

Computational vibrational spectroscopy for molecules adsorbed on the metal surface: a case study of aryl isocyanides

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[Introduction] Self-assembled monolayer (SAM) has been a momentous research field because of its expected transport properties for molecular electronic devices. ^[1] The transport properties of SAM are strongly influenced by the nature of bonding and electronic structure of molecules at the electrode surface. Aromatic series molecule with –SH substitute groups ^[2] and aryl isocyanides ^[3] have received a great attention in the design of the molecular electronic devices. Uosaki's group has concentrated on determining the vibrational properties of isocyanide self-assembled monolayer using sum frequency generation (SFG) spectroscopy, trying to measure the transport behavior which occurs at the interface of aromatic isocyanides and gold, silver, platinum and palladium surfaces, respectively. ^[4] Although spectroscopic properties of the isocyanides-metal interface have been investigated experimentally, the interaction between isocyanides and metal surfaces is still not clearly understood.

[Methods] Geometrical, vibrational and electronic properties have been determined by DFT calculations with PBE, functionals and double- ζ plus polarization (DZP) basis set, using the SIESTA 4.0 package. A common energy shift of 50 meV was employed. The energy cutoff of 200 Ry was chosen to guarantee a convergence of the energies and forces. The basis set superposition error (BSSE) was corrected by a counterpoise method, free energy was calculated by including zero-point energy (ZPE) corrections.

[Result] Until now, two typical organic molecules, 4-methylphenylisocyanide (MPI) and 1,4-phenylenediisocyanide (PDI) have been used to declare the substituent effect. Gold, silver, platinum and palladium surfaces have been employed to measure the metal surface effect. Furthermore, to validate our calculated adsorbate systems, we also verified these structural models from the view of vibrational frequency. The models of free organic molecules, the most favorable adsorbate systems and the other less favorable adsorption sites were used to calculate their vibrational frequencies. The computed frequencies agree well with the available experimental values. The surface effect on electronic structure of adsorbed molecules is also investigated, the details will be presented on the poster.

[References]

- [1] W. Y. Wang, T. Lee, and M. A. Reed, *Rep. Prog. Phys.* 68, 523-544 (2005); [2] V. Burtman, A. S. Ndobe, and Z. V. Vardeny, *J. Appl. Phys.* 98, 034314 (2005); [3] R. J. Angelici, and M. Lazar, *Inorg. Chem.* 47, 9155 (2008); [4] M. Ito, H. Noguchi, K. Ikeda, and K. Uosaki, *Phys. Chem. Chem. Phys.* 12, 3156-3163 (2010)