

Chapter 8

Appendix

In the appendix we present some preliminary results without extend discussion. This concerns possible DEA enhancements when halogen compounds are coadsorbed with a polar molecules and vibrational spectroscopy for the identification of compounds on irradiated films.

Medium enhanced desorption at very low energies

This part concerns the interaction of low energy electrons with $\text{C}_2\text{F}_4\text{Cl}_2$ adsorbed in submonolayer amounts on top of ammonia ice. We have only performed some preliminary measurements they, however, indicate a strong influence of the polar molecules on ion desorption at the very low energy region (< 2 eV). These results will be presented without extended discussion due to the complexity of the problem behind the involved processes and insufficient amount of data required for proper interpretation.

Increasing interest in studying the influence of polar environment on CFCs was stimulated by the report of Lu and Madey about the enhancement in ESD from CF_2Cl_2 embedded in polar medium [18, 55]. They have demonstrated a giant enhancement (up to 10^4) in the desorption of Cl^- through the irradiation with 250 eV electrons on going from adsorbtion of CF_2Cl_2 directly on Ru surface to adsorbtion on top of water ice or ammonia [94]. In contrast,

they have shown that coadsorption of CF_2Cl_2 with nonpolar molecules shows only a small increase in ion desorption (most likely controlled by screening the influence of the image charge) [94,95].

Since during electron bombardment at 250 eV the metal substrate is the source of secondary electrons with a yield maximum at 0 – 2 eV, the observed desorptions were attributed to be initiated by DEA processes. The generated low energy electrons may then efficiently be solvated by clusters of molecules with a permanent dipole like water or ammonia [96]. The enhancement in desorption of $\text{Cl}^-/\text{CF}_2\text{Cl}_2$ embedded in polar environment was proposed to proceed by tunneling of the self-trapped (solvated) electrons from water or ammonia clusters to CF_2Cl_2 resulting in its dissociation.

The direct evidence of the low energy electrons to be involved in the above mentioned processes has been reported by Lu and Sanche [91]. They have performed a charge trapping experiments (see section "*Electron transmission and film charging*") at primary electron energies near 0 eV on 0.1 ML CF_2Cl_2 adsorbed on 5 ML H_2O or NH_3 grown on Kr spacer. These measurements are thus not influenced by the metal substrate and only the effect of polar molecules can be studied. They have observed that upon coadsorption of CF_2Cl_2 on water or ammonia ice the DEA cross-section (estimated from film charging) is by about 130 and 970 times larger than that in the gas phase, respectively [91]. In addition, the mechanism responsible for the observed enhancements has been correlated to the previous one in the way that rather transfer of presolvated electrons than fully solvated electrons is operative. The reason is that a considerable energy (3.2 eV in H_2O bulk [97]) is required to liberate the solvated electrons and direct transfer of an electron to an adsorbate would be very unlikely. From the femtosecond time-resolved laser studies it is known that in the polar liquids solvation of the electrons proceeds through two steps [97]. Before an electron becomes fully solvated, the electron is weakly bound to a preexisting precursor state with a lifetime of picoseconds, which increases when going from liquids to solids up to the milliseconds [98]. Since the time of electron transfer is in the range of femtoseconds [99], there is a high probability for an electron to be transferred from a precursor state to a molecule with a high electron attachment rate.

