Scientific Report

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Title of the project: Temperature effects for DEA to Halohydrocarbons

Purpose of the visit

The collaboration between the experimental physics group at Comenius University Bratislava and the institute of Ion physics at the university of Innsbruck has been launched a few years ago. Several projects have been successfully accomplished in collaboration between mentioned institutions.
The research was focused to the study of electron impact processes with various gaseous molecules at different gas temperatures by using the crossed electron – molecular beams apparatus constructed in Bratislava. The thermo-regulated source of molecular beam enables to stabilize the temperature of tested gas within the temperature interval (298 – 700℃K).hence the tempe rature dependence of cross section for various electron impacts stimulated processes can be studied over the relatively large interval of temperatures. The low energy electron attachment mechanism to a large number of halohydrocarbons have been measured at the University of Innsbruck using a high electron energy resolution monochromator. Electron attachment to molecules is of great importance for understanding electron-molecule interactions and formation of negative ions. In particular it is important to know after the initial electron capture the destiny of the transient negative ion (TNI) complex, that is either leading to auto detachment or to the production of a stable negative ion via dissociative electron attachment. It is clear, the efficiency and dynamics of DEA is determined by the competition between auto detachment and dissociation of the intermediate ion .
In particular, the efficiency will depend on the coupling between the initial electronic state of the intermediate ion and the final antibonding state that leads to dissociation of this ion. As long as the dissociation along the X^- + M potential surface is a fast process (i.e., in the case of strong coupling leading to a quick passage of the point of no return marked by the cross-over point between the XM potential curve and the X^- + M potential curves where no longer auto detachment can occur) the X^- signal intensity in the zero electron energy resonance of an endothermic reaction (1) should follow the Arrhenius temperature dependence:

$$\sigma = \sigma_0 \cdot \exp(-E_a/kT) \qquad (1)$$

The activation energy E_a can be obtained by fitting the measured data following the temperature dependence given by (1).
The aim of the visit was to study the electron attachment reactions to 1-Bromo-2-chlorobenzene, 1-Bromo-3-chlorobenzene and 1-Bromo-4-chlorobenzene. These molecules have been measured during my visit. The crossed beams apparatus at Department of Experimental Physics is equipped with trochoidal electron monochromator, quadrupole mass spectrometer and temperature controlled effusive molecular beams source .
These reactions at low electron energies is important for several reasons . The reactive species produced, a halogen anion X^- and a hydrocarbon radical M, play an important role in dry etching plasmas used in VLSI manufacturing and in excimer and chemical laser plasmas. Moreover, such species are possibly also involved in the processes leading to ozone depletion in the atmosphere. Furthermore, there exists a similarity between the dissociative electron attachment to halohydrocarbons and the process of reductive dehalogenation promoted by bacteria in anaerobic sediments, sewage sludge and aquifer materials. Therefore, an understanding of the energetics and dynamics of DEA to these XM molecules is important also for possible improvements in technological applications as well as for understanding and better control of environmental processes.

Description of the work carried out during the visit

During the visit we have studied dissociative electron attachment reaction to the Bromochlorobenzenes:

$$e^- + C_6H_4BrCl \rightarrow (C_6H_4BrCl)^- \rightarrow Br^- + C_6H_4Cl \qquad (2)$$
$$(C_6H_4BrCl)^- \rightarrow Cl^- + C_6H_6Br \qquad (3)$$

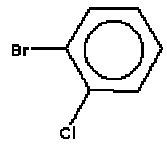
Isomers of C_6H_4BrCl : 1-Bromo-2-chlorobenzene
1-Bromo-3-chlorobenzene
1-Bromo-4-chlorobenzene

The DEA reaction is a two step process involving first formation of transient negative ion (TNI) followed by dissociation into thermodynamically stable fragments. The formation of the TNI is a resonant process in which the free electron is captured by the neutral molecule and a negative ion in its electronic ground or electronically excited state is formed. The thermodynamically unstable TNI decays then by an emission of the extra electron (autodetachment) or dissociation (DEA) into energetically accessible channels consisting of one negatively charged fragment and one or more neutral fragments. The TNI in case of DEA may dissociate in two reaction channels (1) and (2) . The DEA is characterized by cross section which depends on electron energy and gas temperature.
Using the experimental setup we have measured the gas temperature dependence of the cross sections to these molecules in the gas temperature range from 298 to 643°K.
In this case DEA reactions have been studied in the electron energy range 0 to about 2eV. We have studied the temperature dependence of DEA reactions for the Br- and Cl- reaction channel.
On The first two days we worked on the gas inlets. There was a big leak and we were trying to find and fix it.

