Evolution of Negative Ion Resonances at Surfaces: Effect of Environment and Orientation

Petra Tegeder and Eugen Illenberger

1 Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin, Germany
2 Freie Universität Berlin, Institut für Chemie – Physikalische und Theoretische Chemie, Takustrasse 3, D-14195 Berlin, Germany
E-mail: tegeder@physik.fu-berlin.de

Abstract. The influence of the environment and orientation on the evolution of negative ion resonances at surfaces following low energy (0–15 eV) electron attachment to adsorbed and condensed molecules is studied by means of electron stimulated desorption (ESD) of negative ions. In the low energy regime ESD of anions usually proceeds via dissociative electron attachment (DEA) to an individual molecule at or near the surface. Three prototypical cases are discussed in the light of the corresponding gas phase process. (i) ESD of F\(^-\) from a multilayer film of NF\(_3\) shows desorption features which are considerably narrower compared to the corresponding gas phase DEA analogues. This is a mirror of the particular dynamics of the unimolecular reaction in relation to the energy constraints operative in ion desorption. In addition to the strong F\(^-\) desorption it is demonstrated by applying surface vibrational spectroscopy that (resonant) dissociative electron attachment at low energies (0–5 eV) is responsible for chemical changes within the NF\(_3\) film, viz. formation of NF\(_2\) radicals and N\(_2\)F\(_4\) molecules. (ii) In the ESD of Cl\(^-\) from submonolayer Cl\(_2\) adsorbed on rare gas surfaces a strong dependence of both the signal intensity and shape of the desorption resonance on the angle of incidence of the electron beam with respect to the surface normal is observed. This behavior points towards a preferential orientation of the molecules perpendicular to the surface. (iii) The absolute DEA cross-section can appreciably be enhanced by the medium due to an increase of the autodetachment lifetime of the negative ion resonance. This is demonstrated in ClCN for an electronically excited resonance.

1. Introduction

Electron induced reactions play a key role in nearly any field of pure and applied sciences, in the gas phase as well as in condensed phases or at interfaces. This include surface photochemistry, which is often driven by hot electron transfer to the reactant molecule [1], radiation damage of biological material [2], reactions stimulated by electrons in scanning tunneling microscopy (STM) [3, 4, 5], or any kind of plasma used in industrial plasma processing [6]. In each of these fields the electron-molecule interaction represents a key step within an eventually complex reaction sequence.

In any kind of plasma, it is primarily the electron-molecule interaction from which the feed gas molecules receive energy and which maintains the plasma. These primary interactions generate molecules in various excited states, in ionized forms (cations and anions) and finally as fragmentation products, also in excited and ionized forms [6]. All these particles mutually
interact, including photons from emission processes. It is hence a vast variety of different interactions between primary and secondary particles which characterize a plasma. In principle, knowledge about the relative density of the components in their different states and the respective cross-sections would be necessary to model and eventually control the plasma. In actual practice, however, it is often sufficient to restrict on two body interactions between the most abundant components which, in the case of laboratory plasmas, are usually electrons and neutral gas molecules.

In a so-called thermal plasma, the three major constituents, the electrons, neutrals and ions have the same average energy and thus the same temperature and may range from a few thousand degrees of Kelvin (K) in welding torches to millions of K inside of a fusion plasma. In contrary, the plasmas used in materials processing are often so-called cold or anisothermal plasmas [7]. Although they contain a variety of high energy species (neutrals, radicals and ions in excited states) the plasma does not substantially heat its container, i.e., the excited species are far from equilibrium. In particular, the electron energy distribution in such a cold plasma peaks at a few eV and is hence much higher than the average energy of the heavy particles (kT (300K) = 0.026 eV). The weak coupling between the electrons and heavy particles is a consequence of the large difference in masses. From energy and momentum conservation it follows that in a collision, an electron can only transfer an energy amount of the order \( m/M \) (\( m \): electron mass, \( M \): mass of the heavy particle) onto the heavy target. Exceptions are low energy electron collisions with polar molecules, and collisions when resonances are involved (see below). Non-thermal plasmas hence represent systems where very effective chemical processes can occur. These reactions are driven by the hot plasma electrons, while the plasma temperature (defined by the heavy particles) is not far from ambient temperatures.

In reactive plasmas used in chemical vapor deposition (CVD) or dry etching it is obvious that in addition to collision processes between gas phase particles also processes in the gas-surface area and processes inside the solid are important to characterize, model and eventually control the plasma in order to obtain a maximum of the desired products [8]. However also in non-reactive plasmas (high pressure lamps, etc.) and in particular in micro plasmas collisions between electrons and particles at the surfaces are important [9].

In this contribution we consider the interaction of low energy electrons (0–15 eV) with molecules under different phase conditions, i.e., from free molecules in the gas phase to adsorbed or condensed molecules. In the low energy range many molecules exhibit large cross sections for resonant electron capture, leading to the formation of a negative ion resonance (NIR) (synonymously the term transient negative ion (TNI) is used). The NIR is unstable towards the loss of the extra electron (autodetachment) and in competition to this process it can decompose into fragments consisting of an ion and one or more neutrals. The overall process is called dissociative electron attachment (DEA):

\[
e^{-} + M \rightarrow M^{-\#} \rightarrow R + X^{-}
\]  

where \( M^{-\#} \) assigns the NIR formed via a Franck-Condon transition. If DEA channels are energetically accessible at low energies, the cross section for DEA in the gas phase can reach values exceeding 100 Å² \( (10^{-18} m^2) \) [10].

In this contribution the formation and evolution of negative ion resonances on the surface of solids or thin molecular films will be considered. The aim of the studies is to obtain information on how the intrinsic reactivity of the molecules towards low energy (0–15 eV) electrons is affected when proceeding from the gas phase to a condensed environment. A powerful technique to study negative ion resonances at surfaces is electron stimulated desorption (ESD) of negative ion fragments.

In the gas phase the (dissociative) electron attachment reaction yielding fragment ions or the undissociated relaxed ion (M⁻) can directly monitored by means of a mass spectrometric
approach. In contrast, the complementary process in the condensed phase is only observable via the desorption of fragment anions. In principal electron initiated reactions at the surface or in the bulk can directly be followed by probing adsorbate vibrations with infrared reflection absorption spectroscopy (IRAS) [11, 12] or by high resolution electron energy loss spectroscopy (HREELS) [13, 14, 15].

