

Versuch FP-B-03 – Electron attachment

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Aims: In the present lab experiment an overview of the process of inelastic electron scattering process should be gained. More precisely, negative ion formation formed by free electron attachment will be studied.

Based on this experiment, you will learn (i) how anions can be formed upon electron attachment to molecules and how they will decay, (ii) how these processes can be measured and (iii) how the measurements can be interpreted. By writing the protocol you will learn how scientific data can be described and presented in a written report. Due to feedback these skills can be further improved. The grade for this experiment is based on the preparation and the quality of the protocol.

In the following chapter a basic review of negative ion formation by electron attachment is presented.¹ In addition, information about the experimental setup is given.

PART I: THEORETICAL OVERVIEW

1- Introduction :

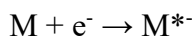
Direct scattering

Depending on the result of the interaction between a free incident electron and a target molecule, the scattering process is either *elastic* or *inelastic*. In an elastic scattering process, the incident electron and the target particle retain practically their initial energy and their momenta. In an inelastic scattering process, the state of the target molecule is changed. It could be a simple excitation of the molecule (rotational, vibrational or electronic excitation) or an ionization event. It can even lead to the dissociation of the molecule.

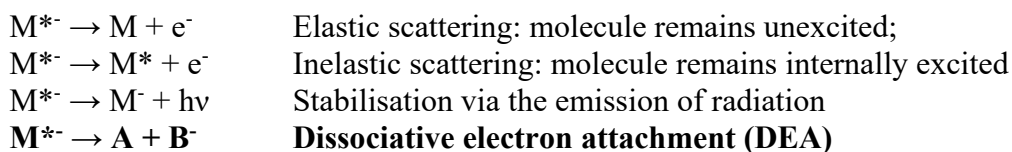
The collision process can also take place indirectly via a resonant state (negative ion resonance).

Resonant scattering (indirect scattering)

Whenever the electron energy matches a resonant state of the molecule, it stays longer than the timescale for direct scattering in the vicinity of the molecule. This complex, consisting of electron and a molecule M is called a "**temporary negative ion**" (TNI).



This reaction leads to an excited anionic molecule, which cannot be stable due to its excess energy. Therefore one of the following reactions will happen:



The first two processes are also called autodetachment (AD), since the electron spontaneously leaves the molecular complex. All processes listed are competitive. However, they have

¹ Ilko Bald et al., Int. Journal of Mass Spectrometry, Vol. 277, p.p. 4–25, 2008

different timescales. For example, emission of radiation takes typically ns and AD/DEA processes are often faster.

2- Dissociative electron attachment (DEA)

The process of dissociative electron attachment can be explained by the use of a Born-Oppenheimer potential energy diagram. Strictly speaking this representation is only applicable for diatomic molecules. In Figure 1 such a potential energy diagram is shown for the diatomic molecule AB and the corresponding anion AB^- . The potential energy is shown as function of the nuclear distance $Q(A-B)$, which in this case represents the reaction coordinate. The electron capture is represented by a vertical transition from the ground state of AB to some excited state of AB^- . This is in accordance with the Franck-Condon principle which states that an electronic transition occurs while the position of the nuclei is fixed.

As already discussed the TNI is a thermodynamically unstable species and is hence subjected to autodetachment (AD) and dissociation (DEA) into B^- and A. Autodetachment can occur until the crossing point R_c is reached, afterwards dissociation is the only possible relaxation channel in the situation shown in Figure 1.

The formed anionic products of a dissociation process (like B^-) can be detected by means of mass spectrometry (analogous to positive ions formed upon electron ionization). The ion yields of mass selected anions will generally show a resonant profile in dependency of the initial electron energy. The resonance shape can be considered as a reflection of the initial ground state vibrational wave function at the potential of the anion (reflection principle) which is schematically shown in Figure 1.

