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Electron stimulated desorption from molecules on a noble gas solid: an analysis of cluster and island formation upon deposition

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Abstract

Desorption of negative fragment ions following low energy electron impact to a two monolayer (ML) adsorbate of CHF₂Cl is studied. Results are compared for a deposition of the 2 ML quantity directly on a monocrystalline gold substrate with that on the surface of a Xe film as a spacer to the metal. The desorption intensity (Cl⁻, F⁻) is strongly suppressed when going from the metal to the rare gas film. For a uniformly covered surface one would expect the opposite behaviour, namely an enhanced desorption from molecules on the rare gas spacer. We interpret this observation by cluster and island formation on the rare gas film after CHF₂Cl deposition. A general analysis of cluster and island format for the fluorochloromethanes on a rare gas surface is performed. (Int J Mass Spectrom 205 (2001) 331–337) © 2001 Elsevier Science B.V.

Keywords: Negative ions; Desorption; Island formation

1. Introduction

The formation and evolution of negative ion resonances at surfaces has gained particular attention within the last years [1–4] as resonances are involved in many surface phenomena, like those relevant for the photochemistry of adsorbed molecules [5]. A negative ion resonance at a surface can be generated by either the interaction of free electrons with the

adsorbed molecule or by the transfer of an excited substrate electron to it. When a photoexcited substrate electron is transferred, the negative ion resonance thus formed can act as a driving force for the respective photochemical reaction [5]. This may lead to desorption of negatively charged fragments [6] or to desorption of the (re-neutralized) undissociated molecule. This latter mechanism is known as substrate mediated transient negative ion state mechanism [7] which is a modification of the established Menzel-Gomer-Redhead model for desorption [8].

The experiments so far involving free electrons include (1) desorption of negative ions as a function of the primary energy (typically in the energy range 0–20 eV) [1–3] or at a fixed primary energy (250 eV when secondary electrons contribute to the overall

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

process) [4], and (2) the measurement of the accumulated negative charge following electron beam exposure [9,10]. When desorbed fragment anions are recorded, the underlying primary process is usually dissociative electron attachment (DA) of the adsorbed molecule. In isolated molecules the cross section for electron capture increases with decreasing electron energy and thus DA can be a very effective process at low energies [11,12]. If DA of a molecule at a surface occurs, desorption of the fragment ion and hence the observation of the process by mass spectrometric techniques is a possible pathway among various others. In comparison to DA in gas phase molecules, however, the observation of desorbed fragment anions is subjected to particular constraints as (1) the fragment ion must gain sufficient translational energy to overcome the polarization energy with the environment and (2) those orientations of the molecule will be preferred allowing an unhindered ejection of the fragment into vacuum. Thus by far not every DA event at the surface will lead to the desorption of an ionic fragment.

Some of the electron attachment studies to adsorbed molecules (including charge accumulation [13,14]) have been performed on rare gas layers condensed on the cold metallic substrate. This has been done for two purposes, firstly to use the rare gas layer as a spacer thereby studying the varying influence of the metal substrate with the thickness of the layer [15] and secondly to study effects induced by the rare gas substrate. For submonolayer amounts of particular molecules on rare gas surfaces it was found that the desorption cross section exhibits sharp enhancements near the energy of the corresponding rare gas excitons [3,16,17]. These features were explained by the initial formation of an electron–exciton complex which transfers the electron and energy to the adsorbed molecule which then undergoes DA eventually followed by desorption of the negative fragment. In all these experiments it was implicitly assumed that the molecules are randomly distributed on the rare gas surface.