In the condensed phase, the NIR created at or near the surface of a molecular film is principally subjected to the following DEA reactions (the subscript (ad) denotes the particle at the surface)

\[
M_{ad}^- \rightarrow R_{ad} + X^- \quad (2)
\]

\[
R + X_{ad}^- \rightarrow R_{ad} + X_{ad}^- \quad (3)
\]

\[
R_{ad} + X_{ad}^- \rightarrow \quad (4)
\]

In addition, relaxation of the undissociated ion \(M_{ad}^-\) and autodetachment is also possible. The branching ratio between the channels (2 – 4) will depend on the orientation of the molecule at the surface and also on the energetics of the underlying DEA reaction. Among the three routes operative at the surface, channel (2) is energetically the least favourable, since a desorbing fragment ion has to overcome the polarization barrier. In the usual case when attractive polarization interaction is larger than the repulsive exchange interaction (Pauli repulsion), the fragment \(X^-\) must gain sufficient translational energy to overcome the polarization energy. Figure 1 compares DEA from a molecule in the gas phase with DEA from a condensed phase molecule. Due to polarization interaction, the ionic curve is generally more shifted than the neutral one. Stabilized molecular anions \(M_{ad}^-\) as well as DEA fragments remaining at the surface \(X_{ad}^-\) contribute to charging of the film under exposure to the electron beam. In fact, charge trapping preferentially occurs at energies where resonances are present [16, 17].

**Figure 1.** Schematic potential energy diagram illustrating DEA in the gas phase and in the condensed phase. The subscript (ad) assigns a particle bound to the surface.
Apart from this energy constraint, it is clear that desorption preferentially occurs for those orientations of the target molecule with the molecular axis along the surface normal thereby allowing direct emission of the ionic fragment. For other orientations DEA is still possible, however, post-dissociation interactions (PDI) of the fragment ion with the surrounding molecules will always be accompanied by some energy dissipation which will reduce the desorption probability to some degree.

In this report we shall illustrate the behaviour of negative ion resonances at surfaces for a few prototypical case studies. The results will be discussed on the background of the intrinsic properties of the gas phase analogues.

2. Experimental
2.1. Electron stimulated desorption (ESD) of negative ions

Electron stimulated desorption of negative ions is studied using an ultrahigh vacuum (UHV) apparatus consisting of a trochoidal electron monochromator (TEM) [18], a cryogenic cooled monocrystalline Au substrate mounted on a manipulator, and a commercial quadrupole mass spectrometer with an ion extraction system (Fig. 2).

![Figure 2. Schematic of the experimental arrangement to study electron stimulated desorption (ESD) of anions at low electron energies.](image)

The substrate can be cooled down to approximately 35 K by means of a closed cycle He refrigerator and resistively heated up to several hundred degrees Kelvin. The molecules are condensed on the metallic substrate by exposing it to a volumetrically calibrated gas quantity effusing from a capillary located 0.7 cm from the gold crystal. The thickness of the film is obtained from thermal desorption measurements by monitoring the pressure in the chamber while heating the film. Since a monolayer and a multilayer can easily be distinguished in the desorption peaks, dosing can be performed with an accuracy of approximately 30%. Experiments are carried out on the target molecules deposited either in multilayer amounts directly on the metallic substrate or in sub-monolayer quantities on a noble gas (Xe, Kr) surface. In the latter case Kr or Xe is condensed in a particular amount on the metallic substrate prior the target molecule deposition. The base pressure in the chamber was in the $10^{-10}$ mbar range.

The TEM operates with a weak homogeneous magnetic field ($\approx 30$ G) which guides the electrons, thus preventing spreading of the beam. The instrument has therefore proved to be particularly suited to studying electron induced processes in the low energy domain. The electron energy is calibrated by the onset of electron transmission to the substrate (the electron injection
curve) representing the vacuum level (0 eV). From the steepness of the onset curve the energy width of the electron beam can be estimated as 0.2 eV at a current of 30 nA. For multilayer Cl$_2$ and CICN coverages, charging of the molecular film following electron beam exposition is inherently present due to stabilized anions and otherwise trapped electrons. This results in a shift of the electron injection curve with respect to the monochromator potential (due to the repulsive potential of the accumulated charge) [19]. All desorption spectra presented here are calibrated with respect to the onset of the injection curve and refer to the first scan on a newly prepared adsorbate. Charging of the film, on the other hand, can be used to identify whether electrons (e.g., at a particular energy) are trapped by the film.

Desorbing anions are extracted and focused into a quadrupole mass filter equipped with an ion lens system. The axis of the mass filter is aligned perpendicular to the electron beam. After traversing through the filter the ions are detected by means of a secondary electron multiplier. The ion signal is maximized by adjusting the angle ($\vartheta$) of the crystal with respect to the fixed axis of the electron beam and the quadrupole. $\vartheta$ refers to the angle between the electron beam axis and surface normal.

2.2. Infrared-Reflection-Absorption-Spectroscopy (IRAS)

The surface vibrational spectroscopy was performed in the same ultrahigh vacuum chamber as the ESD of anions.

For the IRAS studies, the infrared light from a commercial FT-IR spectrometer, is focused through a zinc selenide viewport onto the Au(111) surface inside the UHV chamber at an incidence angle of $\approx 84^\circ$ with respect to surface normal (grazing angle of incidence). The reflected light from the sample is recollimated and focused on a broad-band liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Figures 3 shows a schematic representation of the experiment. The low-frequency cutoff of the detector is near 450 cm$^{-1}$. The spectra were collected in a form of double-sided interferograms using a forward mirror speed of 20 kHz and 4 cm$^{-1}$ resolution. The interferograms were zero-filled and apodized by triangular apodization.

![Figure 3](image.png)

**Figure 3.** Scheme of the experimental setup to study electron induced reactions in thin molecular films by means of infrared absorption-reflection spectroscopy.

The absorption of IR light by molecules adsorbed on a metal surface is dominated by the dielectric behavior of the metal, since the electric field of the incident light as well as that of the dipole moment of the molecular vibrations will interact with the metal electrons. As a consequence, only vibrational modes having a component of the dipole moment perpendicular to
the surface can be excited (metal surface selection rule) and only at grazing angles of incidence one can expect appreciable IRAS intensities [20, 21].

In order to study electron induced reactions the molecular films were exposed to low energy electrons generated by the TEM at different primary energies (0–10 eV). The energy resolution of the electron beam was around 0.5 eV at a current of $\approx 0.8 \mu$A. Note that the current used here is much higher and resolution is lower in comparison to the desorption experiments (see chapter 2.1).