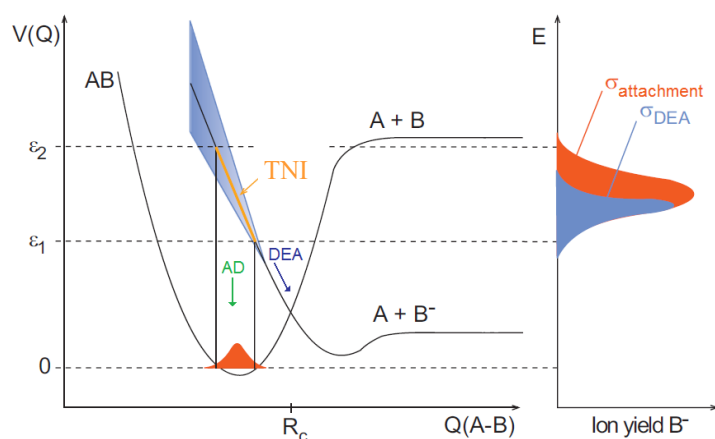


Figure1: Potential energy diagram representing DEA to the diatomic molecule AB. On the right side the corresponding ion yield of B^- is expressed as $\sigma_{\text{attachment}}$ (with neglecting of autodetachment) and σ_{DEA} (including the possibility of autodetachment) is schematically shown.

Some other important definitions related to anions:

The energy difference between the neutral molecule in ground state and the anion (via a vertical transition) is called "**vertical attachment energy**" (VAE).

The "**vertical detachment energy**" (VDE) refers to the energy which is necessary to leave the anion from its ground state (see Fig.2).

The "**adiabatic electron affinity**" (AEA) represents the energy difference between the ground state of the neutral molecule and ground state of the anion (in case of a bound state). To form a thermodynamically stable anion the molecule needs to possess a positive adiabatic electron affinity (AEA) as a precondition. This means that the ground state of the anion lies at lower energy than the ground state of the neutral (as in the case of Figure 2).

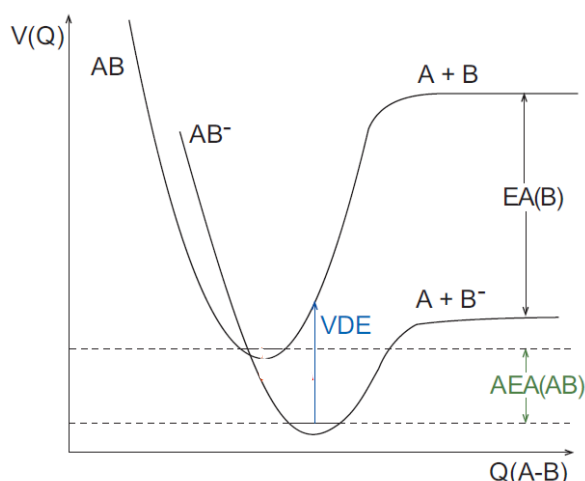


Figure 2: Potential energy diagram schematically depicting the terms adiabatic electron affinity (AEA) and vertical detachment energy (VDE).

Thermodynamics of DEA (see Fig.3):

The experimentally observed appearance energy AE of the fragment B^- is defined by:

$$AE(B^-) = D_0(A - B) - EA(B) + E^*$$

with $D_0(A-B)$ the dissociation energy for the bond $A-B$,
 $EA(B)$ the electron affinity of B
 E^* the excess energy.

The thermodynamic threshold of the process $\Delta H_0(B^-)$ which is the minimum energy necessary for the dissociation of the molecule is given by the following equation.

$$\Delta H_0(B^-) = D_0(A - B) - EA(B)$$

Thus the excess energy of the process is the difference between the experimentally observed appearance energy and the thermodynamic threshold for the formation of the corresponding fragment. The excess energy can be transferred either in translational energy or in internal degrees of freedom (electronic, vibrational and rotational excitation) of the corresponding molecule.

