

# Chapter 4

## Theoretical considerations

In this part we will discuss electron-molecule interactions in the gas phase (under single-collision conditions) and in condensed matter. We will concentrate on resonant processes, where an electron is trapped for a certain time to an unoccupied molecular orbital (MO), forming thus a negative ion resonance (NIR). The term transient negative ion (TNI) is also used, because the lifetime of the created ion is usually short and principally unstable with respect to autodetachment. Types and decomposition reactions of a NIR will be explained. The resonant collisions are mostly operative in the low energy regime ( $< 20\text{eV}$ ), which is just the core of our investigations.

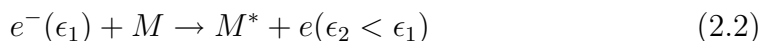
Also at the surface, NIRs can be generated via free electron attachment to adsorbed and condensed molecules. However, different surrounding conditions may considerably modify formation and evolution of the intermediate ion. In the section "*electron attachment to condensed molecules*" we give an overview on the problems how an environment can affect the dissociative electron attachment processes. This concerns changes of energy and lifetime of a NIR, its decomposition pattern and shift of appearance energies of fragmented ions.

## 4.1 Electron-molecule interactions in the gas phase

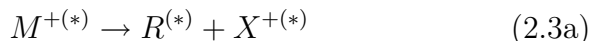
The electron-molecule collisions can in general be divided into two main types, the *direct* and the *resonant* interactions. *Direct* collisions have short interaction times characterized by the usual duration of the electron transit through the dimensions of a molecule. On the other hand, by *resonant* scattering, the electron resides in the vicinity of the molecule for a relatively longer time via capturing into the free molecular orbital (MO).

Depending on the amount of transferred energy from the electron to the target, we speak about *elastic* or *inelastic* electron scattering. In elastic collisions, (4.1) no excitation of the internal energy occurs and the electron loses part of its initial energy only according to momentum conservation. Because of the very small electron mass compared to even the lightest atom H (1:1836), the energy transfer to the atom or molecule is in the order of  $m/M$  of the electron's initial energy (with  $m$  the mass of electron,  $M$  the mass of the target) thus almost negligible. By *inelastic* collisions an amount of the electron energy is transferred to the internal energy of the target. Direct inelastic collisions may create electronically excited states. Direct rotational and vibrational excitation of the molecule is generally very weak due to the argument above ( $m \ll M$ ). Anyway, electronic excitation may result into vibrational excitation through different mechanisms like internal conversion. The direct electron scattering with polar molecules can, however, lead to effective vibrational and rotational excitation, because of the electrostatic forces between the electron and the molecular dipole.

The direct elastic scattering and some subsequent reactions can be expressed as



Process (2.2a) is *dissociative excitation*, (2.2b) *ion pair formation* and (2.2c) *autoionization*. In the last case an electronically excited state above the first ionization energy is formed, which converts into the continuum. In contrast to that, process (2.3) describes direct ionization of the molecule, with possible further fragmentation of the created cation, (2.3a).



*Resonant electron scattering* occurs, when the colliding free electron is bound for a certain time (longer than that of direct electron molecule transit) into discrete level of the target, thus generating a *transient negative ion* (TNI) or synonymously *negative ion resonance* (NIR), according to



We assign the NIR formed by a Franck-Condon transition as  $M^{-\#}$ . This ion can represent an electronically and/or vibrationally excited species. In a polyatomic temporary negative ion, there are the following unimolecular decomposition and stabilization pathways:

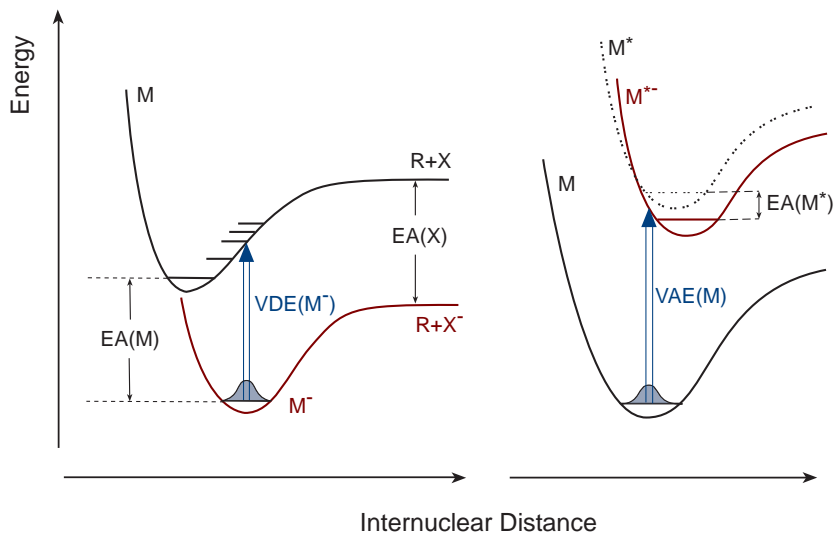


Reaction (4.4a) is called autodetachment and if the energy of the detached electron equals that of the incoming electron, we speak of *elastic resonant scattering*, otherwise it is *inelastic resonant scattering* thereby exciting vibrational modes. The reaction (4.4b) is known as *dissociative electron attachment* (DEA), which leads to the fragmentation of the transient ion into a neutral radical and a negatively charged ion. The last reaction (4.4c) is called *radiative cooling* and relaxation into thermodynamically stable negative ion occurs by photon emission. The time needed for emitting a photon by radiative stabilization is about  $10^{-9} - 10^{-8}$  s, thus this reaction path is less

probable than the first two competitive processes (4.4a) and (4.4b) with lifetimes in the range of  $10^{-14} - 10^{-6}$  s for the former and about  $10^{-14} - 10^{-12}$  s for the latter. The lifetime  $\tau$  and energy width  $\Gamma$  of a TNI are coupled by Heisenberg's uncertainty principle expressed by

$$\Gamma \approx \frac{\hbar}{\tau} \quad (4.5)$$

with  $\hbar = h/2\pi$  and  $h$  the Planck constant. For typical lifetimes the linewidth is very narrow, therefore the energy width of a resonance is mostly controlled by the Franck-Condon transition.



**Figure 4.1:** Schematic diagrams illustrating the terms electron affinity ( $EA$ ), vertical detachment energy ( $VDE$ ) and vertical attachment energy ( $VAE$ ) for two molecules with hypothetical Born-Oppenheimer potential energy curves.