3. Results and Discussion

3.1. Narrow resonances in the low energy (0–4 eV) desorption yield: ESD of $F^-$ from NF$_3$

The electron impact behaviour of gas phase NF$_3$ has attracted considerable interest in recent years as this compound is used as feed gas in various plasma etching processes [22, 23, 24, 25] and also as a fluoride source in excimer gas laser media [26, 27]. Owing to the comparatively high dissociative electron attachment (DEA) cross-section it is also used to generate $F^-$ in the course of ion-molecule reactions [28, 29]. The DEA cross-section in NF$_3$ generating $F^-$ is $\approx 2.2 \times 10^{-16}$ cm$^2$ [30]. In the gas phase, the DEA products F$_2^-$ and NF$_2^-$ are also observed [30, 31], but with a cross-sections about two orders of magnitude below that of $F^-$. Figure 4(a) shows the desorption of $F^-$ from a 5 monolayers (ML) NF$_3$ film and for comparison the DEA gas phase spectrum. As can clearly be seen, the gas phase spectrum consists of a comparatively broad resonance in the low energy region (0–4 eV) with an unresolved structure at 1.2 eV [31].

![Figure 4](image_url)

**Figure 4.** (a) Comparison between gas phase DEA yielding $F^-$ and desorption of $F^-$ from a 5 ML NF$_3$ film in the low energy region (adapted from Ref. [38]). The dashed line in the gas phase spectrum indicates the overlapping two resonances (see text). (b) Schematic potential diagrams relevant in low energy DEA to NF$_3$ yielding $F^-$. The dotted curve represents the excited anion which may also couple to some degree into the limit NF+F+F$^-$. The desorption spectrum differs remarkably due to the appearance of two separated peaks. This is a rather surprising observation as from most of the previous studies the opposite was observed, i.e. a smearing out of gas phase structures when going to the condensed phase [32]. This behavior can be explained by the particular energetics and mechanism of the DEA reaction. The kinetic energy analysis of $F^-$ ions from gas phase NF$_3$ [31] showed that in the energy range up to $\approx 2$ eV ions with appreciable excess energy are generated, whereas above that
energy an additional low energy component appears, becoming more dominant towards higher electron energy. This was interpreted by the existence of two different, energetically overlapping precursor states: one precursor state (NF$_3^-$) related to the electronic ground state of the anion (NF$_3^-$) and another (NF$_3^*$) related to an electronically excited negative ion state (NF$_3^*$) at higher energy (core excited resonance, see Fig. 4(b)). The precursor ion associated with the electronic ground state then decomposes via direct electronic dissociation into F$^-$ + NF$_2$. The associated kinetic energy distribution was shown to be quasi-discrete with the mean energy of F$^-$ increasing from 0.7 to 1.5 eV when the primary electron energy is increased from 0.2 to 2 eV. In contrast, the electronically excited precursor decomposes into F$^-$ with a quasi-thermal energy (mean kinetic energy of F$^-$ below 0.3 eV), indicating a less direct decomposition mechanism. This decomposition process is strongly suppressed in the fragment ion desorption yield.

In the gas phase the two lowest DEA channels leading to F$^-$ are due to the following processes

$$e^- + NF_3 \rightarrow F^- + NF_2 \quad \Delta H_0 = -0.76\text{eV} \quad (5)$$

$$\quad \rightarrow F^- + NF + F \quad \Delta H_0 = 2.12\text{eV} \quad (6)$$

which are exothermic by -0.76 eV and endothermic by 2.12 eV, respectively [33]. From the quasi-thermal kinetic energy release it is likely that the excited precursor ion decomposes into NF$_2^*$ + F$^-$. Above 2.1 eV the excited radical may decompose, leading to the three fragments NF + F + F$^-$. It may therefore appear that the different kinetic energy release is responsible for the different features between gas phase DEA and desorption yield. As mentioned above, the ESD of ions will depend on the orientation of the molecule at the surface and it is subjected to particular energy constraints.

The low energy precursor state ejects F$^-$ ions with appreciable kinetic energy (having a quasi-discrete distribution) which will effectively contribute to the desorption signal. The dissociation of the precursor state at higher energy, on the other hand, yields a quasi-thermal kinetic energy distribution and only a small fraction within the high energy tale of the associated translational energy distribution will contribute to the desorption signal. This explains both, the comparatively low desorption yield from the second state but also the appreciable shift of the maximum in the desorption resonance with respect to that of the gas phase analogue by more than 1 eV.

In conclusion, for the NF$_3$ system it can be seen that two overlapping features in the gas phase DEA can appear as separated features in ESD of anions from an NF$_3$ film. This effect is due to the particular energy constraints for ion desorption in relation to the energetics of the associated DEA reaction.

3.2. Modification of an NF$_3$ film by sub-excitation electrons

In the following we will show that sub-excitation electrons, viz. electrons appreciable below the threshold for electronic excitation, can induce chemical changes in a thin NF$_3$ film. Figure 5(a) shows IRAS spectra of 10 ML NF$_3$ film before and after exposure to an electron beam for different times (i.e., exposed charge in mC) at an electron energy of 1.5 eV. Clearly visible is the symmetric stretch ($\nu_1$) and asymmetric stretch ($\nu_3$) at 1030 and 931 cm$^{-1}$, respectively.

While the $\nu_3$ vibration has components of the dynamical dipole moment perpendicular to the C$_{3v}$-axis of the molecule, that of the $\nu_1$ vibration is oriented parallel to it. From the fact that both modes are active in IRAS we conclude that there is no preferential orientation of the NF$_3$ molecule in the film. The $\nu_3$ mode is shifted with respect to the gas phase value (908 cm$^{-1}$ [34]) but corresponds to that obtained from Raman spectroscopy (930 cm$^{-1}$) recorded on condensed NF$_3$ at 62 K [35]. It should be noted that we do not observe a measurable degradation when the
Figure 5. (a) IRAS signature of the asymmetric ($\nu_3$) and symmetric ($\nu_1$) stretch vibration from a 10 ML NF$_3$ film before and after electron irradiation at an energy of 1.5 eV. The ordinate is in units of milli-absorbance (mAbs). (b) Change in the absorbance ($\Delta$) of the asymmetric stretch ($\nu_3$) mode as a function of electron irradiation time (corresponding to the charge Q in mC) at an electron energy of 1.5 eV. The dotted curve corresponds to a fit using the saturation function Eq.7 (adapted from Ref. [12]).

IR spectrum of the NF$_3$ film is recorded without electron exposure but for times exceeding those of electron irradiation. At an electron exposure above 35–40 mC degradation reaches saturation. The $\nu_3$ intensity is then dropped to about 20% of the initial value. This is probably due to an incomplete overlap between the surface area covered by the electron beam and that by the IR beam. Otherwise we can assume that degradation is operative through the entire 10 ML film as the electrons are transmitted into the metallic substrate. It is likely that electron transmission occurs via an electronic conduction band like in rare gas films [36] or in non-polar insulating liquids [37].

