Electron Induced Processing at the Molecular Level (EIPAM)

Exchange Grant: Linda Feketeova

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Title: "A study of cold electron-solid interactions: polar molecules and their characteristics"

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Scientific Report

The project involved work in the field of the interaction of very low energy ("cold") electrons with condensed molecules. The aim of this work is thus to study topics of prime interest in the EIPAM programme of work. This area of research is almost entirely new. It seems likely that very low energy electrons, with energies down to a few meV, by analogy with gas phase processes, may have very large cross-sections for interaction with molecules within thin films of material. Processes relate to the structural rearrangement of molecules laid down on surfaces, the breakdown of molecules and the synthesis of molecules by irradiation with electrons. Since the subject is so little explored, we need to lay down the groundwork and establish new principles. This was the situation ten to fifteen years ago for cold electron scattering in the gas phase.

The state-of the-art of the subject of electron interactions with solids material is that experiments have been performed down to energies of a few hundred meV with an energy resolution of perhaps one hundred meV. Several European groups, with whom the host laboratory has good contact through EU and ESF networks, e.g. Freie Universität, Berlin (Illenberger), Laboratoire Collisions Atomiques et Moléculaires, Paris XI (Azria), are at the forefront of pioneering research, for example demonstrating remarkable complete transformation of a molecular film with 1 eV electrons impacting on 1,2 $C_2F_4Cl_2$ (Balog,Illenberger, Phys.Rev.Lett. **91** (2003) 213201). The host laboratory was a major node of the EU research network "Electron and Positron Induced Chemistry" (EPIC) under FP5, and takes part in the EU COST P9 project "Radiation Damage in Biomolecular Systems", in the ESF network "Electron Induced Processing at the Molecular Level" (EIPAM) and in the related network "Collisions of Atoms in Traps". These networks draw together expertise in numerous European nations and have been valuable in the furtherance of the work achieved so far in this project.

The most ground-breaking feature of the experiments is that films of material are irradiated (i) with very low currents, perhaps one thousand times lower than in any earlier work (ii) we achieve much lower energies in the electron beam impinging on the substrate, typically down to tens of meV energy, compared with > several hundred meV or higher characteristic of earlier

studies (iii) there should be very high energy resolution in the incident electron beam, potentially as good as 1-2 meV. In this experiment a synchrotron based electron source is used; see Figure 1. This operates through photoionization of Ar at threshold of 15.75 eV (78.65 nm) using monochromatized synchrotron radiation from the ASTRID storage ring at Aarhus. Photoelectrons formed at a few meV energy have the energy resolution of the photons, typically 1 meV to 1.5 meV. These electrons are then formed into a beam. The electrons are allowed to fall upon a thin film of material deposited on tantalum. The current transmitted through the thin film, as a function of incident electron energy, is measured using a femtoammeter.

The mechanics of the apparatus is as follows. The entire system is UHV and baked. Typical base pressures are 2-3 x 10^{-10} mbar. There is an upper chamber, containing the photoionization electron source, where the experiments involving electron irradiation take place. There is a lower independent chamber for the preparation and analysis of samples. The target is moved under UHV between these two chambers. In the lower chamber the sample may be rotated and set at any angle to the vertical as desired. In the lower chamber material is quantitatively dosed onto the tantalum substrate which is presently cooled with liquid nitrogen to a temperature of typically 130K, see Figure 2. We therefore know the film thickness, which is typically a few to more than 50 monolayers (ML). This chamber also includes a mass spectrometer (quadrupole 1-2048 mass range). Temperature programmed desorption (TPD) may be performed here. There is also an Ar ion sputter gun for cleaning of the Ta surface.

The experiment is performed as follows. The Ta surface is sputter-cleaned and then cooled to ~130K. Vapour of the compound to be studied is admitted from a sample inlet system, via a dosing volume, to a known pressure in the sample preparation chamber to prepare a film of known thickness. The target with this film is then raised until it is positioned 90 mm from the region in which photoelectrons are formed by synchrotron radiation, the focal point of the electron optics. The target can be irradiated with currents of a few hundred femtoamps at a fixed energy or the energy can be swept between zero and up to ~10 eV. The latter yields a transmission spectrum.