To generate a thermodynamically stable negative ion, the atom or molecule must possess a positive electron affinity. The *adiabatic electron affinity* ( $EA$ ) of a molecule is defined as the difference in energy between the neutral molecule  $M$  and the negative ion  $M^-$  in their ground states [19]. By definition the molecule has a *positive*  $EA$ , if the ground state of  $M^-$  lies below that of  $M$ , and *negative*, if the ground state energy of  $M^-$  is higher than

M. Anyway, a negative EA of the target molecule does not exclude the formation of a TNI. In any case the intermediate anion is unstable towards autodetachment. Next quantities related to electron attachment processes are the *vertical detachment energy* (VDE) and *vertical attachment energy* (VAE). The VDE is defined [19], as the minimum energy needed to eject an electron from the negative ion in its ground (electronic and vibrational) state without changing the internuclear distance. The VDE is the value obtained from a Franck-Condon transition in photodetachment from anions. The VEA is then defined [19] as minimum energy needed to build the negative ion from the neutral molecule in its ground state without changing the internuclear separation. Fig. 4.1 illustrates the quantities discussed above. In atoms we have  $EA(M) = |VDE(M^-)|$

## 4.2 Cross-section and rate coefficient

An important quantity in describing the effectivity and kinetics of electron-molecule collisions are the *total collision cross-section* ( $\sigma_t$ ) and the *rate coefficient* ( $\beta$ ). The total scattering cross section can be defined by Lambert-Beer law. Let  $N$  be the concentration of target particles per unit volume and  $I$  the intensity of the incident monoenergetic electron beam per unit area and per sec. The scattering probability of an electron in the transition region  $\langle x, x + \delta x \rangle$  is expressed by

$$\frac{dI}{I} = -N\sigma_T dx \quad (4.6)$$

from which by integration we get

$$I = I_0 e^{-N\sigma_T x} \quad (4.7)$$

The term  $\exp(-N\sigma_T x)$  is probability that electron will not be scattered during the depth penetration  $x$  and  $I_0$  is the initial electron beam intensity. The total scattering cross-section includes the sum of all particular types of collisions as elastic ( $\sigma_{el}$ ), excitation ( $\sigma_{ex}$ ), attachment ( $\sigma_{at}$ ), ionization ( $\sigma_{ion}$ ) and

all other interactions ( $\sigma_{oth}$ ). So we can write for  $\sigma_T$

$$\sigma_T = \sigma_{el} + \sigma_{ex} + \sigma_{at} + \sigma_{ion} + \sigma_{oth} \quad (4.8)$$

From the theoretical point of view the maximum value for the total collision cross-section can be predicted from a simplified model (*method of partial waves*) expressed by electron scattering on a spherically symmetric potential. Here the incoming electron beam is treated as a plane wave, which is expanded in *Legendre polynomials*. These polynomials are connected to the electron angular momentum, defined with respect to target (*partial wave*). The partial wave method gives for the total collision cross-section

$$\sigma_T = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l \quad (4.9)$$

with  $k = \sqrt{2\mu\epsilon/\hbar^2}$ ,  $\hbar = h/2\pi$  and  $h$  the Planck constant,  $\epsilon$  the electron energy,  $\mu$  the reduced mass of the electron-molecule complex,  $\eta_l$  represents the phase shift between the electron wave function after and before the collision and  $l$  the angular momentum quantum number. Because the electron is much lighter than molecule, the reduced mass can be replaced by the mass of the electron,  $\mu \approx m_e$ . From equation (4.9) it is obvious, that the cross-section is periodically changing with  $\sin^2 \eta_l$ . At given electron energy the maximum limited value for a particular wave we obtain when the phase shift  $\eta_l$  is odd multiple of  $\pi/2$ , thus

$$(\sigma_l)_{max} = \frac{4\pi}{k^2} (2l+1) \quad (4.10)$$

which gives

$$(\sigma_l)_{max} \approx \frac{1}{\epsilon} \quad (4.11)$$

here,  $\epsilon$  is the electron incident energy.

At very low energies only s-wave ( $l = 0$ ) interaction have to be considered. From theoretical predictions of Wigner the cross-section for s-wave attachment behaves according to (4.11) and changes to  $\sigma_0 \propto \epsilon^{-1/2}$  at very low energies [15, 20]. The measurements performed by Hotop et.al. [21] confirm the  $\epsilon^{-1/2}$  behavior of the electron attachment cross-section to SF<sub>6</sub> in gas

phase at energies less than 1meV.

The relationship between the cross-section and the rate coefficient of a reaction can be expressed as follows

$$k(T) = \int_0^{\infty} \sigma f(v, T) v dv \quad (4.12)$$

here  $v$  is the electron velocity and  $f(v, T)$  is Maxwell-Boltzmann distribution function at the temperature  $T$ .

### 4.3 Types of negative ion resonances (NIRs)

When a free electron of a particular energy is trapped by a molecule, a negative ion is formed. Such anions are called *transient negative ions* (TNI) or *negative ion resonances* (NIR). NIRs are characterized by their limited lifetimes since they are thermodynamically unstable towards autodetachment. If dissociation channels are energetically accessible, they are also unstable with respect to dissociation. According to internal excitation of the intermediate ion, we distinguish between two main types of NIRs.

1. When an extra electron is trapped to a previously unoccupied molecular orbital (MO) without electronic excitation of the target molecule, the NIR is known as a *single particle (1p) resonance*.
2. If the attachment event proceeds via electronic excitation of the molecule, we speak of a *two particle-one hole (2p-1h) resonance* or *core excited resonance*. In that case two electrons occupy previously nonoccupied MOs with a hole in one of the lower lying orbitals.

In a first approximation, the capturing mechanism can be described using the long range polarization interaction between the incoming electron and the (nonpolar) target molecule. The corresponding charge-induced dipole interaction is responsible for their attraction, which consequently may deflect an approaching electron from its initial direction. As a reaction on these changes in momentum, centrifugal force acts repulsively on the electron. On this basis, the superposition of an attractive polarization potential  $V_p$  and