The degradation of the NF$_3$ film is studied by monitoring the $\nu_3$ signal for different electron beam exposure times and different electron energies. This is exemplarily shown in Fig. 5(b) for an electron energy of 1.5 eV. The ordinate corresponds to the change of absorbance ($\Delta$) in units of milli-absorbance (mAbs). The time dependence of $\Delta$ can be approximated [11] by an exponential saturation function:

$$\Delta = \Delta_\infty[1 - exp(-\sigma Q/eA)]$$

with $Q$ the charge quantity corresponding to a particular electron beam exposure time, $\sigma$ the degradation parameter, $A$ the interaction area between the electron beam and the molecular film, $e$ the elementary charge and $\Delta_\infty$ the asymptotic change of the absorbance. Note that both $\Delta$ and $\Delta_\infty$ are negative numbers. For one single monolayer the degradation parameter directly corresponds to the degradation cross-section.

An evaluation of data sets shown in Fig. 5(b) obtained at different electron energies yields the energy dependence of the (relative) degradation cross-section. Figure 6(a) indicates that this degradation cross section peaks at low energy (near 4 eV) and increases again at energies above 6 eV. Although Fig. 6(a) contains only five data points it must be emphasized that each of these data points is obtained from a series of independent measurements (see Fig. 5(b)). This behaviour can directly be related to the electron scattering and electron capture properties of
the target molecule as can be seen by comparing with gas phase studies [31, 30] and studies on electron stimulated desorption of anions from an NF$_3$ film [38] (see chapter 3.1).

Figure 6. (a) Relative degradation cross-section as a function of the electron energy extracted from the fitting procedure (Fig. 5(a), adapted from Ref. [12]). (b) Comparison of F$^-$ formation from gas phase NF$_3$ and from an NF$_3$ film at a thickness of (10 ML) also used for the IRAS studies (see also chapter 3.1).

Figure 6(b) shows the F$^-$ yield from gas phase NF$_3$ and the desorption yield obtained from a 10 monolayer film. While degradation observed by IRAS is operative through the entire molecular film, desorption of ions is restricted to reactions at or near the surface. As discussed in chapter 3.1, F$^-$ formation exhibits pronounced resonant structures in the low energy region, both from gas phase NF$_3$ and as a desorption product from condensed molecules.

From the energy dependence we conclude that the degradation cross section can directly be related to resonant electron capture as the only initial process. This is in fact the only process which can initiate chemical changes in that energy domain. Another process operative in that energy regime is vibrational excitation of the neutral molecule. Since the vibrational excitation functions also exhibit a low energy resonance [39] one can conclude that effective vibrational excitation also proceeds via resonant inelastic scattering, i. e. the transient negative ion can either dissociate (formation of F$^-$) or eject the extra electron with some energy loss recovering the neutral molecule in a vibrationally excited state. In a condensed environment, this energy will immediately dissipate and no chemical change can occur. It should also be noted that undissociated neutrals can in fact desorb via short-lived negative ion resonances: once an ion is formed at or near the surface, it will first be accelerated towards the surface and after electron detachment the neutral system may eventually find itself in the desorption continuum (Antoniewicz picture of neural particle desorption [40]) [41]. By performing thermal desorption spectroscopy, however, we can safely say that the amount of material in the adsorbate does not significantly change upon electron exposition and desorption of neutral molecules can hence be excluded as a major source of the degradation observed by IRAS.

In contrast to the low energy domain the increase of the degradation cross-section at higher energies can no longer be associated with one single process as at those energies electronic excitation associated with inelastic electron scattering contribute. The electronically excited states can, e. g., dissociate into neutral fragments and the inelastically scattered electrons can be captured by further NF$_3$ molecules.
We have also performed an extended IR analysis of the NF$_3$ film after electron irradiation to get information on new species formed in the course of degradation. Although these measurements still suffer from a weak signal to noise level there is evidence that irradiation at 1.5 eV creates NF$_2$ radicals and N$_2$F$_4$ molecules. The latter may be formed by the exothermic association of two adjacent NF$_2$ radicals. In contrast to that exposure of 8 eV electrons gives evidence for NF and NF$_2$ but not N$_2$F$_4$. This may indicate that N$_2$F$_4$ which is eventually formed at 8 eV is degraded by subsequent electron collisions and that degradation is not (or less) operative at low electron energies. Hence the ideal system to perform a controlled modification using low energy electrons is a molecule having a large cross-section for dissociative attachment into a particular channel thereby generating new products which are nonreactive towards electrons of that energy.

In conclusion, by applying the IRAS technique and ESD of negative ions we demonstrate that a 10 ML film of NF$_3$ is degraded in the course of low energy electron irradiation in the range 0–5 eV which is far below electronic excitation of NF$_3$. Degradation is accompanied by the desorption of F$^-$ fragment ions from the film and formation of NF$_2$ radicals and N$_2$F$_4$ molecules in the film. The energy dependence of the degradation cross-section follows that for resonant (dissociative) electron attachment in the low energy region ($\approx 0$ eV–5 eV) and increases above 6 eV. We therefore identify (dissociative) electron capture at low energy as the only initial reaction responsible for the chemical changes in the NF$_3$ film.

3.3. Effect of different environments and orientation: ESD of Cl$^-$ from Cl$_2$

Chlorine is known to be one of the most effective gases for etching and is widely used for semiconductor and thin-film manufacturing [42] as well as in other technological applications e.g. excimer lasers [43]. Cl$_2$ is also important in the perturbed chemistry of the polar stratosphere, i.e. the chemistry on surfaces of particles in polar stratospheric clouds (PSC) [44]. Attachment of low energy electrons to molecular chlorine plays an important role in all these processes.

The interaction of low energy electrons with chlorine molecules in the gas phase has been studied intensively [for a review see ref. [45]]. Beam experiments [46, 47, 48, 49] have demonstrated that the molecule effectively captures low energy electrons yielding a narrow peak near 0 eV (see Fig. 8) due to the process

$$e^- + \text{Cl}_2^{(2\Sigma_g^+)} \rightarrow \text{Cl}_2^{# (2\Sigma_u^+)} \rightarrow \text{Cl}^-(1S) + \text{Cl}(2P) \quad \Delta H_0 = -1.10\text{eV} \quad (8)$$

which is considerably exothermic in consequence of the high electron affinity of the Cl fragment (3.62 eV) compared to the bond dissociation energy ($D(\text{Cl}^-\text{Cl}) = 2.52$ eV) [33]. In eq. 8 Cl$_2^{-\#}$ denotes negative ion resonance (NIR) formed by free electrons with the electronic configuration ...($\sigma_g3p)^2$ ($\pi_u3p)^4$ ($\pi_u^\ast3p)^4$ ($\sigma_u^\ast3p)^1$.

