

Symmetry of bonding states determined by resonant inelastic x-ray scattering: Ethylene/Cu(110)

P. Väterlein¹, L. Triguero², M. Weinelt¹, A. Föhlisch¹, J. Hasselström¹, N. Wassdahl¹, O. Karis¹, L.G.M. Petterson², H. Ågren³, J. Stöhr⁴, and A. Nilsson¹

¹Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala Sweden.

²FYSIKUM, University of Stockholm, Box 6730, S-113 85 Stockholm, Sweden.

³Institute of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden.

⁴IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA.

INTRODUCTION

During the last years *X-ray emission (XE)* spectroscopy has become a powerful tool in the study of the bonding of molecules on solid surfaces [1]. It combines the element and (atomic) site specificity of a core level spectroscopy with a sensitivity towards the chemical environment similar to valence photoelectron spectroscopy. In a XES experiment the fluorescence photons from the sample are analyzed following a core excitation. If the primary excitation is resonant, i.e. corresponds to a NEXAFS resonance, excitation and decay have to be treated as one single inelastic scattering process [2]. In comparison with “ordinary” XE spectra *resonant inelastic x-ray scattering (RIXS)* spectra of well-defined adsorbate systems contain additional information about the symmetry of the participating electronic states since primary excitation and radiative decay are governed by dipole selection rules [3]. These can be exploited by studying the dependence of the RIXS spectra on the polarization of the incoming light and the angle dependence of the emitted radiation.

For strongly coupled adsorbates, however, the difference between RIXS and XE spectra should (almost) vanish since the core excited electron is delocalized rapidly, which leads to a less well defined core excited intermediate state. Such observations have been reported for resonantly excited Auger spectra of chemisorbed molecules [4].

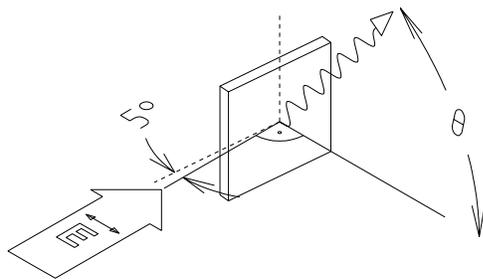
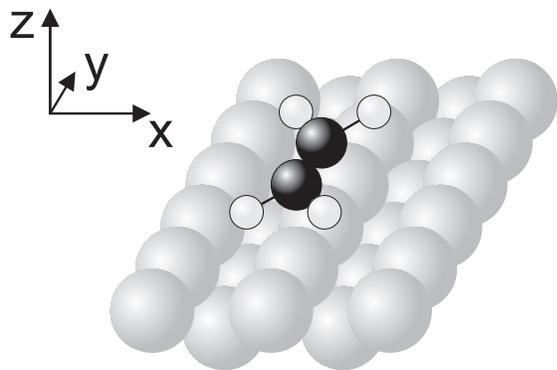


Figure 1: Top: adsorption geometry of ethylene on Cu(110). Bottom: schematic view of the experimental geometry used in the present work. In this geometry the π^* -resonance of the ethylene molecule could be excited with maximum efficiency.

In the present abstract we report RIXS measurements of ethylene adsorbed on the Cu(110) surface, where significant changes in the decay spectrum in dependence of the primary excitation are observed. To interpret these changes and to elucidate the coupling mechanism between the ethylene molecules and the Cu-surface, model calculations have been performed within the framework of *Density Functional Theory (DFT)*.

EXPERIMENTAL SETUP AND DATA EVALUATION

The experiments have been performed at Beamline 8.0. The endstation consists of two UHV chambers for sample preparation and analysis. The base pressure in the system was $1 \cdot 10^{-10}$ mbar. The analysis chamber is rotatable around an axis parallel to the incoming beam and houses an electron energy analyzer (Scienta SES 200) [5], an x-ray emission spectrometer [6] (both mounted perpendicular to the beam) and a multichannel plate de-

detector for x-ray absorption (XA) measurements. Two Cu(110) single crystals were mounted on a manipulator at an angle of about 5° between the surface and the direction of the incoming light (cf. Fig.1) with their [1-10] directions parallel and perpendicular, respectively, to the plane of incidence. The crystals could be rotated about the axis of the incoming beam thus enabling independent variation of the polarization of the incoming light (by rotation of the sample) and the direction of detection of the emitted light (by rotation of the spectrometers). Saturated monolayers were prepared by dosing ethylene on the Cu surface at a temperature of 80K.

RIXS spectra were measured in normal ($\theta = 0^\circ$) and grazing ($\theta = 80^\circ$) emission geometries on both crystals. From these raw spectra the background signal from the substrate and the elastically scattered peak were removed. Due to the only twofold symmetry of the Cu(110) surface and to the „di- σ “ adsorption geometry of the ethylene molecules with their C-C bond parallel to the [1-10] direction of the surface (cf. Fig. 1), spectra for all three polarization directions of the emitted light could be extracted from the measured spectra assuming equal population of the C $2p_x$ -, p_y -, and p_z -orbitals contributing to the different molecular orbitals and of dipolar distribution of the emitted fluorescence photons.

