Chapter 3

The Experiment

In this work the interaction of free electrons with molecules in three different states of aggregation are presented, namely free molecules, molecular clusters and condensed molecules. Most of the experiments were performed on single molecules in the gas phase and on homogeneous molecular clusters at a crossed electron/molecular beam setup at the Freie Universität Berlin. Additionally, experiments on electron induced reactivity in molecular films on a cold substrate were carried out at the *LCAM (Laboratoire des collisions atomiques et moléculaire), CNRS - Université Paris-Sud in Orsay, France.* The two different experimental setups will be described in the following.

3.1 Study of single molecules and molecular clusters

3.1.1 Experimental setup

The experimental setup for the study of electron attachment to single molecules and molecular clusters is shown schematically in Fig. 3.1. It consists of two separately pumped vacuum chambers: the expansion chamber and the reaction chamber. These two chambers are separated from each other by a skimmer.
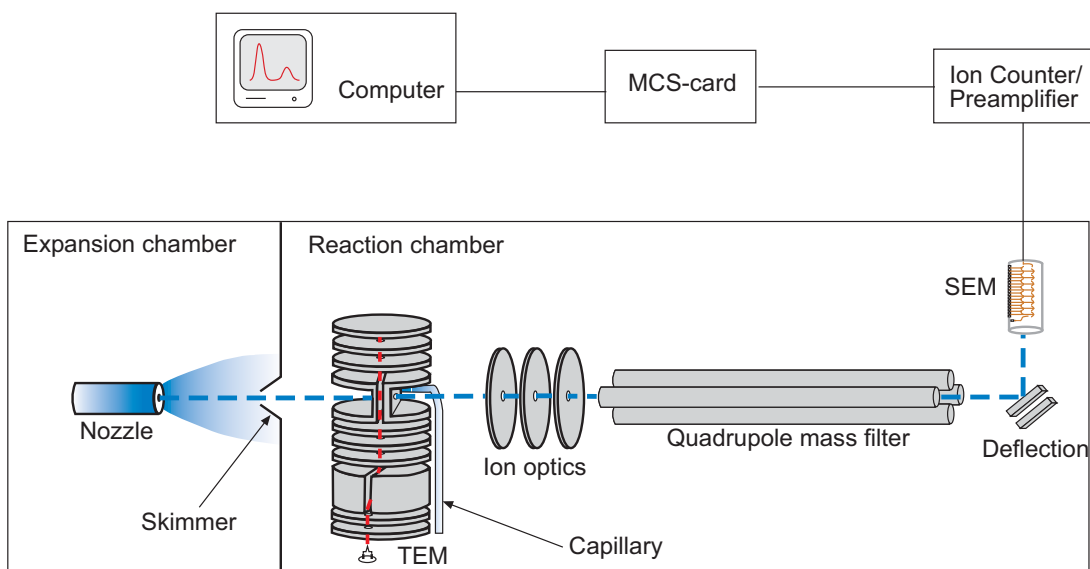

Figure 3.1: Schematic view of the experimental setup.

To achieve the necessary vacuum conditions in the spherical expansion chamber ($\varnothing = 51\,\text{cm}$) two different pump systems were used during this work. In the beginning it was pumped by an oil diffusion pump (Balzers DIF 320) which was separated from the vacuum chamber by a water cooled baffle (Balzers BFA 320 W) to reduce the contamination of oil vapor. Later the oil diffusion pump was replaced by a turbomolecular pump (Pfeiffer TPH 1500). In the configuration with the oil diffusion pump a pumping speed of around $3000\,\text{l/s}$, with the turbomolecular pump of $3500\,\text{l/s}$ is obtained. Thus a base pressure which is measured by a cold cathode gauge (Pfeiffer IKR 251) around $8 \cdot 10^{-8}$ mbar is achieved. The backing pressure for the expansion chamber is generated by a rotary vane pump

(Pfeiffer DUO 35). To maintain a working pressure below $1 \cdot 10^{-4}$ mbar a roots pump (Pfeiffer WKP 250 A) is introduced in between the rotary vane pump and the turbomolecular pump and additionally used during cluster preparation.