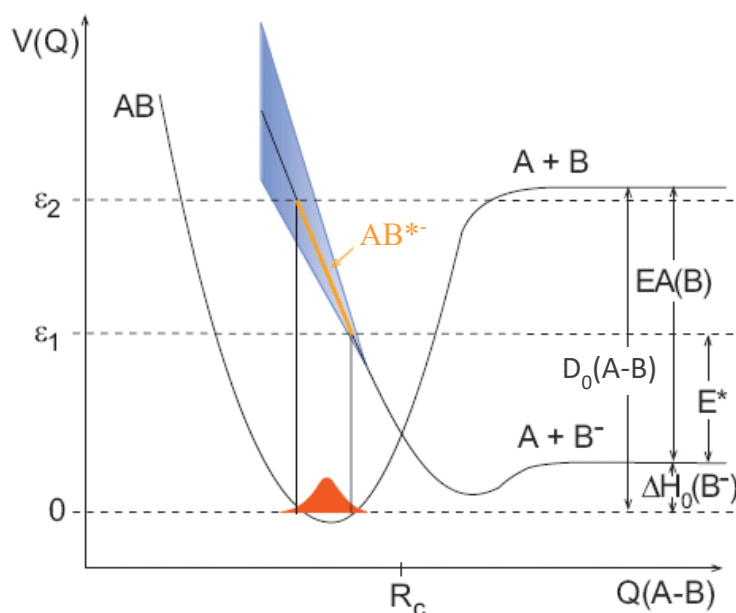


Figure 3: Potential energy diagram representing DEA to the diatomic molecule AB : $D_0(A-B)$ represents the bond dissociation energy of $A-B$, $EA(B)$ the electron affinity of B , E^* the excess energy and $\Delta H_0(B^-)$ the thermodynamic threshold for the formation of B^- .

3- Example : Cl/CCl_4

Carbon tetrachloride (CCl_4) is used in this experiment to calibrate the energy scale of the used electron monochromator and to determine the energy resolution of the electron beam (more details on this topic are given in Part II). Measurements of the Cl^- ion yield will be done during the course of this experiment.

The CCl_4 molecule consists of four chlorine atoms which are placed in the corners of a tetrahedron with the carbon at the centre. Chlorine exists in two stable isotopes ^{35}Cl and ^{37}Cl with natural abundance of 75% and 25% respectively.

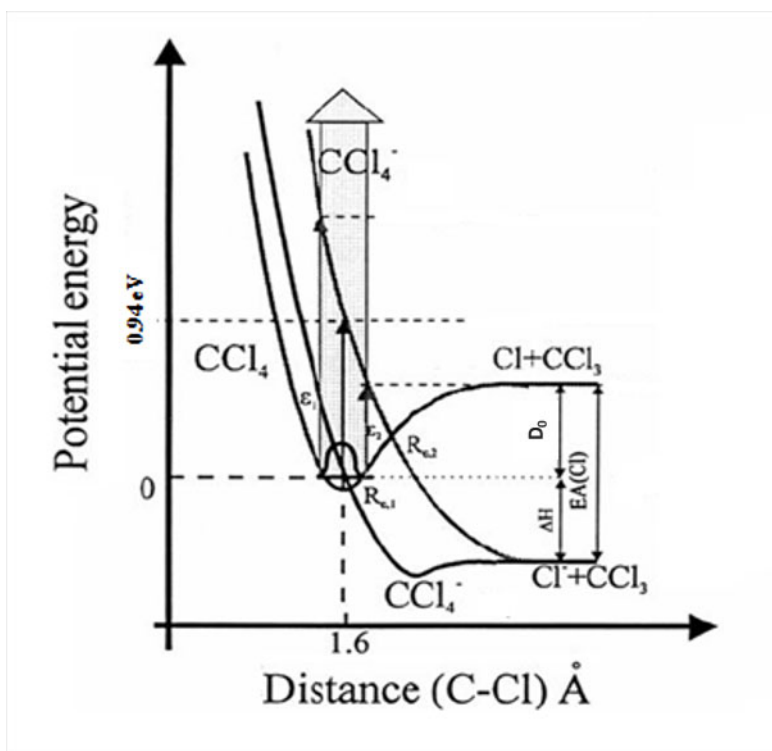


Figure 4: Potential energy diagram of CCl_4 and CCl_4^-

The potential energy curves of CCl_4 and CCl_4^- are schematically shown in Figure 4 (not scaled).² As CCl_4 is a polyatomic molecule, Figure 4 represents a 2D-cut through hyperdimensional surfaces along one specific reaction coordinate.