As we shall demonstrate for the system CHF_2Cl the desorption intensity is drastically suppressed when the compound is deposited on the Xe spacer instead

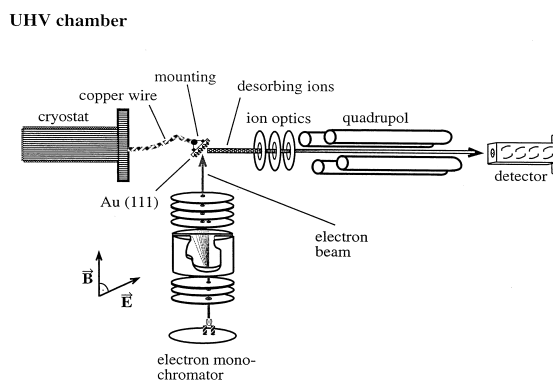


Fig. 1. Experimental setup for the study of electron stimulated desorption of F^- and Cl^- from condensed CHF_2Cl .

directly on the metal. A reasonable explanation is formation of clusters and islands upon deposition on the rare gas surface within the time scale of the experiment. The energetics of such processes will be analyzed for the class of the fluorochloromethanes.

2. Experimental

Desorption of negatively charged ions from adsorbed and condensed molecules following low energy (0–15 eV) electron impact is studied in an UHV apparatus schematically shown in Fig. 1 and described in detail in a previous review article [18]. In brief it consists of a trochoidal electron monochromator [19], a monocrystalline Au substrate mounted on a manipulator and a commercial quadrupole mass spectrometer for identifying the desorbed ions. The trochoidal monochromator was invented three decades ago by Stamatovic and Schulz and is also known as Stamatotron. The presently used Stamatotron generates an energy selected beam of electrons [energy resolution ≈ 0.2 eV (FWHM), electron current ≈ 30 nA]. The electrons are aligned by a homogeneous magnetic field which prevents spreading of the beam at low energy. The Au substrate is electrically insulated but thermally connected to the cold tip of a closed cycle He refrigerator which cools the sample down to ≈ 30 K. A volumetrically determined amount of gas (Xe, CHF_2Cl) is condensed on the cold

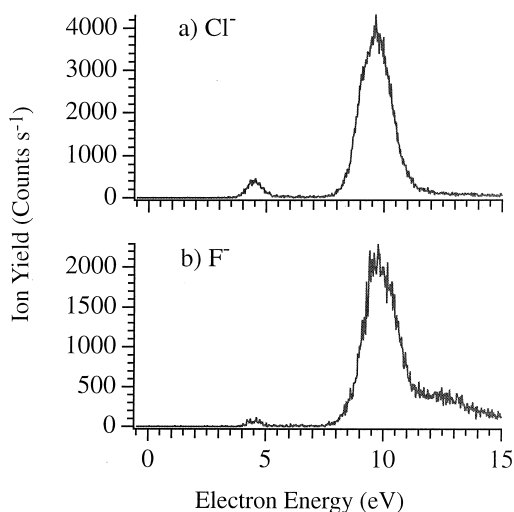


Fig. 2. Desorption of Cl^- and F^- from a 2 monolayer CHF_2Cl film deposited directly onto the metallic substrate.

substrate by means of a capillary which can be placed near the sample. To avoid surface contamination and extensive charging of the film, the desorption spectra presented here always refer to one short scan on a newly deposited system after evaporating the previous one by heating the substrate. Calibration of the electron energy scale is performed by taking the onset of the electron injection curve into the substrate as zero (vacuum level) [18].

3. Results and Discussion

3.1. Desorption of negative ions

In Fig. 2 we present the desorption spectra of Cl^- and F^- from a 2 monolayer (ML) dose of CHF_2Cl directly deposited on the metallic substrate and in Fig. 3 the corresponding yields when the same amount of CHF_2Cl is deposited on a 6 ML of Xe as a spacer to the metal. Formation and evolution of negative ion resonances from gas phase molecules, clusters and condensed phase CHF_2Cl has been discussed in detail in a previous publication from our laboratory [20]. In the gas phase we observed a weak resonance on the Cl^- channel peaking near 1.1 eV and a further on the F^- channel at 3.4 eV (and also a very weak H^- signal