In Bratislava, they use shared gas inlets for both calibrating gas (SF_6) and sample. Then it is very difficult to manage how to regulate sample vapor and SF_6 going through the inlets to the oven. As SF_6 has high pressure compared to the compounds which were supposed to be measured, it didn't let the vapor of the sample passes the inlets and enters the oven. As I needed SF_6 to be inside the reaction chamber during the whole measurements at different temperatures (for energy calibration at different temperatures), then I couldn't introduce SF_6 once at the beginning of the measurement and close SF_6 valve. After working a lot on that, finally I could solve this problem.
All the measurements at different temperatures have been reproduced and remeasured once more to get reliable data.
After I finished 1-Bromo-2-Chlorobenzene and 1-Bromo-3-Chlorobenzene measurements it was the time to measure 1-Bromo-4-chlorobenzene but I was facing something strange. The plastic bottle of this compound which had been ordered from Sigma Aldrich company and was completely packed was empty.

Description of the main results obtained

1)1-Bromo-2-chlorobenzene



Formula: C6H4ClBr
mass %
190 77.3 _____
191 5.0 __
192 100.0 _____
193 6.5 ___
194 24.2 _____
195 1.6 _
196 0.0
Vapour Pressure: 0.397 mmHg at 25℃

After tuning monochromator for zero energy electrons ,I did negative mass scan to detect which anions are produced. Working a lot on monochromator and also SF_6 as a calibrating gas and get much more experience, I know that I can not trust only the shape and also energy resolutions. even with good signal shape and energy resolution it happens that man is far from the zero energy electrons distributions. To solve this problem I always measure SF_5^- with well known resonances, one at zero and the other one at 0.3eV (Fig.1 and Fig. 2)
I have to mention that although there are the other calibrating gas, the best CCl_4, but as the whole compounds which I measure, contain Cl in their structure so it is impossible to use it.

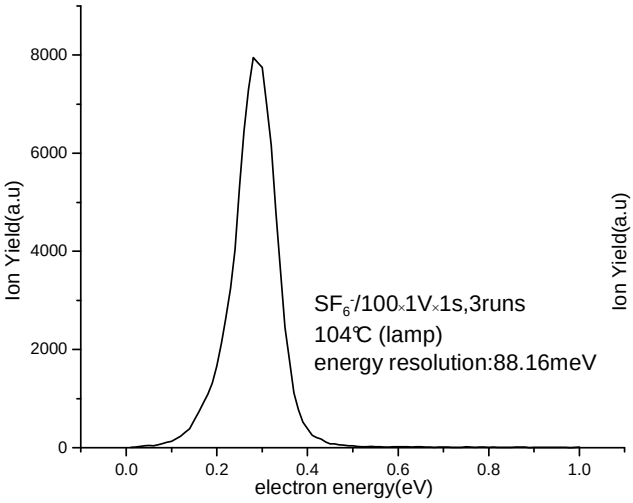


Fig.1 *Energy calibration signal SF_6^- from SF_6 With energy resolution of 88meV for the Present results.*

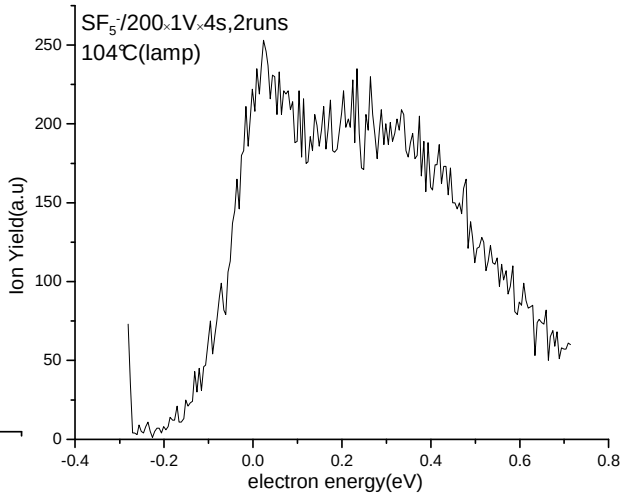


Fig. 2 *SF_5^- signal obtained from electron attachment to SF_6 under single Collision conditions*

it is evident from Fig.3 that The possible channels through DEA for 1-Bromo-2-chlorobenzene is Br^- and Cl^- . Although Br has lower electron affinity compared to Cl but Fig. 1 shows that the weak bond energy and also high cross section of Br^- channel makes that much prominent.

