

Chapter 2

Theoretical Considerations

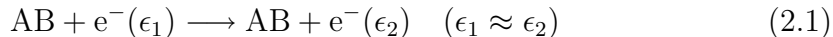
In this chapter some general considerations that are important for the discussion of the results are presented. The first part will deal with the interaction of electrons with molecules in the gas phase under single collision conditions. In the second part the basics for the preparation of molecular clusters and the molecular interactions in such a cluster will be discussed. Finally, we will show how a molecular surrounding can change the electron attachment processes in case of studies with molecular clusters or in the condensed phase.

2.1 Electron-molecule interaction

Generally the interaction of a free electron with a molecule can be divided into two groups: direct scattering and resonant interactions. These processes are discussed in this chapter on the example of the molecule AB under single collision conditions.

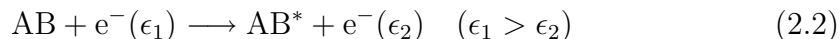
2.1.1 Direct scattering

The process of direct scattering is characterized by short interaction times, i.e. the interaction occurs only in a time scale corresponding to the usual transit time of an electron through the dimensions of a molecule. This is generally considerably shorter than a vibrational period of a normal mode which is in the order of magnitude of 10^{-14} s. The electron-molecule interaction is considered as *direct elastic scattering* if no internal degrees of freedom of the molecule are excited.



Energy transfer occurs only according to momentum conservation so that the transferred energy is in the order of the ratio m_e/m_M of the initial energy of the electron with m_e the mass of the electron and m_M the mass of the molecule. As this ratio is already for the lightest atom hydrogen 1:1836 the transferred energy is generally almost negligible.

If the electron-molecule interaction leads to the excitation of internal degrees of freedom of the target molecule the process is called *direct inelastic scattering*. Thereby some amount of the initial energy of the electron is transferred to the molecule AB leaving it in an excited state. There is no restriction for the amount of transferred energy as the electron is in the continuum before and after scattering.



Due to the low mass of the electron ($m_e \ll m_M$) rotational or vibrational excitation is not likely so that mainly electronic excitation occurs. Nevertheless, the energy transfer can be sufficient to excite low vibrational quanta which is applied e.g. in high resolution electron energy loss spectroscopy (HREELS) as will be

discussed in Section 3.2.4. The excitation of vibrational or rotational degrees of freedom is further possible by e.g. internal conversion.

After formation of the excited molecule AB^* there are several possibilities for relaxation:

- Dissociative excitation



- Dipolar dissociation

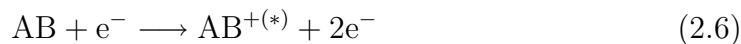


- Autoionization



Here the energy of the electron needs to be above the first ionization energy of AB so that an excited state in the ionization continuum can be formed.

An alternative route leading to ionization is given in (2.6). This process is called direct ionization where further fragmentation of the cation $AB^{+(*)}$ is possible. This process is applied in positive ion mass spectrometry.



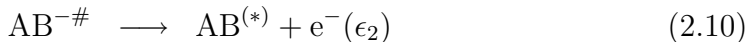
This process is applied in positive ion mass spectrometry to produce fragment cations of the molecule under investigation.

2.1.2 Resonant interactions

A second possibility for electron-molecule interaction is resonant scattering. In this case the electron stays a longer time in the vicinity of the molecule than necessary for electron transit through the dimension of the molecule thereby forming a temporary negative ion (TNI) with the electron in a quasi-bound state (2.8). This process is a resonant interaction because it can be regarded as an electronic transition from a continuum state ($AB + e^-$) to a discrete state ($AB^{-\#}$) of the molecular anion.



There are three possibilities for stabilization and decomposition of the thermodynamically unstable TNI that are given in (2.9 – 2.11).



The first reaction (2.9) is called *radiative cooling* which means that the intact molecular anion AB^{-} is stabilized by the emission of photons.

Reaction (2.10) describes *autodetachment* where the electron is emitted from the molecule. The lifetime varies in a broad range from 10^{-15} s for small molecules to 10^{-3} s for larger molecules, one example with such a long lifetime is SF_6^{-} [13, 102] that is frequently used for calibration measurements. Depending on the energy of the electron released in autodetachment it can either be elastic resonant scattering ($\epsilon_1 \approx \epsilon_2$) or inelastic resonant scattering ($\epsilon_1 > \epsilon_2$). The latter process is also a basic scattering mechanism used in HREELS (see Section 3.2.4).

The third reaction defines *dissociative electron attachment (DEA)*. Here the molecule forms by bond breaking a thermodynamically stable anion B^{-} and one or more neutral fragments A. For DEA the lifetimes are in the 10^{-14} – 10^{-12} s range. A comparison of the lifetimes of the processes clearly shows that autodetachment and dissociative electron attachment occur on a comparable timescale. Thus these two processes are competitive ones. As the performed experiments in this work analyze the products of DEA it will be discussed in more detail in the following sections.

2.1.3 Negative ion resonances

As the formation of a temporary negative ion is only possible at certain energies the term resonance is synonymously used. Generally such negative ion resonances (NIR) can be divided into two main groups: single particle resonances and two particle-one hole resonances.

- **Single particle (1p) resonances:** In this case the electron occupies a virtual molecular orbital of the target molecule while its electronic configuration of the ground state remains unaffected.

- **Two particle-one hole (2p–1h) resonances:** Here electron attachment goes along with electronic excitation of the target molecule so that two electrons occupy previously unoccupied orbitals and a hole is left in one of the lower lying molecular orbitals. Such resonances are also denoted as *core-excited resonances*.

The mechanism of electron trapping to form a TNI can be described as follows. The negatively charged electron approaching the neutral molecule induces a dipole in the molecule. This results in an attractive interaction of the two particles at long distances which can be described by the following potential V_a

$$V_a(r) = -\frac{\alpha e^2}{2r^4} \quad (2.12)$$

with α the polarizability of the molecule, e the elementary charge and r the distance of the electron to the molecule. A repulsive centrifugal potential $V_r(r)$ is generated due to the angular momentum of the electron

$$V_r(r) = \frac{\hbar^2 \ell(\ell + 1)}{2m_e r^2} \quad (2.13)$$

with $\hbar = h/2\pi$, h the Planck constant, ℓ the angular momentum quantum number of the incoming electron and m_e the mass of the electron.