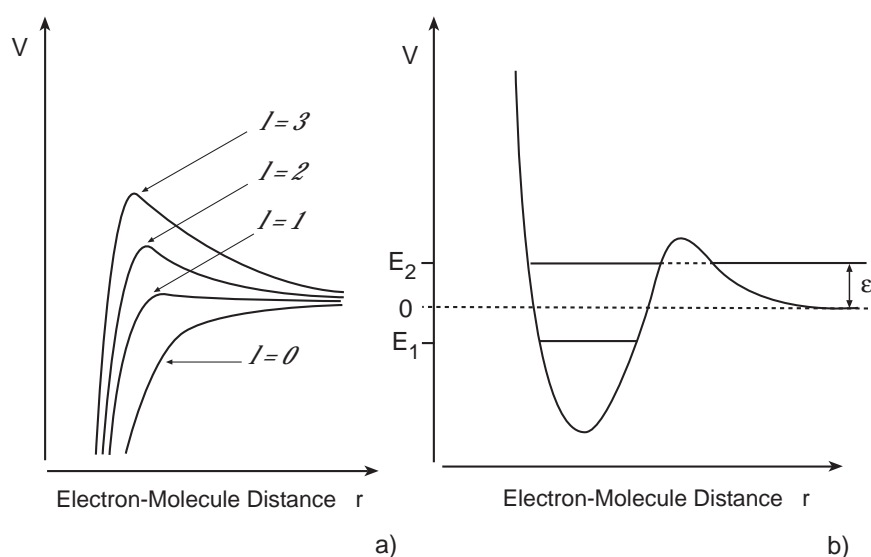
a repulsive centrifugal potential  $V_r$  gives an effective potential energy of an incoming electron  $V_{\text{eff}}$  pictured on Fig 4.2 a).  $V_{\text{eff}}$  for the charge-induced dipole interaction is then expressed as follows,

$$V_{\text{eff}}(r) = V_p + V_r = -\frac{\alpha e^2}{2r^4} + \frac{L^2}{2m_e r^2} \quad (4.13)$$

with  $\alpha$  being the polarizability of the molecule,  $r$  the electron-molecule distance,  $m_e$  the mass of electron and  $L$  the angular momentum of the electron. The angular momentum is defined with respect to the target molecule and is quantized,

$$L = \hbar\sqrt{l(l+1)} \quad (4.14)$$

here  $\hbar = h/2\pi$  with  $h$  being the Planck constant and  $l$  is the angular momentum quantum number. From Fig. 4.2 a) it is obvious that the potential curve is strongly depending on the angular momentum, resulting in a poten-

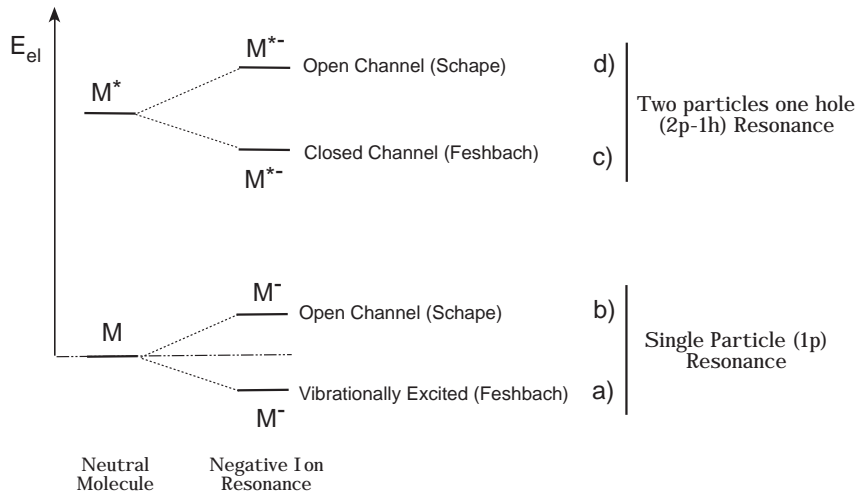


**Figure 4.2:**

**a)** *Effective potential energy curve of the interaction between an electron and a neutral molecule at large distances for different angular momentum values.*

**b)** *Potential energy curve of the interaction between an electron and a neutral molecule (including Pauli repulsion at short distances).*





**Figure 4.3:** Classification of negative ion resonances (NIRs) according to their electronic energy.

tial barrier for  $l > 0$ . At very short distances the electron-electron repulsion (Pauli repulsion) dominates, which leads to a final potential energy curve schematically pictured on Fig. 4.2 b). The resulting potential energy curve between an electron and a molecule depends on whether the molecule is in its ground or electronically excited state. Excited molecules are easier to polarize, therefore such interaction may be very efficient. Existence of one or more molecular orbitals inside the potential well (pictured on Fig. 4.2 b) at energies  $E_1, E_2$ ) enables an extra electron to be trapped by the molecule and form NIR.

According to the electronic energy of the NIRs with respect to their neutral parents ( $M$  or  $M^*$ ), we speak then of *shape resonances* or *Feshbach resonances*. The energy of the first type is higher (Fig. 4.3 b), d)), while the energy of the second type is lower than that of corresponding neutral, (Fig. 4.3 a), c)).

*Shape resonances* are characterized by short lifetimes ( $10^{-14}$  s -  $10^{-12}$  s), since the transition to the neutral parent via autodetachment is possible.

Depending on the energy amount, which the electron has transferred to the molecule, the parent neutral can stay in its ground or excited state (rotationally, vibrationally, electronically). On the basis of the potential energy curve on Fig 4.2 b), a shape resonance can be assigned as follows: an excess electron is trapped to an unoccupied molecular orbital lying at an energy  $E_2$  above the vacuum level. Such discrete states in the continuum can only exist within the centrifugal barrier. Therefore, shape resonances can not be formed via s-wave attachment ( $l = 0$ ).

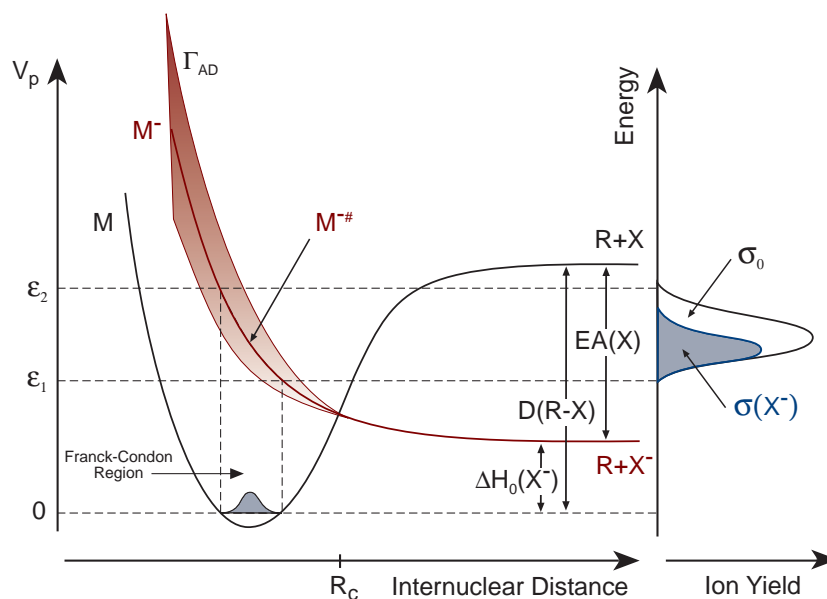
*Vibrational Feshbach resonances* are characterized by relatively longer lifetimes. They can be formed if the corresponding parent neutral possesses a positive electron affinity, thus relaxation of an intermediate ion into a stable parent anion is possible. In the case of Feshbach resonances, when using the illustration on Fig 4.2 b), an extra electron is trapped to an MO lying below the vacuum level at an energy  $E_1$ . In that case the s-wave attachment can take place accompanied by efficient electronic-vibrational energy transfer. *Vibrationally Feshbach resonances* formed at thermal electron energies show usually very high cross-sections ( $10^{-14}\text{cm}^2$ ) with lifetimes often as long as  $10^{-6}\text{s}$ . As we have discussed earlier, at very low impact energies ( $< 10\text{ meV}$ ), s-wave attachment starts to predominate, because p,d,f.. attachments are subjected to a potential barrier preventing low energy electrons to access the potential well.

