

New Crossed Electron-Molecule Apparatus, Electron Attachment Studies to SF₆, CCl₄, CCl₂F₂, CHCl₃ and CHBr₃

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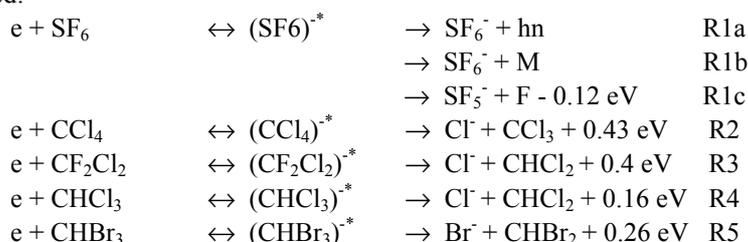
Abstract: Using a new crossed electron-molecule beam apparatus relative cross sections for dissociative electron attachment to SF₆, CCl₄, CCl₂F₂, CHCl₃ and CHBr₃ molecules have been measured at low electron energies from about 0 to 2 eV. The electron energy resolution measurements of the electron beam and the calibration of the electron energy scale have been performed with SF₆ and CCl₄ as a test and calibrant gases. Using a trochoidal electron monochromator electron energy resolution of the electron beam with FWHM of 17 meV has been achieved. The present measurements of dissociative electron attachment to first four molecules are in excellent agreement with previous studies. The dissociative electron attachment to CHBr₃ has been measured in a crossed beam experiment for the first time. Two resonances have been observed at about 0 eV and at about 0.6 eV.

1. Introduction

Electron attachment (EA) studies to the molecules are of fundamental importance to the understanding of electron-molecule interactions at low electron energies and negative ion formation in low temperature plasma. Electron attachment reactions play an important role in various fields of chemistry and physics and in a large number of technological applications (gas dielectrics in high-voltage devices, certain types of discharges and plasma) [1, 2]. Due to this, EA reactions have attracted scientific attention and have been studied in many experiments using both beam [3-5] and swarm techniques [6-8]. Previous EA studies to large number of molecules demonstrated that electron attachment reactions depend strongly on the kinetic energy of electrons (or in case of swarm experiments in the electron temperature T_e) and in many cases dissociative electron attachment (DEA) to the molecules is strongly enhanced by heating the attaching gas to higher temperatures (gas temperature T_g). In most crossed beams EA experiments, EA cross sections have been measured as a function of kinetic energy of the electrons (E). In case of swarm experiments rate coefficients for EA have been measured as a function of electron temperature (T_e).

The present paper is devoted to the studies of DEA relative cross sections to some important electron attaching molecules (SF₆, CCl₄, CCl₂F₂, CHCl₃ and CHBr₃). This study has been performed with a new high-resolution electron/molecular crossed beams apparatus built at the Department of Plasma Physics of the Comenius University in Bratislava. In this report careful description of this new apparatus is done and the first measurements documenting reliability of this new apparatus are presented. In order to test the ability of the

new apparatus to measure relative DEA cross sections, the following molecules have been measured:



Reactions R1-R4 have been already measured in crossed beam experiment and therefore their relative cross section are known. For this reason they are suitable as a test molecules for the new apparatus. The electron attachment to CHBr_3 (R5) has been measured for the first time in a crossed beams experiment.

EA to the molecules is a reaction processing trough two steps i) formation of a transient negative ion (TNI) and ii) dissociation of the TNI or electron detachment from TNI, which is a concurrent process to the dissociation. Formation of TNI is a resonant process and is effective only in a narrow interval of electron energies.

2. Experiment

The present studies were carried out with a new high-resolution electron-molecular beam apparatus. Schematic view of the apparatus is presented in Fig. 1. The electron beam formed by Trochoidal Electron Monochromator (TEM) and accelerated on desired energy is perpendicularly crossed by a molecular beam formed by Effusive Molecular Beam Source (EMBS). Negative ions produced in the reaction chamber are extracted by weak electric field from the interaction region and focused into the entrance of Quadrupole Mass Spectrometer (QMS). The mass selected negative ions are detected as a function of electron energy in single-ion counting mode using a secondary electron multiplier, ion counting electronic and PC acquisition system. The whole system is located in a high vacuum chamber and pumped out with 500 ls^{-1} turbo-molecular pump. The vacuum chamber is heated by a system of two lamps ($2 \times 500 \text{ W}$) inside the chamber, in order to achieve clean surfaces of the TEM (limit pressure of the apparatus $p < 5 \cdot 10^{-7} \text{ pa}$). During the measurements, when molecules flow trough EMBS inside the vacuum chamber, the pressure in the vacuum chamber is usually below $8 \cdot 10^{-6} \text{ pa}$.