By the combination of the attractive and the repulsive potential one obtains the effective potential $V_{eff}(r)$ of the interaction

$$V_{eff}(r) = V_a(r) + V_r(r) = -\frac{\alpha e^2}{2r^4} + \frac{\hbar^2 \ell(\ell + 1)}{2m_e r^2} \quad (2.14)$$

which results in a potential barrier for $\ell \neq 0$ as depicted in Fig. 2.1. The electron can tunnel through the barrier and occupy a quasi-bound state (a discrete electronic state lying in the continuum) if the molecule possesses an unoccupied molecular orbital of a symmetry with a defined value for ℓ that is in accordance with the angular momentum of the incoming electron. At short electron-molecule distances the Pauli-repulsion gets important which finally results in a potential energy curve as shown schematically in Fig. 2.1. As electron capture is described by the shape of the effective interaction potential this resonance is denoted as *shape resonance* [5, 93, 92].

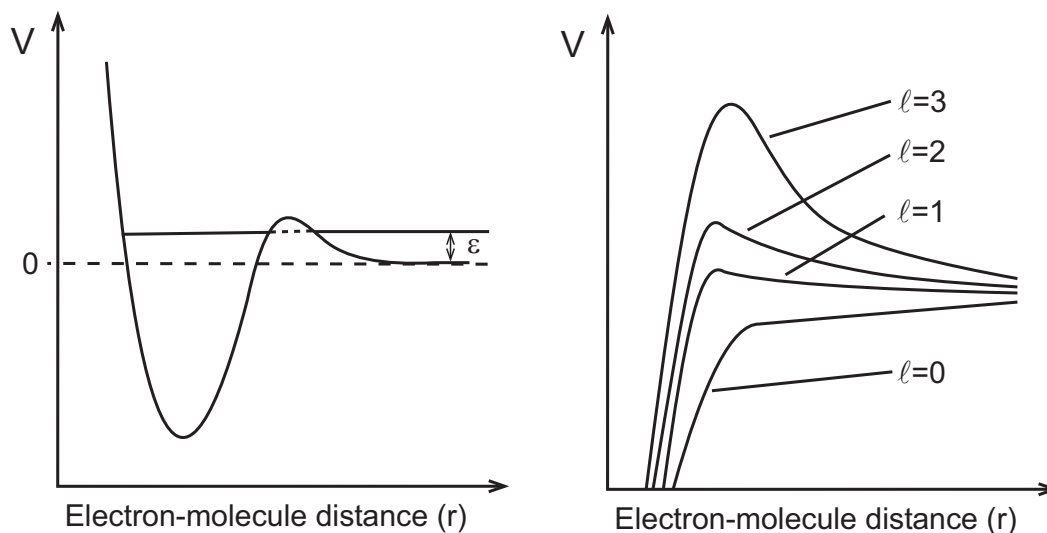


Figure 2.1: Effective potential describing the electron-molecule interaction including Pauli repulsion at small distances (left side). On the right side the potential barrier for different angular momentum values ($\ell=0, 1, 2, 3$) is depicted.

In addition to the above mentioned general classification of NIRs with respect to the number of particles involved in this process one can further distinguish between different types of resonances according to their energy in comparison to the neutral molecule [5, 93, 92].

As depicted in Fig. 2.2 the energy of shape resonances lies generally above the corresponding ground state or electronically excited state of the neutral and they are thus considered as open channel resonances. If the energy of the resonance lies below the associated ground state or electronically excited state it is referred to as Feshbach resonance. In the following the characteristic differences between the resonance types will be described in more detail.

Shape resonances: Shape resonances are mostly formed via a one-particle mechanism but they can be as well of the core-excited resonance type. Their energetic position is generally 0–4 eV above the corresponding state in the neutral (electronic ground state or electronically excited state). The typical lifetimes of such resonances are quite short (10^{-15} – 10^{-10} s) as they can easily decay into the respective neutral state [93].

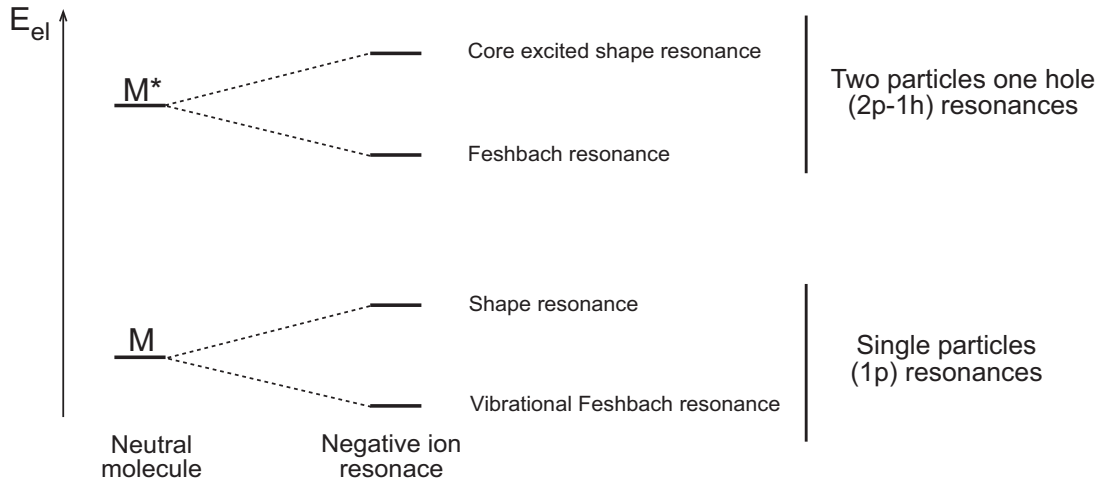


Figure 2.2: Classification of negative ion resonances according to their energy with respect to the neutral molecule.

