Scientific report on the Exchange Grant for visiting Prof. Dr. Petra Swiderek

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Purpose of the visit

Reactions in pure and mixed films of C_2H_6 and CD_3CN induced by low-energy electrons have been investigated by use of thermal desorption spectroscopy (TDS). This system serves as a model for material systems consisting of a hydrocarbon surface (represented by C_2H_6) and a reactive agent (CD_3CN) that will hopefully provide a means of functionalising the hydrocarbon material.

Functionalised organic surfaces are important because they allow to tailor the properties of a material or form the basis for more complex molecular architectures. While simple hydrocarbon materials like polymers but also self-assembled monolayers of alkanethiols and similar materials are readily available, more complex functional molecules usually require a sophisticated synthetic strategy and are therefore costly. Electron beam exposure is a cheap method to functionalise the surfaces of hydrocarbon materials and therefore it is highly desirable to examine the reactions that occur in the irradiated samples of alkanes with functional molecules. The main goals of this study were to determine both the conditions needed for the desired reactions to occur as well as to identify the products of bimolecular reactions and most importantly those between C_2H_6 and CD_3CN.

Description of the work carried out during the visit

Thermal desorption spectroscopy (TDS) of both mixed (with a ratio of 1:1) and pure films of C_2H_6 and CD_3CN exposed to low-energetic electron irradiation has been performed. The energy (E_0) of the non-monochromatized electron beam with an estimated resolution of the order of 1 eV was set to several energies in a range of $5 - 15$ eV. The experiments were performed in an ultrahigh vacuum chamber pumped by a turbomolecular pump to a pressure of about 10^{-10} Torr with the residual gas consisting mainly of hydrogen.

For each experiment, thin films of C_2H_6 and/or CD_3CN were deposited onto a 2 cm^2 Au substrate cooled by means of a closed-cycle He cryostat by dosing a volumetrically calibrated amount of gas through a gas-inlet located directly in front of the substrate. The thickness of the films was estimated to be of the order of 30 monolayers. At this thickness, effects from the Au surface can be largely excluded due to the limited mean free path of low-energy electrons in the organic film.
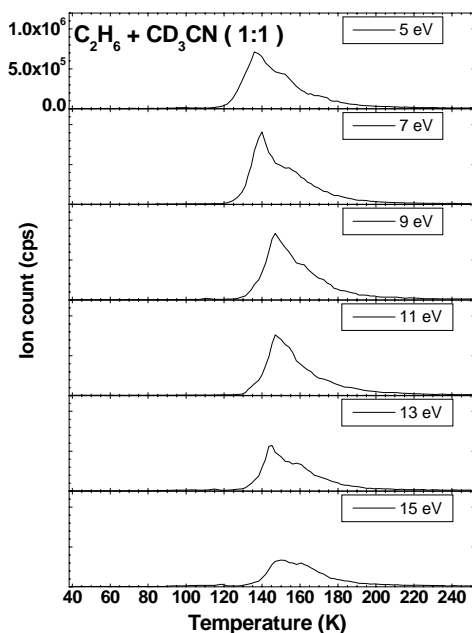
After an irradiation time corresponding to an electron exposure of 5000 μC the surface was heated from 35 K up to 250 K. In each experiment TDS curves were recorded for four different molecular masses using a Quadrupole Mass Spectrometer (QMS) residual gas analyser. The chosen signals were characteristic of specific desorbed molecules and correspond usually to the parent positive ions formed after 70 eV electron impact at the entrance of the QMS.
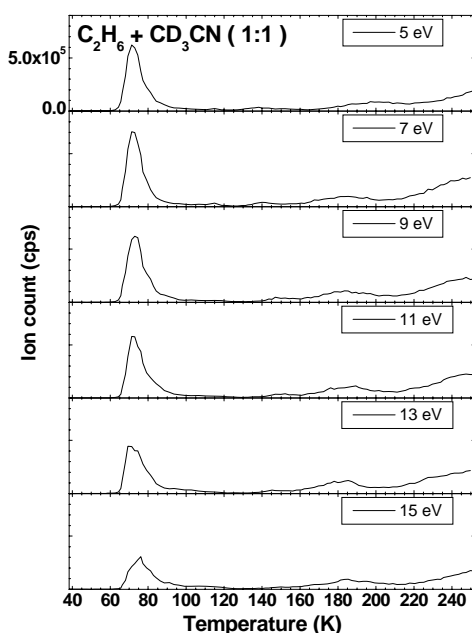
Description of the main results obtained

Each molecule can be identified in a TDS curve corresponding to a characteristic molecular mass by the temperature at which desorption from the surface occurs. The partial pressure of a molecule increases at this specific temperature, peaks and drops in about 30 K. Since the area under a desorption peak of a specific molecular

ion is proportional to the amount of its neutral precursor molecule on the surface, the magnitude of this signal reveals the variation of the concentration of a reaction product under electron exposure and also upon variation of E_0.