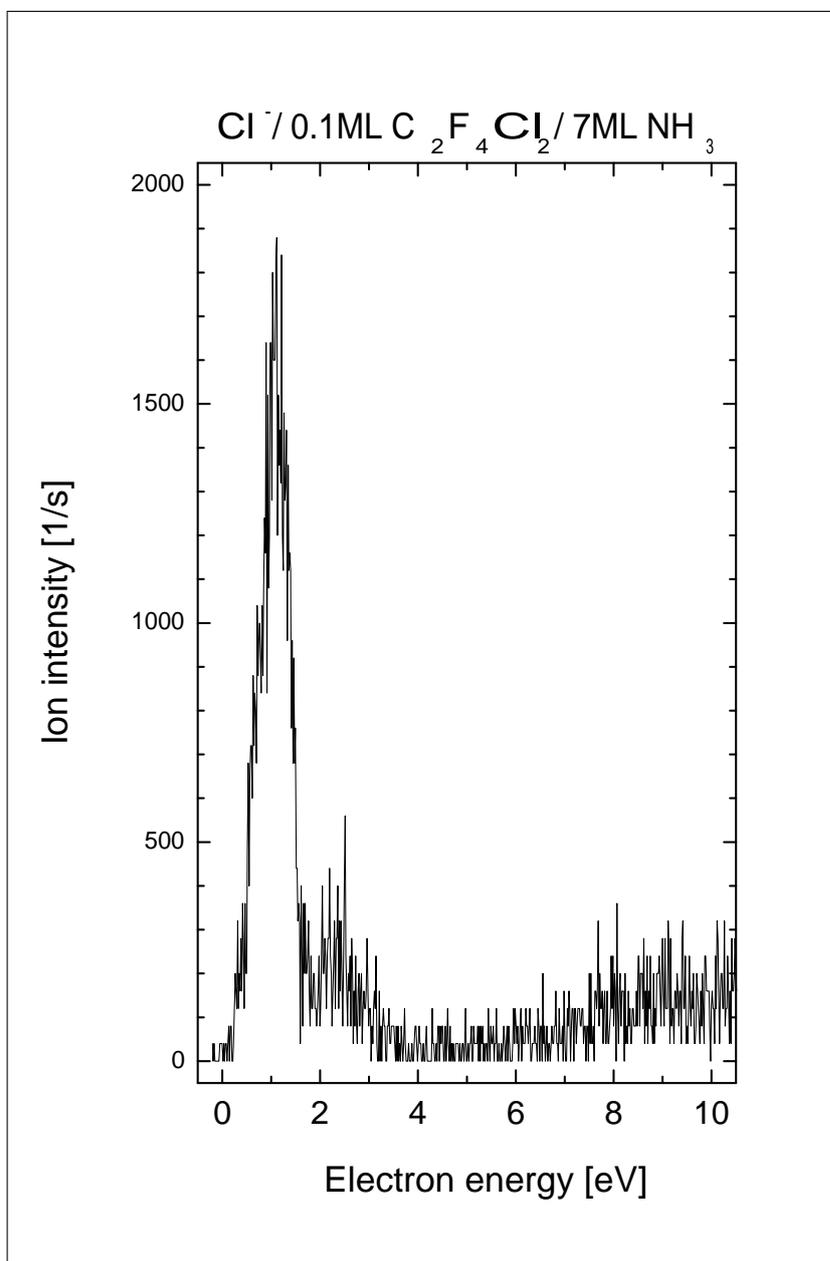


Figure 8.1: *Cl⁻ desorption from 0.1 ML of C₂F₄Cl₂ adsorbed on top of the 7 ML film of NH₃. Ion yield represents the first energy scan, scan duration 25 s, I = 60 nA.*

On the basis of these results we have performed ESD experiments on $C_2F_4Cl_2$ and $C_2F_3Cl_3$ adsorbed in submonolayer amounts on top of ammonia ice, Fig. 8.1. The intensity of electron beam is about 60 nA with an estimated resolution of about ± 0.3 eV.

Fig. 8.1 shows desorption of Cl^- ion yield from 0.1 ML $C_2F_4Cl_2$ adsorbed on top of 7 ML film of NH_3 as a function of energy. The pattern of the yield function resembles to that obtained from DEA to gas phase $C_2F_4Cl_2$. This is a very surprising observation as we extensively have stressed on the preferable desorption at higher energies. As seen on Fig. 8.1, the ion desorption predominates in the low energy region with the most intense feature peaking near 1.1 eV. From the yield pattern we can distinguish between three resonant states located at 1.1, 2.2 and near 9 eV, but both higher energy desorption resonances are relatively suppressed. Taking into account the hypothesis with the presolvated electrons, the electron transfer may cover only the lowest lying resonant state as the other states would most likely not be energetically accessible. On the other hand, Cl^- ions generated near 1.1 eV must possess considerable kinetic energy as they have to overcome the polarization potential induced by the polar medium. It is not really clear why the ions are so effectively ejected into the vacuum at very low energies and only the tunneling of the presolvated electrons to the adsorbate would not explain the observed desorption enhancement. We should also note, that within the first energy scan considerable film charging occurs and charge accumulated at the surface may play an important role in ion desorption. Anyway, further investigation are needed in order to explain the processes involved in the observed phenomena.