Vibrational Feshbach resonances: If the molecule possesses a positive electron affinity vibrational Feshbach resonances can be formed. The energy of the TNI lies in this case below the corresponding electronic ground state of the neutral molecule. For vibrational Feshbach resonances also s-wave attachment ($\ell=0$) is possible. The energy of the captured electron is effectively transferred to vibrational degrees of freedom of the molecule. These resonances are generally found at very low electron energy and show very high cross-sections [38]. A further characteristic is the long lifetime of the resonance that can range up to microseconds.

Two particle one hole Feshbach resonances: In this case the formation of the TNI goes along with electronic excitation of the molecule. In contrary to core excited shape resonances the energy of the resonance lies below the corresponding level of electronic excitation of the neutral molecule. Thus the emission of the excess electron is only possible if the electronic configuration is changed which results in lifetimes in the range 10^{-13} – 10^{-12} s and longer [93].

2.1.4 Dissociative electron attachment (DEA)

The process of dissociative electron attachment can be explained in more detail by the use of a Born-Oppenheimer potential energy diagram. Strictly speaking this representation is only applicable for diatomic molecules, for polyatomic molecules it describes a cut through hyperdimensional surfaces along the corresponding reaction coordinate Q .

In Fig. 2.3 such a potential energy diagram is shown for the diatomic molecule AB and the corresponding anion AB^- . The electron capture is represented by

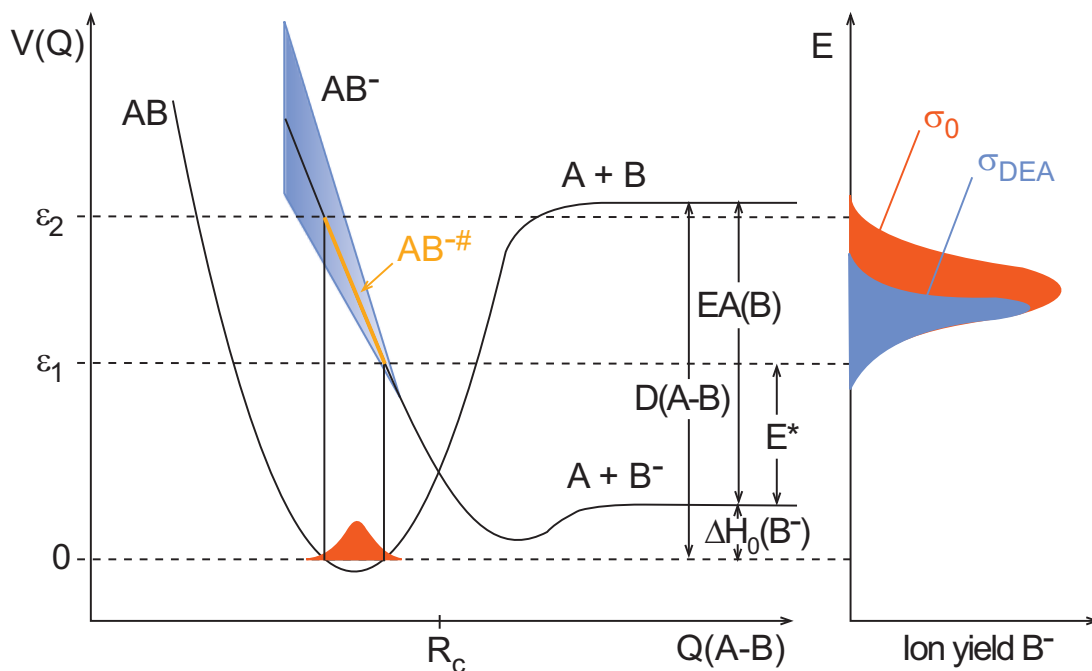


Figure 2.3: Potential energy diagram representing DEA to the diatomic molecule AB . On the right side a corresponding ion yield is schematically shown. $D(A-B)$ represents the dissociation energy of $A-B$, $EA(B)$ the electron affinity of B , E^* the excess energy and $\Delta H_0(B^-)$ the thermodynamic threshold for the formation of B^- .

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. Generally the

probability for an electronic transition from the ground state to an electronically excited state is given by the Franck-Condon factor (FCF).

$$FCF = |\langle \Psi_i | \Psi_f \rangle|^2 \quad (2.15)$$

Here Ψ_i represents the vibrational wave function of the ground state while Ψ_f is the one of the final state. In Fig. 2.3 the corresponding region where the formation of the TNI is possible is marked in orange. Thus the TNI is generally formed in a vibrationally excited state (one particle resonances) or in a vibronically excited state (two particle one hole resonances). As already discussed the TNI is a thermodynamically unstable species and is hence subjected to autodetachment and dissociation. Autodetachment can occur until the crossing point R_c is reached, afterwards dissociation is the only possible relaxation channel.

For the formation of a thermodynamically stable anion the molecule or atom needs to possess a positive adiabatic electron affinity (AEA). This means that the ground state of the anion lies at lower energy than the ground state of the neutral. The energy difference of the neutral ground state and the excited state of the anion formed by the initial Franck-Condon transition is denoted as vertical electron affinity (VEA). As vertical detachment energy (VDE) the energy necessary to detach the electron from the anion at fixed position of the nuclei is considered. Fig. 2.4 pictures the explained terms.

The formed anionic products of the dissociation process can be detected by means of negative ion mass spectrometry in dependency of the electron energy. The obtained ion yields will generally show a resonant profile with a shape that 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 Fig. 2.3 [41, 66]. Generally the cross-section for electron attachment is higher at low electron energies as given by the relation $\sigma(\epsilon) \propto \epsilon^{-1}$ [109]. At very low energies close to the threshold the s-wave electron attachment cross-section increases with decreasing electron energy according to $\sigma(\epsilon) \propto \epsilon^{-\frac{1}{2}}$ [109, 45].