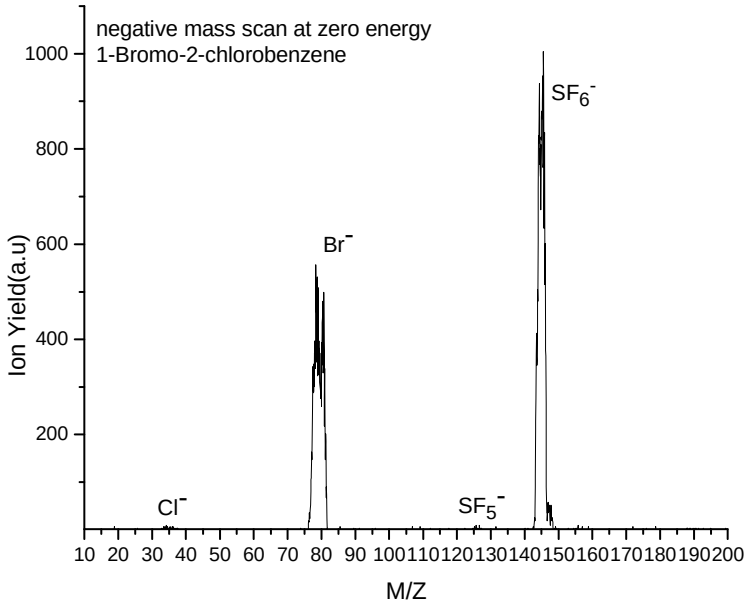


Fig3. *Negative mass scan of 1-Bromo-2-Chlorobenzene done at zero energy electrons.*

In Figure 4 the Br^- ion yields for DEA to 1-Bromo-2-Chlorobenzene measured at from 377 till 643ºK temperature are presented. The ion yields measured at different temperatures show dependence on the gas temperature in the measured temperature range.