The TEM (Fig. 2) has been for the first time developed by Stamatovic and Schulz [9]. The electrons are produced by thermal emission from a hairpin filament directly heated by passing current. The electron beam is formed by a system of electrodes, is directed in the x-direction and enters dispersive element of TEM. As a dispersive element of this monochromator, region with crossed homogenous electric (y-direction) and magnetic field (x-direction) is used. In this dispersive element the electrons are separated according to their x-component of velocity. After passing the dispersive region, slow electrons are more deflected (in z-direction) then the faster ones. Using an aperture with diameter of 1 mm, only electrons with a narrow energy spread leave the dispersive region and are further ac-

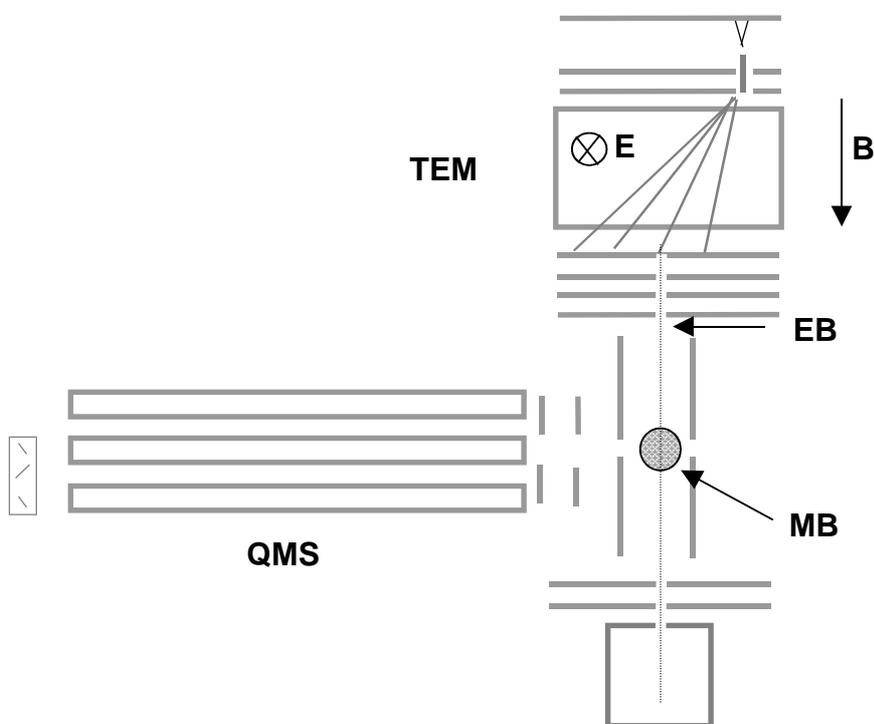


Fig. 1. Schematic view of the electron-molecular beam apparatus, TEM - trochoidal electron monochromator, EB - electron beam, MB - molecular beam, QMS - quadrupole mass spectrometer.

celerated or decelerated by a system of three electrodes on desired energy. The electrons enter the reaction chamber and react with the molecules. The kinetic energy of the electrons is defined by the potential difference between filament and reaction chamber. The homogeneous electric field of the dispersive region is formed by a system of two planar electrodes (E about 1 V/cm). The homogeneous magnetic field is produced by a pair of Helmholtz coils mounted outside of the vacuum (typical value of the magnetic field B is about 0.01 Tesla). Adjusting separately the electric and magnetic field of the TEM, the energy distribution function of the electrons in the beam is affected. The energy spread of the electrons in the electron beam measured as a Full Width at Half Maximum (FWHM) can vary on this way from a very broad (more than 200 MeV, electron current more than 200 nA) to a very narrow (20 MeV electron current lower than 10 nA).