The cross-section for dissociative electron attachment σ_{DEA} is defined as

$$\sigma_{DEA} = \sigma_0 \exp\left(\frac{-\tau_{DEA}}{\tau_{AD}}\right), \quad P = \exp\left(\frac{-\tau_{DEA}}{\tau_{AD}}\right) \quad (2.16)$$

with σ_0 the cross-section for the formation of the resonance, τ_{DEA} the lifetime of

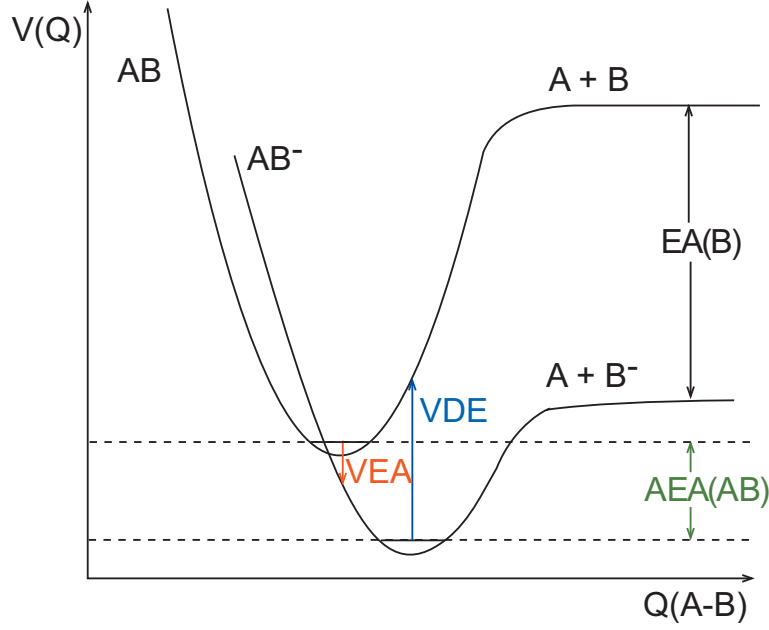


Figure 2.4: Potential energy diagram schematically depicting the terms adiabatic electron affinity (AEA), vertical attachment energy (VAE) and vertical detachment energy (VDE).

the TNI with respect to dissociation and τ_{AD} the autodetachment lifetime while P is the survival probability. The dissociation time τ_{DEA} is defined as

$$\tau_{DEA} = \int_{R_0}^{R_c} \frac{dR}{v(R)} \quad (2.17)$$

with R_0 the distance of the nuclei at the time of the transition from the neutral to the anion and $v(R)$ the radial velocity between A and B^- which is given by the following equation.

$$v(R) = \sqrt{\frac{2(E^* - V_a)}{\mu}} \quad (2.18)$$

The excess energy of the underlying process is denoted as E^* while V_a represents the potential energy of the anion AB^- and μ is the reduced mass of A and B^- . The lifetime of a TNI with respect to autodetachment τ_{AD} and its width Γ are related by the Heisenberg uncertainty principle as follows.

$$\tau_{AD} \approx \frac{\hbar}{\Gamma} \quad (2.19)$$

The survival probability is dependent on the energy and is generally higher with lower energy. Additionally, the time until R_c is crossed is shorter. Thus the peak maximum of the corresponding ion yield is red shifted (*survival probability shift*) as shown in Fig. 2.3 by the blue curve.

Finally we would like to consider the thermodynamics of DEA. The experimentally observed appearance energy AE of the fragment B^- is defined by

$$AE(B^-) = D(A - B) - EA(B) + E^* \quad (2.20)$$

with $D(A-B)$ the dissociation energy for the bond A-B, $EA(B)$ the electron affinity of B and 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.

$$\Delta H_0(B^-) = D(A - B) - EA(B) \quad (2.21)$$

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.

2.2 Molecular aggregates

The term cluster is in a general sense used for an aggregation of atoms or molecules with a number of two up to several thousands of particles. According to the binding properties in the clusters one can distinguish between different groups of clusters like metallic clusters, ionic clusters, clusters bound by hydrogen bonds, covalent clusters and van der Waals clusters. Thus the binding energy of the clusters varies in a broad range from very low energy in case of induced dipole interaction, like for noble gas clusters, up to 4 eV for ionic binding or covalent interaction in clusters. A prominent example for covalently bound clusters are fullerenes [47].

In this work molecular clusters of organic molecules are investigated. Hence the intermolecular interactions between the molecules as well as the interaction of an ion with neutral molecules in the cluster will be discussed. Then the preparation of molecular clusters will be described briefly.

2.2.1 Intermolecular interactions

Interaction between neutral molecules

Van der Waals forces generally describe the attractive interaction between neutral molecules. These interactions can be divided into three different types, namely the electrostatic interaction between two dipoles (1), the interaction between a dipole and an induced dipole (2) and the interaction between two induced dipoles (3) [57]. A specific type of intermolecular interaction is hydrogen bonding.

1. Dipole-dipole interaction

The potential energy of a dipole-dipole interaction is determined by the orientation of the two dipoles as follows

$$V_{\mu,\mu} = \frac{\mu_1\mu_2}{4\pi\epsilon_0 r^3} (2 \cos \vartheta_1 \cos \vartheta_2 - \sin \vartheta_1 \sin \vartheta_2 \cos \varphi) \quad (2.22)$$

with μ the dipole moment of the particles 1 and 2, ϵ_0 the dielectric constant of the vacuum and r the distance between the centers of mass. The bracket term defines the relative orientation of the dipoles with ϑ_1 and ϑ_2 the angles between the dipole vectors $\vec{\mu}_1$, $\vec{\mu}_2$ and the axis defined by r whereas

φ describes the angle between the two dipoles perpendicular to this axis. Considering the various possible orientations of the molecules to each other the average interaction potential becomes zero. Since the potential energy depends on the orientation of the dipoles the molecules aim for an energetically favorable orientation. The thermal motion of the particles acts against this orientation. Thus the average potential energy of two rotating particles is given in Eq. 2.23 with k the Boltzmann constant and T the temperature.

$$V_{\mu\mu} = -\frac{2}{3kT} \left(\frac{\mu_1\mu_2}{4\pi\epsilon_0} \right)^2 r^{-6} \quad (2.23)$$

As Eq. 2.23 shows, the interaction energy is proportional to r^{-6} . Typical energies for molecules at room temperature with a dipole moment of 1 D in a distance of 0.5 nm are $0.07 \text{ kJ}\cdot\text{mol}^{-1}$ [7]. At higher temperatures this equation is no more valid as the rotation of the molecules overcomes the attractive interaction. Going to low temperatures rotation plays no role and the two molecules can be considered as stationary, the interaction is then proportional to r^{-3} with interaction energies about $2 \text{ kJ}\cdot\text{mol}^{-1}$.

