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LETTER TO THE EDITOR

Substrate-dependent UV-induced dissociation of physisorbed SF_6 in the monolayer regime

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Abstract. UV- or x-ray-induced excitation often leads to fragmentation of isolated or condensed molecules but is usually less harmful to molecules adsorbed on a metal surface due to known quenching mechanisms. By comparison of UV photoemission results from SF_6 on different substrates, Ni(111), Ge(100), and NaCl(100), we show that this quenching works well for a metal and a semiconductor surface, and even for a $\sim$ 6 Å thick epitaxial NaCl layer on Ge(100). However, for thicker NaCl layers ($\geqslant$ 15 Å) the quenching mechanism (probably reneutralization by electron tunnelling from the substrate) is less efficient, or, in other words, is slow compared to the time scale of nuclear motion. Consequently, rapid SF_6 dissociation is observed upon UV irradiation for isolating spacer layers around and above $\sim$ 15 Å thickness.

For a basic understanding of the interaction between matter and radiation, as well as for many applications, it is necessary to study photon- (and electron-) stimulated dissociation and/or desorption processes of adsorbates. Typical examples for which a detailed knowledge about such processes is needed are the wall (or vacuum problem) in plasma machines, storage rings, or accelerators, and radiation-stimulated chemical reactions on surfaces. Also for the application of surface analysis methods using energetic electron or photon beams it should be a prerequisite to understand the principles of excitation and de-excitation mechanisms in adsorbate systems [1].

For various reasons the relatively large inorganic molecule sulphur hexafluoride (SF_6) has been chosen as a chemically inert and highly symmetric adsorbate. It has a high cross section for electron capture because of low-lying and localized unoccupied electronic states and because of a dynamical rearrangement of the bonding geometry (for PF_3 see [2]; SF_6 shows a very similar behaviour [3]). Therefore, it is also a well-known electron scavenger in accelerators.

From the literature it is known that gaseous or solid SF_6 dissociates by irradiation in the UV range [4, 5]. Berkowitz gives a value of 18.1 eV for the onset of SF_4^+ formation [4], and electron impact studies of (isolated) SF_6 yielded a threshold at 15.29 eV for the formation of SF_4^+ ions [5]. It is also known that SF_6 reacts with sodium on the Ni(111) surface [6].

In a previous publication we carefully studied the photon-induced dissociation of physisorbed SF_6 on Ni(111) [7]. From this study we know that for x-ray excitation (x-ray photoelectron spectroscopy (XPS)) subsequent Auger transitions lead to a highly excited molecule with at least two holes in the valence band. This excitation remains

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localized on the molecule and causes dissociation of SF_6 in the multi- and monolayer regime. F and S atomic fragments which are directly adsorbed on the Ni(111) surface were identified. For UV excitation (ultraviolet photoelectron spectroscopy (UPS)) we only observed dissociation in SF_6 multilayers as, for monolayer SF_6, the (single-particle) excitation is rapidly transferred to the substrate.

In this letter we demonstrate the influence of the substrate on the UV induced dissociation of SF_6 in the monolayer regime by comparison of SF_6 adsorption on Ni(111), Ge(100), and NaCl(100) surfaces.

The experiments were performed in a modified VG ESCAlab MkII chamber comprising a standard twin anode x-ray tube, a UV source with polarizer, a 150° spherical sector analyser, a VG low-energy electron diffraction (LEED) system, a Balzers QMG 112A quadrupole, and a Leybold He-flow cryostat. With this equipment the sample was cooled to 40 K. All measurements were made at a base pressure of $< 6 \times 10^{-11}$ mbar.

The Ge single crystal was cleaned by repeated cycles of argon sputtering and heating up to 900 K. After the cleaning procedure no impurity signal was detected by XPS and a clear (2×1) LEED pattern which is typical for the reconstructed clean Ge(100) surface was observed. Following the results of Fölsch *et al* [8] the NaCl layers on Ge(100) were formed by evaporating NaCl (99.999%) out of a Al_2O_3 crucible. NaCl forms a perfect epitaxial film on Ge(100) with the same orientation as the substrate. The first fully closed layer on Ge(100) is a doublelayer. The quality and thickness of the NaCl adlayers were checked by LEED, XPS, UPS, and also by SF_6 and xenon TPD spectra, as these spectra are also very sensitive to surface roughness (see also [9]).