The Franck-Condon transition near 0 eV creates the anion in its electronic ground state, however, well above the relaxed geometry (see Fig. 7(a)). Further peaks in the ion yield are observed around 2.5 and 5.8 eV.

A detailed analysis of the contribution close to zero eV by means of a high resolution ($\approx 1$ meV) study using the laser photoelectron attachment (LPA) method showed a p-wave attachment-threshold behaviour of the DEA cross section at very low energies with a peak at 50 meV at a cross section of $\sigma_{DA} \approx 10^{-20}m^2$ [50, 51]. These results are in agreement with theoretical predictions [51, 52] and also an electron beam study at a resolution of $\approx 80$ meV [49].

Fig. 8 shows a comparison between the gas phase DEA yielding Cl$^-$ [49] and the Cl$^-$ desorption yield from a 6 ML Cl$_2$ film adsorbed directly on the metallic substrate [54]. A remarkably strong Cl$^-$ desorption signal is observed peaking at 5.5 eV and a comparative weak feature around 3 eV. The ESD resonances presently observed are located at similar energies as
Figure 7. (a) Potential energy curves relevant for DEA to Cl$_2$(1$\Sigma^+$) in the low energy regime (reproduced from [51, 53]). (b) Experimental situations for a Cl$_2$ molecule oriented parallel and perpendicular to the surface, respectively. $\theta$ assigns the angle between the electron beam and the molecular axis (adapted from Ref. [54]).

Figure 8. Comparison between gas phase DEA yielding Cl$^-$ (adapted from Ref. [49]) and the Cl$^-$ yield obtained from 6 ML Cl$_2$ condensed directly on a monocrystalline gold crystal at 35 K, as a function of incident electron energy taken at grazing incidence ($\theta = 85^\circ$). $\theta$ assigns the angle of incidence of the electron beam with respect to the surface normal (adapted from Ref. [54]).

those observed from DEA to gas phase molecules, however, the strong low energy gas phase feature close to zero eV is completely suppressed in ESD.

Suppression of low energy resonances and enhancement of the higher energy features is the usual situation when comparing ESD with gas phase DEA (except for the F$^-$ desorption from condensed NF$_3$ as shown in chapter 3.1) and a consequence of the energy constraints for ion desorption but also the influence of the surrounding medium on the lifetime of a NIR (see below) [55, 56]. The non-observation of an ion desorption signal in the low energy regime, however, does not necessary imply that (dissociative) electron attachment is no longer operative at the
surface. We observe charging of film at low energies (<2 eV) which indicates that electron attachment at those energies is still operative (eventually involving inelastic scattering events prior to electron localization).

If we approximate the decomposition of the NIR at the surface as unimolecular and assume the same polarization energy \( V_a \) for the NIR (\( \text{Cl}_2^- \# \)) and the fragment ion (\( \text{Cl}^- \)), the energy threshold for desorption \( \epsilon_d \) can be expressed as [19]

\[
\epsilon_d = \frac{m_i}{m} V_a + \Delta H_0
\]

with \( m_i \) and \( m \) representing the mass of the ionic and neutral fragment, respectively, and \( \Delta H_0 \) the thermodynamic limit of the corresponding gas phase DEA process. Note that in this context \( V_a \) is a positive number. A rough estimate for the bulk value of the polarization energy can be obtained from the Born formula [57], by using the value of 2.15 for the dielectric constant of Cl\(_2\) and \( R(\text{Cl}) = 180 \text{ pm} \) [33] for the ionic radius yielding a value of 2.14 eV. If for the present situation we assume that the ions desorbing from the surface are subjected to half of the bulk polarization energy and that the influence of the metallic substrate is negligible we arrive at \( V_a = 1.07 \text{ eV} \). With this value the threshold for Cl\(^-\) desorption becomes \( \epsilon_d = -0.6 \text{ eV} \), i.e. desorption of Cl\(^-\) is energetically accessible by free electrons at any energy.

The fact that desorption of Cl\(^-\) is not observed below 2 eV must then be explained by effective energy dissipation during decomposition of the ion Cl\(_2\) \( (^2\Sigma^+_u) \) which reduces the desorption signal below the detection limit. Note that eq. (9) refers to an energy threshold taking into account polarization but no energy dissipation. We may thus conclude that low energy electrons (<2 eV) are still attached (eventually via inelastic scattering events) forming the molecular ion in its electronic ground state but considerably off the relaxed geometry. The molecular ion then either decomposes according to process 8 with Cl\(^-\) ion remaining at the surface or the parent ion relaxes into a stable configuration below the dissociation limit by intermolecular collisions between the ion and the environmental molecules. Energy dissipation and hence relaxation into a stable configuration of Cl\(_2\) is favored by the appreciable adiabatic electron affinity of Cl\(_2\) (2.38 eV [33], see Fig. 7(a)). From the present charging experiments we cannot conclude to which degree the reaction at low energies is dissociative or associative.

In contrast, the NIR created near 3 eV and near 5.5 eV dissociates in such a way that Cl\(^-\) is effectively ejected into vacuum. A study by Hedhili et al. [58] demonstrated appreciable kinetic energy released to the desorbed fragment ions.

In the spirit of the above discussion and in agreement with a former study on electron stimulated desorption of Cl\(^-\) from condensed Cl\(_2\) [59], we ascribe the 3 eV feature to the transition Cl\(_2\) \( (^1\Sigma^+_g) \rightarrow \text{Cl}_2\) \( (^2\Pi_g) \) and the strong 5.5 eV feature to the transition Cl\(_2\) \( (^1\Sigma^+_g) \rightarrow \text{Cl}_2\) \( (^2\Pi_u) \) (see Fig. 7(a)).