The EMBS consists of absolute pressure sensor (MKS Barratron, pressure range $1\text{-}7$ Pa) and heatable stainless steel gas container with a single 4 mm long 0.5 mm diameter channel. A narrow molecular beam is formed by effusion of the molecules through this channel. Between the EMBS and reaction chamber of TEM a 3 mm aperture is located in order to reduce the flow of the gas in the reaction chamber and TEM. The gas inlet system of the EMBS is working at higher pressure (typically $10^5\text{-}100$ Pa) and the gas is introduced to the EMBS through a precise diaphragm regulating valve, reducing the gas pressure to

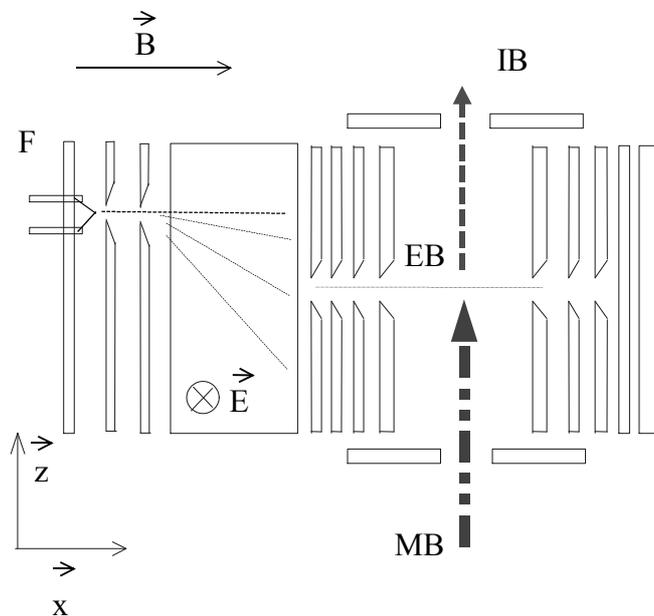


Fig. 2. Schematic view of the trochoidal electron monochromator (TEM), F - filament, B - magnetic field, E - electric field, EB - electric beam, MB - molecular beam, IB - ion beam

0.5-7 Pa. At this pressure mean free path of the molecules in the EMBS is longer than the typical dimension of the EMBS.

Molecules SF_6 and CCl_4 are usually used to calibrate the electron energy scale and to estimate electron energy resolution of the electron beam [10]. Both molecules possess very high cross-sections for EA in the threshold region (electron energies close to the zero). These cross-sections have been recently measured with high sub-millivolt resolutions by Klar et al. [11, 12] and Hotop et al. 1994 using their laser photo ionisation technique. In these studies, threshold behaviour of the EA cross-section has been measured and strong decrease of the cross-section with electron energy has been observed ($E^{-1/2}$ at very low energies and E^{-1} at higher electron energies). Strong dependence of EA cross-section on electron energy close to the threshold is the reason why both molecules are used for electron energy calibration and estimation of the energy spread of the distribution function of the electron in the electron beam in experiments with free electrons [13].

3. Results

The TNI of SF_6 molecule (SF_6^*) is observable in mass spectrometer due to its long lifetime against autodetachment and dissociation. Temporary negative ion is even the most intense ion at low electron energies (below 100 MeV). The cross-section for non-dissociative EA to SF_6 has a maximum at very low energies due to electron attachment of slow s-wave electrons and thus the cross-section varies with the electron energy as $E^{-1/2}$ [11]. In crossed beam experiments and also in swarm experiments radiative stabilisation of $(\text{SF}_6)^*$ (reac-

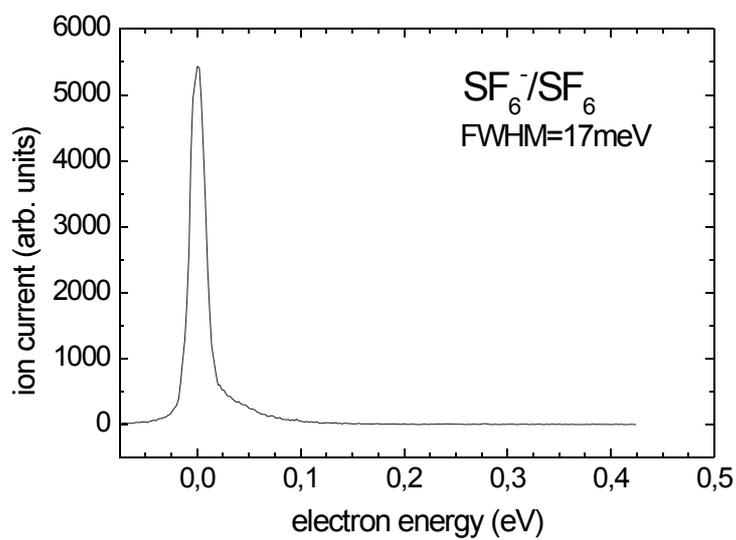


Fig. 3. Relative cross-section for electron attachment to SF₆ at room temperature.