2. Induction

A molecule with a permanent dipole moment μ_1 can induce a dipole moment μ_2^* in another polarizable molecule. This induced dipole moment is dependent on the electric field of the permanent dipole E and the polarizability α_2 of the molecule in which the dipole is induced.

$$\mu_2^* = \alpha_2 E \quad (2.24)$$

Thus the interaction energy of the two molecules can be described as follows.

$$V_{ind} = -\frac{\mu_1^2 \alpha_2}{\pi \epsilon_0} r^{-6} \quad (2.25)$$

As the induced dipole is always acting in the same direction as the permanent dipole the rotation of the molecules does not play a role and the interaction is attractive in every orientation. Thus there is no temperature dependence and the interaction potential is proportional to r^{-6} . Taking

again into account a dipole moment of 1 D for the molecule with the permanent dipole, a distance of 0.3 nm between the molecules and a polarizability of $10 \cdot 10^{-30} \text{ m}^3$ the interaction energy becomes $\approx 0.8 \text{ kJ} \cdot \text{mol}^{-1}$ [7].

3. London dispersion force

Two non-polar molecules (no permanent dipole moment) attract each other due to fluctuations in their electron density distribution. These fluctuations induce a dipole moment μ_1^* in an adjacent molecule. The electric field of this dipole then induces in turn a dipole moment μ_2^* by polarizing a neighboring molecule. Thus an attractive interaction between the two molecules is generated. Although the dipole moment μ_1^* will change the orientation the interaction remains attractive as the two dipoles are correlated. A good approximation of this intermolecular interaction is given by the London formula

$$V_{disp} = -\frac{2}{3}\alpha_1\alpha_2\frac{I_1I_2}{I_1+I_2}r^{-6} \quad (2.26)$$

with I_1 and I_2 the ionization energy of the two molecules. The relation between the potential energy V_{disp} and the distance r is again given by $V_{disp} \propto r^{-6}$. As an example one can consider the interaction energy between two methane molecules that is about $5 \text{ kJ} \cdot \text{mol}^{-1}$ [7].

All these types of intermolecular interactions have in common that they show the same dependence on the distance between the molecules by $V_{\mu\mu}$, V_{ind} and $V_{disp} \propto r^{-6}$. The molecules are generally subjected to the attractive intermolecular interaction as described above at long distances and the Pauli repulsion at small distances. An empirical model that represents this behavior is the Lennard-Jones potential.

$$V = -ar^{-6} + br^{-12} \quad (2.27)$$

The parameters a and b are constants that depend on the corresponding substance.

Hydrogen bonds: A very specific type of intermolecular interaction is a hydrogen bond. A general definition for this interaction was given by *Pauling*. He stated “Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be

acting as a bond between them. This is called a hydrogen bond.” Additionally, he claimed that a hydrogen bond can only be formed between the most electronegative atoms [74]. Nowadays, a variety of intermolecular interactions are defined as a hydrogen bond that are not necessarily between two electronegative atoms. There are for example hydrogen bonds of the structure $-C-H \cdots Y$ and $-X-H \cdots C-$ with non-electronegative atoms as proton donor or proton acceptor [103]. A typical value for a hydrogen bond strength is $\approx 20 \text{ kJ}\cdot\text{mol}^{-1}$ which corresponds to 0.21 eV [7].

Interaction between an ion and a neutral molecule

The described electron attachment processes lead to the formation of anions. The presence of a charged particle in a cluster induces further attractive intermolecular interactions that will be described in the following.

1. Interaction of an ion with an induced dipole

The charged particle can induce a dipole in a neighboring neutral molecule. This kind of interaction was already explained in Chapter 2.1 and is proportional to r^{-4} .

$$V_{ind} = -\frac{1}{2} \frac{\alpha e^2}{4\pi\epsilon_0} r^{-4} \quad (2.28)$$

2. Interaction of an ion with a dipole

This interaction of a charged particle with a permanent dipole is described by

$$V_{\mu,e} = -\frac{\mu e}{4\pi\epsilon_0} r^{-2} \quad (2.29)$$

and is proportional to r^{-2} .

In comparison with the intermolecular binding energies of neutral molecules the interaction with an anion is quite strong and thus the potential energy for an ionic cluster is lowered.

2.2.2 Preparation of molecular clusters

Kantrowitz and Grey [44] first published a theoretical consideration of supersonic beams originally following the aim to increase the intensities in molecular beams. Such supersonic beams nowadays find a broad application in cluster production or in molecular spectroscopy of cold molecules, ions or radicals [23, 97]. The preparation of molecular clusters in supersonic beams will be briefly discussed in the following.

Adiabatic expansion of an ideal gas

Generally one can distinguish between effusive molecular beams and supersonic beams by their Knudsen number K which is defined as

$$K = \frac{\lambda}{d} \quad (2.30)$$

with λ the mean free path of the particle in the gas reservoir before the expansion and d the diameter of the nozzle. A Knudsen number $K > 1$ represents an effusive beam while a $K < 1$ describes a supersonic molecular beam. An effusive beam is characterized by a Maxwell-Boltzmann velocity distribution according to the temperature in the gas reservoir.