The reaction $\text{e}^- + \text{CCl}_4 \rightarrow (\text{CCl}_4)^{-*} \rightarrow \text{Cl}^- + \text{CCl}_3$ is exothermic by 0.45 eV.

As mentioned in Section 2, the thermodynamic threshold of the reaction is given by the bond dissociation energy of CCl_4 $D_0(\text{Cl}-\text{CCl}_3)=3.22\text{eV}$ minus the electron affinity of chlorine $\text{EA}(\text{Cl})=3.67\text{eV}$.

In the low energy range, two CCl_4^- anion curves are accessible within the Frank-Condon principle. Therefore two peaks are observable in the Cl^- ion yield curve. As the potential energy curve of the lower state passes the vibrational ground state of the neutral molecule, already electrons of zero kinetic energy may be captured by the molecule, which will then dissociate into $\text{Cl}^- + \text{CCl}_3$. This first peak is due to s-wave³ capture.

The second resonance has a vertical attachment energy of 0.94 eV and has been assigned to p-wave scattering.

² PhD-Thesis Daniel Muigg, Universität Innsbruck, 1998

³ In quantum mechanics a free electron at defined energy can be represented by a plane wave which represents a superposition of partial waves with different angular momentum l , i.e. s-waves for $l = 0$ and p-waves for $l = 1$. When only s-waves contribute, the attachment cross section rises at low energies ($\sigma \sim 1/E$).

PART II : HEMISPHERICAL ELECTRON MONOCHROMATOR (HEM)

1- Introduction :

As for light, it is possible to create lenses to focus an electron beam by creating an appropriate electric field. The shape of the electric field created in the gap between two cylinders (set at different potential V_1 and V_2) bends the electron trajectory toward the axis, and therefore acts as a lens as it focusses the electron beam. In order to keep the image position constant while varying the energy, one more element (at a potential V_3) needs to be added to the previous system. The properties of the “3 elements” lens system depend on both the lens geometry (length of the different cylinders) and the voltage ratios V_3/V_1 and V_2/V_1 . In short, the ratio V_2/V_1 changes the focussing strength of the lens whereas the ratio V_3/V_1 changes the energy of the image (where $V_3/V_1 > 1$ for an accelerating mode and $V_3/V_1 < 1$ for a decelerating mode). In addition, a radial electrostatic field between two concentric hemispheres has an energy dispersive character which allows to reduce the energy distribution of an electron beam.

2- Description

The present electron monochromator consists of (see Fig.5):

- an electron source
- a set of electron lenses to transport electrons away from the source
- an energy selector (hemispherical in our apparatus)
- a further set of electron lenses to transport the energy resolved beam and focus it to the collision region

Electron Source

Electrons are emitted from common hairpin filament. A current of about 2.35 A is passed through the filament and the emission current is a few tens of μA . Electrons emitted have a broad energy distribution ($\sim 0.8\text{eV}$ energy spread; Maxwell-Boltzmann distribution) and also a wide angular spread. These electrons are accelerated towards an anode plate (AN) kept at voltages between 60-100V.

From the source to the hemisphere

A multitude of electrostatic lenses is necessary to focus and guide the beam into the hemispherical electrostatic sector, where the broad energy distribution is cut down to a narrow (50-100meV) Gaussian-like shape.