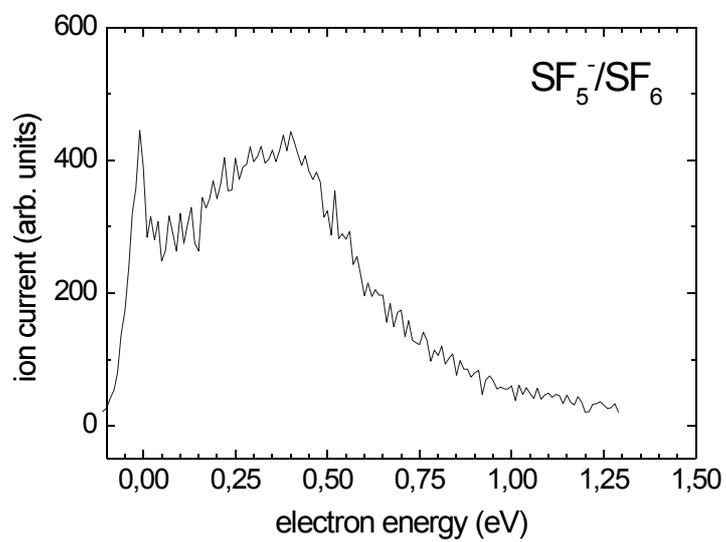


Fig. 4. Relative cross-section for dissociative electron attachment to SF₆.

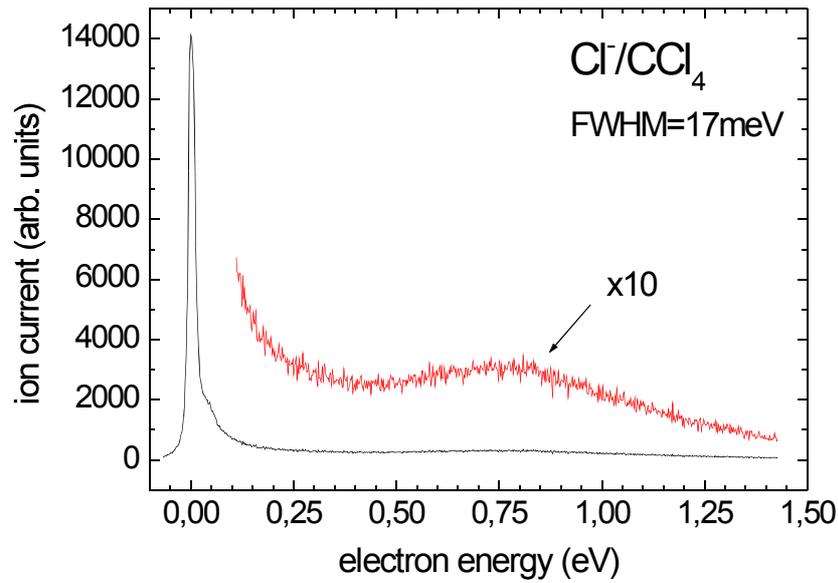


Fig. 5. Relative cross-section for dissociative electron attachment to CCl.

tion R_a) can be neglected, due to a very low probability to release the excess energy in form of electromagnetic radiation. In swarm experiments collisional stabilisation of the $(SF_6)^{-*}$ plays an important role [14]. In crossed beam experiments (at single collision conditions) collisional stabilisation does not occur and due to this fact an important difference between swarm and crossed beam experiments exists. In crossed beam experiments much more SF_5^- ions are observed than in swarm experiments. Due to absence of collisional stabilisation of $(SF_6)^{-*}$ ion in crossed beam experiments the dissociation is much more significant. With increasing electron energy fragment ion SF_5^- becomes more and more important and at energies above 100 MeV the SF_5^- ions become the dominant ion. The cross section for DEA to SF_6 possesses two distinct peaks, the first close to the zero electron energy, due to EA to the vibrational and rotational excited molecules and the second at about 380 MeV due to direct DEA to the SF_6 in a vibrational ground state. Brüning et al. [15] observed enhancement of the DEA cross section to SF_6 at very low electron energies by CO_2 laser radiations.