Figure 9 (a) shows the desorption spectrum of Cl\(^-\) from a sub-monolayer Cl\(_2\) condensed on a multilayer Xe. In contrast to Cl\(^-\) desorption from multilayer Cl\(_2\) directly condensed on the metallic substrate, a separated desorption resonance peaking at 2.5 eV is clearly visible apart from the strong peak around 5.5 eV. Apparently the noble gas environment enhances the desorption probability, in particular from the Cl\(_2\) \( (^2\Pi_u) \) state. In the case of Cl\(^-\) desorption from the sub-monolayer Cl\(_2\) coverage on the Xe spacer the ion intensity at 5.5 eV is approximately one order of magnitude higher than that from the 6 ML Cl\(_2\) film deposited directly on the metallic substrate (Fig. 8). Since the polarisability of Xe \( (4.0 \times 10^{-24} \text{ cm}^3 \text{ [33]}) \) is not far below that of Cl\(_2\) \( (4.6 \times 10^{-24} \text{ cm}^3 \text{ [33]}) \) it is in fact unlikely that the different polarisability alone is responsible for the effect. It has been shown that using a rare gas spacer of 15 ML the interaction of a charge with the metallic substrate (image charge) can be neglected [60]. Therefore we conclude that the reduced influence of the metal surface is responsible for the increase in the ion desorption yield.
Figure 9. Desorption of Cl$^-$ from sub-monolayer Cl$_2$ co-adsorbed on the surface Xe and Kr, respectively, which act as a spacer to the metallic substrate. $\vartheta$: angle of incidence of the electron beam with respect to the surface normal.

While the desorption spectra shown in Figs. 8 and 9(a) are taken at an angle of incidence of the electron beam with respect to the surface normal of approximately $\vartheta = 85^\circ$ (grazing incidence, leading to maximum ion yields, see Fig. 7(b)) the spectra in Figure 9(b)+(c) are measured under an angle of $\vartheta = 45^\circ$. Under these conditions we observe (apart from the lower count rate) a significant change in the shape of the high energy Cl$^-$ peak around 5.5 eV. Two separated features are visible peaking at 5.0 and 6.2 eV, whereas the shape of the Cl$^-$ desorption yield at 2.5 eV remains unchanged, albeit with an increase of its relative intensity.

We consider that the appearance of these structures is related with the pronounced angular dependency obtained in gas phase DEA [48] pointing towards a preferential orientation of the molecules on the noble gas surface.

From the analysis of the measured angular distributions of the Cl$^-$ ions in the gas phase [48] the 2.5 eV feature was attributed to the transition Cl$_2$ ($^1\Sigma_g^+$) $\rightarrow$ Cl$^-$ ($^2\Pi_u$) with the final state electron configuration $\ldots(\sigma_g3p)^2 (\pi_u3p)^4 (\pi_u^*3p)^3(\sigma_u^*3p)^2$ representing a core excited resonance. The third feature peaking near 5.8 eV (and extending from 3.5 eV to 7.5 eV) should consequently arise from the $^1\Sigma_g^+ \rightarrow ^2\Pi_u$ transition, the negative ion having the electronic configuration...
....(σ_3p)^2(π_u3p)^4(π^*_u3p)^4(σ^*_u3p)^2. This feature, however, seems to consist of two components peaking at 5.4 eV and 6.0 eV visible at particular observation angles (θ) of the mass spectrometer with respect to the incident electron beam. An analysis of the partial waves contributing to this transition revealed that the two components in the ion yield arise from a change of the mixing of the partial waves with energy in the ^3Π_u resonance.

Figure 7(b) illustrates both limiting scenarios for the orientation of an adsorbed Cl_2 molecule with the molecular axis flat along the surface and perpendicular to the surface (along the surface normal), respectively. In the latter case the reference angle used here (ϑ) corresponds to that relevant for the angular distribution in the gas phase DEA beam experiment, ϑ = θ. Accordingly, for the flat orientation we have ϑ = θ − 90°.

The structure at ϑ = 45° together with the pronounced intensity change is compatible for a perpendicular orientation but definitely not a flat orientation. This is confirmed by comparing with the gas phase angular distributions [48] which at ϑ = 90° (close to the grazing incidence situation in the present experiment) show an unstructured resonance peaking at 5.4 eV while at ϑ = 45° the leading peak is near 6 eV with a structure near 5 eV. It has to be noted that in the gas phase experiment the molecules are oriented randomly and the detector selects a particular angle while in the present experiment the angle of incidence with respect to the surface normal is changed, while the orientation of the molecules at the surface is fixed. Hence there are two arguments pointing towards the perpendicular orientation, namely the changing structure in the ion yield curve in an analogous way to the gas phase results and the change of intensity. At grazing incidence the desorbing Cl− ions are ejected directly towards the quadrupole entrance thus increasing the collection efficiency.

It has to be admitted that these observation are not an ultimate proof that the majority of the molecules are oriented perpendicular. If one assumes that other orientations exist, in particular flat lying molecules which do not contribute to the ESD signal, only the perpendicular oriented and ESD active molecules would be responsible for the observed effects.

In conclusion, while any Cl− signal below 2 eV associated with the molecular ion in its electronic ground state, is completely suppressed in ESD, we observe intense desorption of negative ions from the two core excited resonances which is particularly strong when the molecule is adsorbed in sub-monolayer amounts on noble gas films. The strong dependence of both the signal intensity and shape of the desorption resonance from the angle of incidence of the electron beam indicates a preferential orientation of the molecules perpendicular to the surface.

3.4. Medium enhanced dissociative electron attachment: ESD of anions from ClCN

The cyano radical CN is a well-known pseudo halogen with a remarkably high electron affinity (3.82 eV [61]) exceeding even those of the halogen atoms. In analogy to the conventional bihalogen molecules (FCl, BrI, etc.) the compounds XCN (X: halogen atom) may be viewed as pseudo-bihalogens. Cyanogen halides represent an interesting intermediate in the classification of electrophilic compounds, viz. their performance with respect to electron attachment. In saturated halogenated hydrocarbons DEA generally occurs via impact of an electron into an orbital with considerably antibonding σ*(R–X) character which leads to a direct electronic dissociation generating the halogenide (X−) [62]. In contrast, cyanogen containing molecules capture the extra electron in a π*(CN)-orbital finally leading to dissociation of the (R–CN)-bond along a vibrational predissociation mechanism [63].

With the bond dissociation energy D(Cl–CN) = 4.2 eV [64] and the well known electron affinities of the halogen atom (EA(Cl) = 3.621 eV [33]) and CN from above (3.82 eV) the energetic threshold (ΔH_0) of the complementary DEA reactions

\[ e^- + ClCN \rightarrow Cl^- + CN \quad \Delta H_0 = 0.58 \text{eV} \quad (10) \]
\[ \rightarrow Cl + CN^- \quad \Delta H_0 = 0.38 \text{eV} \quad (11) \]
becomes nearly endothermic.

![Comparison between Cl⁻ and CN⁻ desorption from a 7 ML ClCN film (adapted from ref. [65]) and gas phase DEA yielding Cl⁻ and CN⁻ in the energy range 0–15 eV (adapted from ref. [66]).](image)

**Figure 10.** Comparison between Cl⁻ and CN⁻ desorption from a 7 ML ClCN film (adapted from ref. [65]) and gas phase DEA yielding Cl⁻ and CN⁻ in the energy range 0–15 eV (adapted from ref. [66]).