During the three months of work in Aarhus, a large number of experiments have been performed. Only a small fraction of the most significant will be reported here. A good deal of work was performed proving that the apparatus was yielding reliable data free from artefacts due to for example electrostatic phenomena not directly connected, or unconnected, with the passage of cold electrons through the substrate. We have concentrated on water ice layers, since these turned out to be very interesting. There are also quite extensive data for propanoic acid, fluorobenzene and some

data for acetic acid. The water ice data are complete but the other species may be subjected to further study.

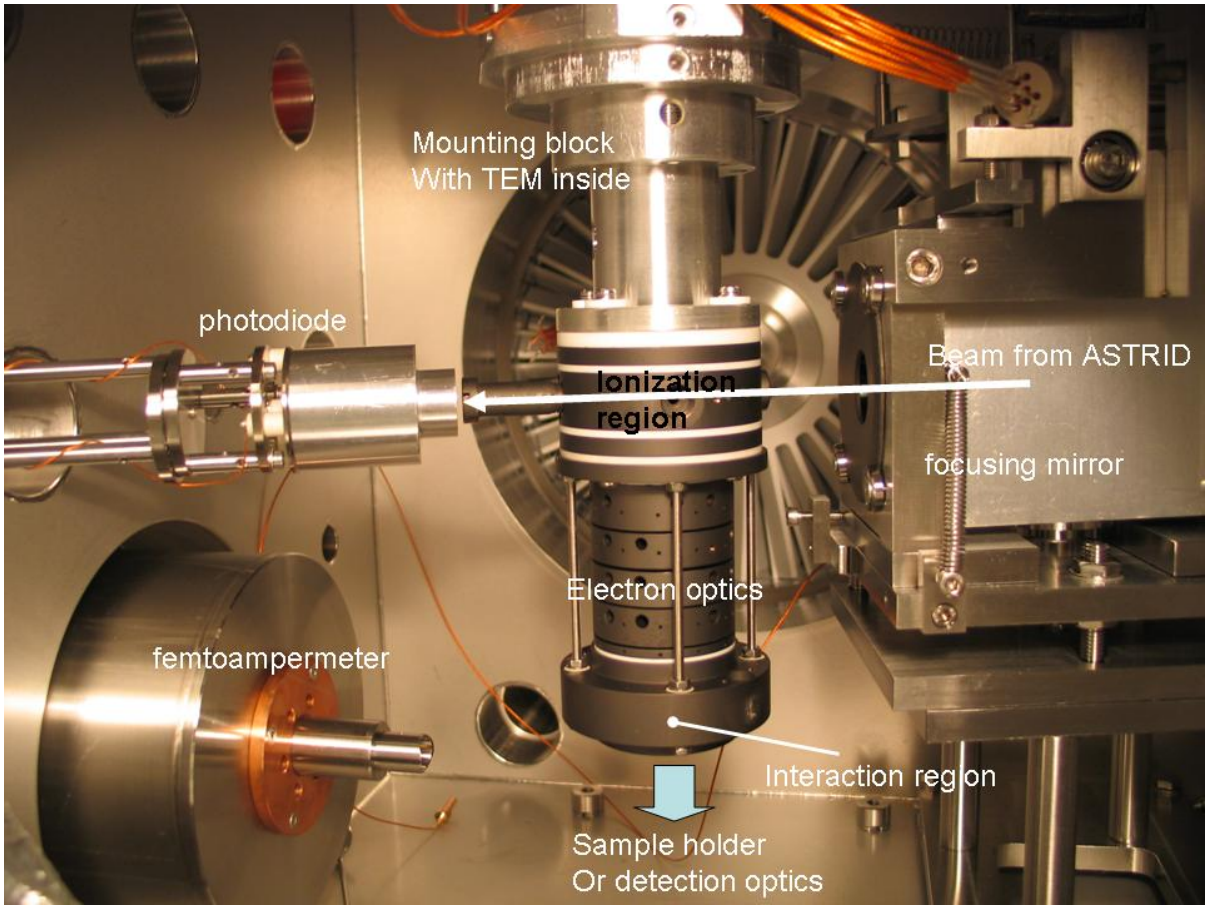

Figure 1: The experimental system.