*Two particle one hole Feshbach resonances* or *closed channel resonances* are as well characterized by their longer autodetachment lifetimes compared to their equivalent *electronically excited shape resonances* (*open channel resonances*). This may easily be seen from Fig. 4.10. Here a vertical transition from the potential curve of the negative ion to that of electronically excited neutral is not possible. Stabilization into neutral parent can only proceed via two electron processes. Accordingly, the lifetime of the intermediate ion is prolonged.

## 4.4 Dissociative electron attachment (DEA)

As we have discussed above, NIRs are principally unstable with respect to autodetachment. If the evolution of the intermediate ion leads to dissociation, we speak then of *dissociative electron attachment* (DEA). In this part we will analyze the principle and energy balance for the simplified model of DEA to a diatomic molecule  $M$ .

The process of ion formation followed by its decay is schematically pictured on Fig. 4.4. Here the Born-Oppenheimer (BO) potential energy curve of a diatomic molecule  $M$  and its corresponding ion  $M^-$  is shown. The capturing event is figured as a vertical transition from the potential energy of  $M$  to that of  $M^-$ . This approximation is reasonable, because the process of electron trapping is much faster than the vibrational movement of the constituent atoms  $R, X$ . The atoms are thus frozen in their position during the electron attachment (*Franck-Condon principle*).



**Figure 4.4:** Schematic of dissociative electron attachment (DEA) for a diatomic molecule with purely repulsive potential for the negative ion.

The captured electron then resides for a certain time (NIR lifetime) on a previously unoccupied molecular orbital (MO). In Fig. 4.4, the potential

energy of  $M^-$  ion is purely repulsive, which means, that the excess electron is trapped to an antibonding MO. The repulsive force between the constituent atoms drives them to separate. Up to the crossing point of the potential curves at the distance  $R_c$ , (*point of no return*), detachment of the extra electron can occur. Depending on the energy amount transferred from the electron to the target, the molecule can then remain in its ground or vibrationally excited state. However, if the NIR survives until a distance larger than the crossing point, only the fragmentation can take place. After the *point of no return*, the conversion from  $M^-$  to  $M$  is no longer possible through a vertical transition.

From Fig. 4.4 we can analyze the energy balance of the DEA process. The electron energy  $\epsilon$  required to generate negative ion  $X^-$  is expressed as

$$\epsilon = D(R - X) - EA(X) + E^* \quad (4.15)$$

with  $D(R - X)$  binding energy of the constituents R and X,  $EA(X)$  electron affinity of X and  $E^*$  the excess energy of the process. The minimum energy necessary for dissociation is called the *thermodynamic threshold energy* ( $\Delta H_0$ ) and is equal to

$$\Delta H_0(X^-) = D(R - X) - EA(X) \quad (4.16)$$

If the  $\Delta H_0$  is known for the specific reaction, the excess energy is calculated using

$$E^* = \epsilon - \Delta H_0(X^-) \quad (4.17)$$

In general, the excess energy can be transferred into internal (rotational, vibrational, electronic) and kinetic energy of the fragments.

$$E^* = E_T + E_i \quad (4.18)$$

where  $E_T$  represents the total translational energy of the fragments and  $E_i$  denotes the internal energy imparted to all fragments. The translational energy released to the negative fragment  $X^-$  can then be determined using

the principle of linear momentum conservation, giving

$$E_T(X^-) = \frac{m}{M} E_T = \frac{m}{M} (\epsilon - \Delta H_0(X^-) - E_i) \quad (4.19)$$

where  $m$  and  $M$  is the mass of neutral fragment and parent molecule, respectively.

The equation (4.19) can also be written using the mass of the anionic fragment  $m_i$ , giving

$$E_T(X^-) = \frac{M - m_i}{M} E_T \quad (4.20)$$

From eq. (4.20) it is clear that *the lighter fragment gains more translational energy than the heavier one.*

From the kinetic energy imparted to all fragments, we can get information about the energy distribution of the DEA process. Under collision free conditions the kinetic energy of the negative fragment can be measured either directly, using an energy analyzer [22, 23], or indirectly using time-of-flight measurements [24, 25].

Also the shape of  $X^-$  ion signal with respect to electron impact energy is shown on Fig 4.4. The cross-section for this particular dissociation channel can be expressed as,

$$\sigma(X^-) = P\sigma_0 \quad (4.21)$$

where  $P$  is the probability for a NIR to survive until the point of no return, the so called *survival probability* and  $\sigma_0$  represents the cross-section for NIR formation. The survival probability  $P$  is expressed as

$$P = \exp\left(-\frac{\tau_{AD}}{\tau_D}\right) \quad (4.22)$$

where  $\tau_{AD}$  is the NIR lifetime with respect to autodetachment and  $\tau_D$  is the NIR lifetime with respect to dissociation. The latter can be expressed as

$$\tau_D = \int_{R_0}^{R_c} \frac{1}{v(R)} dR \quad (4.23)$$

here  $R_0$  is the distance between the atoms at the moment of electronic transition and  $v(R)$  relative velocity of the atoms as a function of their separation.

The velocity can be determined from the excess energy  $E^*$  by

$$v(R) = \sqrt{\frac{2}{\mu}(\epsilon - V_a(R))} \quad (4.24)$$

with  $\mu$  the reduced mass of the constituents and  $V_a$  the potential energy of the parent anion.

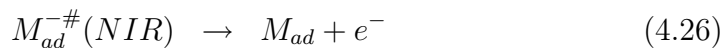
The lifetime  $\tau_{AD}$  and the energy width  $\Gamma_{AD}$  of the NIR are coupled together by the Heisenberg uncertainty principle as follows

$$\tau_{AD}(R) \approx \frac{\hbar}{\Gamma_{AD}(R)} \quad (4.25)$$

From equation (4.23) and (4.25) we can see, that survival probability  $P$  is a function of energy. The exact behavior of the function is not easy to determine. In general survival probability increases with decreasing the energy, which results in red shift of  $\sigma(X^-)$  maximum with respect to  $\sigma_0$  maximum, known as *survival probability shift*, see Fig 4.4.