In the present experiment electron attachment to SF_6 has been measured with high electron energy resolution. Non-dissociative attachment to SF_6 has been observed with strong single peak at zero energy, from the shape of the peak energy resolution of the electron beam of 17 MeV has been estimated (Fig. 3). Cross section for DEA to SF_6 has two peaks, the first one at about 0 eV and the second one at about 0.4 eV (Fig. 4). Peak positions in the cross sections for non-dissociative EA and DEA to SF_6 are in excellent agreement with previous beam studies. The main advantage of present studies is the high electron energy reso-

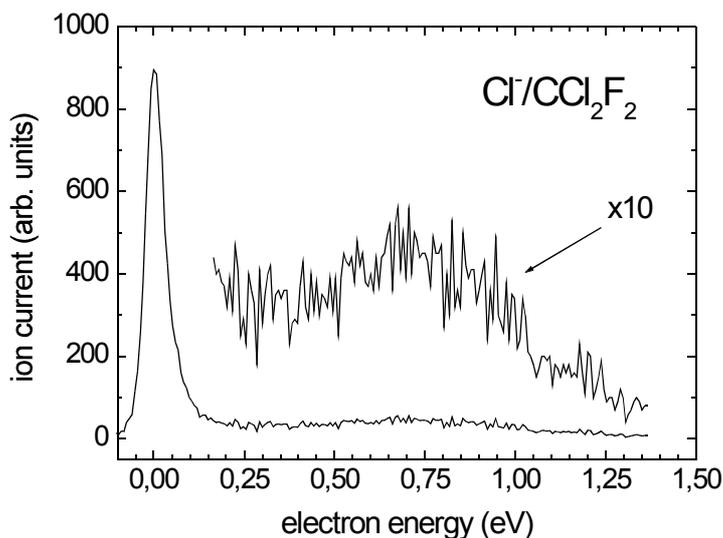


Fig. 6. Relative cross-section for dissociative electron attachment to CF_2Cl_2 .

lution. Better resolution has been achieved only in photoelectron experiment, which is, however, limited to very low electron energies.

In case of CCl_4 molecule, TNI is short living (in pico-second range [16]) and therefore no parent molecular ions can be observed in crossed beam experiments at low electron energies (below 2 eV). The only product of the DEA reaction is the Cl^- ion. The cross section for DEA to CCl_4 has two peaks, the first one at very low energies due to DEA of slow s-wave electrons, and second at around 0.8 eV due to DEA to excited state of the negative ion [3, 17]. In the present study, DEA cross section to CCl_4 has been measured with a high electron energy resolution of 17 MeV (Fig. 5). The first most intense peak has been found at zero energy and the second broad peak at about 0.8 eV. The shape of the cross section and positions of the peaks are in very good agreements with previous studies.

The molecule CF_2Cl_2 (freon 12) is of a great importance for atmospheric chemistry. The role of this molecule was recognized in destruction of the stratospheric ozone. For this reason, studies of reactivity of this molecules attracted high attention. In beam experiments Illenberger et al. [18] have measured DEA to CF_2Cl_2 at room temperature. At low electron energies one peak for production of Cl^- at around 0.8 eV has been observed. Chen et al. [19] have measured DEA of low-energy electrons to this molecule in the temperature range from 300 to 1 000 K using retarding potential cross beam technique. In their experiment zero energy peak has been observed and activation energy of 130 MeV has been estimated. At low electron energies at about 0 eV a strong peak has been observed with a shoulder up to about 0.8 eV. In the present experiment relative cross section for DEA to CF_2Cl_2 has been measured (Fig. 6). The relative cross section possesses two peaks, the first one at 0 eV and the