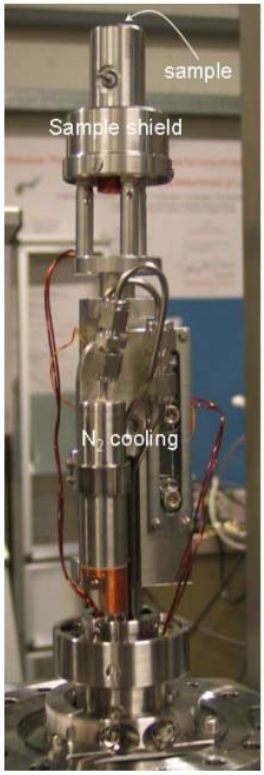

Figure 2: The sample holder.

A summary of Experimental Results

The transmitted current is measured as a function of electron energy. At present the energy scale is assigned by assuming that the onset of electron current is at zero energy. This may be in error by tens of meV. This remains an outstanding source of uncertainty in the experimental data.

1. Fluorobenzene

In order to validate the higher energy behaviour of the instrument we have studied the passage of electrons through films of fluorobenzene. This material was chosen since the transmission spectrum shows two characteristic peaks at 4.8 and 7.5 eV (see the red curve in Fig.3) [L. Sanche, J. Chem. Phys 71 (12), 4860 (1979)]. We reproduce the form of this spectrum satisfactorily with peaks at 4.9 and 8.2 eV (black curve in Fig.3).

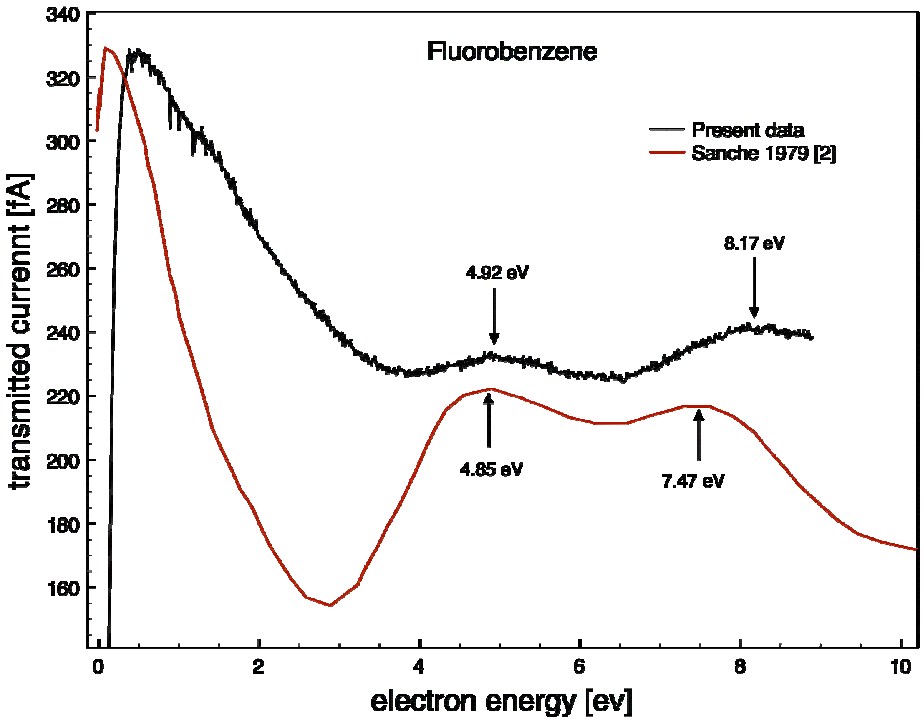

Figure 3: Transmitted current vs. electron energy for fluorobenzene at 130K. The black curve is the present experiment, and the curve refers to 5 monolayers. Data of Sanche (the red curve) with an arbitrary current scale are shown for comparison and refer to about 60 monolayers.