## 4.5 Electron attachment to condensed molecules

In this work, the interactions of low energy electrons ( $< 20$  eV) with adsorbed and condensed molecules is studied. The following modifications have to be considered with respect to NIRs, when going from collision free conditions to the condensed phase:



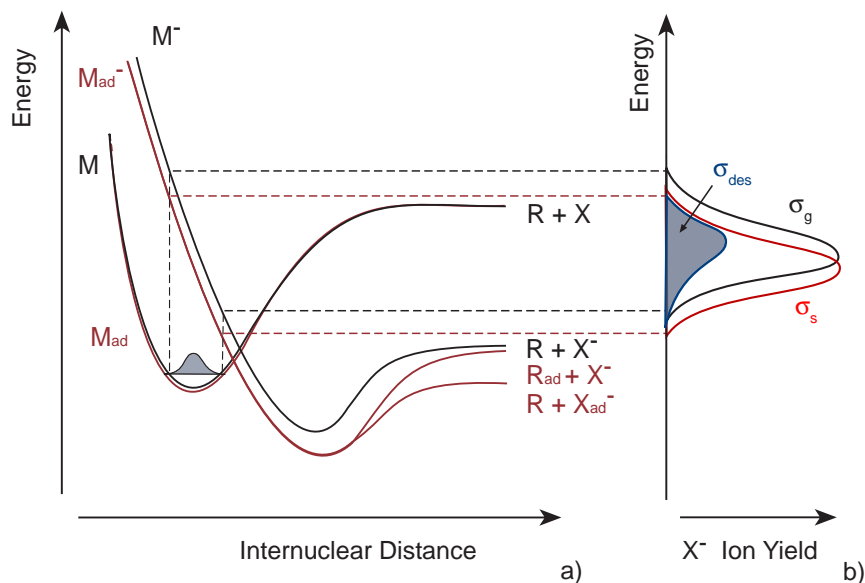
here, the index *ad* assigns a particle adsorbed at the surface. The reaction (4.26) is called *autodetachment*, which principally can also lead to vibrational and/or electronic excitation of the target molecule. In reaction (4.27),

NIR is stabilized into stable negative parent (if  $EA(M) > 0$ ). In that case, the excess energy is efficiently dissipated into the surrounding medium. Note, that under collision free conditions, relaxation pathway (via radiative cooling) is very unlikely. The reactions from (4.28) to (4.30) lead to the dissociation into radical and negative fragment (DEA). Principally, both fragments can remain at the surface (4.28), or one of them can be desorbed (4.29),(4.30). When a radical or negative fragment is emitted from the surface, we speak of *electron stimulated desorption* (ESD). From the energetic point of view, the negative ion desorption, (4.30) is less favorable compared to neutral fragment desorption, (4.29). This is due to the fact, that charged particles polarize the environment. As a result, attractive electrostatic forces between the anion and induced charge in the medium create a polarization potential, which must be overcome in desorption.

Now we will restrict the discussion to ESD processes experimentally observed in the present work, when the negative fragments are emitted from the surface. The process is affected by the environment in the following way:

- The energy of a NIR is usually lowered by attractive polarization interaction of the excess electron with the surrounding molecules, Fig. 4.5 a).
- In order to desorb, the negative fragment must overcome attractive polarization force, induced by its own charge.
- The orientation of the parent anion at the surface should be directed in the way, that dissociation lead directly to the desorption of the negative fragment. Otherwise, post dissociation collisions may suppress ion desorption to some degree, see below.

Fig. 4.5 a) illustrates the influence of an environment on DEA channel for a diatomic molecule by means of hypothetical potential curves. The black curves represent the potential energies of a neutral molecule M and its corresponding ion  $M^-$  in the gas phase, while the red curves represent their potential energies in the bulk. The difference in energy between the solvated and free ion is higher than that between the solvated and free neutral. This leads to the downshift (*red shift*) in NIR formation. In the first approximation we can consider that the energy required to form a TNI is lowered



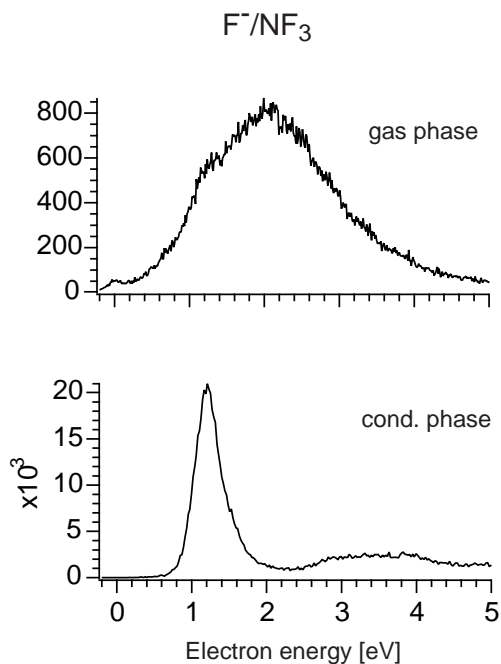
**Figure 4.5:**

a) Comparison between the potential energy curves in the gas phase (black potential curves) and condensed phase (red potential curves).  
 b) The black and red curve represent the  $X^-$  formation in the gas phase ( $\sigma_g$ ) and at the surface ( $\sigma_s$ ), respectively. The blue curve represents the ion yield after the desorption ( $\sigma_{des}$ ).

by the polarization energy of the parent ion, see Fig. 4.5 a). Because the negative ions with insufficient translational energy can not desorb, the final desorption resonance may thus be even *blue shifted* with respect to corresponding gas phase DEA resonance, Fig. 4.5 b). This happens in consequence of the fact, that in a diatomic molecule the kinetic energy of the fragments is directly proportional to the electron attachment energy. In some cases (e.g. for heavy fragments, etc...), the polarization effect leads to the total suppression of the ion emission [26]. However, the decrease in ion desorption yield from the condensed phase does not automatically imply suppression of dissociative channel, since the generated fragments may remain at the surface. On the contrary, the dissociation pathway can even be enhanced (see below). Basically, suppression of desorption results in charge accumulation at the surface. Evidently, the charging effect is more probable at thermal electron energies than at higher impinging energies.