At the beginning of this work a new cluster source was installed in the expansion chamber. For the formation of molecular clusters a mixture of the molecule under investigation in an excess of Argon or Helium is prepared and then expanded adiabatically into the vacuum through a $50\,\mu m$ nozzle. The position of the nozzle can be optimized in x-, y- and z-position to allow the supersonic molecular beam an ideal pass through the conical skimmer ($\varnothing = 0.4$ mm). For the adjustment of the nozzle position a calibration laser is integrated in the cluster source. As the temperature of the nozzle influences the formation of clusters it can be cooled by means of a liquid nitrogen cycle and heated by resistive heating if necessary. For temperature controll a Pt 100-sensor is mounted on the nozzle.

The reaction chamber is pumped by two turbomolecular pumps (Pfeiffer TPH 330 U, Pfeiffer TMU 071 P), a rotary vane pump (Pfeiffer DUO 018 B) is used as a fore pump. In this configuration a background pressure of $5 \cdot 10^{-8}$ mbar, measured by a cold cathode gauge (Pfeiffer IKR 251), can be reached. The cluster beam enters the reaction chamber via the skimmer that separates the outer part of the molecular beam with a velocity compound perpendicular to the beam.

In the collision zone the cluster beam interacts with a monochromatized electron beam of defined and variable energy that is generated by a trochoidal electron monochromator (TEM) located perpendicular to the cluster beam. As the study of single molecules in the gas phase is also possible with this setup, an effusive molecular beam can be introduced via a capillary pointing directly to the collision zone. The negative ions formed in the collision zone are accelerated by a weak electric field to a quadrupole mass spectrometer (QMS) which is mounted in the axis of the cluster beam. The transmitted ions are detected by a secondary electron multiplier (SEM) in a 90° off-axis configuration.

A beam shutter located directly behind the entrance of the cluster beam into the reaction chamber helps to distinguish if an observed ion signal originates from electron attachment (EA) to a molecular cluster or to a single molecule traveling in the cluster beam.

3.1.2   Trochoidal electron monochromator

With the experiments presented in this work, mainly electron-molecule interactions at low electron energies (0–15 eV) are studied . Therefore an electron beam with a defined and variable energy that achieves also at very low electron energies close to 0 eV reasonable intensities is required. A suitable system that meets these demands is a trochoidal electron monochromator (TEM) first established by Stamatovic and Schulz [100, 101]. Here, a perpendicular electric and magnetic field allows a selection of the electrons according to their energy.

A schematic view of the TEM is depicted in Fig. 3.2, the region of electron energy selection is marked in yellow, the reaction zone in blue.
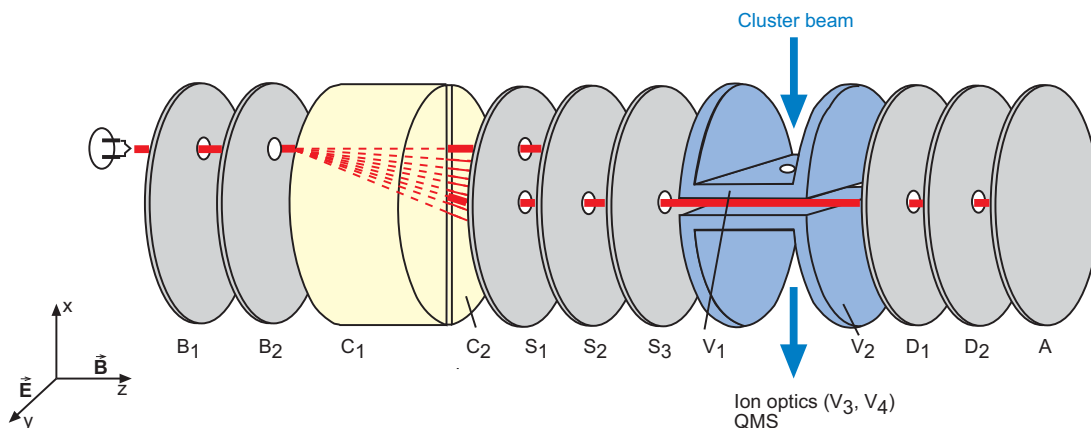

Figure 3.2: Schematic view of the TEM.