The adsorption layers were prepared by dosing through a capillary array beam doser. The carefully studied adsorption system SF_6/NaCl/Ge(100) is presented elsewhere [9]; we used the results from this study for the preparation of SF_6 mono- and multilayers, respectively. The XPS/UPS binding energies (BE) are referred to the Fermi level of the Ge sample and have an absolute accuracy of ±0.1 eV based on an established calibration procedure [10].

We give a brief summary of our results for SF_6 on Ni(111) [7]. Figure 1 shows UPS spectra of SF_6 on Ni(111) taken with monochromatized HeI and HeII radiation. At first we concentrate on the monolayer spectra. With both UV excitation lines we observe the molecular valence orbitals of SF_6: $1t_{1g}$, $1t_{2u} + 5t_{1u}$, $3e_g$, $1t_{2g}$, and $4t_{1u}$ (as indicated in figure 1). The peak intensities and energy separations are nearly identical to those of gas-phase spectra [11, 12]. This is, by the way, a clear indication of undissociated, physical adsorption. The major difference from isolated SF_6 is an overall BE shift which is caused by the adsorption, i.e. by local potential and screening effects.

If we now compare the mono- and multilayer spectra of figure 1 we notice surprising differences. In the case of HeI excitation of the multilayer we find only one broad peak with hardly any structure, whereas the corresponding HeII spectra look very similar to those from the monolayer. The major difference in the HeII spectra is a 0.8 eV shift to higher BE. This shift is typical for rare gases and physisorbed molecules. It is mainly due to a reduction of final-state screening which is more effective in a monolayer (image potential screening by the substrate) than in multilayers (extramolecular screening only by polarization of neighbours). A (small) contribution to the shift from differences of the local potential in both cases cannot be excluded.

Another difference is the interesting variation of relative peak intensities in the HeII spectra for the mono- and multilayer, respectively. This is an effect of the energy dependence of the inelastic mean free path [13], but irrelevant in the present context.

Additional time-dependent measurements with unmonochromatized UV irradiation

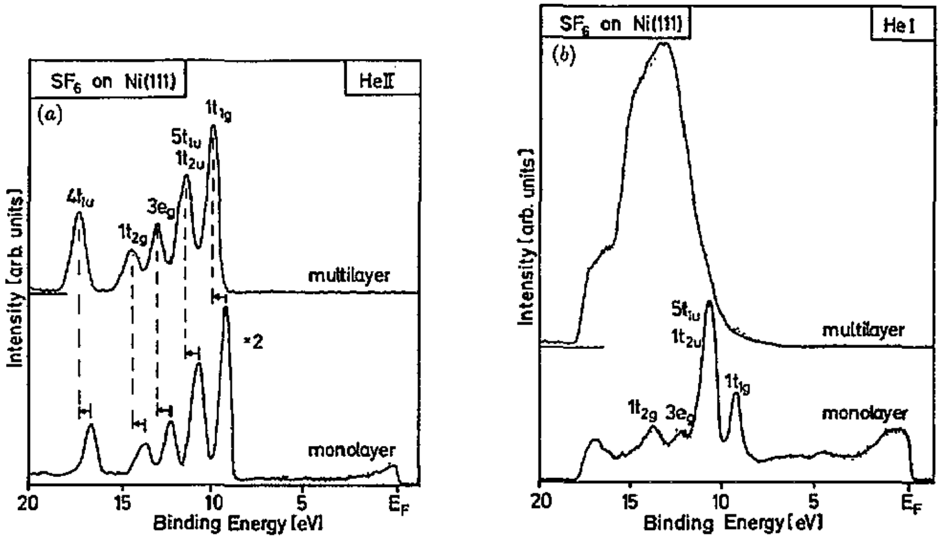

Figure 1. UPS spectra taken with monochromatized (*a*) HeII and (*b*) HeI radiation from SF_6 on Ni(111); top: multilayers, bottom: monolayer.