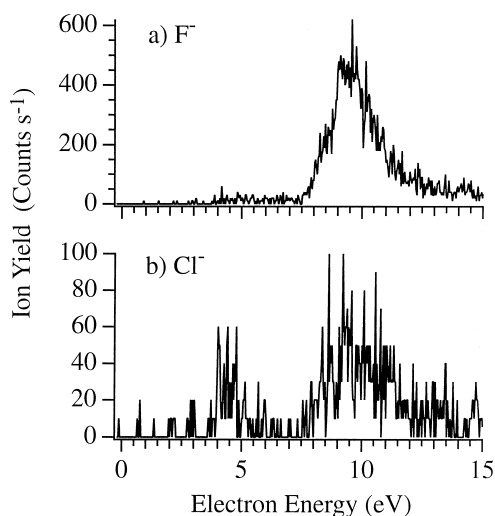


Fig. 3. Desorption of Cl^- and F^- from a 2 monolayer CHF_2Cl film deposited onto a 6 monolayer Xe as a spacer to the metallic substrate.

which we shall not discuss here). Electron impact to condensed CHF_2Cl leads to remarkably strong resonance features in the desorption yield with a dominant peak located around 9.7 eV. At that energy only a very weak feature was seen in the corresponding gas phase DA yield. It was shown that the absolute cross section for ion desorption is at least 2 orders of magnitude higher than the gas phase analogue (surface enhanced DA [20]).

As can be seen by comparing Figs. 2 and 3 the desorption yield from the rare gas layer is significantly suppressed with the effect more pronounced on the product Cl^- . For a uniformly covered surface one would rather expect the opposite behaviour, namely an increased desorption efficiency from CHF_2Cl on the noble gas surface due to the lower solvation energy: apart from the orientation of the molecules at the surface, desorption of an ion into vacuum is constrained by the interaction energy of the charge with the medium. Desorption requires that the kinetic energy of the ion must be larger than this interaction energy. If the decomposition of the precursor ion at the surface is approximated as unimolecular the energetic threshold for desorption becomes [18]

$$\varepsilon_d = (m_i/m)V_p + \Delta H_0 \quad (1)$$

with m_i and m the mass of the ionic and neutral fragment, respectively and ΔH_0 the thermodynamic limit of the corresponding gas phase DA process and V_p the solvation energy which is essentially due to polarisation. Note that in this context V_p is a positive number. The gas phase ΔH_0 numbers are 0.14 ± 0.1 eV for the Cl^- channel and 1.76 ± 0.2 eV for the F^- channel [20].

Expression (1) indicates that the desorption threshold is directly proportional to the interaction energy and for a given DA system desorption of a heavy ionic fragment is energetically less favourable. This last fact is simply a consequence of the principle of linear momentum conservation which results in less kinetic energy release to the heavy fragment.

The interaction energy of the negative ion is composed of the polarization energy with the neighbouring CHF_2Cl molecules plus the effect of the image charge in the metal. In both cases we have a 2 ML coverage of CHF_2Cl molecules and hence a comparable contribution from polarization. The image potential can be expressed by

$$V_p = e^2/16\pi\epsilon_m\epsilon_0z$$

with e the elementary charge, ϵ_m the dielectric constant of the material ϵ_0 the vacuum permittivity, and z the distance of the charge from the metal surface. For bulk Xe we have a dielectric constant of 1.88 [21] leading to

$$V_p(\text{eV}) = 1.9/z(\text{\AA})$$

for a charge located on the Xe spacer with thickness z . It is obvious that an ion located on the surface of the noble gas layer is subjected to a considerably weaker solvation energy than directly on the metallic substrate. We hence interpret the present observation of a considerably decreased intensity by the formation of clusters or islands on the rare gas film which reduces the effective area (surface) for electron attachment and negative ion desorption. The additional observation that this effect is more pronounced on Cl^- than on F^- may be related to the structure of the clusters or islands with the F atoms preferentially located on the spheres.