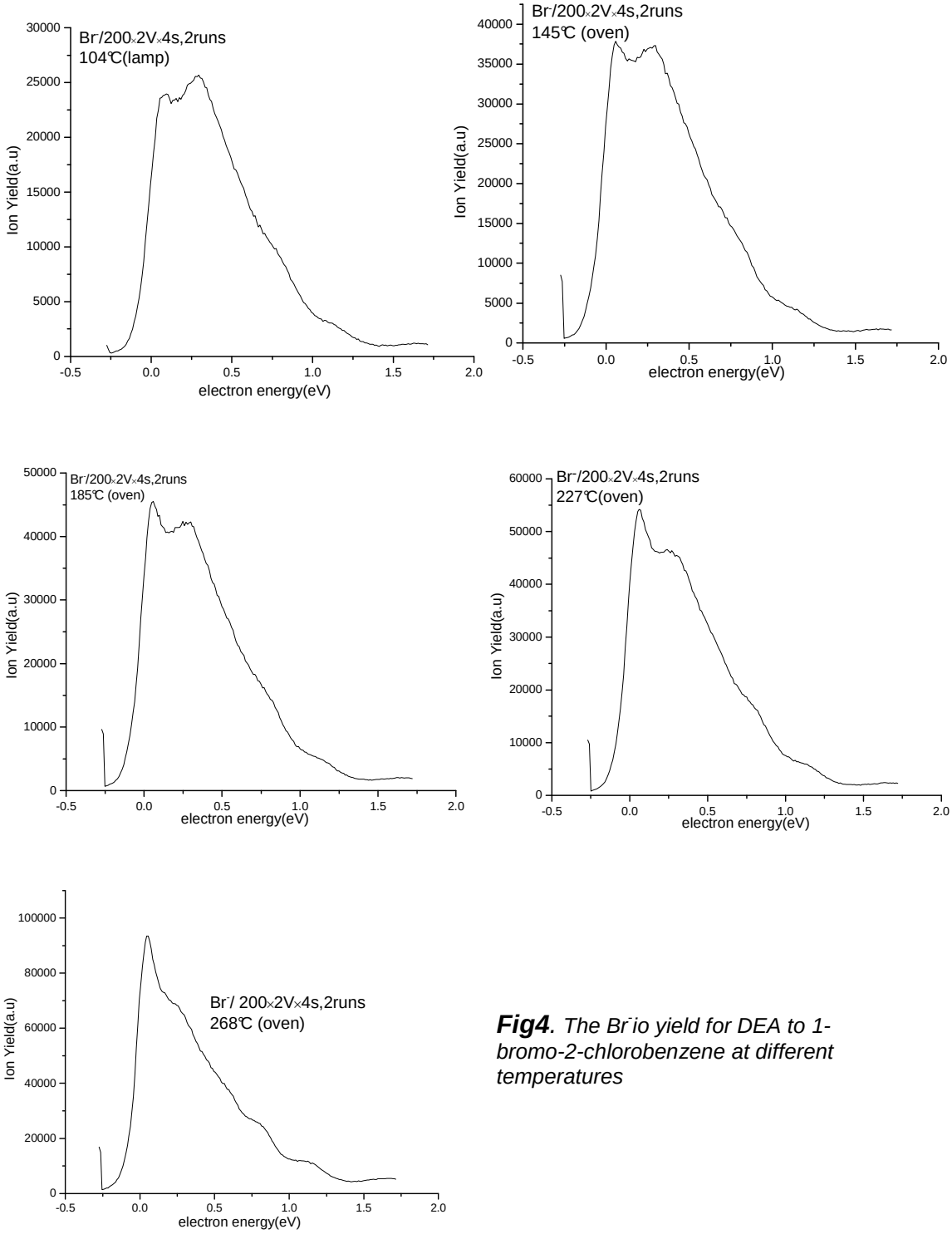


Fig4*. The Br^- io yield for DEA to 1-bromo-2-chlorobenzene at different temperatures*

In the case of Cl^- we observed temperature dependency but it appears at very high temperature compared to Br^- (Fig5).

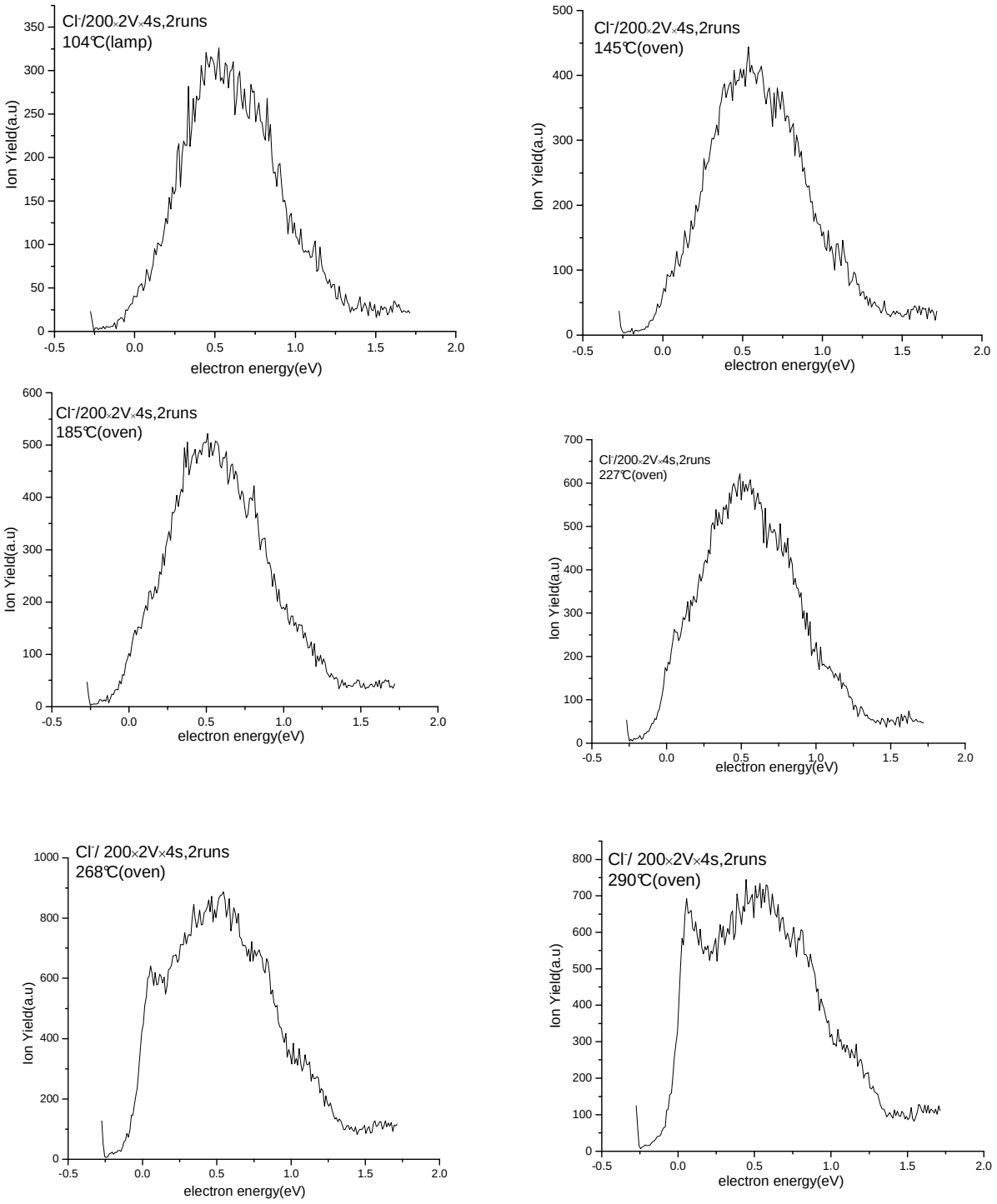
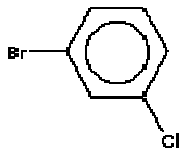