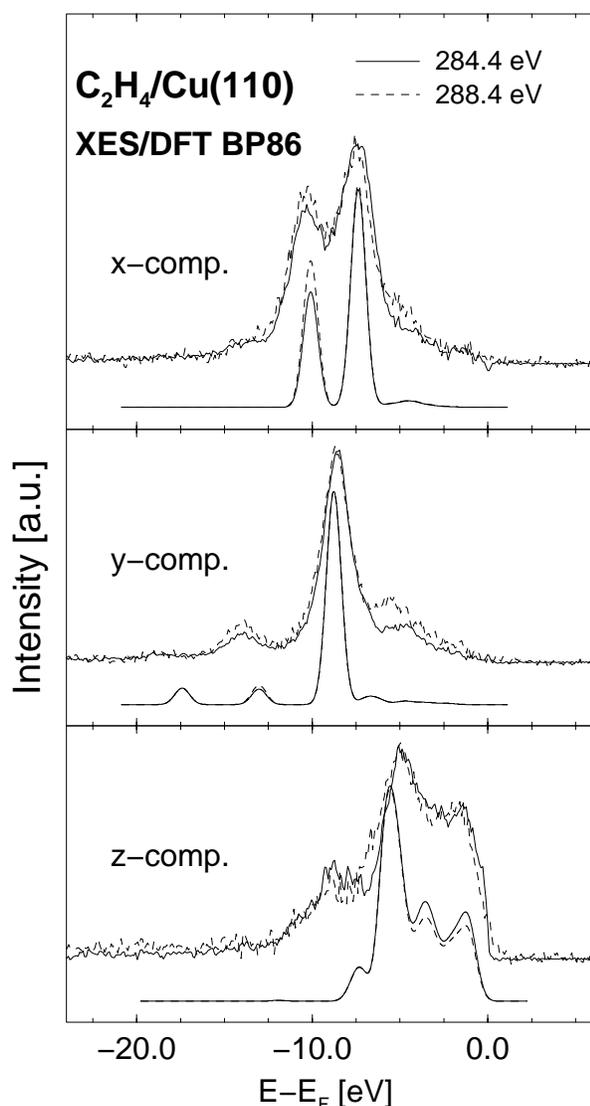


Figure 2: Experimental and calculated RIXS spectra of ethylene/Cu(110) for three different polarizations of the emitted radiation after excitation at two different photon energies.

THEORETICAL BACKGROUND

For the model calculations the „deMon“ program package [7] was used which allows self consistent calculation of the electronic structure of molecules and clusters using the Kohn-Sham formalism. For the exchange and correlation interactions the gradient corrected functionals described by Becke [8] and Perdew and Wang [9], respectively, have been used. The substrate was simulated by a cluster consisting of 86 Cu atoms. For a central cluster of 14 atoms all electrons were treated explicitly while for the rest of the Cu atoms only the 4s electrons were included explicitly into the calculation. The geometry of the adsorbate was optimized during the calculations while the geometry of the cluster was fixed to the experimental bulk values. The dipole matrix elements for the primary excitation and the radiative decay were calculated using ground state wave functions (frozen orbital approximation) and the Kramers-Heisenberg equation [10] was employed to calculate the RIXS intensities. To facilitate comparison with the experimental data, the spectra have been broadened by a gaussian of 0.8 eV width (FWHM).

RESULTS AND DISCUSSION

Figure 2 shows the RIXS spectra for three different polarizations of the emitted light after excitation at two different photon energies. Below the experimental spectra the corresponding calculated spectra are plotted. All spectra have been normalized to maximum intensity. The lower excitation energy (284.8 eV) corresponds to an exci-

tation into the π^* resonance of ethylene while the higher energy (288.4 eV) corresponds to an excitation into the rydberg manifold. The x - and y -components comprise those states derived from “ σ -orbitals” of the ethylene molecule, while the z -component contains the “ π -orbitals”. The energy scale of the plot is with respect to the Fermi level which corresponds to an emission energy of 284.3 eV as was determined by photoelectron spectroscopy (PES). In the experimental spectra for all three polarizations subtle but significant differences between the two excitation energies can be observed which are well reproduced in the calculations.