The formation of a supersonic beam will be discussed by means of an adiabatic expansion of an ideal gas. The gas with the pressure p_0 in the gas reservoir is expanded adiabatically to the pressure p through a nozzle with a diameter d . According to $K < 1$ the diameter of the nozzle is bigger than the mean free path of the gas and thus many collisions will occur during the passage of the nozzle. The random atomic motion (defined by p_0 and the temperature in the reservoir T_0) is converted into directed translational energy. Taking into account the principle of energy conservation under the assumption of isentropic conditions, the following equation can be derived to describe the conditions before and after the expansion.

$$H_0 + \frac{1}{2}mv_0^2 = H + \frac{1}{2}mv^2 \quad (2.31)$$

The index 0 represents the condition before the expansion with H the enthalpy of the gas and $\frac{1}{2}mv^2$ the kinetic energy of the flow. Before the expansion the flow velocity $v_0 = 0$ and thus this condition is only described by the enthalpy. The

substitution of the enthalpy H by the term $H = c_p T$ with c_p the heat capacity of the gas at constant pressure results in the following equation.

$$c_p T_0 = c_p T + \frac{1}{2} m v^2 \quad (2.32)$$

From this equation it is obvious that an increase of flow velocity goes along with a cooling of the beam. As the local speed of sound u is defined by

$$u = \sqrt{\frac{\gamma k T}{m}} \quad (2.33)$$

it further leads to a decrease of the speed of sound. In this equation k represents the Boltzmann constant and γ the heat capacity ratio ($\gamma = c_p/c_v$) at constant pressure (c_p) and constant volume (c_v). The Mach number M defined by

$$M = \frac{v}{u} \quad (2.34)$$

increases. Taking into account the above defined terms, the following equation can be derived.

$$\frac{T}{T_0} = \left(1 + \frac{1}{2} (\gamma - 1) M^2\right)^{-1} \quad (2.35)$$

Considering the translational energy a comparison between an effusive and a supersonic molecular beam shows that the Maxwell-Boltzmann distribution in an effusive beam with a maximum at $v = \sqrt{(3kT/m)}$ changes in case of a supersonic molecular beam to a narrower distribution and a maximum at higher energy. The differences in velocity distribution are shown in Fig. 2.5.

A description of pressure p , temperature T and density ρ of the beam is given by the combination of Eq. 2.35 with the Poisson equations.

$$\frac{T}{T_0} = \left(\frac{p}{p_0}\right)^{\frac{(\gamma-1)}{\gamma}} = \left(\frac{\rho}{\rho_0}\right)^{\gamma-1} \quad (2.36)$$

Thus the cooling is efficient at low T_0 or at high p_0 . The Mach number M can further be defined by

$$M = A \left(\frac{x}{d}\right)^{\gamma-1} \quad (2.37)$$

where A is a constant that depends on γ and x is the distance from the nozzle. Thus one can estimate the dependence of p , T and ρ from x/d . The expansion leads to a decrease of p , T and ρ and an increase of M . The Mach number grows

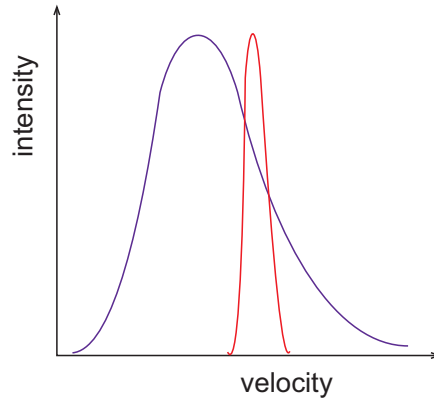


Figure 2.5: Comparison of the velocity distribution in an effusive beam (blue curve) and in a supersonic beam (red curve).

until a finite Mach number is reached, this represents the distance of the nozzle at which no more collisions occur and thus pressure, temperature and density will remain constant.

Adiabatic expansion of a molecular gas

In contrast to an ideal monoatomic gas, internal degrees of freedom can be excited in molecular gases by the excitation of rotation and vibration. This can lead to a decrease of the adiabatic coefficient γ as shown in the following equation where f is denoted as the number of excited degrees of freedom of rotation and vibration.

$$\gamma = \frac{5 + f}{3 + f} \quad \lim_{f \rightarrow \infty} \gamma = 1 \quad (2.38)$$

Cooling is no more operative in case of $\gamma=1$ which will lead to $T = T_0$ according to Eq. 2.35.

To avoid this problem the seeded beam technique is applied where the molecule of interest is diluted in an excess of a carrier gas (He or Ar) that acts as a cooling bath. The adiabatic coefficient is then defined as

$$\gamma = 1 + \left[\sum_i \frac{x_i}{\gamma_i} - 1 \right]^{-1} \quad (2.39)$$

with x_i the mole fraction of the components. Working with a huge excess of the carrier gas, the flow velocity of the molecule under investigation will equal that of the carrier gas.

Condensation in the supersonic molecular beam

The formation of clusters by condensation needs to proceed via three-body collisions due to the principle of energy and momentum conservation. At very small Knudsen numbers such three-body collisions in and after the nozzle are more probable and thus such experimental conditions are applied if the supersonic beam is used for cluster preparation. As explained above the adiabatic expansion causes a cooling in the beam. In case the temperature of the beam falls below the binding energy of the dimer, it can be stabilized as shown for the noble gas Ar.



The formed dimers then act as condensation nuclei and grow fast to bigger aggregates. By the release of the interatomic binding energy the cluster is reheated.