Via desorption restrictions at surface, two different resonant states of the  $\text{NF}_3$  molecule have been resolved, Fig 4.6. Under the collision free conditions, the  $\text{F}^-$  ion yield shows a broad resonance in the energy range from 0 to 4 eV, with an unresolved feature near 1.2 eV [27]. However, from the kinetic energy distribution of generated  $\text{F}^-$  ions it is clear, that two overlapping  $\text{NF}_3^-$  precursor states contribute to the final  $\text{F}^-$  ion yield. The analysis shows high kinetic energy of generated  $\text{F}^-$  ions at lower impinging energies  $\approx 2\text{eV}$ , associated with the fragmentation of the  $\text{NF}_3^{\#-}$  to fragments in the electronic ground state. On the other hand at higher impinging energies ( $> 2\text{eV}$ ), *quasithermal*  $\text{F}^-$  ions are formed from the electronically excited parent anion. As a result of energetic restrictions at the surface, two separate  $\text{F}^-$  peaks are observed in ESD measurements from condensed  $\text{NF}_3$  [28].



**Figure 4.6:** Comparison between the  $\text{F}^-$  ion yields from  $\text{NF}_3$  molecule under collision free conditions and adsorbed on the surface, according to Tegeder et al. [28].

Generally the orientation of the molecule at the surface changes considerably the desorption efficiency [29–31]. A favorable orientation for ion desorption is when the relevant molecular axis is parallel to the surface normal with the negative fragment pointing away from the surface. For example, it has been shown, that the cross-section for ESD of  $\text{CF}_3^-$  from condensed  $\text{CF}_3\text{I}$  exceeds the gas phase  $\text{CF}_3^-$  DEA cross-section by more than 2 orders

of magnitude. Enhancement was explained by a preferential orientation of the molecule at the surface and particularly by a medium enhanced desorption mechanism, based on the conversion from an open-channel resonance to a closed-channel resonance [30, 32]. It was found, that  $\text{CF}_3\text{I}$  when condensed in multilayer amounts, the I – C molecular axis is tilted from the surface plane, with  $\text{CF}_3$  fragment pointing out of it. Anyway, the result is surprising, since the desorption of a polyatomic fragment is very unusual in condensed phase measurements. One would expect redistribution of the excess energy into internal energy of the fragment. Here, on an average 80% of the excess energy was converted into translational energy of the fragments.

If the ion precursor dissociates parallel to the surface or if the negative fragment moves toward the film, desorption cross-section is suppressed. In that case, the generated fragments collide with surrounding molecules, which is known as *post dissociation interactions* (PDIs). Via PDIs new chemical reactions within the molecular films can be induced. We speak then of *secondary reactions*, because they are primarily initiated by electron-molecule interactions. Secondary reactions can proceed through both, negative fragments and radicals. Examples of such processes are: formation of  $\text{O}_3$  from condensed  $\text{O}_2$  [33], synthesis of  $\text{Cl}_2$  molecules from condensed  $\text{C}_2\text{F}_4\text{Cl}_2$  (investigated in this work) [34] and  $\text{CF}_2\text{Cl}_2$  [35] or  $\text{O}_2$  generation following electron impact to water ice [36, 37].

### 4.5.1 Energetics of ESD

The energetics of ion desorption via DEA can be treated in analogy to DEA in the gas phase. In general the translational energy imparted to all fragments can be expressed using eq. (4.17) as

$$E_T = E^* - E_i \quad (4.31)$$

where  $E_i$  is the internal energy of the fragments. Because the energy of the intermediate ion in the bulk is lowered by its polarization energy, the energy

required to form a NIR can be expressed as

$$\epsilon = \Delta H_0 + E^* - V_p(M^-) \quad (4.32)$$

Here  $V_p(M^-)$  represents the polarization energy of the parent anion  $M^-$ . Putting equations (4.31) and (4.32) together and using eq. (4.19), we get the translational energy of the negative fragment before desorption to be

$$E_T(X^-) = \frac{m}{M} E_T = \frac{m}{M} (\epsilon - \Delta H_0 - E_i + V_p(M^-)). \quad (4.33)$$

with  $m$  and  $M$  the mass of neutral fragment and parent molecule, respectively. Anyway, an anionic fragment also polarizes the environment. In order to desorb it must overcome the polarization forces induced by its own charge. Hence, the kinetic energy of the  $X^-$  fragment after the desorption is

$$E_T(X^-)' = \frac{m}{M} (\epsilon - \Delta H_0 - E_i + V_p(M^-)) - V_p(X^-) \quad (4.34)$$

The negative ion is emitted from the surface if it satisfies condition  $E_T(X^-)' > 0$ . We can thus derive energetic threshold for an ion desorption as

$$\epsilon_{thr} = \frac{M}{m} V_p(X^-) - V_p(M^-) + \Delta H_0. \quad (4.35)$$

Accordingly eq. (4.35) can be simplified, when the polarization energy of the parent ion is similar to that of negative fragment ( $V_p(M^-) \approx V_p(X^-) = V_p$ ). The threshold energy for ion desorption is then

$$\epsilon_{thr} = \frac{m_i}{m} V_p + \Delta H_0 \quad (4.36)$$

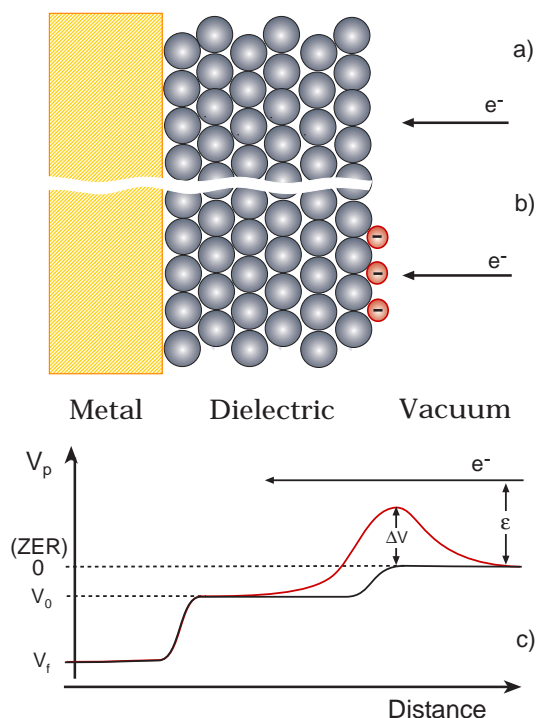
where  $m_i$  is the mass of anionic fragment. From eq. (4.36) it is clear that threshold energy is directly proportional to the anionic mass. Considering also that most of the gained translational energy is imparted into light fragments, we can see, that desorption of heavy fragments is unfavorable.

The equations above are valid if the dissociative process is unimolecular. It means, there is no energy dissipation to the surrounding environment during the dissociation. However, in reality there is always more or less

energy transfer from the solvated ion into surrounding molecules.