All the electrostatic lenses of the monochromator are made of molybdenum and they are electrically insulated from each other by ruby balls in between the plates. The lenses of the collision zone (V_1 and V_2) and the ion optics (V_3 and V_4) are made of non-magnetic stainless steel. To prevent adsorption of the investigated chemicals on the metal surface two halogen lamps are mounted close to the monochromator to heat the device.

Thermal heating of a tungsten filament produces electrons with a broad energy distribution. These thermal electrons are collected and focused through the non-axial holes of the first two lenses B_1 and B_2 to the energy selection zone. There an electric field $\vec{E}$ generated by the potential difference between C_1 and C_2, perpendicularly crosses an axial magnetic field $\vec{B}$ acting along the z-axis (see

Fig. 3.2). For the generation of the magnetic field ($\approx 82\,\text{Gauss}$) two Helmholtz coils are located outside of the reaction chamber.

Charged particles in an electric and magnetic field experience the Lorentz force $\vec{F}$ given by

$$\vec{F} = q(\vec{E} - \vec{v} \times \vec{B}) \tag{3.1}$$

with q the charge and $\vec{v}$ the velocity of the particle. For the situation depicted in Fig. 3.2 the electron is initially accelerated along the electric field (y-direction). Then the combined action of the electric and magnetic field results in cycloidal or trochoidal trajectories depending on their initial velocity $\vec{v}_z$, whereas the center of rotation is moving with a constant velocity $\vec{v}_x$.

$$\vec{v}_x = \frac{\vec{E} \times \vec{B}}{|\vec{B}|^2}, \quad \vec{E} \perp \vec{B} \quad \Rightarrow \quad v_x = \frac{E}{B} \tag{3.2}$$

As the holes of the lenses after the energy selection zone are in axial position and therefore displaced by the distance Δx with respect to the holes in the electrodes B_1 and B_2, only the electrons deflected by a distance that equals Δx are transmitted to the collision zone. Thus the time T_z necessary to pass the length L of the selection zone in z-direction must equal the time T_x needed to travel the distance Δx in x-direction.

$$T_z = \frac{L}{v_z} = \frac{\Delta x}{v_x} = T_x \tag{3.3}$$

Hence the kinetic energy of the electrons $E_{kin,z}$ that leave the energy selection zone is given as follows

$$E_{kin,z} = \frac{1}{2} m_e \left(\frac{EL}{B\Delta x} \right)^2 \tag{3.4}$$

with m_e the mass of the electron.

The following electrodes S_{1-3} extract and focus the beam of a defined energy to the collision zone that is given by the lenses S_3, D_1, V_1 and V_2, where the interaction with the molecular beam occurs. After passing the reaction room the electrons are accelerated by D_1 and D_2 and the electron current as a measure for the beam intensity is detected at lens A.

To calibrate the absolute electron energy scale and to determine the energy resolution of the electron beam, electron attachment to SF_6 is applied. Sulfur

hexafluoride forms near $0\,\mathrm{eV}$ electron energy metastable SF_6^- ions with a cross-section of $2 \cdot 10^{-17}\,\mathrm{m}^2$ (at $\mathrm{E} = 1\,\mathrm{meV}$) [18, 45]. This cross-section for the formation of SF_6^- decreases by five orders of magnitude in the range 0–$200\,\mathrm{meV}$ [13]. In this work the full width at half maximum (FWHM) of the peak for SF_6^- formation as an indication for the energy resolution of the electron beam could be determined generally to values between $120\,\mathrm{meV}$ up to several hundreds of meV. The energy resolution of the monochromatized electron beam is limited by the physical dimensions of the used monochromator, and furthermore adsorption of the substance under investigation on the surface of the monochromator lenses can deteriorate the resolution. Moreover, most of the substances studied in this work have a low cross-section for electron attachment, thus sometimes a poor resolution in favor of a higher electron current is applied.