Preliminary results from IRAS and EELS experiments

IRAS: The comparison between the infrared spectrum of nonirradiated 20 ML film of $C_2F_4Cl_2$ with that after the irradiation with electrons at 10 eV (5 mC dosage) shows only a decrease in intensities without appearing of new vibration bands. The observed decrease in intensity is attributed to the film evaporation, see Fig. 8.2. We assume that the probability for a detection of new species is very small using the IRA technique as the IR spectrum represents the absorption through the whole 20 ML film while the modified area takes only about 10% of the upper layer of the film.

EELS: The EELS technique has the advantage that the electron beam used for sample irradiation is afterwards used for the analysis and therefore the areas of irradiation and probing coincide. Fig. 8.3 shows the EEL spectra of the nonirradiated and irradiated sample. As can clearly be seen, after irradiation with electrons of 10 eV energy, a new feature at 234 meV $\approx 1887\text{ cm}^{-1}$ appears, which is close to that of C = C stretch from C_2F_4 (1872 cm^{-1} in the gas phase). We assume thus that C_2F_4 (or polymers) are formed at the surface. The spectra after film irradiation at energy of about 1 eV could not be obtained due to considerable charging of the film at this energy, which inherently deflected the electron beam out of the detector.

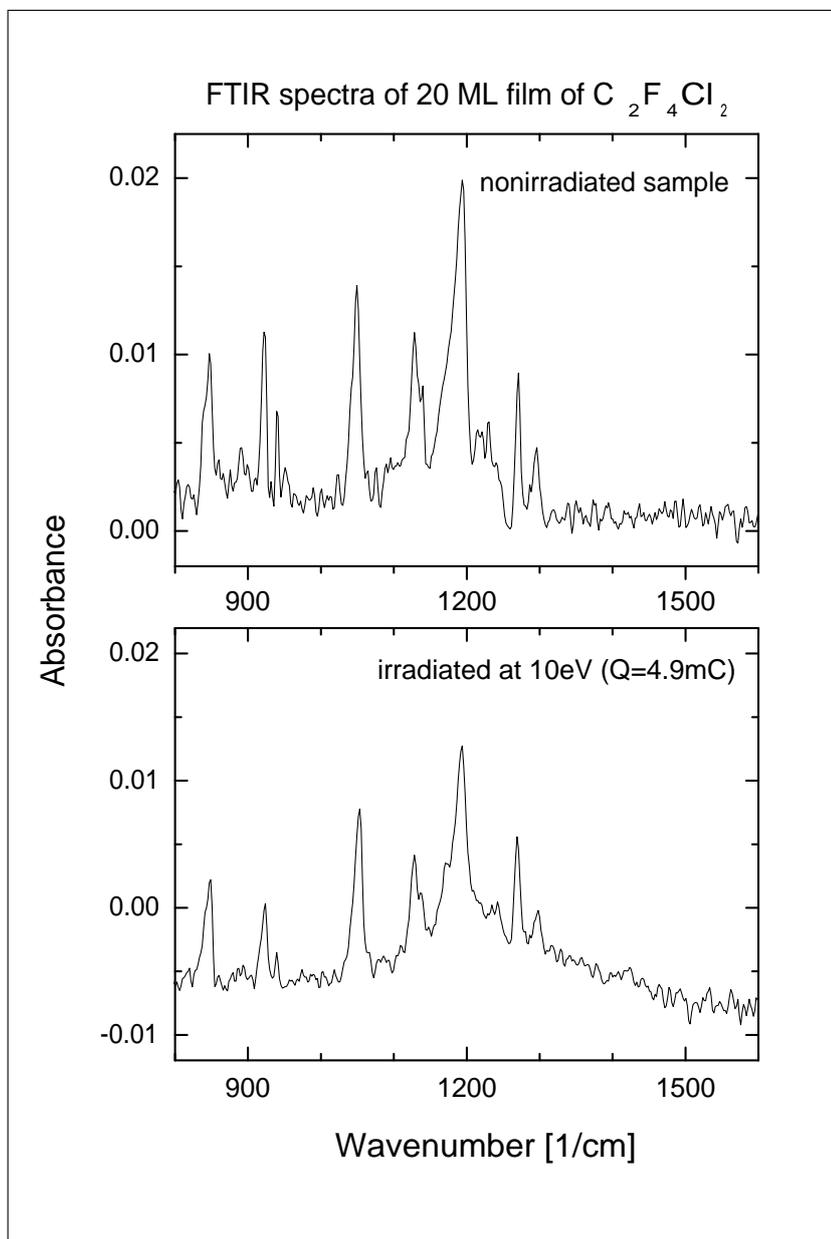


Figure 8.2: Infrared spectrum of the nonirradiated 20 ML film of $C_2F_4Cl_2$ (top) and that of irradiated at 10 eV and particular dosage (bottom).