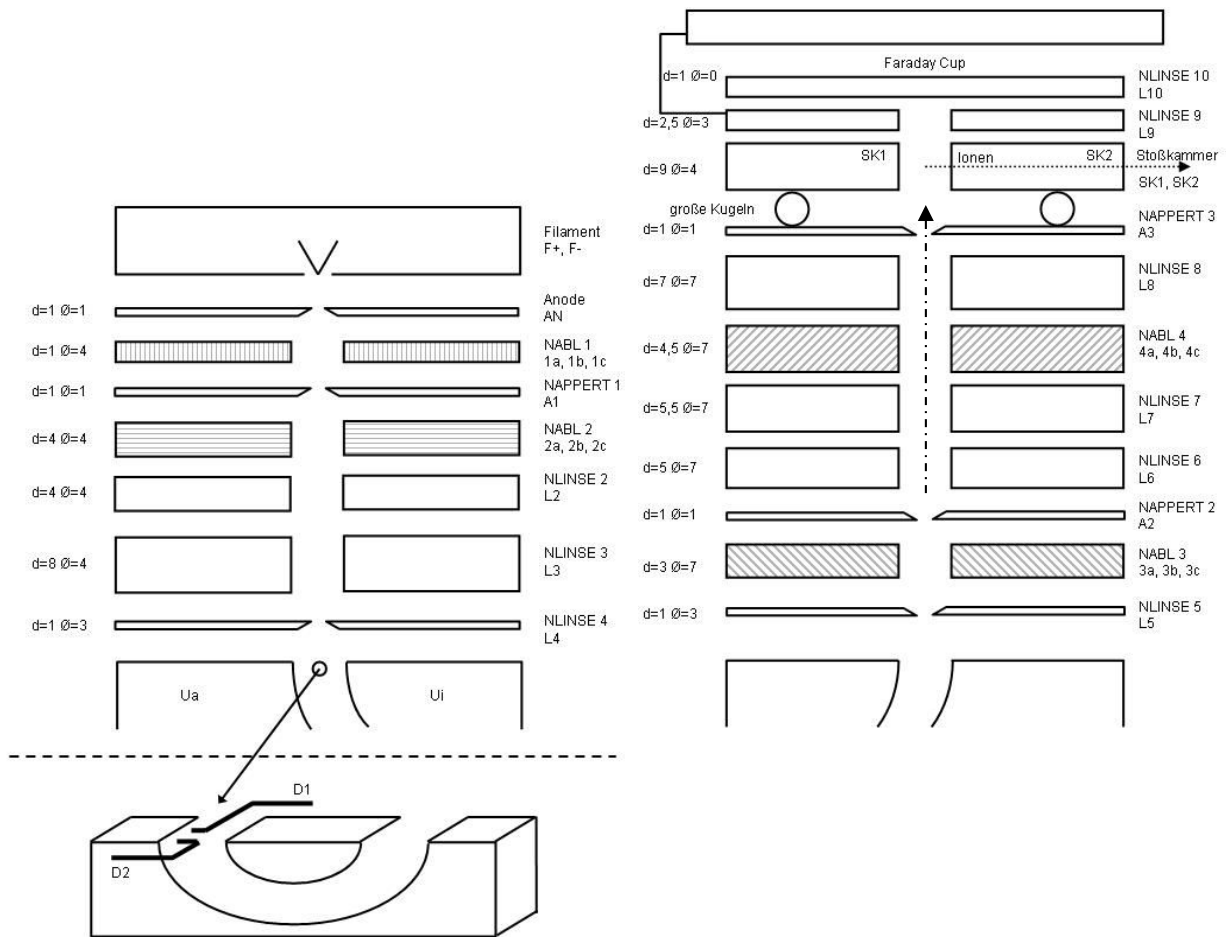


Figure 5: Diagramm of the Hemispherical Electron Monochromator. The letter d on the left means the thickness of the concerning lens, whereas the symbol Ø stands for the diameter of the orifice where the electrons pass through (both values in mm). On the right the names of the single lenses and their identifications on the corresponding electrical power supplies are given. If a lens is hatched it means, that it consists of four parts (4/4), whereas two parts are electrically connected (e.g. NABL1 is segmented in 1a(1/4), 1b(1/4) and 1c(2/4)).

Hemispherical energy selector

The energy selector consists of two concentric hemispherical surfaces, the inner hemisphere at potential U_i and the outer hemisphere at potential U_a . Inside this hemispherical energy selector, the electrons “see” a spherically symmetric electrostatic field created by the potential difference between the two hemispheres. Electrons with energies above the mean energy U_{exmitte} have larger elliptic radii while those with lower energy have smaller radii. Therefore only electrons which are within a certain interval around the mean energy leave the selector. At the entrance of the hemisphere a deflector D1 and D2 is added to adjust the vertical position of the beam.

