ESRF	**Experiment title:** Correlating Organic Molecule - Metal Distances with Charge-Transfer Efficiency	**Experiment number:** SI-1359
Beamline: ID 32	**Date of experiment:** from: 12/04/2006 to: 18/04/2006	**Date of report:** 24/07/2006
Shifts: 18	**Local contact(s):** Dr. Jörg Zegenhagen	*Received at ESRF:*

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Report:

1. Introduction

As outlined in the proposal, the purpose of the project was to measure bonding distances and thus the conformation of organic electron acceptor molecules on metal surfaces as function of interaction strength (*i.e.*, the amount of charge transfer) by variation of (i) acceptor electron affinity, (ii) metal chemical potential, and (iii) temperature. This would be a significant step towards establishing a comprehensive correlation of these parameters for our general understanding of molecule/metal interactions and interface energetics. The information obtained will be very useful in highlighting the potential of an interface modification scheme that we have recently proposed [1,2]. In particular, XSW data should not be the only experimental technique that is used for sample characterization. The combination of a number of surface science techniques (XSW, photoelectron spectroscopy, scanning tunneling spectroscopy) in conjunction with state-of-the-art theoretical modeling should lead to progress in the field, and will allow to benchmark and improve presently available theoretical models.

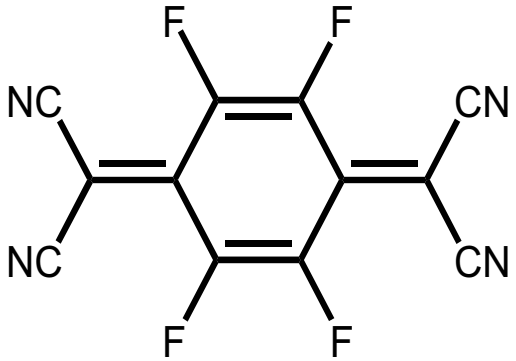

Illustration 1: Chemical structure of F_4TCNQ.

Specifically, the electron acceptor molecule tetrafluoro-tetracyanoquinodimethane (F_4TCNQ; Fig. 1) was chosen for the present study. Metal single crystal surfaces used were Ag(111) and Cu(111). Unfortunately, the quality of our Ag(111) crystal did not suffice since the normal incidence rocking width of > 1.2 eV did not allow for meaningful XSW measurements. However, the Cu(111) substrate turned out to be of high quality, with the a normal incidence rocking width of *ca.* 0.90 eV (close to the intrinsic value), and could successfully be used for XSW measurements. Due to a lack of time (long XSW scans, see below) we could not perform experiments with a second electron acceptor molecule. - Below we give a short summary of results from the beamtime (SI-1359) at ID32.

2. XPS and XSW measurements on monolayers of F_4TCNQ

The relatively weak photoelectron signals from a submonolayer of F_4TCNQ/Cu(111) required relatively long integration times. Since the stability of the monochromator allowed only for short XSW scans of approximately 30 minutes, we generally took several XSW scans which were added later.
Several films of F_4TCNQ with different coverages in the submonolayer and monolayer regime were prepared, using the quartz crystal microbalance and the XPS signal as thickness monitor. Representative core level spectra are displayed in Fig. 2.

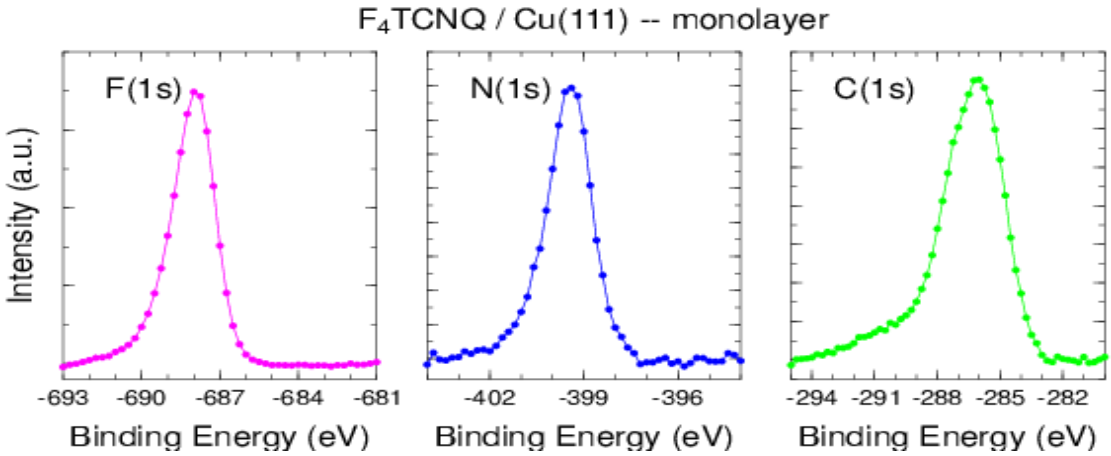

Illustration 2: XPS signal from a submonolayer of F_4TCNQ on Cu(111)