In the following we will consider the energetics

and kinetics of such formation processes. We note that recent experiments on the related compound CHFCl_2 resulted in a comparable effect [22] as in the present system while the desorption intensity from NF_3 was appreciably higher from the rare gas layer [23]. In the context of the present interpretation this means that upon NF_3 deposition cluster formation does not occur. This is easily rationalized by the lower intermolecular interaction as obvious from the much lower boiling temperature of NF_3 (-130°C compared to 9°C in CHFCl_2 [21]).

3.2. Structures of electronegative molecules on a rare gas lattice

We consider here the deposition of electronegative molecules on a rare gas lattice. Bulk rare gases (with the exception of He) prefer the face centered cubic (fcc) lattice. Adsorption of rare gases on metallic substrates has been extensively investigated in the past (see, e.g. [24–26]) and it appears that they prefer the (111) face on metal surfaces. If the interaction between the adsorbed molecules is dominated by their dipole moments this interaction will control the three dimensional lattice structure of the polar molecules. The dipole moments of nearest neighbours must then have opposite directions and from the symmetry of the problem it follows that the molecular bulk lattice must be the body centered cubic system (bcc, see below). On the other hand, the symmetric compounds (CX_4 , X = halogen atom) do not have a dipole moment and they hence form the face centered cubic (fcc) lattice. In the latter case the density of the solid ρ is connected with the distance between nearest neighbour by $\rho = m\sqrt{2}/b^3$ where m is the molecular mass. Table 1 contains values of the mean binding energy per molecule ϵ obtained from the pressure of the saturated vapor p_{sat} on the basis of its temperature dependence $p_{\text{sat}} \propto \exp(-\epsilon/T)$. These numbers refer to the temperature regime where p_{sat} has been measured and the accuracy is in the order of the thermal energy in this range. The numbers in parentheses give the intermolecular binding energy at the boiling point as obtained from the enthalpy of vaporization. For comparison the ϵ values for the rare gases are 960 ± 70 K

for Ar, 1330 ± 30 K for Kr and 1850 ± 60 K for Xe. All input data are from [21].

For the molecules of Table 1 the solid density is known and with the critical molecular volume V_{cr} the scaling law $V_{cr}/b^3 = 2.0 \pm 0.2$ holds. The average accuracy for the distances between nearest neighbours in Table 1 is ± 0.2 Å.

Whereas solid bulk halomethanes with no dipole moment have the fcc structure, polar halomethanes will have the fcc or the bcc structure, dependent on the value of the dipole moment. As mentioned, it is energetically favourable to have nearest neighbours with opposite dipole moments in the case when the dipoles dominate the intermolecular interaction. The lattice then consists of two cubic lattices, each of them containing molecules with parallel dipole moments. We hence have the bcc lattice with the dipole moment of the central molecule opposite to those located in the vertices. With b the distance between nearest neighbours we have for the length of the elementary cell $l = 2b/3^{1/2}$ (lattice constant). The interaction energy per one molecule can be expressed by

$$\begin{aligned}
 U &= -\mu^2 \sum_{i,j,k} \left[\left(\frac{1}{2} + li \right)^2 + \left(\frac{1}{2} + lj \right)^2 + \left(\frac{1}{2} + lk \right)^2 \right]^{-3/2} \\
 &\quad + \mu^2 \sum_{i,j,k} [(li)^2 + (lj)^2 + (lk)^2]^{-3/2} \\
 &= -U_0 \sum_{i,j,k} \frac{1}{\left[\left(\frac{1}{2} + i \right)^2 + \left(\frac{1}{2} + j \right)^2 + \left(\frac{1}{2} + k \right)^2 \right]^{3/2}} \\
 &\quad + U_0 \sum_{i,j,k} \frac{1}{(i^2 + j^2 + k^2)^{3/2}} \quad (2)
 \end{aligned}$$

with $U_0 = \mu^2/l^3$. The values i, j, k are negative and positive integers which characterize the position of a molecule in the three dimensional lattice, if a test molecule is located in the origin ($i = j = k = 0$). This allows one to calculate the sum directly. Taking into account the positions of approximately 1000 molecules we get for the above sum $U = (5.0 \pm 0.1) \times U_0$.