## 4.6 Electron transmission and film charging

We will consider now an electron beam impinging directly onto a dielectric film condensed on the metal substrate. Principally, a fraction of the beam will be reflected at the surface while the rest will be transmitted through the film to the metal.



**Figure 4.7:**

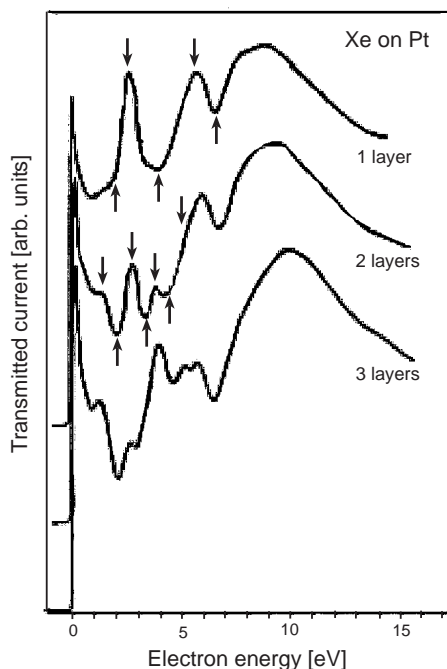
*a) Rare-gas solid adsorbed on a metal substrate.*

*b) Rare-gas solid with charged particles at the surface.*

*c) Potential energy experienced by an incoming electron for an uncharged (black curve) and charged dielectric film (red curve).*

The potential energy for an incoming electron is pictured on Fig. 4.7. Here, the vacuum level is defined as *zero energy reference* (ZER). For the heavier rare gas solids ( $\geq \text{Ar}$ ), the bottom of the conduction band, assigned as  $V_0$ , is located below ZER, with a typical values ranging between 0 and  $-1$  eV for most of the dielectrics [19, 38]. Consequently, an electron entering the rare-gas film (from a vacuum side) will gain additional kinetic energy. Inside the dielectric film the motion of the electron is considered to be quasi elastic, so far as the energy of the electron is below the first electronically excited state of the rare-gas atoms. The electron, however, can lose part

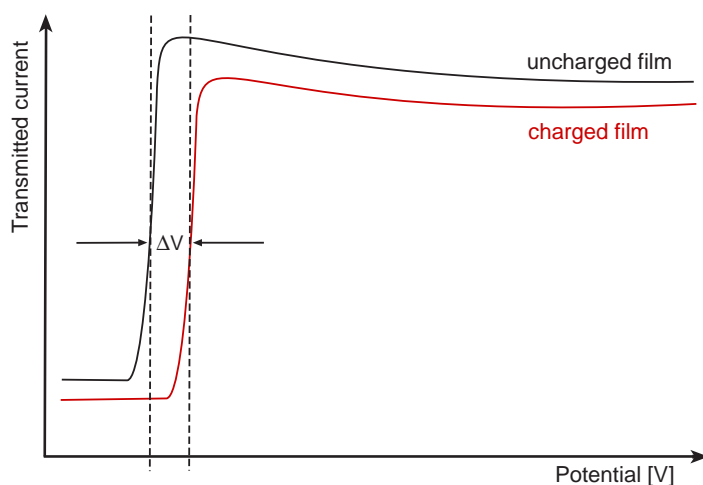
of its energy via interaction with phonons, which is, however, a negligible amount. Two interfaces, vacuum/dielectric and dielectric/metal, effect the electron motion in the way that it may be multiply reflected and interfere with electrons moving directly into the metal. The transmitted current then shows interference structures in its intensity with respect to the electron energy, Fig 4.8. Observed phenomena, also called *quantum size effects*, appear in the low energy region, where the associated de Broglie wavelength of the electron is comparable with film thickness [39].



**Figure 4.8:** *Electron current transmitted through the Xe film as a function of energy. The arrows indicate the position of structure for a given number of monolayers, according to Perluzzo et al. [40].*

When coadsorbing a compound on top of the rare-gas film, part of the impinging electrons will be trapped thus causing charge accumulation at the surface, Fig. 4.7 b). Characteristic film charging is usually associated with solvation of the negative fragments and parent anions and provides hence some information about the EA processes at the surface. The negatively charged surface then acts as a retarding potential and decelerates incoming electrons. In Fig. 4.7 c) this is pictured as potential barrier  $\Delta V$ . If the kinetic energy of the electrons is higher than that of the potential barrier, electrons can pass through the film, otherwise they will be reflected. The charge accumulated at the surface may be determined when measuring the

transmitted current, Fig. 4.9. In the case of a nonirradiated film, the onset of the transmitted current represents ZER. After the electron bombardment the retarding potential at the surface shifts the current onset to higher energies. The difference in potential (equal to the potential barrier  $\Delta V$ ) between the nonirradiated and irradiated film is then directly proportional to the accumulated charge.



**Figure 4.9:** *Transmitted current for an uncharged and charged film.*

As already mentioned above, the charged particles (negative fragments, parent anions) trapped at the surface are a measure of the EA cross-section  $\sigma(\text{EA})$ . In that case *the charge trapping method* is used to determine the corresponding cross-section values [41–43]. Here the investigated molecules are condensed in submonolayer amounts on top of the multilayer rare-gas solid. While the submonolayer amounts are necessary to avoid inhomogeneous charging of the irradiated surface area, the inertness of the noble gas prevents from extra charging via the solvation of the electrons in the bulk. The charge accumulated at the surface is thus only due to contribution of the anionic species, generated via electron attachment to investigated compound. After the irradiation, the molecular film is treated as a parallel plate capacitor, where on dielectric/vacuum side the negative charge is stabilized and the opposite side is grounded via metal substrate. When the density of

the investigated molecules  $\sigma_0$  is small and the irradiation time  $t$  is short, the accumulated charge can be expressed as

$$Q \approx It\sigma_0\sigma(EA) \quad (4.37)$$

with  $I$  the impinging current. This assembled charge creates a difference in potential given by

$$\Delta V(t) = EL = \frac{QL}{\epsilon S} \quad (4.38)$$

where  $\epsilon$  and  $L$  are the dielectric constant and film thickness, respectively, and  $S$  is the irradiated area. The area  $S$  is given by the diameter  $d$  of the electron beam,

$$S = \frac{\pi d^2}{4} \quad (4.39)$$

The time derivation at  $t = 0$  of  $\Delta V$  determines the electron attachment cross-section  $\sigma(EA)$  and is equal to

$$A_s = \frac{d\Delta V(t)}{dt} = \frac{LI\sigma_0\sigma(EA)}{\epsilon\pi r^2} \quad (4.40)$$

the term  $A_s$  is called *charging coefficient*.