3.1.3   Ion detection and measurement categories

For ion detection a commercially available mass spectrometer from Balzers (QMG 422) is used that consists of further ion optics, the mass filter, the deflection plates and the secondary electron multiplier (SEM). The formed negative ions are extracted from the collision zone by a weak electric field between V_1, V_2 and then focused and accelerated to the quadrupole mass spectrometer by the lenses V_3, V_4 that are mounted on the monochromator. The ion optics of the mass spectrometer further focus the ions to the mass filter. There four rods are electrically connected pairwise and a high frequency alternating voltage together with a direct voltage is applied to them. Thus the ions move on different paths according to their mass/charge ratio and a transmission through the mass filter is possible only for a given frequency at a certain mass/charge ratio. After transmission through the mass filter the ions are deflected and accelerated by the application of a high voltage ($> 3\,\mathrm{kV}$) to the first dynode of a $90°$ off-axis SEM. Thereby an electron cascade is induced that is further multiplied by the following dynodes until an electron pulse arrives at the last dynode. This pulse is amplified by the preamplifier and passes then via the ion counter to an MCS (multi channel scaler) card and is finally read out and displayed by the corresponding software.

There are different measurement categories to analyze the processes of interest. Both the analysis of anions and cations is possible with the described spectrometer. In case of detection of cations the internal ionization source of the quadrupole mass spectrometer is used. This mode is mainly applied for the analysis of the background gas in the apparatus. In principle two different kinds of spectra can be recorded:

1. Mass spectra: The ion intensity is measured in dependency of the m/z ratio, the Quadstar 422 Version 6.02 software developed by Balzers is used to read out and display the signal.

   - Positive ion mass spectra: A tungsten filament as the internal ionization source emits electrons that are generally accelerated to about 70 eV to ionize the neutral molecules. The electron current and the electron energy are variable.

   - Negative ion mass spectra: The negative ions formed by the interaction of the monochromatized electron beam with the substance are analyzed at a fixed electron energy.

2. Ion yields: Here the ion intensity is recorded in dependency of the electron energy at a fixed mass/charge ratio. Therefore the linear variation of the electron energy is carried out by the MCS card connected with an analog/digital converter. To display the experimental data a LABVIEW program is used.

3.2   Study of molecular films

3.2.1   Experimental setup

In addition, results on the electron interaction with molecular films studied by means of high resolution electron energy loss spectroscopy (HREELS) are presented. These experiments have been carried out in close collaboration with the *LCAM (Laboratoire des collisions atomiques et moléculaire), CNRS - Université Paris-Sud, Orsay, France.* In the following the corresponding experimental setup will be discussed briefly, for further details see the PhD Thesis of *M. Bertin.* [10]

Generally, the experimental setup consists of three different separately pumped ultra high vacuum (UHV) chambers that can be separated from each other by gate valves. By the use of ionic, turbomolecular and titanium sublimation pumps a base pressure in the 10^{-11} Torr range can be maintained. The mentioned three chambers are named according to their function as preparation chamber, ESD (electron stimulated desorption) chamber and HREELS chamber.

The preparation and analysis of the crystalline substrate can be performed in a preparation chamber with different instruments for cleaning, characterizing and passivating the substrate. For example low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) can be applied to analyze the surface. Moreover, an atomic hydrogen source is present for passivating (hydrogenating) the substrate.

The second chamber serves for three different functions:

1. thin film preparation by vapor deposition.

2. electron irradiation of molecular films with a high electron dose.

3. electron stimulated desorption (ESD) measurements.

Finally, the HREELS spectrometer for the vibrational analysis of the molecular films, is located in a third separate chamber.

The performance of the presented experiments incorporates four different steps:

1. preparation of molecular films.

2. control of the prepared film by means of HREELS.

3. electron irradiation of the film.

4. analysis of the irradiated film by means of HREELS.

These different steps will be described more detailed in the following.