From the dipole interaction energies (Table 1) it can be seen that for the completely substituted meth-

Table 1

Parameters for some fluorochloro methanes; b : distance between nearest neighbours in the lattice, ϵ : mean binding energy per molecule in the liquid, the number in parentheses refer to the mean binding energy at the boiling temperature, μ : dipole moment, U : dipole interaction energy calculated from Eq. (2). All input data are taken from [21].

Molecule	b (Å)	ϵ (K)	μ (D)	U (K)
CF ₄	4.9	1700 ± 200	0	0
CF ₃ Cl	5.3	2300 ± 200	0.50	250
CF ₂ Cl ₂	5.6	2900 ± 200	0.51	220
CFCl ₃	5.9	3500 ± 300	0.46	160
CCl ₄	6.1	4500 ± 900 (3900)	0	0
CHF ₃	4.8	2300 ± 100	1.65	3700
CH ₂ F ₂	4.6	2900 ± 300	1.60	4000
CH ₃ F	4.5	2500 ± 300	1.86	5800
CH ₄	4.3	1170 ± 70 (1000)	0	0
CH ₃ Cl	4.9	3300 ± 500 (2600)	1.89	4600
CH ₂ Cl ₂	5.5	4000 ± 300 (3500)	1.60	2300
CHCl ₃	5.8	4000 ± 300 (3800)	1.04	840
CHF ₂ Cl	5.2	3100 ± 200	1.42	2100

anes this value is small compared to the real intermolecular energy, but it is obviously essential for hydrogen containing compounds. We may hence conclude that the completely substituted compounds have the fcc and those containing hydrogen the bcc structure.

In any case for halomethanes on a rare gas surface the interaction is dominated by the intermolecular energy in contrast to molecules on a metallic surface. Molecules on rare gas lattices will then cover the surface not uniformly but rather form clusters or three dimensional islands. We shall now consider the statistical physics of these islands.

For simplicity we assume that each island has a hemispherical form and assume the same radius for each island. We shall evaluate a typical island size under realistic experimental conditions. We will work with the free energy $F = -T \ln z$ where z is the partition function. Thermodynamic equilibrium corresponds to the minimum of F , i.e. the maximum of the partition function.

We introduce the number of islands k and a number of positions m which they can possess. Evidently, $m = S/4r^2$ with S the target area and r the island radius. The partition function is

$$z = C_m^k \exp\left(-\frac{E}{T}\right)$$

with C_m^k the number of combinations for the position of the islands and the energy of the system

$$E = -\varepsilon n + E_{\text{sur}} \quad (3)$$

The first term is the volume energy (ε is the binding energy per molecule in the solid, and n the total number of molecules at the substrate) and E_{sur} the surface energy of the island which can be expressed as

$$E_{\text{sur}} = \left[2\pi \left(\frac{r}{b}\right)^2 2D + \pi \left(\frac{r}{b}\right)^2 2(D - D') \right] k \quad (4a)$$

Here D is the binding energy between two molecules and D' the binding energy between a molecule and a rare gas atom and k the number of islands. For the fcc structure the binding energy per atom is $\varepsilon = 6D$. For simplicity we assume the sphere surface having the {100} plane, so that the surface energy per on atom is $2D$, and the surface area per atom is b^3 . Assuming that the boundary between rare gas crystal and island is the same plane, the total surface energy of the island can be expressed through the total number of molecules (n) and the number of islands (k)

$$E_{\text{sur}} = 2\pi \left(\frac{r}{b}\right)^2 (3D - D')k = 3k^{1/3}n^{2/3}(3D - D') \quad (4b)$$

