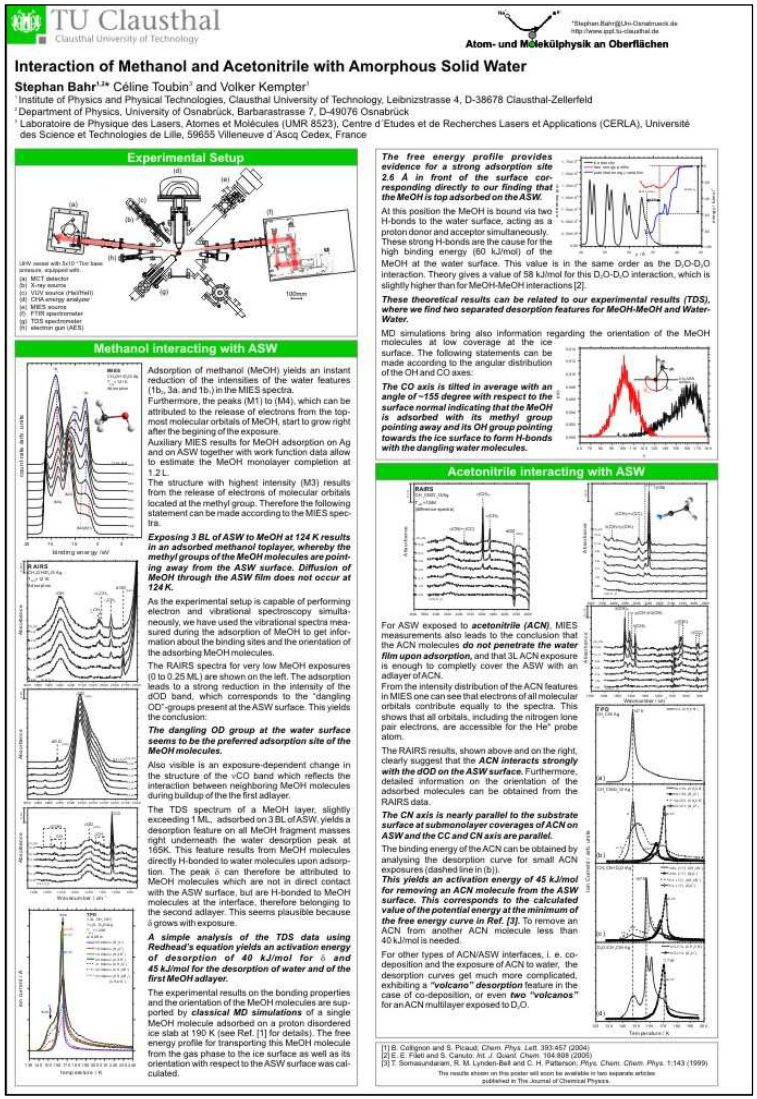
Poster #1



TU Clausthal
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Atom- und Molekülphysik an Oberflächen

Interaction of Methanol and Acetonitrile with Amorphous Solid Water

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Experimental Setup

Methanol interacting with ASW

Adsorption of methanol (MeOH) yields an instant reduction of the intensities of the water features ($1b_1$, $3a_1$ and $1b_2$) in the MIES spectra. Furthermore, the peaks (M1) to (M4), which can be attributed to the release of electrons from the topmost molecular orbitals of MeOH, start to grow right after the begining of the exposure.
Auxiliary MIES results for MeOH adsorption on Ag and on ASW together with work function data allow to estimate the MeOH monolayer completion at 1.2 L.
The structure with highest intensity (M3) results from the release of electrons of molecular orbitals located at the methyl group. Therefore the following statement can be made according to the MIES spectra.

Exposing 3 BL of ASW to MeOH at 124 K results in an adsorbed methanol toplayer, whereby the methyl groups of the MeOH molecules are pointing away from the ASW surface. Diffusion of MeOH through the ASW film does not occur at 124 K.