From hemisphere to the interaction region

After this energy filtering another set of lenses is used to focus and guide the beam into the collision chamber (“Stoßkammer”), where electrons with a chosen energy E may attach to neutrals and anions are extracted. The neutral gas is added via a so-called leak valve to the monochromator chamber. The energy E of the electrons is given by the output voltages of the

power supply U_e , the power supply U_{efein} and the scanning voltage U_{scan} ⁴, i.e. $E = U_e - U_{\text{efein}} + U_{\text{scan}}$.

These resulting ions are extracted by a weak electric field in the direction of the quadrupole mass filter, whereas the remaining electrons are collected in a Faraday “cup” (which is actually in the current setup only a plate), which is connected to a picoamperemeter.

3- “Tuning” the HEM

A separately adjustable voltage can be applied to every single element of the HEM. If we speak about “tuning”, the aim is to maximize the electron current reaching the Faraday cup while simultaneously minimizing the electron energy spread. This procedure is always a compromise, as the total electron current decreases with the energy spread getting narrower. Less electron current means finally less ion yield and therefore a reduced signal-to-noise ratio in the obtained data.

To tune the monochromator for maximum electron current regardless the resolution, one sets the electron energy manually to approximately 1eV and looks at the picoamperemeter connected to the Faraday cup. By carefully changing all the voltages of the lenses shown in Figure5 the electron current is maximized usually.

Important: During the lab course you should briefly (15-20 min) optimize the monochromator before starting the measurements. Due to time reasons we will restrict us to few lenses. These are (see Figure 5): L4, D1, D2, Ua, Ui, L5, 3a, 3b, 3c, A2, L6, L7, 4a, 4b, 4c and L8. Do not change the A3, SK1, SK2 and L10 at all; otherwise the electron beam may become unstable for the rest of the day and your data will be wrong.

It turned out that for the optimization it is much better to do this rather quickly and to repeat the whole procedure several times (optimize from e.g. from L4 to L8, go back to L4 and optimize again, ...), instead of spending a lot of time for every single lens.

4- Magnetic Field Compensation

It is absolutely crucial that no magnetic fields influence the electron beam. Three pairs of Helmholtz-coils are mounted around the whole machine to compensate the magnetic fields of the earth or those of any other devices in the lab.

5- Determining the energy resolution of the electron beam

CCl_4 is an ideal calibration gas for DEA measurements for two reasons:

- The narrow 0eV peak makes it possible to calibrate the energy scale.
- The electron energy resolution can be deduced directly from the width of the 0eV peak (usually at the “full width at half maximum”; FWHM).

⁴ For U_{scan} two options are available: Either one uses directly the output (0-10V) of the National Instruments Card of the measurement computer or another power supply (0-100V) with the voltage of the NI card as input. The latter option is chosen, if the scan range of the electron energy should be larger than 10eV.

PART III : QUADRUPOLE MASS SPECTROMETER

1-Description :

In the quadrupole mass spectrometer, the ions are separated according to their mass to charge ratio m/z . The quadrupole consists of a parallel array of four rod electrodes mounted in square configuration. The voltage applied to two opposite rods is :

$$\phi_0 = U + V \cos(\omega t) \quad \text{and} \quad \phi_0 = -(U + V \cos(\omega t))$$

where U is the amplitude of the direct voltage and V the amplitude radiofrequency voltage.

Within the rod-system the ions oscillate under the influence of the high frequency electrical field. Only ions with a certain mass to charge ratio are successfully passing the analyser, the other masses undergo an oscillating trajectory of increasing amplitude so they will ultimately be collected on one of the electrodes.

To achieve the best possible ion signal an electrostatic 3 elements system is placed at the entrance of the quadrupole. The first element is called "Optik außen" (outer optics) and the second one "Optik innen" (inner optics) whereas the third one is connected to ground potential and therefore not adjustable. By applying appropriate voltages to these elements the ions can be focussed to the entrance aperture of the quadrupole.