On the basis of the XPS spectra we found indications of beam damage after prolonged exposure to X-rays (on the order of several hours), evidenced by the appearance of a low binding energy component of the F(1s) core level. This indicated the formation of F-Cu bonds, and consequently the loss of molecular integrity. For further data evaluation, we only used spectra that did not exhibit the low binding energy component in the F(1s) spectra.

First, the XSW signal from the clean copper surface was measured to characterize the substrate. After evaporation of the organic layers we obtained high quality XSW data from the F_4TCNQ layers.
By comparison of the N(1s), C(1s), and the F(1s) signals (Fig. 3) already their different shape and position indicates that the nitrogen is located closer to the metal surface than the fluorine. Due to the comparably low coherent fraction in the C(1s) scan no reliable information can be obtained on the position of the carbon atoms. Furthermore, the fact that nitrogen and fluorine exhibited different positions indicates that the adsorbed molecule is not planar, and consequently a number of different distances for chemically inequivalent carbons is expected. From the preliminary analysis of the photo yield we obtain the coherent position of the nitrogen (~ 2.69 Å) and fluorine (~ 3.28 Å) atoms in the molecule. At present, theoretical calculation using density functional theory are being conducted on model systems, in order to provide a microscopic understanding of the highly distorted adsorption-geometry of F_4TCNQ on Cu(111).

By heating the samples to different temperatures between T=30°C and T=300°C we studied annealing effects within the F_4TCNQ layers. However, no systematic changes were found.

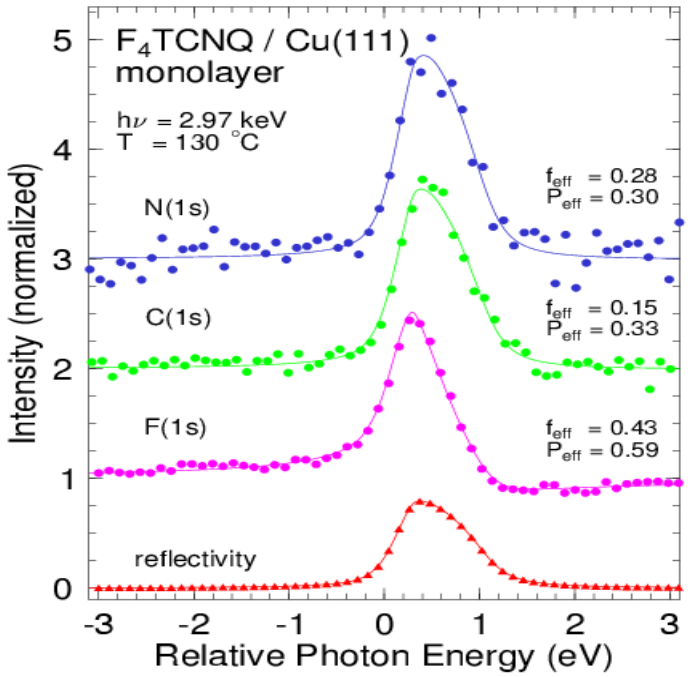

Illustration 3: XSW from signals from a submonolayer of F_4TCNQ on Cu(111) with a preliminary analysis

3. Summary

Overall, the experiment was very successful and we are currently working on the further analysis of the data and the preparation of a manuscript for publication, including XSW, photoemission, and theoretical results [3].

We wish to thank our local contact for the excellent support on ID32.

4. References

[1] N. Koch, S. Duhm, J. P. Rabe, S. Rentenberger, R. L. Johnson, J. Klankermayer, F. Schreiber, *Tuning the Hole Injection Barrier Height at Organic/Metal Interfaces With (Sub-) Monolayers of Electron Acceptor Molecules,* Appl. Phys. Lett. **87** (2005) 101905.

[2] N. Koch, S. Duhm, A. Vollmer, J. P. Rabe, R. L. Johnson, *Optimized hole injection with strong electron acceptors at organic-metal interfaces*, Phys. Rev. Lett. **95** (2005) 237601

[3] L. Romaner, G. Heimel, J.-L. Bredas, A. Gerlach, F. Schreiber, R. L. Johnson, S. Duhm, N. Koch, E. Zojer, *Impact of charge transfer and molecular distortions on the electronic sttructure of metal-organic interfaces,* to be submitted