Fig5. *The Cl^- ion yield for DEA to 1-bromo-2-chlorobenzene measured at different temperatures*

2) 1-Bromo-3-chlorobenzene



Formula: C6H4ClBr (liquid)

mass %
190 77.3 _____
191 5.0 __
192 100.0 _____
193 6.5 ___
194 24.2 _____
195 1.6 _
196 0.0

Vapour Pressure: 0.609 mmHg at 25°C

it is evident from Fig.6 that The possible channels through DEA for 1-Bromo-3-chlorobenzene is Br^- and Cl^-. Although Br has lower electron affinity compared to Cl but Fig. 6 shows that the weak bond energy and also high cross section of Br^- channel makes that much prominent.

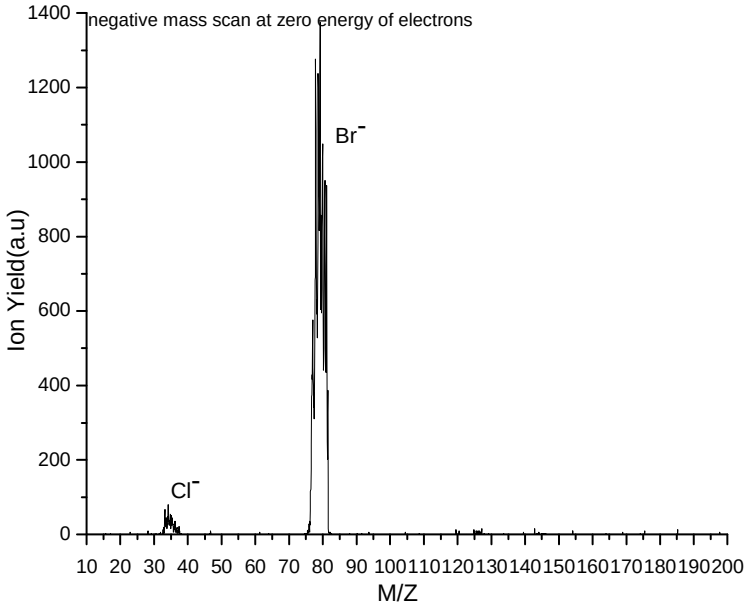


Fig 6*. Negative mass scan of 1-Bromo-3-Chlorobenzene done at zero energy electrons.*