2-Operating and optimizing the quadrupole

Operating the quadrupole is very user-friendly as it is mostly automated and computer controlled. The high-frequency generator that is in use currently is suitable for masses between 1 and 1024 m/z (mass per charge). To obtain maximum transmission at a suitable mass resolution, the quadrupole has to be tuned. However, there are much less parameters to be taken care of than for tuning the monochromator.

"Optik außen" (power supply OA) does usually not need any changing (a value of about +80V is recommendable; for higher voltages electrons may also be extracted into the quadrupole) whereas "Optik innen" (power supply OI) has to be optimized frequently. Note: There is more than one setting where "Optik innen" has a maximum. However, these maxima of ion yield differ in intensity and it is therefore important to check to whole voltage range while tuning "Optik innen" and not only the small range of one single maximum.

The speed of the ions passing the quadrupole is mainly influenced by the adjustable "Feldachse" (field axis) and has a major effect on the actual mass resolution.

Note: As the monochromator is on "Ionenenergie" potential, the voltage applied as "Feldachse" has to be subtracted from "Ionenenergie" to obtain the real value (e.g. "Ionenenergie" = 28V, "Feldachse" = 26V, i.e. the "real" field axis is 2V). A "real" field axis value around 3V is recommendable to achieve a reasonable mass resolution.

After the mass analysis anions are deflected off-axis by an electrostatic deflector (outer deflector has power supply Da and inner deflector Di) and are detected by a channeltron type secondary electron multiplier (see Figure 6 for the basic working principle).

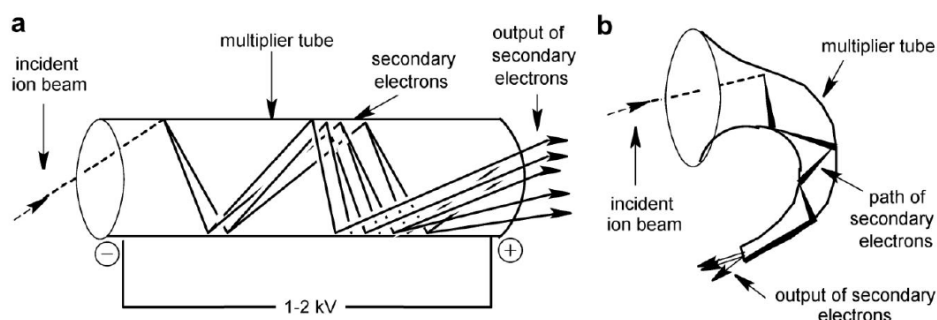


Figure 6. General schematic of a linear channel type secondary electron multiplier (a) and a curved one (a), used for the detection of ions in mass spectrometry. Figure taken from Mass Spectrometry, J.H. Gross, Springer Verlag, Heidelberg, 2004

PART III : TYPICAL RESEARCH CARRIED OUT WITH THE MONOCHROMATOR

The apparatus is also used for current scientific research. Electron scattering from phase molecules (biomolecule, explosives ...) and atomic or molecular clusters, i.e. small agglomerates of Ar, Ne, CO₂, N₂O, etc., have been measured previously. Currently we study electron attachment to so-called radiosensitisers (used in radiation therapy to increase the sensitivity of cancer tissue towards radiation), which should be highly electron-affinic.