2. Water ice.

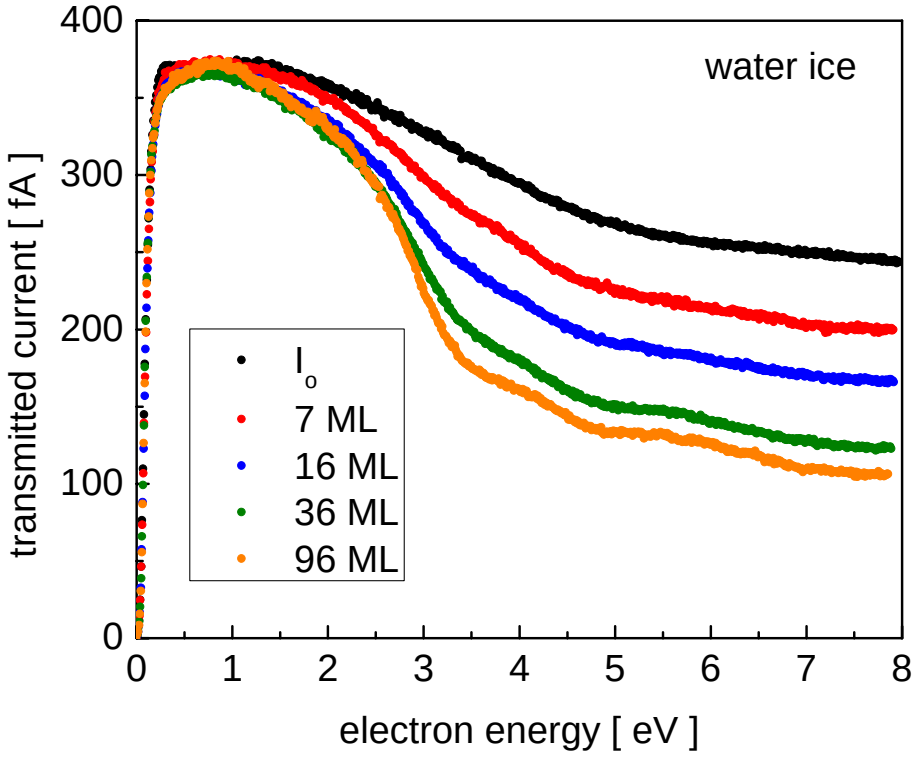

Figure 4: Transmitted current vs. electron energy for polycrystalline water ice at 130K. The top curve is for bare tantalum, and the curves refer successively to 7, 16, 36 and 96 monolayers.

The data in Figure 4 show a remarkable phenomenon. At very low energy polycrystalline water ice is effectively transparent to electrons. This is demonstrated since the transmitted current to the tantalum substrate is unchanged by the presence of ice layers on the tantalum at very low energy. This is illustrated in more detail in Figure 5 which shows only very low energy data. This is a very surprising result since water ice is of course an insulator. There is no evidence for charging.

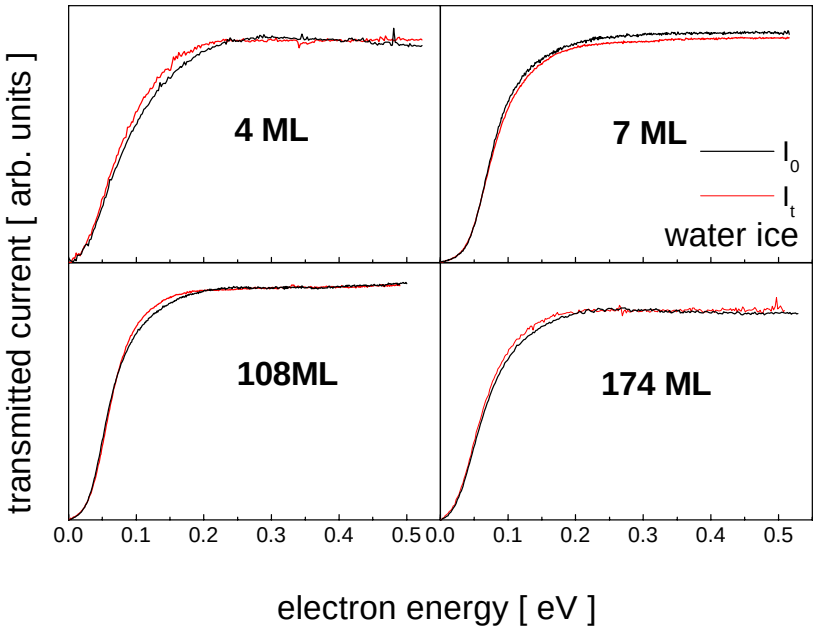

Figure 5: Transmitted current vs. electron energy for polycrystalline water ice at 130 K for different thicknesses. The black curve is for bare tantalum and the red curve is for polycrystalline water ice.