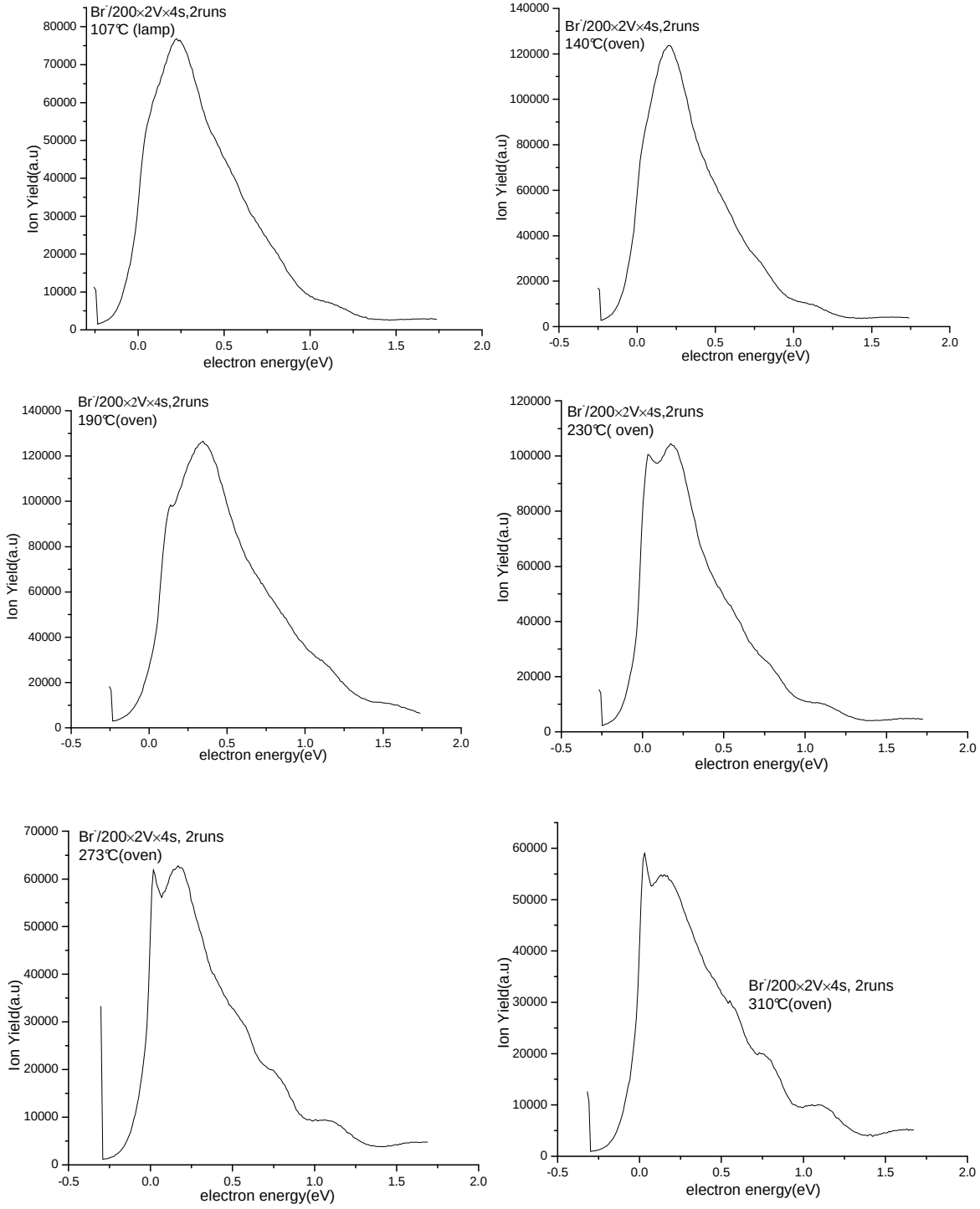


Fig7. *The Br⁻io yield for DEA to 1- bromo-3-chlorobenzene at different temperatures.*