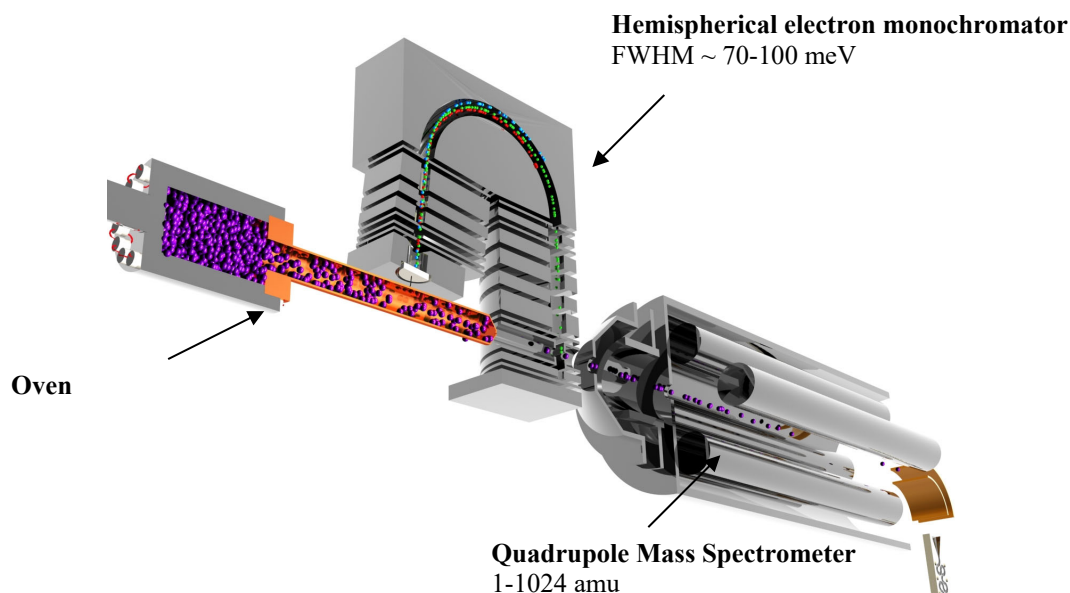


Figure 7: Experimental set-up used for studies with non-volatile compounds.⁵

⁵ D. Huber et al., J Chem Phys **125**, 084304 (2006)

Planned schedule for the afternoon of the experiment (the final one may vary):

- Discussion about this manual
- Introduction to the setup in the lab
- Optimization of the monochromator and ion optics using the Cl^-/CCl_4 anion signal at the maximum of the zero eV resonance.
- Calibration measurement using Cl^-/CCl_4
- Search for anions formed by electron attachment to SF_6 (SF_6^- and F^-) and subsequent measurement of their resonance spectra as function of the electron energy.

Tasks for the data analysis/report:

- Analyze the Cl^-/CCl_4 ion yield: First calibrate the electron energy scale using the first resonance of Cl^- and determine the width of the first resonance (which can be considered as a measure of the energy width of the electron beam). Note that depending on the optimization, zero eV peaks may be slightly asymmetric. Determine then the position and width of the second resonance. The second resonance may be shifted compared to the VAE value shown in Figure 4. (0.94 eV). Discuss possible reasons for this result.
- Calibrate all measured ion yields for the SF_6 sample and analyze resonance positions as well as widths for the SF_6^- and F^- data. As pointed out in <https://www.sciencedirect.com/science/article/pii/S1387380600002803>, the SF_6^- ion yield should also reveal a zero eV peak as Cl^-/CCl_4 . If your determined position is slightly off this value (also taking into account the statistical error), how do you interpret this result?
- Draw a schematic potential energy diagram (employing the Morse potential energy function, see chapter 3.2.5 in the book *Atoms, Molecules and Optical Physics 2* by I.V. Hertel and C.-P. Schulz; the book is available via ULBT) for the ground states of neutral SF_6 and the SF_6^- anion and describe your result (one aspect is if the plot supports your experimental observation). Use the following parameters: $\text{AEA}(\text{SF}_6) = 1.05$ eV, $D_0(\text{SF}_5-\text{F}) = 4.35$ eV, $D_0(\text{SF}_5^--\text{F}) = 1.44$ eV, zero-point-energy (SF_6) = 0.056 eV, zero-point-energy (SF_6^-) = 0.045 eV, equilibrium distance for SF_6 $d(\text{S}-\text{F}) = 1.5$ Å; equilibrium distance for $\text{SF}_6^- = 1.71$ Å.

Concerning the report:

- Reports should not be longer than 10-12 pages and should contain the following sections: Abstract, Introduction, Theory about electron attachment (max. 1.5 pages), Overview experimental setup (max. 1 page), Description of execution including experimental details, Results and Discussion, Summary, References
- The report must be submitted by e-mail to: Stephan.Denifl@uibk.ac.at