The condensation process can be qualitatively described by the phase change of a supersaturated gas as depicted in Fig. 2.6 [30]. The gas in the reservoir (be-

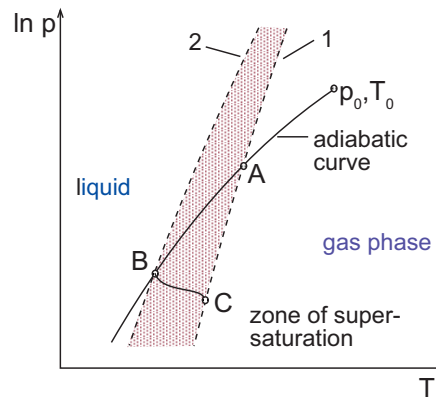


Figure 2.6: Schematic p,T -phase diagram qualitatively explaining condensation in the cluster beam (1 represents the equilibrium vapor pressure curve, 2 is denoted as the supersaturation vapor pressure curve).

fore the expansion) is in an equilibrium state with T_0 , p_0 . During the expansion the adiabatic curve is crossing the equilibrium vapor pressure curve at (A) and enters a zone of supersaturation. In crossing the vapor pressure curve of supersaturation at (B) condensation starts. The released binding energy reheats the cluster and condensation is possible until the equilibrium state at (C) is reached.

2.3 Electron attachment to molecular clusters

The interaction of electrons with molecular clusters is subjected to substantial changes in comparison to single molecules. There are mainly three different categories how a molecular surrounding can influence the process of electron attachment:

1. collective properties
2. scattering of the electron before the attachment process occurs
3. stabilization of the TNI by the medium

These topics will be discussed in detail in the following. The cluster will be denoted M_n with M the molecule under investigation and n the number of molecules that form the cluster.

2.3.1 Collective interaction of the electron with the cluster

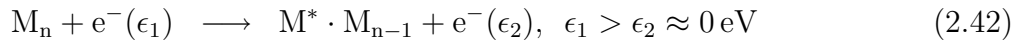
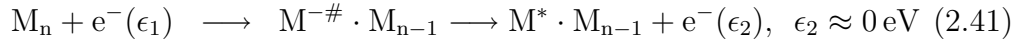
A slow electron with an energy of 1 eV corresponds to a large *de Broglie*-wavelength which is 12.4 Å. This is in the order of magnitude of intermolecular distances in the cluster. Thus electron scattering events are no longer described with a single scattering center but rather as a simultaneous scattering over multiple centers.

Electron attachment may also not exclusively proceed via charge localization at an individual molecule in the cluster. Calculations of *Gianturco et al.* for formic acid suggest that the density of charge is in case of the comparably strong hydrogen bonded dimer distributed over the entire dimer and thus additional resonances appear in comparison to the single molecule [28]. Furthermore, electron attachment is no more restricted to localization of the excess electron in an unoccupied molecular orbital. For NH_3 and H_2O clusters it was shown that an electron can be bound collectively by the dipoles of the molecules above a characteristic number of molecules in the cluster. Electrons that are bound in this way are called solvated electrons or hydrated electrons in case of H_2O . For water it was shown that clusters of the structure $(\text{H}_2\text{O})_n^-$ with $n \geq 2$ do exist [107]. The exact binding properties of the electron in the cluster are a subject of ongoing

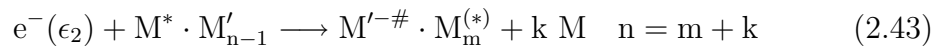
research activity. For small water clusters $(\text{H}_2\text{O})_n^-$ $n=2-7$ the most abundant experimentally observed anions are of the dipole-bound type. The excess charge is in this case localized on the surface of the cluster [31, 95]. In photoelectron spectroscopy studies by *Verlet et al.* three different classes of isomers were observed. The isomer with the largest electron binding energy was assigned to a structure where the electron is bound in the interior of the cluster; the isomers with smaller electron binding energy were attributed to a localization of the excess electron in surface states [105].

2.3.2 Local electron-molecule interaction

In the studies presented here local electron-molecule interactions play an important role. These interactions were already described in Section 2.1. In experiments with molecular clusters autodetachment and inelastic scattering processes may be particularly important in anion formation. The corresponding reaction schemes for electron attachment followed by autodetachment (2.41) and inelastic scattering (2.42) in a cluster are given in the following.



In case the cluster consists of molecules M' that possess high electron attachment cross-sections for quasi-thermal electrons, the scattered electrons can be attached to these molecules and then contribute to anion formation.



This process is called *self-scavenging* if the scattering molecule and the scavenging molecule are the same. If they are of different types the process is named *auto-scavenging*. Such *self-scavenging* processes were observed in this work in case of hexafluoroacetone, further prominent examples are ozone [61], methyl iodide [46] and trifluoromethyl iodide [70]. Auto-scavenging processes were found for the system N_2/SF_6 [42].

2.3.3 Interaction of the TNI with the molecular surrounding

As explained in Section 2.2.1 there are attractive intermolecular interactions between the single molecules of a clusters. Thus the energy of a cluster AB_n is lower with respect to the energy of the single molecule AB . Much stronger than the interaction between neutral molecules is the interaction between the negatively charged ion formed by electron attachment and the surrounding molecules. Hence the energy of the anionic state is lowered to a greater degree than that of a neutral cluster. The energetic situation is schematically represented by the potential energy curves in Fig. 2.7.

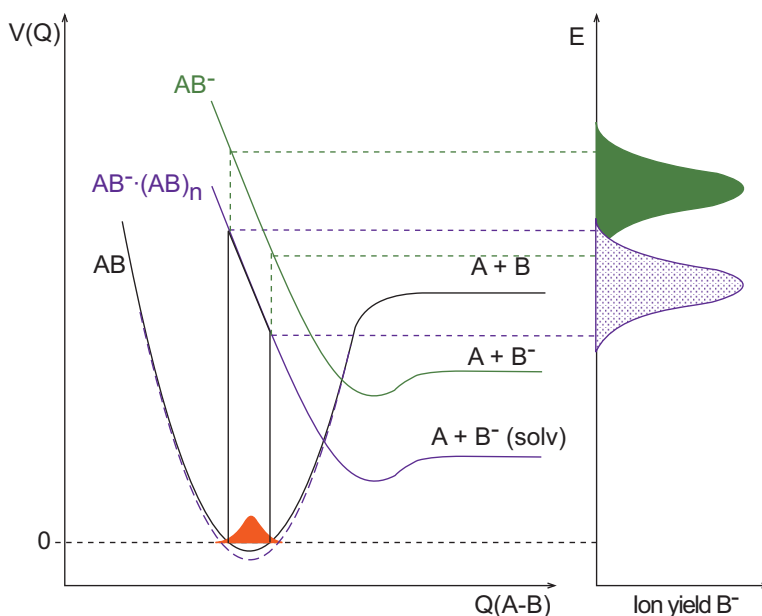


Figure 2.7: Schematic comparison of an electron attachment process to an isolated molecule (green) and to a molecule in the cluster (blue).

