

Figure 1 shows the ion yields for the negative ions recorded at the gas temperature of 321 K. Br^- and Cl^- ions are the only negative ions observable from $CHClBr_2$ in present experiment in the electron energy range from 0 to 8 eV. The molecular ion observed in swarm experiment Cl_2^- [7] was not detected in the current experiment within the sensitivity of the apparatus. The sensitivity of the apparatus was sufficient to detect the Cl_2^- ions at the rate observed in the FALP experiment [7]. The intensities are in arbitrary units but within the same scale for both fragment ions. The ion yields peak at energies close to zero eV. Both curves exhibit apparent shoulders near 1 eV. It should be noted that near threshold (0 eV) the shape of the ion yields is strongly affected by the electron energy distribution function: the measured ion yield is a convolution of the electron energy distribution function $f(E,U)$ and the cross-section $\sigma(E)$:

$$I(U) = K \int_0^\infty \sigma(E) f(E,U) dv \tag{4}$$

where $I(U)$ is the ion yield at the acceleration voltage U, $\sigma(E)$ is the cross-section for the DEA reaction, $f(E,U)$ is

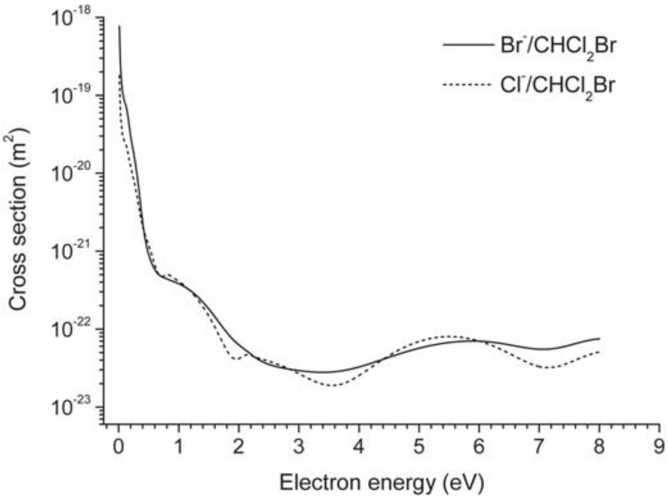

Fig. 2. Partial cross-sections for DEA to $CHCl_2Br$.

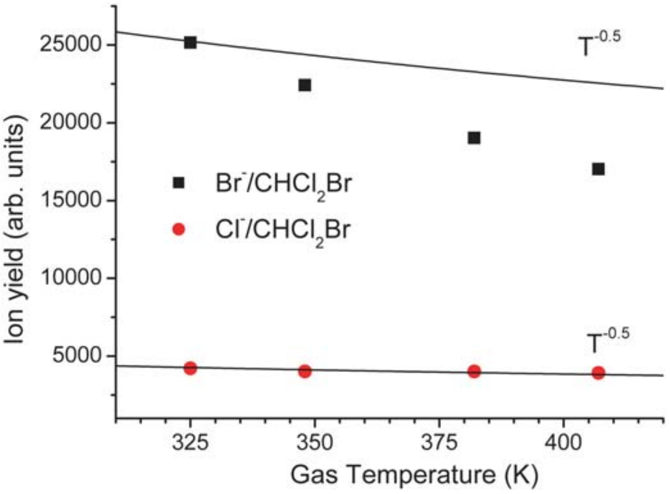

Fig. 3. The temperature dependencies of the overall and Br^- ion yield (■); Cl^- ion yield (●) at low electron energies (∼0 eV). The ion yields are not corrected for the temperature dependence of the gas density $T^{-0.5}$ which are indicated by the full lines.

the distribution function for the electron energy which is directly related to the acceleration voltage U and K express the overall efficiency of the extraction, transmission and detection of the ions. The shape of the ion yield below the 0 eV is due to convolution of the electron energy distribution function with the cross-section for DEA to the molecule.

The next resonances present in the ion yields were observed at 2.2 eV and 5.5 eV in Cl^- and at 5.9 eV for Br^- ion. A resonance corresponding to the 2.2 eV resonance in Cl^- is not apparent in the Br^- ion yield. The positions of the DEA peaks have been obtained by non linear least square fitting of the Gaussian functions to the ion yields.

Figure 2 presents absolute partial cross-sections for reactions (1) and (2). The cross-section curves were obtained by data analysis of the experimental ion yields measured at 321 K (Fig. 1). As mentioned above (Eq. (3)) the measured ion yield is a convolution of the cross-section and the electron energy distribution function and also depends on the detection sensitivity of the apparatus. Measuring the ion yield for the reference molecule SF_6 under well defined experimental conditions we are able to determine the electron energy distribution function $f(E,U)$ and the response function K. Using $f(E,U)$ and K we are able to estimate cross-sections for a molecule measured under comparable conditions as the reference molecule (electron current, $f(E,U)$, pressure, etc.). We assume identical sensitivity of the apparatus K for the detection of the ions. The electron attachment cross-section for the reference molecule SF_6 is well-known [9]. The DEA cross-sections (Fig. 2) were obtained from the ion yields by a deconvolution procedure (see [10] for details).