What is taking place is as follows. Polycrystalline ice has a broad valence band whose lower edge lies about 0.1 eV below the vacuum level. Incoming low energy electrons can enter this valence band, assuming that it straddles the vacuum level. These electrons then undergo inelastic collisions involving energy exchange with low energy phonons of the ice and lose sufficient energy to fall below the vacuum level. At this stage, saving superelastic collisions which re-energise them, the electrons have nowhere to go but to undergo a random walk through the ice layer until they reach the tantalum substrate. At this stage they are conducted away.

When the energy of the incoming electrons exceeds approximately 1 eV, then the inelastic mechanism becomes progressively less efficient and transmission through the ice layer drops. This drop is more marked for thicker layers. We have not yet attempted to identify any origin for the structure between 3.5eV and 7eV clearly apparent for thick layers of ice in Figure 4.

The comparison of the transmitted current through a 33 ML film of water ice and 70 ML of fluorobenzene film layers is shown in Figure 6. The data demonstrate the attenuation of the electron beam for thin layers of fluorobenzene material.

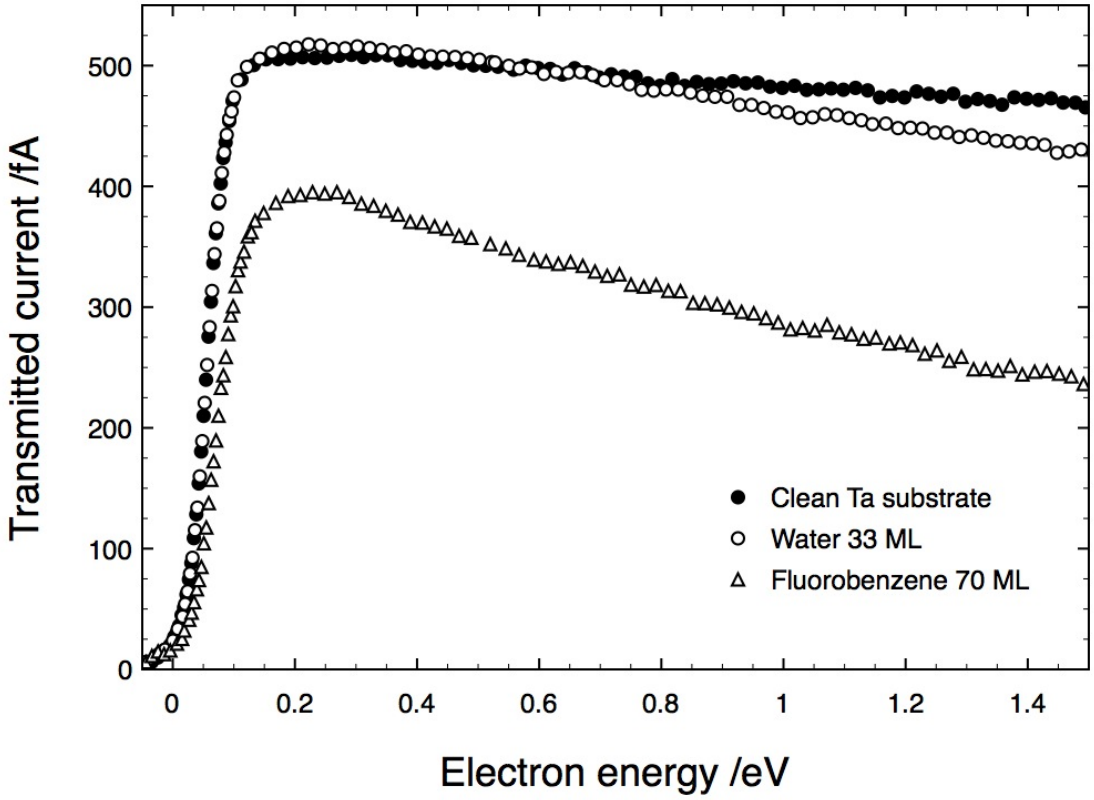

Figure 6: The variation of the transmitted current of electrons with electron kinetic energy in the range between a few meV and 1.5 eV for bare tantalum, tantalum with 33 ML film of amorphous solid water and with a 70 ML film of fluorobenzene, all at 130 K.