If we neglect the interaction in the boundary between the cluster and the rare gas surface we obtain

$$E_{\text{sur}} \approx \frac{3}{2} \varepsilon k^{1/3} n^{2/3} \quad (4c)$$

Since the number density of molecules in the fcc structure is $2^{1/2}/b^3$ the total number of molecules is

$$n = \frac{2\pi\sqrt{2}}{3} \left(\frac{r}{b}\right)^3 k$$

and with l the number of layers which can be formed on the substrate (by a given number of molecules and under uniform distribution) we have $n = Sl/b^2$. We can now express the partition function from above as

$$\ln z = \text{const} + k \ln(m/k) - An^{2/3}k^{1/3} \quad (5a)$$

with $\text{const} = n\varepsilon/T$ and $A = 3\varepsilon/2T$. The parameter A characterizes the ratio of the specific surface

energy to the thermal energy at the temperature of the sample. For the CHF_2Cl molecule on a Xe surface we have for typical conditions of the present experiment ($T = 30$ K, $l = 2$, $S = 0.5$ cm^2) $n = 4 \times 10^{14}$, $m = 4 \times 10^4 k^{2/3}$, and $A \approx 155$. With these values we obtain for the partition function

$$\ln z \approx \text{const} + k[10 - (\ln k)/3] - 8 \times 10^{11} k^{1/3} \quad (5b)$$

Among integer values of k the maximum of the partition function corresponds to $k = 1$, i.e. formation of one single island under thermodynamic equilibrium. The question then is on which time scale cluster and island formation occurs.

3.3. Kinetics of cluster and island formation

In the actual experiment the sample molecules are deposited within some several seconds and the spectra are recorded on a time scale of up to a few minutes. It must be remembered that adsorbates are often grown far away from thermodynamic equilibrium and their structures may be decided in a very early stage of nucleation and island growth. Such phenomena have recently been reviewed [27,28].

The mechanism of diffusion across the surface can be thought as individual hops of particles from their original site to adjacent neighbour sites. In the case of a coverage close to one monolayer a hopping event can thereby lead to dimer formation. The hopping frequency ∂ can be expressed as

$$\partial = \partial_0 \exp(-E_{\text{diff}}/T) \quad (6a)$$

with ∂_0 the pre-exponential factor and E_{diff} the activation energy for surface hopping. In terms of residence times we can write

$$\tau = \tau_0 \exp(E_{\text{diff}}/T) \quad (6b)$$

The pre-exponential factor is composed of the vibrational period of the molecule in the site (10^{-11} – 10^{-13} s) plus a factor accounting for the different “escape routes” from the given site [29]. The pre-exponential

factor can then range between 10^{-7} and 10^{-13} s. Obviously E_{diff} very sensitively controls the residence time of a particle at a particular site. For physisorbed systems, E_{diff} is in the order of 10% of the heat of adsorption [29] and thus typically in the range of 100–500 K. For the present situation (sample temperature 30 K) and assuming an activation energy of 300 K and a pre-exponential factor of 10^{-10} s one arrives at a residence time of a few microseconds. Although strongly dependent on E_{diff} we may conclude that dimer formation can easily occur for electronegative molecules on a rare gas lattice. Once a dimer is formed, its residence time is considerably larger due to the increasing activation energy. Clusters consisting of several molecules may no longer change their positions so that the growth of larger islands is only possible through evaporation of molecules from small islands and attachment to larger ones.

4. Conclusion

We interpret the strong suppression of the desorption intensity from CHF_2Cl adsorbed on a Xe spacer by cluster formation within the time scale of the experiment. The observation that desorption of Cl^- is more suppressed than that of F^- can then be explained by a preferential geometry of the clusters with the Cl atom located inside the complex. Such a geometry is easily rationalized by the comparatively larger polarisability of Cl compared to F.

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