Figure 10 shows a comparison between gas phase DEA yielding CN⁻ and Cl⁻ and the corresponding desorption yield from a 7 ML ClCN film in the energy range between 0 and 15 eV. Both ionic desorption products appear within a strong desorption resonance peaking at 4.3 and 8.8 eV. Cl⁻ arises from an additional low energy peak at 2.0 eV [65]. In the gas phase the most abundant signals are the CN⁻ and Cl⁻ formation close to 0 eV [66]. This intense low energy resonance in the gas phase is completely suppressed in the ESD signal and at the position of the intense desorption resonances (4.3 and 8.8 eV) the gas phase DEA yield does not exhibit any particular structures.

Due to the comparable mass weights of both fragments Cl and CN, the complete suppression of the strong low energy DEA ion yield (< 1 eV) in the desorption signal can fully be accounted to energetic constraints. With eq. 9, we obtain the thresholds \( \varepsilon_d = 1.8 \pm 0.2 \) eV for Cl⁻ and \( 1.1 \pm 0.2 \) eV for CN⁻. The gas phase TOF experiments [66] indicate non-thermal formation of both ionic fragments with kinetic energies of 0.25 eV (Cl⁻) and 0.35 eV (CN⁻), virtually independent of the incident electron energy. From these experiments one would hence not predict any desorbed fragments due to insufficient kinetic energy.

The appearance of two intense and comparatively sharp desorption resonances at energies where the gas phase DEA ion yields are smooth with no particular structures is surprising. Due to a variety of different effects (broadening of transition energies due to inhomogeneous coupling, the energy constraints for desorption, energy dissipation, etc.) one would rather expect the opposite effect, namely a further smearing out ESD structures compared to those observed in gas phase DEA. As discussed earlier [55], however, coupling of a molecule to an environment can change the character of a resonance in a way that negative ion formation is enhanced (in spite of the many possibilities of energy dissipation). This is particularly the case, when electronically excited resonances are involved [56].

The two prominent desorption resonances (peaking near 4.5 eV and at 8.8 eV) are most likely associated with core excited resonances. The lowest optical absorption feature in ClCN is a broad and structureless band (A-band) with a threshold near 5.5 eV and a band maximum at 7.0 eV. This absorption feature is assigned as a \( \sigma^* \leftarrow n \) transition leading to a state with strong
antibonding (Cl–CN) character. The second absorption feature (α-band) consists of discrete features on a broad continuum, the latter due to transitions to dissociative states. These two bands are followed by different Rydberg band systems [67]. While it is not straightforward to associate the 8.8 eV desorption resonance to one of the many possible electronically excited states present in this energy domain, the desorption feature around 4.5 eV must be due to a core excited resonance associated with the lowest optical transition (A-band) or a dipole forbidden transition at some lower energy.

![Diagram](image)

**Figure 11.** Left: Classification of resonances: a) closed channel Feshbach (core excited/two particle one hole) and b) open channel shape (core excited/two particle one hole) resonances [68]. Right: Schematic representation of the conversion of a short-lived open channel resonance into a Feshbach resonance under solvation. The width of the open-channel resonance is due to Franck-Condon broadening and lifetime broadening. The vertical arrows indicate effective autodetachment (one electron transitions) into the associated electronically excited neutral molecule (adapted from ref. [55]).

Irrespective of the exact assignment of the relevant states we can suppose that in the gas phase in the energy range close to 4.5 eV and also near 8.8 eV a core excited shape resonance can be formed in ClCN, i.e. an electronic state with two electrons in normally unfilled molecular orbitals. Such open channel resonances are short-lived since they can decay by autodetachment into the associated electronically excited state of the neutral as indicated by the arrows in Fig. 11. At least in the energy range around 8.8 eV the appreciable density of electronic states leads to many curve crossings and electronic predissociation is expected to be the usual process for DEA. This is in contrast to lower energies (0–3 eV) where single particle resonances are formed which often dissociate directly along a repulsive potential energy surface. Due to its short lifetime with respect to loss of the extra electron, an open channel core excited resonance may hardly be visible through DEA in the gas phase. A closed channel (or Feshbach) resonance is located below the excited neutral and can only decay into the neutral molecule via a two electron process. Therefore Feshbach-type resonances have much longer autodetachment lifetimes. With respect to solvation this means that an open channel resonance in the gas phase can be converted into a Feshbach-type resonance in an environment. The increased autodetachment lifetime will result in an enhancement of the DEA cross section. This simple picture does not include a microscopic description in terms of potential energy surfaces. It simply describes the enhancement of fragment ion formation in the condensed phase by the enhanced autodetachment lifetime.

In conclusion, in gaseous ClCN the most intense reactions occur within narrow resonant features in the energy range below 1 eV. In contrast, desorption of fragment ions is observed from two comparatively sharp structures located around 4.5 eV and 8.8 eV. This behaviour can be explained by a particular lifetime effect of core excited resonances by transforming a
short-lived open channel resonance in the gas phase into a long-lived Feshbach resonance in the condensed phase.

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG), The European Union through the EPIC Network and the Freie Universität Berlin.