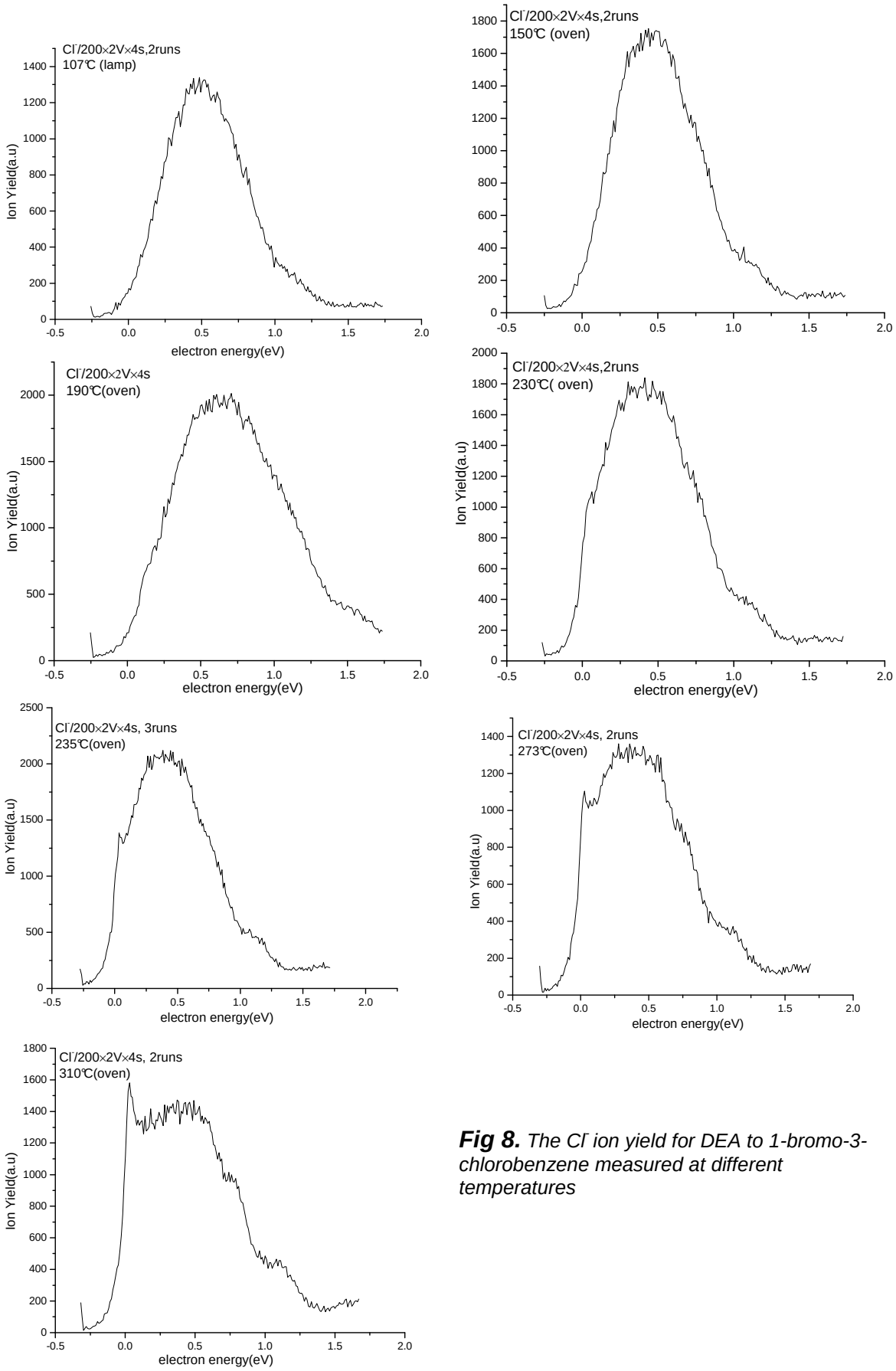


Fig 8. *The Cl^- ion yield for DEA to 1-bromo-3-chlorobenzene measured at different temperatures*

The first temperature is produced by two lamps inside the chamber which heat the monochromator and oven at the same temperature. This temperature was the lowest temperature which we could start our measurements. I checked the lower temperature but at that temperature monochromator doesn't show stable behavior. for the next temperatures I started to heat the oven through an external power supply.
During my stay in Bratislava, we cleaned monochromator twice. As Bratislava monochromator is different in construction from the exist one in Innsbruck so I got a lot of experiences .

Project publication

The obtained results are supposed to be published in a paper by Stefan Matejcik collaboration.

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