As the experimental setup is capable of performing electron and vibrational spectroscopy simultaneously, we have used the vibrational spectra measured during the adsorption of MeOH to get information about the binding sites and the orientation of the adsorbing MeOH molecules.
The RAIRS spectra for very low MeOH exposures (0 to 0.25 ML) are shown on the left. The adsorption leads to a strong reduction in the intensity of the dOD band, which corresponds to the "dangling OD"-groups present at the ASW surface. This yields the conclusion:

The dangling OD group at the water surface seems to be the preferred adsorption site of the MeOH molecules.

Also visible is an exposure-dependent change in the structure of the νCO band which reflects the interaction between neighboring MeOH molecules during buildup of the the first adlayer.
The TDS spectrum of a MeOH layer, slightly exceeding 1 ML, adsorbed on 3 BL of ASW, yields a desorption feature on all MeOH fragment masses right underneath the water desorption peak at 165K. This feature results from MeOH molecules directly H-bonded to water molecules upon adsorption. The peak δ can therefore be attributed to MeOH molecules which are not in direct contact with the ASW surface, but are H-bonded to MeOH molecules at the interface, therefore belonging to the second adlayer. This seems plausible because δ grows with exposure.

A simple analysis of the TDS data using Redhead's equation yields an activation energy of desorption of 40 kJ/mol for δ and 45 kJ/mol for the desorption of water and of the first MeOH adlayer.

The experimental results on the bonding properties and the orientation of the MeOH molecules are supported by ***classical MD simulations*** of a single MeOH molecule adsorbed on a proton disordered ice slab at 190 K (see Ref. [1] for details). The free energy profile for transporting this MeOH molecule from the gas phase to the ice surface as well as its orientation with respect to the ASW surface was calculated.

The free energy profile provides evidence for a strong adsorption site 2.6 Å in front of the surface corresponding directly to our finding that the MeOH is top adsorbed on the ASW.

At this position the MeOH is bound via two H-bonds to the water surface, acting as a proton donor and acceptor simultaneously. These strong H-bonds are the cause for the high binding energy (60 kJ/mol) of the MeOH at the water surface. This value is in the same order as the D_2O-D_2O interaction. Theory gives a value of 58 kJ/mol for this D_2O-D_2O interaction, which is slightly higher than for MeOH-MeOH interactions [2].

These theoretical results can be related to our experimental results (TDS), where we find two separated desorption features for MeOH-MeOH and Water-Water.

MD simulations bring also information regarding the orientation of the MeOH molecules at low coverage at the ice surface. The following statements can be made according to the angular distribution of the OH and CO axes:

The CO axis is tilted in average with an angle of ~155 degree with respect to the surface normal indicating that the MeOH is adsorbed with its methyl group pointing away and its OH group pointing towards the ice surface to form H-bonds with the dangling water molecules.

Acetonitrile interacting with ASW

For ASW exposed to ***acetonitrile (ACN)***, MIES measurements also leads to the conclusion that the ACN molecules ***do not penetrate the water film upon adsorption***, and that 3L ACN exposure is enough to completly cover the ASW with an adlayer of ACN.
From the intensity distribution of the ACN features in MIES one can see that electrons of all molecular orbitals contribute equally to the spectra. This shows that all orbitals, including the nitrogen lone pair electrons, are accessible for the He* probe atom.
The RAIRS results, shown above and on the right, clearly suggest that the ***ACN interacts strongly with the dOD on the ASW surface.*** Furthermore, detailed information on the orientation of the adsorbed molecules can be obtained from the RAIRS data.

The CN axis is nearly parallel to the substrate surface at submonolayer coverages of ACN on ASW and the CC and CN axis are parallel.

The binding energy of the ACN can be obtained by analysing the desorption curve for small ACN exposures (dashed line in (b)).
This yields an activation energy of 45 kJ/mol for removing an ACN molecule from the ASW surface. This corresponds to the calculated value of the potential energy at the minimum of the free energy curve in Ref. [3]. To remove an ACN from another ACN molecule less than 40 kJ/mol is needed.

For other types of ACN/ASW interfaces, i. e. co-deposition and the exposure of ACN to water, the desorption curves get much more complicated, exhibiting a ***"volcano" desorption*** feature in the case of co-deposition, or even ***two "volcanos"*** for an ACN multilayer exposed to D_2O.