showed clearly that similar changes as under pure HeI irradiation also occur in the HeII multilayer spectra but on a time scale seven times longer (see [7] for details). The reason for this difference is a resonant bonding–antibonding excitation process for $h\nu \sim 21$ eV (HeI), most likely the excitation $1t_{2u} + 5t_{1u} \rightarrow 2t_{2g}$. This can be derived from the comparison of measured energies [7] and from the high relative peak intensity of the $1t_{2u} + 5t_{1u}$ orbital in the HeI spectrum (figure 1(*a*), bottom), indicating a resonantly enhanced photoionization cross section for photon energies near 21 eV.

Finally, the different dissociation behaviour of mono- and multilayers upon UV irradiation has to be explained. If a single valence hole is created by a UV photoemission process, this may lead to bond breaking, i.e. dissociation, if this excitation remains localized in the molecule for a time sufficiently long compared to the motion of molecular fragments. This probably happens rather often in the SF_6 solid or in condensed layers. In the monolayer, however, this excitation is apparently transferred to the substrate rather quickly, for instance by tunnelling of an electron from the substrate into the molecule, before possible fragments can move apart. Thus, the dissociation process is quenched in the monolayer by delocalization of the excitation. Such a mechanism has also been suggested in previous publications [14, 15].

Therefore we conclude that generally for SF_6 monolayers on metals the interaction between the adsorbate valence orbitals and substrate wave functions is sufficient to make the tunnelling/delocalization process of a valence excitation fast on the time scale of atomic motion ($\ll 10^{-13}$ s). In order to change the strength of the adsorbate–substrate interaction, and hence the tunnelling probability, we also studied SF_6 monolayer dissociation under UV irradiation on different substrates, i.e. Ge(100) and NaCl(100). Interestingly, UV irradiation of SF_6 on Ge(100) and on a doublelayer NaCl on Ge(100) yielded the same results as on Ni(111). This important finding indicates that the delocalization of the valence excitation also takes place on semiconductor surfaces, and that even a ~ 6 Å thick insulating layer does not prevent this quenching process until dissociation occurs.

The next question is what happens upon increasing the NaCl layer thickness.

Figure 2 shows an SF_6 monolayer on clean Ge(100) and on NaCl(100) layers of different thicknesses as indicated in the figure (the peak at 6 eV BE belongs to the NaCl valence band). For comparison a HeII multilayer spectrum of dissociated SF_6 on Ni(111) is shown at the bottom of figure 2. All spectra in figure 2 were taken with unmonochromatized HeII radiation after preparation of a fresh and undamaged SF_6 monolayer. Only the multilayer spectrum on Ni(111) was recorded after a total UV irradiation time of 100 min and thus shows dissociated SF_6 induced by UV radiation. As the spectra were taken without a monochromator, HeI radiation was also present with approximately three times higher intensity. The HeII spectra are generally a better indicator for SF_6 dissociation, as resonant excitations and band structure effects significantly modify the HeI spectra on NaCl(100) [9].