In the present experiments the amount of the initially deposited molecules C_2H_6 and CD_3CN decreased by about a factor 2 when increasing E_0 from 11 to 15 eV (Fig. 1,2).

The degradation of the initially deposited molecules at lower E_0 was negligible at the given signal-to-noise ratio of the experiment. Nonetheless, the formation of several product molecules could be detected with the amount depending on E_0. The most important findings are the following:

- CD_4 production is important at E_0 above 10 eV (Fig. 3). Electron impact thus leads to efficient dissociation of CD_3CN producing CN and CD_3. These radicals seem to immediately abstract a hydrogen from their nearest neighbour producing other radicals and CD_4. In pure CD_3CN, a smaller amount of CD_3H is also detected, possibly due to reactions with the residual gas in the vacuum chamber. In mixed films of CD_3CN and C_2H_6, however, production of the latter is more important (Fig. 4), hinting towards intermolecular reactions between CD_3CN and C_2H_6.

Fig. 1 TDS curves at 44 amu (CD_3CN).


Fig. 2 TDS curves at 30 amu (C_2H_6).
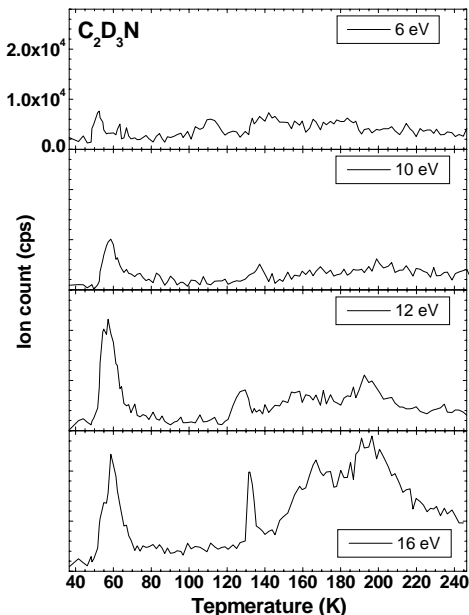
**Fig. 3** TDS curves at 20 amu (CD_4).
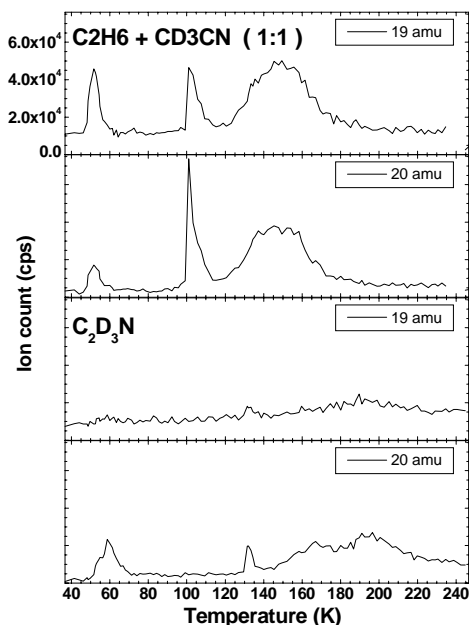
Fig. 4 TDS curves at 15 and 16 eV in mixed and pure film, resp.