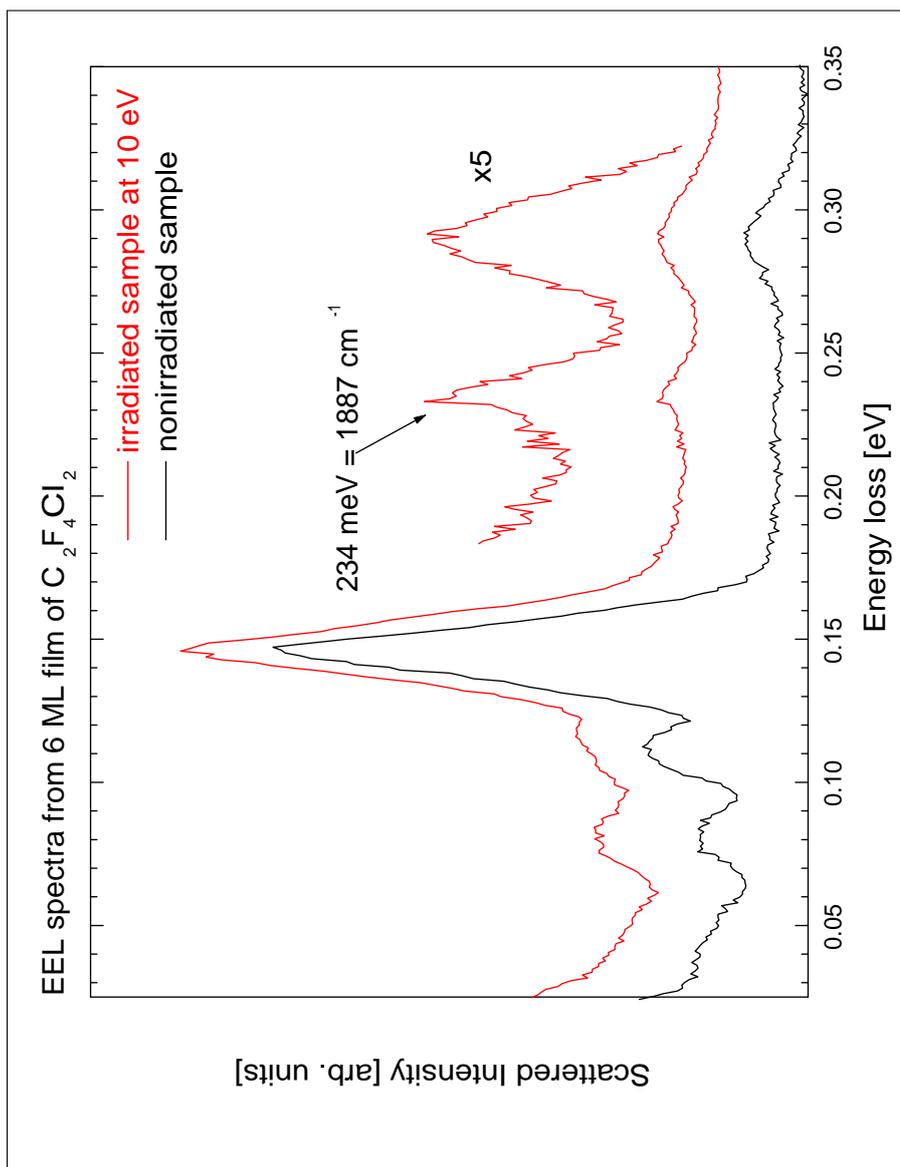


Figure 8.3: Electron energy loss spectrum at an incident electron energy 10 eV of the nonirradiated 6 ML film of $C_2F_4Cl_2$ (blue curve) and that of irradiated with 10 eV, 48 hours, 0.3nA (black curve).