The important point is the observation of various changes in the SF_6 monolayer spectra with increasing NaCl layer thickness, Θ_r^{NaCl}. Firstly, the spectra in figure 2 exhibit an energy shift towards higher BE with increasing insulator thickness. This shift is due to differences of the local potential (the measured contribution of the work function is 1.2 eV for $\Theta_r^{NaCl} = 9$), charging at higher NaCl layer thickness ($\Theta_r^{NaCl} \geqslant 5$, see below), and a reduction of final-state screening on the insulator. Secondly, the monolayer SF_6 spectra on Ge(100) and on the first layer NaCl (doublelayer, $\Theta_r^{NaCl} = 2$) show only a slight 'blurring' of the peaks as compared to Ni(111) (figure 1(*b*)), and, as mentioned above, they did not change with increasing dose of irradiation, identical to the SF_6 monolayer behaviour on Ni(111). Therefore we conclude that in the monolayer no tendency towards dissociation can be detected on these substrates. This finding was corroborated by XPS measurements which did not yield peaks corresponding to atomic F and S on the surface. It is very interesting that the 'smearing' of structure increases with NaCl layer thickness. At first sight one would guess that this is an effect of charging. A comparison of the full width at half maximum (FWHM) of the NaCl valence band peak does indeed show a broadening due to charging for the thickest NaCl layer (top spectrum of figure 2, $\Theta_r^{NaCl} = 9$) as compared to the other spectra. (Incidentally, this charging is also responsible for the further energy shift of the peaks at higher NaCl coverages.) But if one assumes for the SF_6 peaks the same amount of peak broadening as for the NaCl valence band one does not obtain the same degree of 'smearing' as the top spectrum of figure 2 shows. Thus, charging plays only a minor role in this case; the peak shapes are dominated by dissociation of SF_6 in the monolayer. This conclusion is corroborated by further observations. For instance, the SF_6 monolayer spectrum at the top of figure 2 ($\Theta_r^{NaCl} = 9$) is nearly identical to the SF_6 multilayer spectrum of dissociated SF_6 on Ni(111) (bottom of figure 2) recorded after long UV irradiation time (100 min). In addition, the spectrum for a NaCl thickness of 5 layers also shows dissociation of SF_6 (enhanced broadening), and it changes after higher irradiation doses becoming very similar to that of SF_6 multilayers on Ni(111) (bottom of figure 2). The corresponding HeI spectra for SF_6 on different NaCl(100) layers show the same behaviour, and hence are not shown. In particular the one for $\Theta_r^{NaCl} = 9$ is identical to that for SF_6 multilayers on Ni(111) (figure 1(*b*), top spectrum).

Finally, an XPS F1s spectrum (figure 3) was recorded after the HeII spectrum depicted at the top of figure 2. The typical structure for a mixed layer of intact and dissociated SF_6 molecules is seen in this spectrum. The peak at 690.0 eV BE is unambiguously due to molecular SF_6 [16], while that at 684.6 is attributed to dissociated F atoms which are directly attached to the substrate (for comparison on Ni(111) see [7]). This second peak is not visible in F1s spectra from undissociated SF_6 layers. (Both F1s peaks again show the same energy shift towards higher BE as the peaks in the UPS spectra.

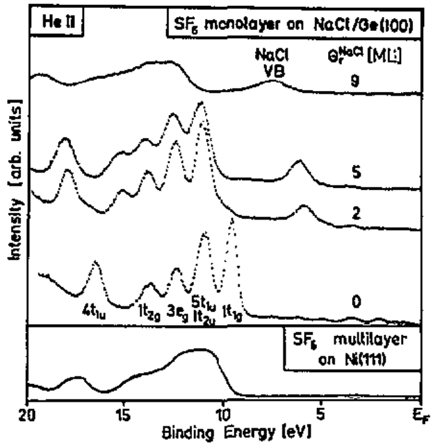

Figure 2. UPS spectra taken with unmonochromatized UV radiation (HeI/HeII ratio ~ 3 : 1) from SF$_6$ monolayers on Ge(100), different epitaxial NaCl(100) layers on Ge(100), and from SF$_6$ multilayers on Ni(111) as indicated in the figure. The spectra were recorded after preparation of a fresh SF$_6$ monolayer with the exception of the multilayer spectrum on Ni(111) (bottom) which was recorded after 100 min of UV irradiation.

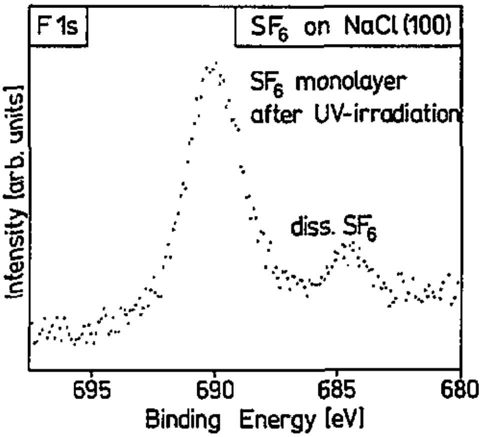

Figure 3. F1s XPS (Mg Kα) spectrum from SF$_6$ on NaCl(100) in the monolayer regime. The spectrum was recorded directly after the topmost UV spectrum of figure 2.