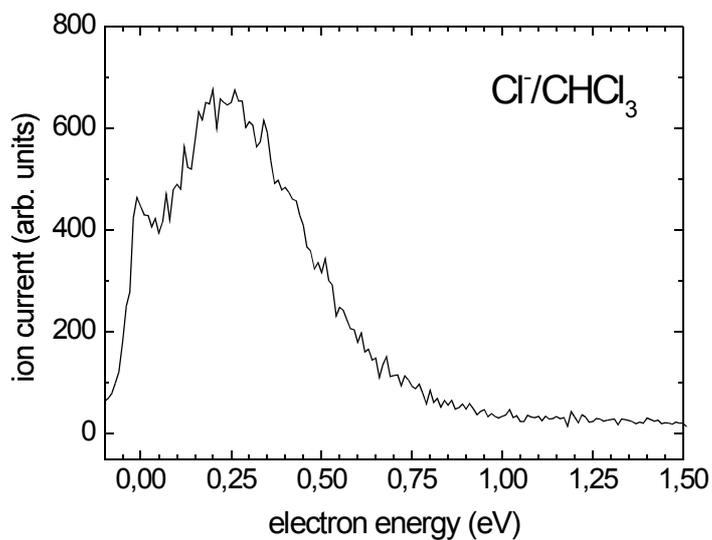


Fig. 7. Relative cross-section for dissociative electron attachment to CHCl_3 .

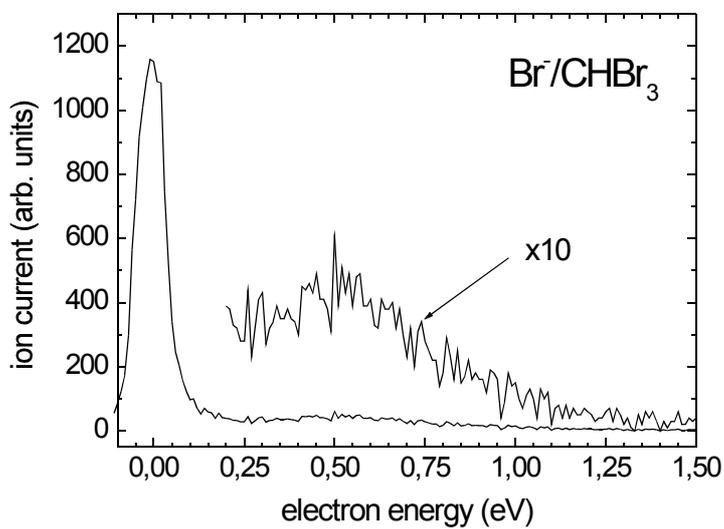


Fig. 8. Relative cross-section for dissociative electron attachment to CHBr_3 .

second one at about 0.75 eV. The agreement with previous experimental result of Hahndorf et al. [20] and Kiendler et al. [21] is satisfactory, however Kiendler et al. did not observe 0.8 eV peak in the DEA cross section (only a shoulder) this was due to strong discrimination of fast ions in this experiment. Schumacher et al. [22] did not detect the zero energy peak in his experiment. Reason for this fact is probably inability to get slow electrons in the reaction chamber. The position of the 0.8 eV peak agrees with the position of a peak in the present experiment.

The first measurement of DEA to CHCl_3 in a crossed beam experiment has been carried out by Spence et al. [3]. The measured DEA cross section as a function of electron energy to CHCl_3 had two peaks, the first one at zero energy and the one second at about 200 MeV. Chu et al. [17] measured the DEA cross section to CHCl_3 at the room temperature and find the position of the first peak at zero energy and the position of the second peak at about 270 MeV. Matejcik et al. [13] measured DEA cross section to CHCl_3 as a function of gas temperature in the temperature range from 310 to 436 K. The position of the two peaks was in agreement with the previous two beam experiments. Present studies of DEA cross section to CHCl_3 (Fig. 7) are in excellent agreement with the previous crossed beam studies. The cross section for DEA to chloroform has two distinct peaks the first at zero energy and the second at about 250 MeV.

The relative cross section for DEA to CHBr_3 (R5) is presented in Fig. 8. The DEA to this molecules proceeds through two resonances, the first one very narrow at 0 eV and the second one at about 0.5 eV. The first resonance is probably due to low energy s-wave electron attachment to the lowest (CHBr_3)- ionic state. The second resonance is probably due to electron attachment to the excited anionic state. There are no other crossed beam data on DEA to bromoform.

4. Conclusions

In the present paper electron attachment and dissociative attachment studies to the molecules in the gas phase have been performed using a new high-resolution electron-molecular beam apparatus. The measured cross-section for electron attachment to the SF_6 , CCl_4 , CCl_2F_2 , CHCl_3 are in a very good agreement with previous experimental findings. DEA cross-section to CHBr_3 has been measured for the first time in a crossed beam experiment.

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