

Monitoring Delocalization of Molecular Orbitals at 4-Flouro-Benzenethoil Monolayer/Au(111)



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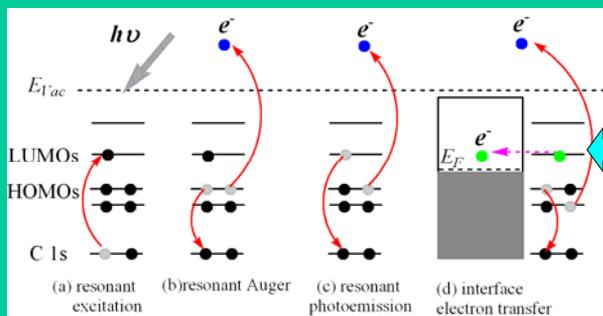
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Introduction

- Molecules containing a high degree of π -conjugation have been of great interest due to their unique properties and their promising applications in molecular electronics.
- The role of molecule-surface interface is one of the most important issues in molecular electronics. Moreover, the electron transfer process across the molecule/electrode junction is still poorly understood and problems related to this topic, such as the dynamics of electron transfer and the transfer mechanism, remain unresolved.

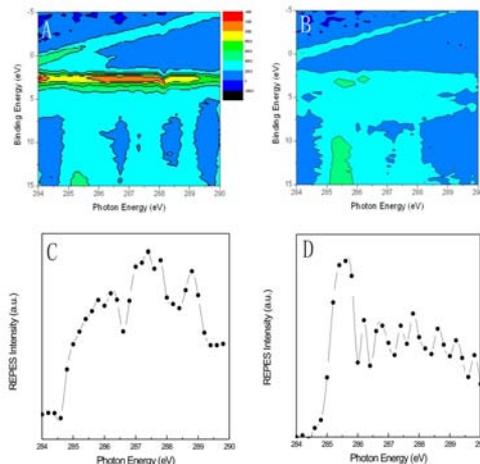
Methodology

Electrons in a particular core level are first photoexcited by soft x-ray photons to a resonant bound state (a); this is followed by the deexcitation of the system via predominantly Auger-like transitions. If the excited electrons are localized at the excited state for a sufficiently long time, two new transitions might be possible: resonant Auger and resonant photoemission.



For strong coupling system, the excited electrons directly decay into the substrate and normal Auger processes are followed.

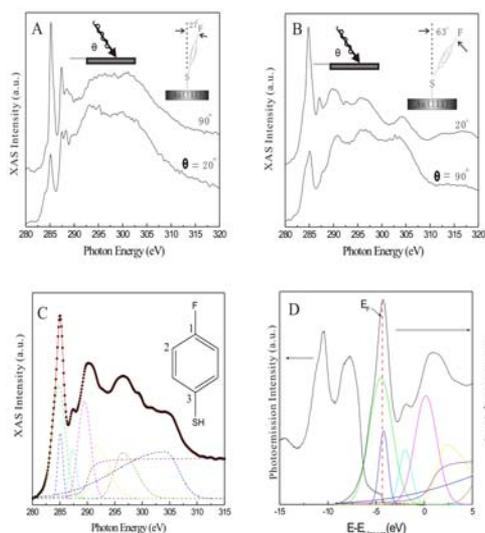
II. Electron transfer dynamic across molecule/Au Interface



Strong resonant enhancements were clearly observed in the monolayer with a molecular orientation of 27° , indicating the localization nature of the involved unoccupied states (a and c); in contrast, an *ultra-fast charge transfer process in the timescale of less than 6 fs* was observed for the molecules lying down on Au(111) (b and d).

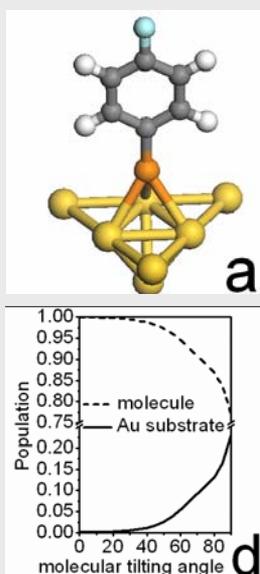
Main Results

I. Two 4-Flouro-Benzenethoil monolayers on Au(111) with different molecular orientations

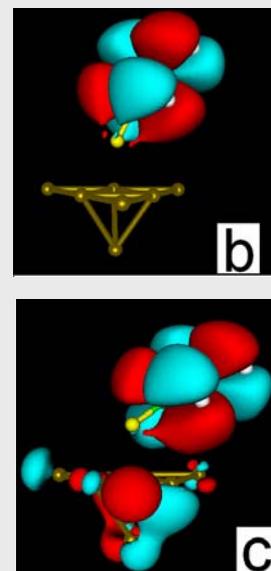


The XAS measurements confirm that the 4-Flouro-Benzenethoil monolayers have the molecular orientations of 27° and 63° , respectively. The XAS spectra are well decomposed into four components related to $1s \rightarrow \pi^*$ orbitals transitions.

Conclusions



DFT calculations demonstrate that the LUMO orbitals for the monolayer with a tilt angle of 30° distribute only around the molecule (b), however, a considerable portion of the LUMO orbitals locates on the Au substrate for the monolayer with larger tilt angle of 60° (c).



- The molecular orbitals experience a localization-delocalization transition with the vary of its molecular orientation due to strong hybridization between the molecule and the metal.
- A simple molecule, such as 4-Flouro-Benzene thiol, can display bistable states that can be used as a molecular switch by simply controlling its orientation.