Considering electron attachment the energetic situation in the cluster leads to a solvation shift of the initial Franck-Condon transition with respect to the isolated molecule. Thus the resonance maximum is shifted to lower electron energy (*red shift*) as demonstrated by the ion yield curves on the right side of Fig. 2.7. This shift in energy can amount up to several hundreds of meV and

may therefore turn a negative electron affinity for the isolated molecule into a positive EA for the molecule in the cluster. Examples for a solvation shift were observed in this work for example in case of trifluoroacetic acid clusters as will be discussed later. Further examples are CO_2 or N_2O [38, 39].

On the other hand, the formed anion needs a higher energy to leave the association with surrounding molecules and thus the corresponding resonance is shifted to higher energy (*blue shift*). These two contrary effects may compensate each other or one of them can dominate and will be therefore visible in the experimentally observed ion yield.

In cluster experiments not only the single newly formed anion B^- is detected but frequently also complexes in which the anion is solvated by one or more intact molecules ($\text{B}^- \cdot \text{M}$). Complexes of this structure are observed in this work for every compound investigated in the cluster experiment. Well analyzed examples which show a variety of such solvated anions are CF_3Cl [35] and $\text{C}_2\text{F}_5\text{I}$ [51]. The formation of further solvated complexes consisting of the neutral co-product of DEA and intact molecules is possible; but due to the use of negative ion mass spectrometry as an analyzing tool, these complexes cannot be identified under the present experimental conditions.

The molecular surrounding present in a cluster offers different stabilization pathways for a TNI. As the average collision frequency in a molecular cluster is

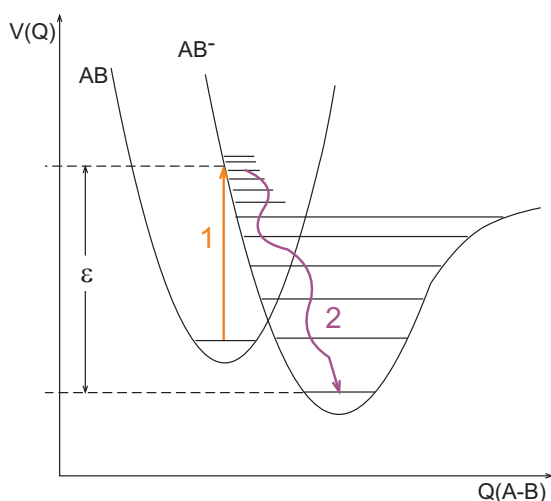


Figure 2.8: Schematic representation of evaporative attachment.

in the range of 10^{12} – 10^{10} s⁻¹ the energy can easily be transferred from the TNI to the neutral neighboring molecules. This can further lead to the evaporation of neutral molecules from the cluster so that the intact molecular anion M⁻ or its higher homologues M_n⁻ can be stabilized. Thus this mechanism is called *evaporative attachment*. The energetic situation is schematically displayed in Fig. 2.8 in a simple representation.

Here only the molecule in the cluster that forms the TNI is considered. In the literature various examples for *evaporative attachment* can be found like CF₃I [70], 1,2-C₂F₄Cl₂ [54] and C₂F₂Cl₂ [52]. Within this work such processes were observed for simple organic acids like HCOOH [60] and CF₃COOH [50] as discussed later.

2.4 Electron interaction with molecular films

As already discussed for electron attachment to clusters, intermolecular interactions play also a particular role in electron interaction with molecular films. Similarly to clusters the potential energy of M and M^- is lowered due to attractive interactions with the environment. The stronger polarization force between the formed anion and the surrounding molecules results in a greater difference (red shift) between the free anion and the solvated anion state than for the neutral compounds. In the dissociation process the excess energy is distributed between the formed fragments and due to energy and momentum conservation the lighter fragment gets the higher amount of translational energy.

These considerations strongly influence the possibilities if a formed anion or radical will remain adsorbed on the surface or if it will desorb. For desorption the corresponding anion needs to overcome its attractive polarization force with the surrounding molecules. Thus the following processes are possible once the TNI is formed:



Process (2.44) represents autodetachment while (2.45) shows the formation of the intact molecular anion that is possible in case of a positive electron affinity by energy dissipation into the surrounding medium. The mechanisms described in (2.46–2.48) all show dissociation into a radical and an anion. The formed fragments may either both remain adsorbed at the surface (2.46) or one of them may desorb (2.47–2.48).

The molecular surrounding in a molecular film can either suppress or enhance the dissociation of a TNI. Especially in the low energy region the cross-section for the desorbing anions is lowered in comparison to the gas phase as the low amount of energy deposited in the system is not sufficient to overcome the polarization energy. Suppression of the desorption of negative ions leads to charge accumula-

tion at the surface. Thus the negatively charged surface will decelerate incoming electrons and they will be reflected in case their kinetic energy is not sufficiently high to overcome the potential barrier caused by charge accumulation.

In contrast there are also medium enhanced DEA processes possible in the condensed phase. As discussed above the negative ion resonance is shifted to lower energy due to polarization. Thus the crossing point R_c of the potential energy curve for the neutral and that for the anionic state is shifted to smaller internuclear distances. Hence the time during which autodetachment is possible is shortened and dissociation of the molecule gets more probable. Furthermore, the lowering of the resonance energy can lead at energies around electronic excitation to a change from an open channel core excited resonance to a closed channel Feshbach resonance. These Feshbach resonances generally show longer lifetimes and dissociation may prevail.