References

[1] Zimmermann F M and Ho W 1995 Surf. Sci. Rep. 22 127
[2] Boudaiffa B, Cloutier P, Hunting D, Huel S M and Sanche L 2000 Science 287 1658
[3] Ha S W and Rieder K H 2003 Annu. Rev. Phys. Chem. 54 307
[4] Pascual J L, Norente N, Song Z, Conrad H and Rust H P 2003 Nature 432 535
[5] Sloan P and Palmer R E 2005 Nature 434 367
[6] Becker K H 2001 Elementary collision processes in plasmas (Low Temperature Plasma Physics) eds Hippler R, Pfau S, Schmidt M, Schoenbach H S(Berlin: Wiley-VCH)
[7] Grill A 1994 Cold Plasma in Material Fabrication. From Fundamental to Applications (New York: IEE Press)
[8] Hatano Y 2000 Adv. At. Mol. Opt. Phys. 43 231
[9] Becker K H, Kogelschatz U, Schoenbach K H and Barker R J 2004 Non-Equilibrium Air Plasmas at Atmospheric Pressure (Bristol: Institute of Physics Publishing)
[10] Klar D, Ruf M W and Hotop H 2001 Int. J. Mass Spectrom. 205 93
[11] Olsen C O and Rowntree P A 1998 J. Chem. Phys. 108 3750
[12] Tegeder P and Illenberger E 2001 Chem. Phys. Lett. 341 401
[13] Lafosse A, Bertin M, Domaracka A, Pliszka D, Illenberger E and Azria R 2006 Phys. Chem. Chem. Phys. 8 5564
[14] Ipolyi I, Michaeilis W and Swiderek P 2007 Phys. Chem. Chem. Phys. 9 180
[15] Swiderek P, Jäggle C, Bankmann D and Burean E 2007 J. Phys. Chem. C 111 303
[16] Bass A D and Sanche L 1995 J. Phys. Chem. 95 2910
[17] Lu Q B and Sanche L 2003 J. Phys. Chem. Lett. 341 401
[18] Meinke M and Illenberger E 1994 J. Phys. Chem. 98 6601
[19] Chaball J Y 1988 Surf. Sci. Rep. 8 211
[20] Hoffmann F.M. 1983 Surf. Sci. Rep. 3 107
[21] Bruno G, Capezzuto P, Cicala G and Manodoro P 1994 J. Vac. Sci. Technol. 12 690
[22] Perrier J, Mest J, Sieffert J M and Schmitt J 1990 Plasma Chem. Plasma Proc. 10 571
[23] Groenbech K E and Verdereyen J T 1985 J. Appl. Phys. 57 1596
[24] Manos D M and Flamm D L 1989 Plasma Etching (Boston: Academic Press)
[25] Chantery P J 1982 Applied Atomic Collision Physics eds. Massey H S W, McDaniel E W and Bederson B (New York: Academic Press) vol. 3, p. 58
[26] Shaw M J and Jones J D J 1977 Appl. Phys. 14 393
[27] Pellerite M J and Brauman J I 1983 J. Am. Chem. Soc. 105 2672
[28] Langer J, Matejcik S and Illenberger E 2000 Phys. Chem. Chem. Phys. 2 1001
[29] Nandi D, Rangwala S A, Kumar S V K and Krishnakumar 2001 Int. J. Mass Spectrom. 205 111
[30] Ruckhaberle N, Lehmann L, Matejcik S, Illenberger E, Bouteiller Y, Periquet V, Mesure L, Desfrançois C and Schernmann J P 1997 J. Phys. Chem. 101 9942
[31] Meinke M, Parenteau L, Rowntree P, Sanche L and Illenberger E 1993 Chem. Phys. Lett. 205 213
[32] Lide D R 1997 Handbook of Chemistry and Physics (Boca Raton: CRC Press)
[33] Shimanouchi T 1972 Tables of Molecular Vibrational Frequencies Consolidated Vol. I (Washington: NSRDS-NBS)
[34] Gilbert M, Nectoux P and Drifford M 1978 J. Chem. Phys. 68 679
[35] Sanche L 1990 J. Phys. B: At. Mol. Opt. Phys. 23 1597
[36] Schmidt W F 1997 Liquid State Electronics of Insulating Liquids (Boca Raton: CRC Press)
[37] Tegeder P and Illenberger E 1999 Phys. Chem. Chem. Phys. 1 5197
[38] Boesten L, Tachibana Y, Nakano Y, Shinozuka S, Tanaka H and Dillon M A 1996 J. Phys. B: At. Mol. Opt. Phys. 29 5475
[39] Antoniewicz P R 1980 Phys. Rev. B 21 3811
[40] Gadzuk J W, Richter L J, Buntin S A, King D S and Cavanagh R R 1990 Surf. Sci. 235 317
[42] Kimura M and Itikawa Y 2001 Electron Collisions with Molecules in Gases: Applications to Plasma Diagnostics and Modeling (Advances in Atomic, Molecular, and Optical Physics) Vol. 44 (New York: Academic Press)
[43] McDaniel E W and Nighan W L 1982 Gas Lasers, Applied Atomic Collision Physics Vol. 3 (New York: Academic Press)
[44] Wayne R P 1991 Chemistry of the Atmospheres (Oxford: Clarendon)
[45] Christophorou L G and Olthoff J K 1999 J. Phys. Chem. Ref. Data 28 131
[46] Tam W C and Wong S F 1978 J. Chem. Phys. 68 5626
[47] Kurepa M V and Belic D S 1978 J. Phys. B: At. Mol. Phys. 11 3719
[48] Azria R, Abouaf R and Teillet-Billy D 1982 J. Phys. B: At. Mol. Phys. 15 L569.
[49] Feketeova L, Skalny D J, Hanel G, Gstir B, Francis M and Mark T D 2003 Int. J. Mass Spectrom. 223-224 661
[50] Barsotti S, Ruf M W and Hotop H 2002 Phys. Rev. Lett. 89 083201-1
[51] Ruf M W, Barsotti S, Braun M, Hotop H and Fabrikant I I 2004 J. Phys. B: At. Mol. Opt. Phys. 37 41
[52] Fabrikant I I, Leininger T and Gadea F X 2000 J. Phys. B: At. Mol. Opt. Phys. 33 4575
[53] Leininger T and Gadea F X 2000 J. Phys. B: At. Mol. Opt. Phys. 33 735
[54] Tegeder P, Balog R, Mason N J and Illenberger E 2005 Phys. Chem. Chem. Phys. 7 685
[55] Le Coat Y, Hedhili N M, Azria R, Trone M, Inglsson O and Illenberger E 1998 Chem. Phys. Lett. 296 208
[56] Illenberger E 2003 Surf. Sci. 528 67
[57] Born M 1920 Z. Phys. 1 45
[58] Hedhili M N, Lanchgar M, Le Coat Y, Azria R, Lu Q B and Madey T E 2001 J. Chem. Phys. 114 1844
[59] Azria R, Parenteau L and Sanche L 1987 J. Chem. Phys. 87 2292
[60] Michaud M and Sanche L 1990 J. Elect. Spec. and Rel. Phenom. 51 237
[61] Klein R, McGinnis R P and Leone S R 1983 Chem. Phys. Lett. 100 475
[62] Illenberger E 2000 Electron Attachment Processes to Free and Bound Molecules (Photoionization and Photodetachment, Part II) ed. Ng C Y (Singapore: World Scientific) Vol.10B pp 1063-1160
[63] Kühn A, Fenzlaff H P and Illenberger E 1987 Chem. Phys. Lett. 135 335
[64] Davis D D and Okabe H 1968 J. Chem. Phys. 49 5526
[65] Tegeder P and Illenberger E 2005 Chem. Phys. Lett. 411 175
[66] Brüning F, Hahndorf I, Stamatovic A and Illenberger E 1996 J. Phys. Chem. 100 19740
[67] Felps W, Rupnik K and McGlynn S 1991 J. Phys. Chem. 95 639
[68] Palmer R E and Rous P J 1992 Rev. Mod. Phys. 64 383