3. Acetic acid (CH_3COOH)

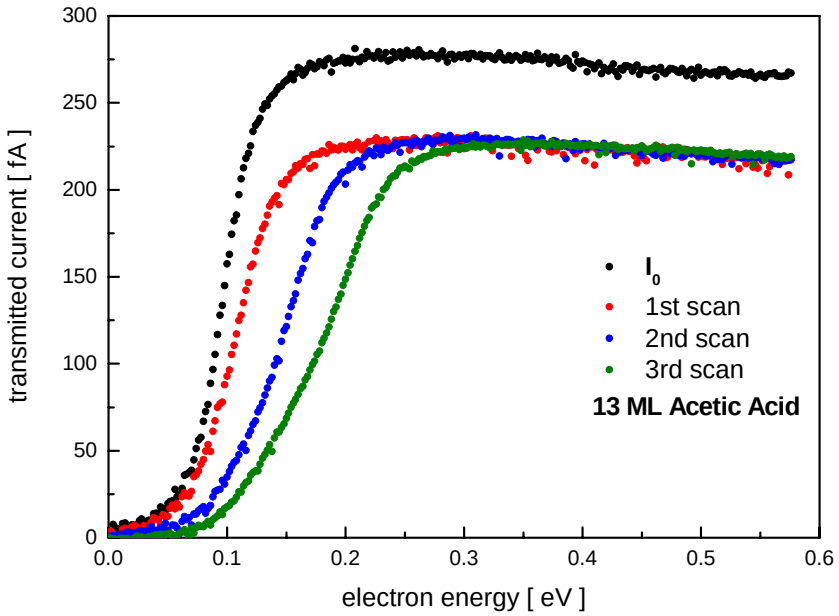

Figure 7: Successive scans through a 13 ML sample of acetic acid at 123 K.

Acetic acid (Figure 7) shows behaviour which strongly contrasts with that of water ice. There is strong apparent charging of the layer of acetic acid (13 ML) shown by the displacement of successive scans labelled 1-3 in Figure 7 as shown in case of propanoic acid and fluorobenzene, too (data not shown). However, the shifts caused by charging were not expected to be as big as shifts observed (35 meV). Thus there might be another cause of these shifts. Experiments with the thinnest layer and lowest electron current possible have been done. The results presented in Figure 8 show no shift. This surprising result may help to explain the origin of the shift. Further investigations are in progress.

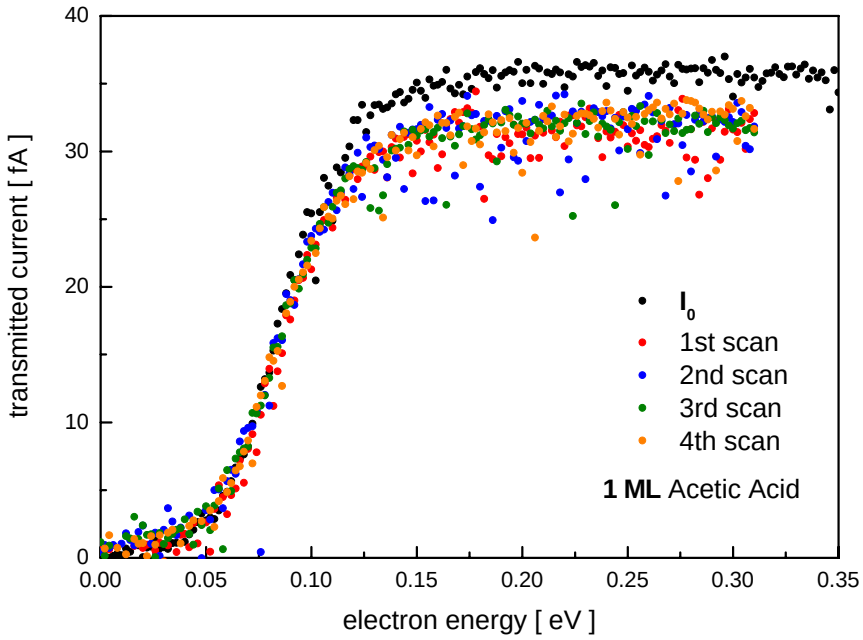

Figure 8: Successive scans through a 1 ML sample of acetic acid at 124 K.

Concluding remarks

During the period of my stay in Aarhus I have been involved in a range of very interesting and successful experiments. These have considerably expanded my knowledge of electron scattering at both the theoretical and experimental level. I have become familiar with a number of new techniques, specifically UHV techniques, dosing methods, temperature programmed desorption and electron optics.

The data for water ice have been submitted for publication. Further experiments are planned using a variety of molecular targets which may include nitrobenzene and other polar species.