At very low electron energies ( $< 1$  eV), the ion desorption is suppressed and the value obtained using eq. (4.40) represents the *absolute EA cross-section*  $\sigma_{\text{abs}}(EA)$ . At higher energies also ion desorption can take place. The accumulated charge is then reduced and lowers the calculated EA cross-section value,

$$\sigma(EA) = (1 - P_{\text{des}})\sigma_{\text{abs}}(EA). \quad (4.41)$$

with  $P_{\text{des}}$  desorption probability for all anions. Since the desorption of the parents anions can be excluded, the product  $P_{\text{des}}\sigma_{\text{abs}}(EA)$  represents the *ESD cross-section* for all anionic fragments.

The charge trapping method is one of the techniques used to analyze the changes in electron attachment processes when going from the collision free conditions to condensed phase.

## 4.7 Medium enhanced DEA.

Over a period of time, many studies have demonstrated a significant influence of the environment to the electron scattering/attachment processes. When speaking about the effect on DEA processes, the surrounding medium can either suppress or enhance particular dissociation pathways. For many adsorbates, fragmentation via DEA processes have been found to proceed with a considerable cross-section. Of course, generated fragments can further react with atoms or molecules in the vicinity, thereby forming new compounds.

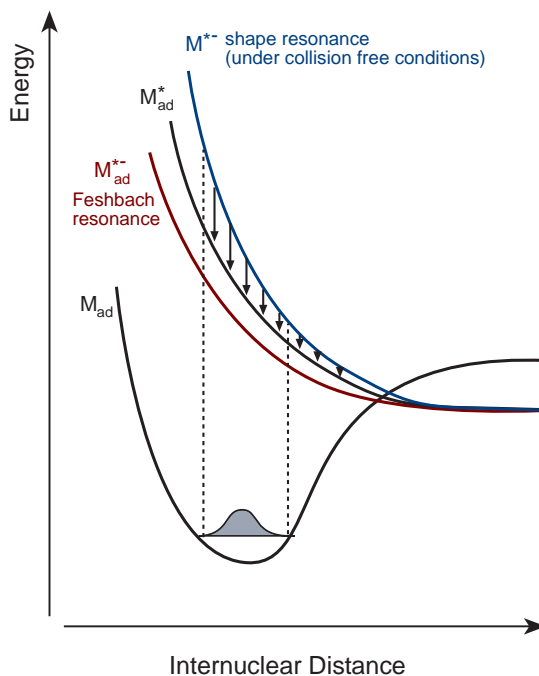
As discussed earlier, the observation of desorbed negative fragments following DEA to condensed molecules is strongly affected by induced polarization force. The desorption cross-section is usually lowered compared to the DEA cross-section under collision free conditions. This is much pronounced in the low energy region, where the energy amount delivered to the system is small. Dissociation of the parent anion can, however, still be operative. For many molecular systems the DEA cross-section is known to be even enhanced when going from collision free conditions to condensed phase.

Compounds like  $\text{CF}_4$  [44],  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  [45],  $\text{CH}_3\text{Cl}$  [46],  $\text{CF}_3\text{Cl}$  [47] coadsorbed in submonolayer amounts on top of the rare-gas solids, show increase in DEA cross-section at electron energies below 1 eV. At that energy, desorption of the negative fragments is suppressed and the *charge trapping method* is used to determine the corresponding cross-section values, see section 2.6. In principle, both dissociative (via anionic fragments) and nondissociative (via parent anions) EA processes contribute to film charging. However, the excess electron is often trapped into antibonding MOs (for molecules above). The question then is on the branching ratio between dissociation and the relaxation into the ground state of the anion. In the case of a purely repulsive state, the cross-section for charge accumulation corresponds to that of DEA. Even at higher impinging energies, where the ion desorption is operative, increase in DA cross-section has been observed using *charge trapping method*. The enhancements at higher energies (3 – 7 eV) were detected for example for  $\text{CO}_2$  [48],  $\text{O}_2$  [49] and  $\text{H}_2\text{O}$  [50] when adsorbed on top of a Krypton spacer. However, here the derived cross-section values



represent the lower limit of the total DEA cross-section, since ion desorption takes place.

The observed medium induced enhancements were explained via an increase in survival probability of the transient anion against autodetachment. As we have discussed earlier, electronic polarization of the environment results in energy downshift of the NIR, Fig 4.5. The crossing point  $R_c$  is thus shifted to a smaller internuclear distance. Accordingly, the time the intermediate ion spends in the area active for autodetachment is shortened and hence the probability for dissociation increases.



**Figure 4.10:** Example of a medium induced conversion from an open channel (shape) resonance into a closed channel (Feshbach) resonance. Arrows on the figure illustrate the possible decay of the intermediate ion via autodetachment.

Despite the kinetic energy filter for desorption, medium enhanced ESD have been detected for many CFC's, however, usually associated with the electronically excited parent ions. The mechanism leading to an increase is similar to that discussed above. Here the environment affects the electronically excited NIR in the following way: Under collision free conditions, the

energy of the excited NIR lies above its corresponding electronically excited neutral. However, when going to the condensed phase, the energy of the resonance is lowered and can even lie below that of the excited neutral. We speak then of *medium induced conversion* from an *open-channel resonance* into a *closed-channel Feshbach resonance*, Fig. 4.10. While the open channel resonance can decay via electron emission the Feshbach resonance can release an extra electron only via two electron process. The survival time of the solvated NIR is then strongly prolonged and dissociation (if available) will prevail [28–31, 46].

Apart from direct free electron attachment to the compound, *substrate mediated electron transfer* reactions can take place within the molecular films. Here the electron is captured by molecules different from the molecule of interest. The captured electron is then transferred to the investigated compound. Electron transfer reactions have been observed for example for rare gases (Xe, Kr, Ar) or polar molecules (H<sub>2</sub>O, NH<sub>3</sub>) when used as a substrate.

It has already been shown, that by submonolayer coverages on top of a multilayer (> 15ML) rare gas solid, desorption of negative fragments exhibits pronounced increase at energies close to that of corresponding rare gas excitons [51–53]. Desorption enhancements are explained by the formation of an *electron-exciton complex* which then transfers the electron and energy to the molecule, forming thus a negative ion resonance which dissociates.

For polar environments like water ice or ammonia, the excess electron is not bound to an individual molecule, but is trapped in the potential well formed by the orientation of the molecular dipoles. We speak then of *solvated electrons*. Giant enhancements in electron attachment processes leading to desorption of a fragment ions (attributed to solvated electrons) have been observed for many CFC's when coadsorbed in submonolayers amounts on top of polar solids [18, 54, 55].