For the free ethylene molecule strict symmetry selection rules apply following resonant excitation: the π^* -resonance is due to excitation of a C 1s electron into an orbital of *gerade* parity ($1b_{3g}$). Thus only orbitals with *gerade* parity contribute to the resonant decay spectrum. For the chemisorbed molecule the inversion symmetry is lifted. The selection rules are now those of the C_{2v} point group. Nevertheless a stronger variation between resonant and off-resonant emission spectra is to be expected. The reason for the experimentally observed weak variations is revealed by the calculations: across the Fermi level a mixing of states derived from the *highest occupied molecular orbital (HOMO)* of the ethylene molecule ($1b_{2u}$) and of states derived from the *lowest unoccupied molecular orbital (LUMO)* ($1b_{3g}$) occurs. Therefore the resonant excitation does not only comprise excitations in π -states of former *gerade* parity, which now belong to the b_1 -representation but also into in π -„ungerade“ states (now a_1) derived from the HOMO. The same is true for the off-resonant excitation but with different weights of the LUMO- and HOMO-like states which is the reason for the observed excitation energy dependence. This mixing of states can be observed directly in the z -component spectra: in the gasphase the XE spectrum of ethylene contains only one peak with π -symmetry ($1b_{2u}$). The z -component spectra in Fig. 2, however, show a broad structure which extends from -12 eV up to the Fermi level. According to the DFT calculations this structure also contains intensity from decay of both HOMO- and LUMO-like states. In contrast the σ -orbitals of the ethylene molecule remain essentially unchanged as can be concluded from the x - and y -component spectra which are very similar to the corresponding components of the gas phase XE spectrum [11]. The observed small differences are basically due to a weak distortion of the molecules upon adsorption. This is also corroborated by the DFT calculations.

Based on these findings a significant contribution of the σ -orbitals to the chemical bond between the ethylene molecule and the Cu(110) surface can be excluded. The bonding is due to a π -donation π^* -backdonation mechanism. The DFT calculations furthermore show a predominant contribution of Cu 3d states to the bonding orbitals

CONCLUSIONS

In conclusion we used the *resonant inelastic x-ray scattering (RIXS)* technique to investigate the chemical bond of ethylene molecules on the Cu(110) surface. Our spectra show a subtle but significant dependency on the exciting photon energy which proves a mixing of states with the symmetries of the HOMO and LUMO of ethylene, respectively, above the Fermi level. A similar mixing can be observed directly as broadening of emission lines in the z -component of the XE spectrum. These experimental findings are supported by model calculations carried out within the framework of *density functional theory (DFT)*. A significant contribution of the σ -orbitals of ethylene to the adsorbate-substrate bond could not be found. Therefore our experimental and quantum-chemical results lead unambiguously to a description of the chemical bond between the ethylene molecule and the Cu(110) surface by a π -donation π^* -backdonation mechanism.

ACKNOWLEDGEMENTS

The authors would like to acknowledge valuable and stimulating discussions with Joseph Nordgren and Nils Mårtensson.

REFERENCES

- [1] A. Nilsson, M. Weinelt, T. Wiell, P. Bennich, O. Karis, N. Wassdahl, J. Stöhr, M.G. Samant, *Phys. Rev. Lett.* **78**(14) 2874 (1997).
- [2] T. Åberg, *Physica Scripta* **21**, 495 (1990).
- [3] P. Glans, K. Gunnelin, P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, H. Ågren, F. Kh. Gel'mukhanov, T. Warwick, E. Rotenberg, *Phys. Rev. Lett.* **76**(14) 2448 (1996).
- [4] W. Wurth, C. Schneider, R. Treichler, D. Menzel, and E. Umbach, *Phys. Rev. B* **37**, 8725 (1988); A. Sandell, O. Björneholm, A. Nilsson, J.N. Andersen, and N. Mårtensson, *Phys. Rev. B* **49**(15) 10136 (1994).
- [5] N. Mårtensson, P. Baltzer, P. Brühweiler, J.O. Forsell, A. Nilsson, A. Stenborg, and B. Wannberg, *J. Electron Spectrosc. Relat. Phenom.* **70**, 117 (1994).
- [6] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, *Rev. Sci. Instrum.* **60**, 1690 (1989).
- [7] D.R. Salahub, R. Fournier, P. Mlynarski, I. Papai, A. St-Amant, and J. Ushio in *Density Functional Methods in Chemistry*, J. Labanowski and J. Andzelm eds., Springer, New York (1991) p. 77; A. St-Amant, PhD thesis, Université de Montréal, 1992. The present version of the program has been substantially modified by L.G.M. Petterson.
- [8] A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [9] J.P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8822 (1986).
- [10] H.A. Kramers and W. Heisenberg, *Z. Phys.* **31**, 681 (1925); J.J. Sakurai, *Advanced Quantum Mechanics*, Addison Wesley (1967).
- [11] J. Nordgren, private communication.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, by the Swedish Natural Science Research Council (NFR), the Swedish Institute (SI), and the Göran Gustafsson Foundation for Research in Natural Science and Medicine. One of us (P.V.) gratefully acknowledges a stipend from the Deutsche Forschungsgemeinschaft .

Principal investigator: Anders Nilsson, Dept. of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden. Email: anders.nilsson@fysik.uu.se. Telephone: +46-(0)18-471-3609. Fax: +46-(0)18-471-3611.