3.2.2 Thin film preparation

For the study of electron interaction in the condensed phase only experiments on trifluoroacetic acid (CF_3COOH) will be presented in this work. This substance is a liquid with a vapor pressure of $141\,hPa$ at $20\,°C$. To remove diluted gases from the liquid before introduction into the UHV chamber the substance has to be purified by freezing it in liquid nitrogen and pumping the non-frozen gases with the turbomolecular pump of the gas inlet system. This step can be repeated several times in order to obtain a pure sample. To prevent impurities of the molecular films the whole system is kept under ultra high vacuum conditions, the remaining impurities are removed from the substrate in several cleaning cycles by resistive heating. In order to achieve sufficiently low temperatures for the condensation of molecular films the surface is mounted at the cold end of a liquid helium flow cryostat. Thereby minimal temperatures around $20\,K$ can be reached which is sufficient to stick e.g. the molecular gas CO_2.

The substance under investigation is then introduced directly into the ESD chamber and vapor deposited on the cold hydrogenated diamond substrate by exposing the surface to a certain pressure of the substance. To control the introduced amount of substance, the pressure in the UHV chamber is regulated by use of an introduction leak valve.

The thickness of the adsorbed films can be estimated by assuming that the adsorbed substance has a sticking coefficient close to unity at deposition temperatures around $30\,K$. Then a thickness of one monolayer (ML) corresponds to one Langmuir, that is defined as the exposition of the substrate to a pressure at $1 \cdot 10^{-8}\,Torr$ for the time of $100\,s$. With the use of this method the error in thickness of the molecular films is estimated to $50\,\%$. The prepared molecular films are checked before irradiation by means of HREELS.

3.2.3 Irradiation of the prepared films

For the experiments on induced reactivity the molecular films were irradiated with electrons at low energies in the range between 1 and $20\,\text{eV}$. To facilitate the observation of electron induced reactions, the films need to be irradiated at a comparably high dose and the irradiated area should cover a relatively big part of the substrate to make the probe of new products by means of HREELS easier. These criteria are fulfilled by an electron gun where the electrons are emitted from a thoriated tungsten filament by the application of a current of around $2.1\,\text{A}$. The electron energy is defined by the difference of the potential at the midpoint of the cathode and the variable potential that is applied to the sample. Electron energies in the range from 0.5–$40\,\text{eV}$ with an energy resolution estimated to approximately $500\,\text{meV}$ can be obtained. By the use of a Wehnelt cylinder, whose potential is determined via maximizing the current detected at the surface, the electron beam is focused onto the sample. With this arrangement electron currents in the microampere range can be reached, the irradiation with a current of $1\,\mu\text{A}$ during $100\,\text{s}$ corresponds to a dose of $6.5{\cdot}10^{14}\,\text{e}^-/\text{mm}^2$ by taking into account an irradiated surface area of $1\,\text{mm}^2$. Typically a dose in the $10^{16}\,\text{e}^-/\text{mm}^2$ range was applied to the molecular films.

3.2.4 High resolution electron energy loss spectroscopy (HREELS)

The HREELS spectrometer

For the performance of HREELS on the molecular films before and after their irradiation, the sample is transferred into the HREELS chamber, where a commercially available HREEL spectrometer from Omicron (IB 500) is provided. This spectrometer consists of a double monochromator and a single analyzer and is schematically displayed in Fig. 3.3.