This energy shift is also attributed to changes in the local potential and to charging.)

Of course, SF$_6$ generally dissociates after x-ray irradiation in the multilayer as well as in the monolayer [7]. But the effect of dissociation normally becomes detectable only after 15 min of x-ray irradiation. As the XPS spectrum of figure 3 was taken directly (~ 2 min) after the UPS spectrum, it shows only effects which are due to the preceding UV irradiation and *not* to the x-ray irradiation during recording of this spectrum. XPS spectra taken from a fresh SF$_6$ layer on NaCl(100), $\Theta_r^{NaCl} = 9$, do not contain structures other than the main peak at 690 eV. Thus it can unambiguously be concluded that the dissociation product which is observed in the F1s spectrum of figure 3 at 684.6 eV BE is caused by UV irradiation, and that the HeII SF$_6$ monolayer spectrum on NaCl(100) for $\Theta_r^{NaCl} = 9$ represents a partly dissociated SF$_6$ layer. We emphasize that the dissociation of SF$_6$ under UV-irradiation starts at a NaCl layer thickness of approximately 5 NaCl layers, or more precisely, between 2 and 5 NaCl layers.

In conclusion, the resulting picture is as follows. With HeI radiation ($h\nu \sim 21$ eV) a resonant transition from bonding $1t_{2u} + 5t_{1u}$ to antibonding $2t_{2g}$ SF$_6$ orbitals is possible. This excitation process is the most likely channel that leads to fragmentation of the SF$_6$ molecule if the excited valence state lives long enough compared to the time scale of nuclear motion (10^{-13} s). For isolated SF$_6$, SF$_6$ in condensed layers, or in a monolayer on an insulating substrate this is apparently the case. In contrast, on metal substrates this excited state is rapidly quenched due to the remaining interaction between metal and molecule, and hence the molecules remain intact. In other words, the missing valence electron is replaced by rapid reneutralization because of electron tunnelling from the substrate into the adsorbate. The important message of the present data is that this quenching process also occurs for SF$_6$ molecules on a semiconductor surface, and even on a doublelayer of the insulator NaCl. Only for insulator thicknesses between 2 and 5 layers, i.e. 6 and 15 Å [17] does the tunnel probability decrease to such an extent that the lifetime of the excitation becomes similar to that of nuclear motion (10^{-13} s), and hence the dissociation probability increases drastically.

We note that this finding has consequences for radiation effects on adsorbates in general, for photoemission investigations of molecules on different substrates including insulating films, and for the dynamical screening properties in photoemission and Auger decay processes. This last point will be discussed in a forthcoming publication [18].

In summary we have shown that: (i) Resonant photo-ionization can be observed for the $5t_{1u} + 1t_{2u}$ molecular orbital with photon energies near 21 eV (HeI). (ii) In the SF_6 multilayer rapid dissociation occurs upon UV irradiation. The dissociation process is seven times more effective for HeI than for HeII radiation, probably because of the resonant bonding–antibonding excitation process $5t_{1u} + 1t_{2u} \rightarrow 2t_{2g}$. (iii) For SF_6 adsorption on metals and semiconductors dissociation in the monolayer *is not* observed for UV excitation. The single-particle excitation is rapidly quenched by the substrate. (iv) For adsorption on insulators dissociation in the monolayer *is* observed under UV irradiation. This was demonstrated by SF_6 adsorption on thick ($\sim$ 15 Å) epitaxially grown NaCl layers on Ge(100). (v) A minimum NaCl layer thickness of less than 5 layers ($<$ 15 Å) is necessary to quench the transfer of the excitation from the molecule to the Ge-substrate by tunnelling processes. In this case, the lifetime of the de-excitation process becomes about 10^{-13} s, the characteristic time for atomic motion.

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