To compare the present cross-section data with the rate coefficients obtained from swarm experiments at room temperature [7] we have calculated the DEA rate coefficient using the present partial cross-sections. The value of the total rate coefficient (sum of the Br^- and Cl^- channels) at $T_e = 321$ K is 5×10^{-8} $cm^3\,s^{-1}$. This value is in very good agreement with the rate coefficient determined by Spanel et al. [7] in their FALP experiment at $T = 300$ K (4×10^{-8} ($\pm 15\%$) $cm^3\,s^{-1}$).

Figure 3 presents the dependence of the ion yields at ≈0 eV as a function of the gas temperature in the temperature range from 321 to 475 K. The Br^- ion yield shows a decrease with increasing temperature. The decrease is stronger than the temperature dependence $T^{-0.5}$ describing the decrease of the gas number density in the molecular beam. This indicates that the partial cross-section for this reaction channel decreases with temperature. The Cl^- ion yield follows the $T^{-0.5}$ function and thus the Cl^- cross-section, is for this electron energy independent of temperature. This means that the overall ion intensity in the present experiment decreases with temperature. Note that the experimental points in Figure 3 are not corrected for the temperature dependence of the gas density.

The observed temperature dependence of the DEA in the gas phase is in disagreement with the swarm experiment. Whilst in the swarm experiment the total attachment rate coefficient rapidly increases with the temperature, the total cross-section in the beam experiment decreases. This difference and also the high temperature data from the FALP experiment indicate that collisional effects i.e. collisions of the transient negative ions with the buffer gas may play an important role in the FALP experiment at higher gas temperatures. This is also supported by the fact that in beam experiment only Cl^- and Br^- ions were observed while in the swarm experiment additionally the molecular ion Cl_2^- was detected [7].

The branching ratios R ($R = Br^-/(Cl^- + Br^-)$ where Br^- and Cl^- are the ion yields of the ions Br^- and Cl^-) are shown in Figure 4 as functions of the electron energy and the gas temperature at 321 and 440 K. The branching ratio at 321 K indicates that Br^- is the dominant product ion. The branching ratio R obtained by Spanel et al. [7] in the FALP experiment at 293 K is in good agreement

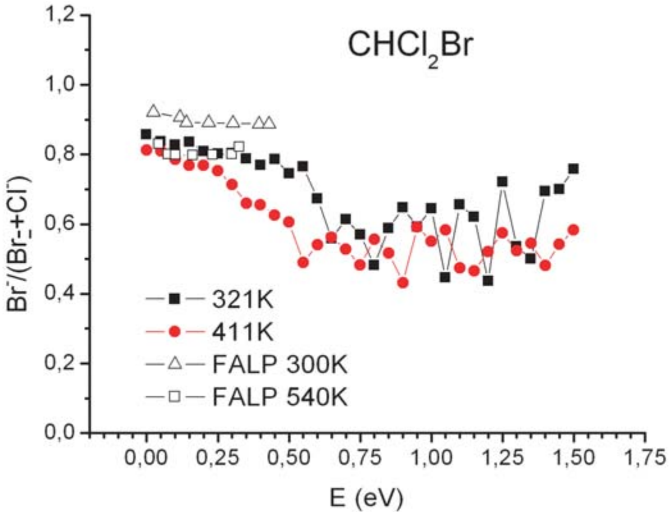

Fig. 4. The branching ratio R ($\mathrm{Br}^-/(\mathrm{Br}^-+\mathrm{Cl}^-)$) as a function of electron energy and gas temperature. For a comparison the branching ratios from FALP experiment [7] are indicated.

with the present results. At 440 K we observe slight decrease of the branching ratio in comparison to 321 K in the low electron energy range, however, in the whole electron energy range Br^- ion is still dominant product. The FALP branching ratio at 540 K was also lower than that at 293 K.

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References

1. *Electron-Molecule Interactions and Their Applications*, edited by L.G. Christophorou (Academic, Orlando, 1984), Vols. I and II
2. D. Smith, P. Spanel, in *Adv. At. Mol. and Opt. Phys.* (Academic Press, 1993), Vol. 32
3. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 – March, 2003 Release, `http://webbook.nist.gov`
4. *CRC Handbook of Chemistry and Physics on CD-ROM*, edited by D.R. Lide (CRC Press, 2003)
5. S. Matejcik, I. Ipolyi, E. Illenberger, Chem. Phys. Lett. **375**, 660 (2003)
6. I. Ipolyi, S. Matejcik, P. Lukac, J.D. Skalny, P. Mach, J. Urban, Int. J. of Mass Spect. **233**, 193 (2004)
7. P. Spanel, D. Smith, Int. J. Mass Spectrom. **205**, 243 (2001)
8. S. Matejcik, V. Foltin, M. Stano, J.D. Skalny, Int. J. Mass Spectrom. **223–224**, 9 (2003)
9. A. Schramm, I. Fabrikant, J.M. Weber, E. Leber, M.-W. Ruf, H. Hotop, J. Phys. B: At. Opt. Mol. Phys. **32**, 2153 (1999)
10. M. Stano, V. Foltin, S. Matejcik, J. Langer, S. Gohlke, E. Illenberger, J. Phys. B: At. Mol. Opt. Phys. **36**, 443 (2003)