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Adsorption of Benzene Derivatives on the Ag(110) at 90K Studied by Collision-energy-resolved Electron Spectroscopy with He*(2^3S) Metastable Atoms

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Penning ionization electron spectroscopy (PIES) is a widely known method for investigating the electron structure of the molecules in the valence band. This method has been even more developed to a powerful tool for investigation of dynamic and anisotropy in interactions between a target molecule and the metastable atoms of the probe gas (mainly He*(2^3S)). In PIES the spectra can be collected in dependence on two parameters: the common electron kinetic energy and the energy of collision between a target and He*(2^3S). This technique, known as 2D-PIES, has been widely used for the study of various molecules in gas phase experiments.

The cuts of two-dimensional data at selected collision energies provide the usual PIES-spectra while cuts at selected ionization bands give the collision energy dependence of partial ionization cross sections (CEDPICS). In the case of a molecular orbital (MO) mainly localizing around repulsive region, the CEDPICS-slope for this MO is positive, because the metastable atom with larger kinetic energy reaches the inner region (where the MO-overlapping and the reaction probability is high) of the target against the repulsive interaction. On the other hand, a negative CEDPICS can be assigned to an attractive interaction with He* around the extending region of corresponding MO, because the metastable atom is deflected to this area of the molecule by the attractive interaction. In this case, the number of deflected trajectories decreases with the increase of collision energy. Since the electron distributions of individual MOs are more or less localized on the different spatial parts of the molecule, different CEDPICSs for various ionic states can be connected to the anisotropy in interaction between He*(2^3S) and the target molecule. Knowing the value of the CEDPICS-slope, the chemical activity for various parts or its functional parts of the target can also be estimated.

The spectroscopy with metastable atoms is also intensively used for investigation on surfaces. This method is also known as MIES (Metastable Impact Electron Spectroscopy) or MAES (Metastable Atom Electron Spectroscopy). On condition that no resonant transfer between He* 2s state and an occupied state of the target takes place, which is typical for dielectric adsorbates, the most important electron process for the surfaces is Auger de-excitation (AD), which is similar to Penning ionization process for gas phase targets. These processes take place when the inner-shell unoccupied 1s orbital of He*(2^3S) overlaps the field of MOs localizing outside the collision boundary surface of the target, then 1s MO is filled by a target electron and the 2s electron is ejected and can be analyzed. Therefore, on the basis of similar kind for interaction of metastable atoms with surfaces and gas targets, application of the 2D-PIES method for investigations on a surface can also be useful.

Adsorption of benzene on Ag(110), which is investigated in the framework of the project for 2D-PIES on the surfaces, is shown in the Figure 1. Along with some irregularities in the electron

energy range 0 – 2.5 eV, which are very likely caused by peculiarity of the experimental setup with a electron analyzer of retarding type, five bands in the energy range 3 – 12 eV, which can be easily assigned to benzene on the basis of the gas-phase spectrum, can be distinctly observed. Due to high surface sensitivity, the intensity of the bands at the adsorption reaches full intensity already at monolayer (ML) covering. Thus after exposition of ca. 35 L, a closed layer is formed on the silver surface at the temperature of the liquid nitrogen. For the 2D-PIES measurements, the films corresponded to the spectra exposed with 15 L and 95 L, with covering ca. 0.5ML and 2 ML respectively, were selected.

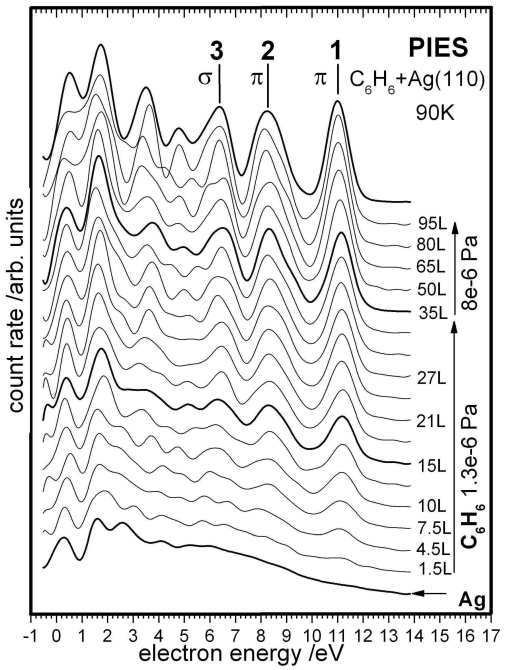

Figure 1. C_6H_6 adsorption on the Ag(110) surface at 90 K

The results for the collision energy dependence of partial ionization cross sections are sown in the Figure 2 for three most intensive bands 1 – 3. The curves for covering of 0.5 ML are drawn taking into account the background correction. As in the case of benzene in the gas-phase, the π MOs 1 and 2 have negative CEDPICS slopes indicating an attractive interaction with He* for related target regions. The band 3, which can be assigned to σ_{CH} MO, has a negative CEDPICS for the case of 0.5 ML while in the gas-phase the σ MOs show usually a repulsive character; taking into account a very strong attractive character of the Ag(110) surface, it may be an evidence of planar adsorption of the benzene molecules, which has been already observed for some metal surfaces. When a benzene molecule is localized apart of the silver surface, like in the case of 3 ML covering, the repulsive character of the σ regions is also indicated by CEDPICS. We can also conclude, that there is an additional factor causing the more intensive repulsive interaction of the σ bands: A comparison of the spectra for ~ 1 ML and ~ 3 ML (~ 35 L and 95 L respectively), shows larger intensity in the region 3 – 7 eV, which is assigned to the σ bands. It may indicate, that σ regions (i.e. edges) of the molecules in next layers can be easier reached by the metastable He* molecules, which means a different (not planar) kind of adsorption.

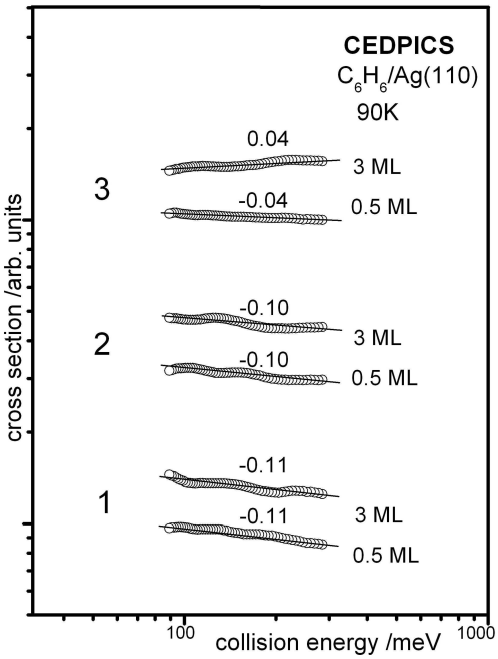

Figure 2. Collision energy dependence of ionization intensitv for bands 1 – 3

Therefore spectroscopy with metastable atoms, especially with resolving collision energy, allows us to obtain electron structure of the adsorbed films as well as information on orientation adsorbed molecules and on the interaction of different regions of the film with metastable atoms.