[1] B. Collignon and S. Picaud, *Chem. Phys. Lett.* 393:457 (2004)
[2] E. E. Fileti and S. Canuto, *Int. J. Quant. Chem.* 104:808 (2005)
[3] T. Somasundaram, R. M. Lynden-Bell and C. H. Patterson, *Phys. Chem. Chem. Phys.* 1:143 (1999)

The results shown on this poster will soon be available in two separate articles published in The Journal of Chemical Physics.

Interaction of Methanol and Acetonitrile with Amorphous Solid Water

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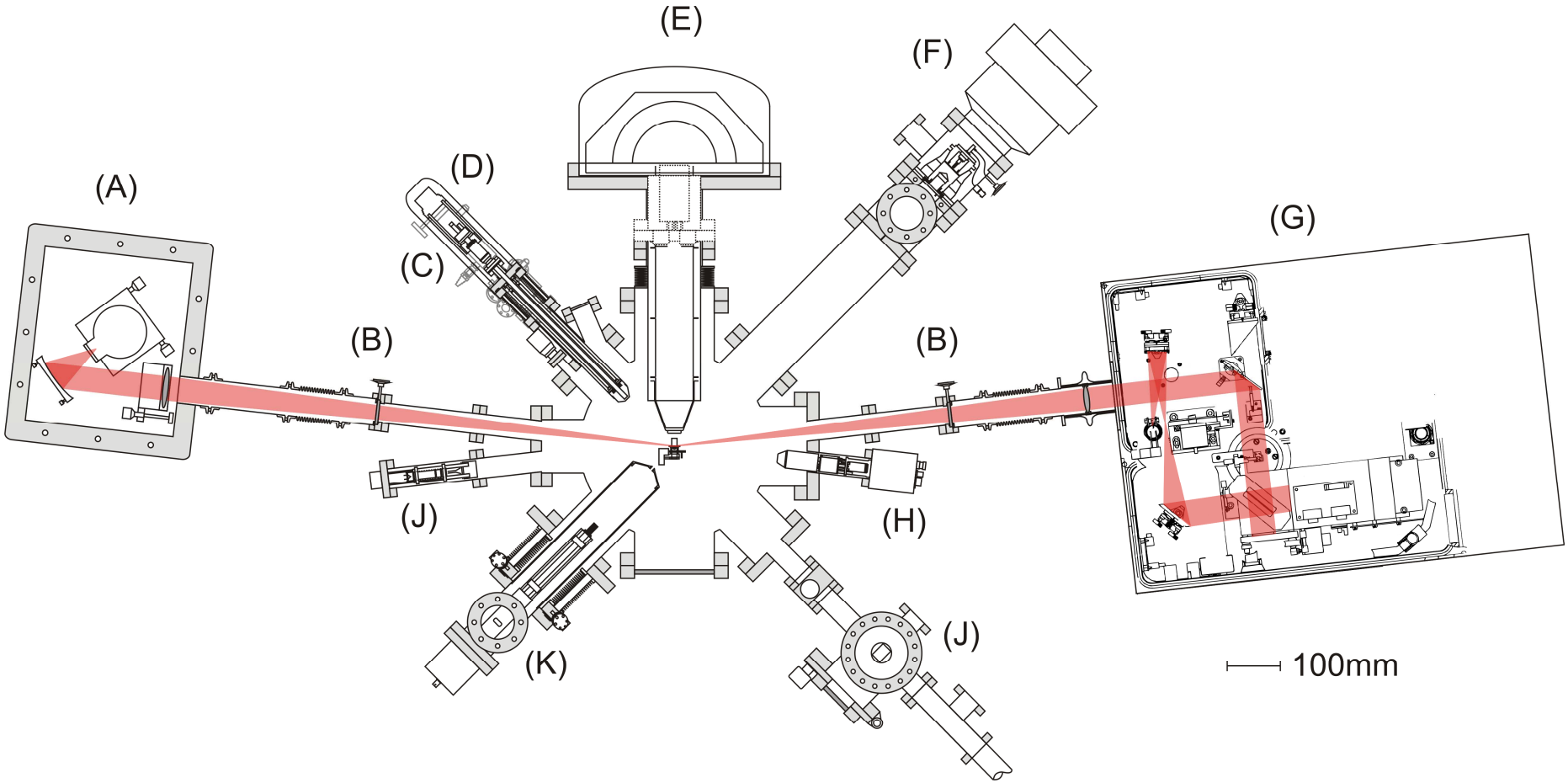
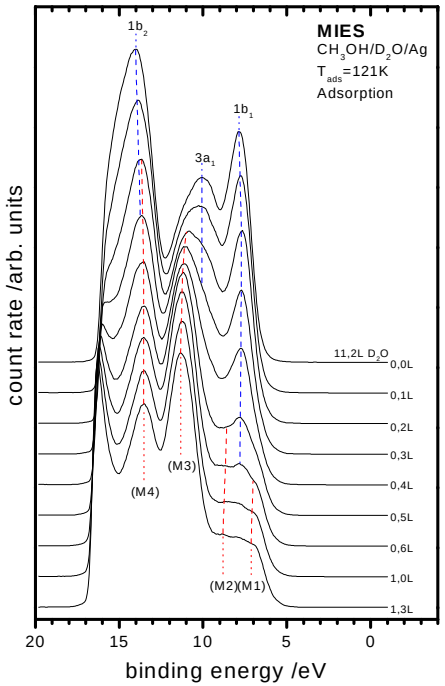
Experimental Setup:



(A) Photodetector
(B) Differentially pumped KBr-viewports
(C) Omicron HIS 13 VUV-source
(D) Fisons XR3E2-234 XPS-source
(E) Leybold Ea10 energy analyzer
(F) MIES-source
(G) Bruker IFS 66v/S FT-IR spectrometer
(H) PHI Model 04-191 sputter ion gun
(J) Sample load lock
(K) Pfeiffer QMG 422 differentially pumped QMS
(L) VSW EG5 electron source

Methanol (CH_3OH)/ASW :



MIES: (***M***etastable ***I***nteraction ***E***lectron ***S***pectroscopy)

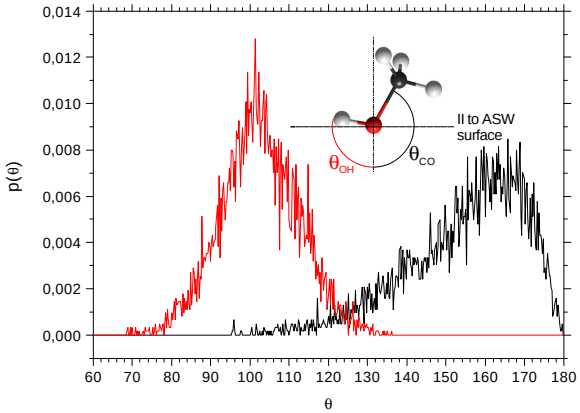
- MeOH is top adsorbed on ASW at 124K
- Methyl group is pointing away from the surface

RAIRS:

- dangling OD group at ASW surface is preferred adsorption site

TPD:

- yields an activation energy of desorption of
  40kJ/mol for removing MeOH of MeOH
  ≥45kJ/mol for removing MeOH of ASW surface



Classical MD simulation:

- The free energy profile provides evidence for
  a strong adsorption site 2.6 Å in front of the surface
- Show that MeOH acts as a proton donor and acceptor,
  thus forming two H-bonds with the ASW surface
- Theory also provides information on the binding geometry
  of the MeOH on top of the ASW surface

Acetonitrile (CH_3CN)/ASW:

MIES:

- ACN is top adsorbed on ASW

RAIRS:

- As for MeOH the dangling OD on the ASW surface is the preferred adsorption site
- CN and CC axes are nearly parallel to the substrate surface at submonolayer-coverages of ACN on ASW
- Re-organization of the ACN monolayer on ASW occurs during further exposure

TPD:

- yields an activation energy of desorption of
  39kJ/mol for removing an ACN from ACN
  ≥45 kJ/mol for removing an ACN from the ASW surface

- other adsorption scenarios result in much more complicated TPD spectra