The electrons emitted from a LaB_6 filament are accelerated and focused by some electrostatic lenses to the entrance slit of the premonochromator and enter afterwards the following monochromator. Both are $127°$ cylindrical monochromators. In this case the energy E_0 to pass on a circular orbit is linearly dependent
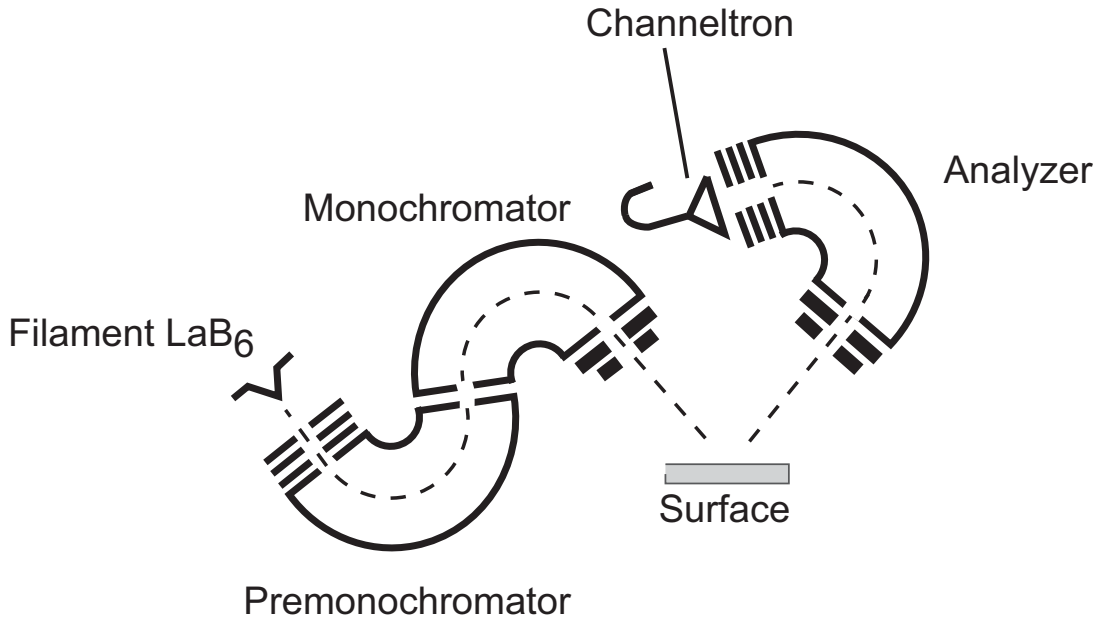
Figure 3.3: Schematic view of the HREEL spectrometer.

on the potential difference ΔV between the two plates with the radii R_1 and R_2 and is given by [24, 41]

$$E_0 = \frac{1}{2}e\frac{\Delta V}{ln\frac{R_2}{R_1}} \qquad (3.5)$$

The monochromatized electrons leaving the monochromator are focused by two lenses onto the sample where they are elastically or inelastically scattered. For the analysis of the energy loss of the electrons due to vibrational excitation in the molecular film, the scattered electrons are focused by two electrostatic lenses to a cylindrical analyzer (similar to the monochromators) and finally detected by a channeltron. The signal is read out and displayed with a corresponding software.

The obtained spectra show the intensity of the electron energy losses in dependency of their energy. With high intensity a peak corresponding to the signal of the elastically scattered electrons is observed. Taking the full width at half maximum (FWHM) of this elastic peak, the energy resolution of the electron beam can be determined. With weaker intensity the characteristic peaks for the substance appear, each of them associated with the excitation of specific vibrations in the molecular film or the substrate.

The spectra were generally taken in specular geometry at an angle of 55° with respect to the surface normal and an incident electron energy of 5 eV. The resolution obtained in these experiments, is determined by the FWHM of the elastic peak and is in this kind of experiments typically around 5 meV.

The mechanisms of vibrational excitation

In HREEL spectroscopy three modes of electron-surface interaction lead to vibrational excitation. These are dipolar scattering, impact scattering and resonant scattering [24, 26, 36].

Dipolar scattering   Dipolar scattering is a long range interaction ($\approx$100 Å) of the electron with the dynamic dipole moment of the absorbat/surface. Thus only IR active modes will be observed via this scattering mechanism, i.e. only modes related with a dipole moment perpendicular to the surface. The angular distribution of scattered electrons peaks in this case in the close vicinity of the specular direction.

Impact scattering   Impact scattering is operative at short distances (1–10 Å) as scattering is due to the repulsion of the incident electron by the electronic structure of the probed system. Here, no particular selectivity concerning the scattering angle is observable. Therefore spectra taken in specular geometry are a superposition of the two described scattering mechanisms, and hence also modes that do not fulfill the selection rules for dipolar scattering are detectable. In every other geometry only impact scattering is operative and thus the comparison of the obtained spectra can provide information on the underlying mechanism.

Resonant scattering   The process of resonant scattering was already described in Section 2.1. In this case the electron is in a first step attached to the molecule and forms a TNI, then the electron can be emitted again by autodetachment and the molecule will be left in a vibrationally excited state.