Dr. Serge Monturet

Universität Potsdam

Institut für Chemie

Theoretische Chemie

Karl-Liebnecht-Strasse 24-25,

Haus 25, 14476 Potsdam-Golm,

Germany.

Brief scientific report. Stay in San Sebastian, Spain, hosted by Prof A. Arnau from 15/03 to 28/03 2009. Reference code: COST-STSM-CM0601-04515.

Motivated by the experimental results obtained in the group of Prof. J. I. Pascual (Freie Universität, Berlin, Germany), and the theoretical approach developed by Prof. Arnau and co-workers (Universidad del Pais Vasco, San Sebastian, Spain), we investigate the formation of dispersive bands in π-stacked tetrathiafulvalene (TTF) molecules adsorbed on lead (Pb 111).

The measures obtained by M. Konschake in his diplomarbeit[1] show that the chemisorption geometry of the TTF molecules is qualitatively different when adsorbed on gold and on lead. Actually, in the case of Au(111), the molecule tends to be flat, slightly tilted due to the formation of sulfur-gold bonds with the surface. When adsorbed on Pb (111), its plane is perpendicular to the metal surface. And when studied in high coverage conditions, it has been shown that the TTF molecules tend to form dimers.

On the other hand, it is known that the TTF is a strong charge donnor, and calculations have shown that, when adsobed on gold, the TTF positively charges leading to strong coulombic interactions between them[2]. The idea of calculating the dimer structure measured by M. Konschake and the adsorbed isolated molecule on lead came rapidly as a first step. Prof. A. Arnau also suggested the possibility of calculating a chain of adsorbed π-stacked TTF molecules, taking advantage of both theoretical and experimental results concerning the aforementioned dimer structure. The chains can evetually give rise to a band structure if the molecules are close enough. In figure 1, we show the dispersion of the bands actually formed by the TTF chains, they have been calculated using density functional theory as implemented in the VASP code[3]. The distance between two consecutive molecules is 4 Å. As the measured distance is shorter, the bands are expected to be even more dispersive.

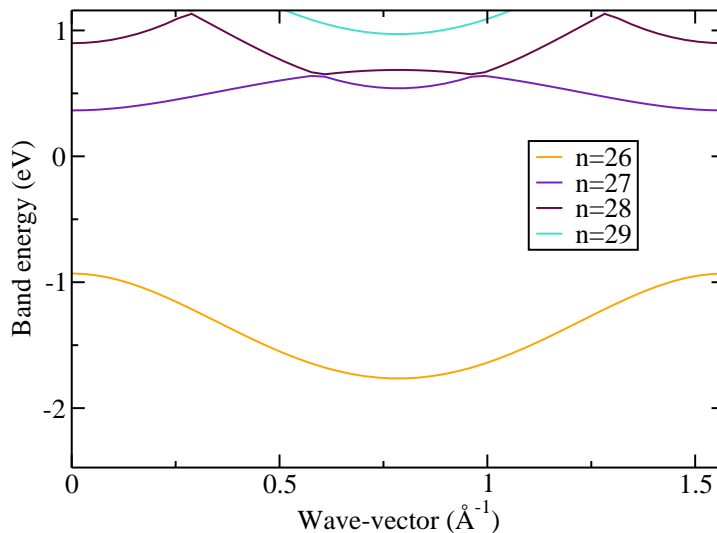The next step, is to adsorb the chain on the surface following the indi-

Figure 1: *Band structure of a TTF chain along the stacking direction. Band index n=26 corresponds to the highest occupied band.*

cations of the experimental results, namely the measured distance between TTF molecules forming a dimer. Once fully relaxed, each TTF is expected to give charge to the surface depleting the band associated with the highest occupied molecular orbital. If this occurs, a one-dimensional metal is obtained because the Fermi level would lie below the maximum energy of the highest occupied band.

A satisfying way to study the coupling of the molecules to the surface is the calculation of the projected density of states (PDOS). The role of the molecular states can be revealed by projecting the DOS on the TTF molecular orbitals. However, if the molecules interact with each other in such a way that the orbitals of the TTF lose molecular character, giving rise to bands, some wave-vector dependence is to be expected in the energy of the molecules orbitals. This is the reason why the PDOS is not sufficient to describe this kind of systems. Instead, a wave-vector-resolved PDOS can be calculated. As shown in reference[4], the k-resolved PDOS is a powerful tool to investigate these periodic systems. The next step will consist in fully relaxing the TTF chains and applying this method to obtain the behaviour of the bands, and conclude on the nature of the electronic structure of the adsorbed TTF molecules.

References

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