- C_2D_6 is produced both in pure CD_3CN and in mixed films. Important amounts are detected between 5 and 7 eV in both types of samples, whereas the production observed in pure CD_3CN at 15 eV is largely suppressed in the mixed film (Fig. 5 and 6) This is reasonable given that this product stems from the recombination of CD_3 radicals produced upon dissociation of CD_3CN. The production in the 5-7 eV range probably relates to the resonant formation of CH_3^- and CN^- observed with a maximum at 7 and 8 eV in the gas phase previously [1].
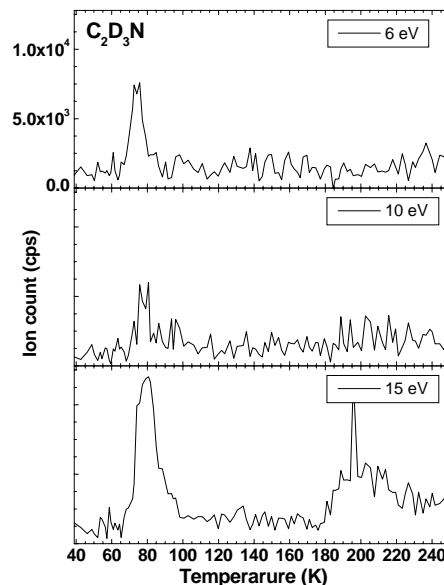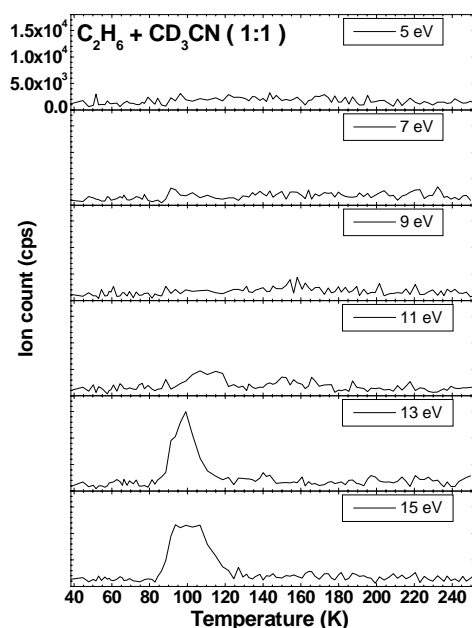

Fig. 5 TDS curves at 36 amu (C_2D_6).
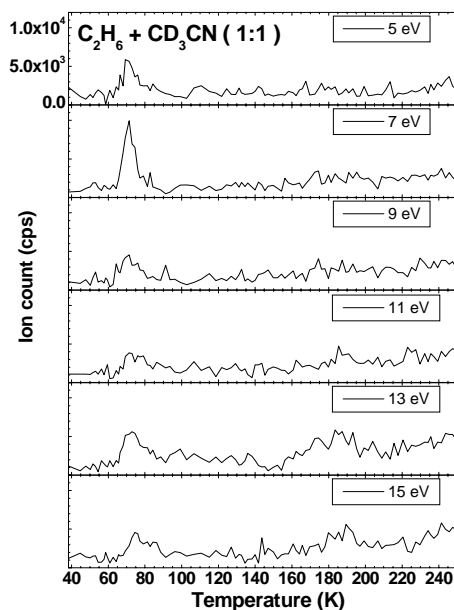
Fig. 6 TDS curves at 36 amu (C_2D_6).

- $C_2H_5CD_3$ resulting from an intermolecular reaction between C_2H_6 and CD_3CN is observed at higher E_0 (Fig. 7). The complementary product C_2H_5CN was not detected unequivocally.

Fig. 7 TDS curves at 47 amu ($C_2H_5CD_3$).

In addition, attempts were undertaken to monitor formation of HCN and DCN. The interpretation of the data was so far hampered by lacking information on the desorption temperature of these species. Also, further investigation of other than studied and possible reaction products is a subject of discussion.

The acquired TDS results so far do not allow to resolve resonant processes in the energetic spectrum below 10 eV with a similar quality as the previous gas phase dissociative electron attachment spectra [1]. This is partly caused by the much lower energetic resolution of the electron source in the TDS apparatus but may also reflect differences in the experimental conditions of the two methods e.g. single molecule impact vs. bulk molecules in the film. Nonetheless, several products giving insight into the dominant reactions pathways in the model system C_2H_6 / CD_3CN have been monitored. More comprehensive and quantitative follow-up studies to the present fast screening of the reactions taking place in this system as well as in CH_3CN deposited on top of hydrocarbon layers will be undertaken in the future.

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Future collaboration with host institution
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A longer collaboration, probably lasting one year, is very likely after the end of my doctoral studies i.e. with a launch most likely in 2006.

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Projected publications/articles resulting or to result from the grant
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The manuscript of a publication as well as a presentation for LEEMI IV are in preparation.

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Other comments
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A program for the analysis of TDS data was developed to increase the production efficiency. Since the new program uses the same interface as was used here before and automates all notoriously repeated steps of the data analysis, it saves most of the time that was spent on this non-scientific part of the research.

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[1] Chem. Phys. Letters 381 (2003) 216-222