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

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### **[Abstract]**

The aim of this study is to develop a methodology for computations of vibrational spectra for molecules adsorbed on the metal surfaces. The configurational and electronic structures of the two typical organic molecules, i.e., 4-methylphenylisocyanide (MPI) and 1,4-phenylenediisocyanide (PDI), adsorbed on gold, silver, platinum and palladium surfaces have been studied. For each selected metal surface, atop, bridge and hollow sites have been generated for aryl isocyanides adsorption. The adsorption configuration, adsorption energy and the vibrational frequency of bond stretching of the organic molecule adsorbed on metal surfaces have been compared with other metal species, as well as with the experimental results.

### **[Introduction]**

Self-assembled monolayer (SAM) has been a momentous research field because of its expected transport properties for molecular electronic devices.<sup>[1]</sup> 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<sup>[2]</sup> and aryl isocyanides<sup>[3]</sup> have received a great attention in the design of the molecular electronic devices. The vibrational spectra of an adsorbed molecule are fingerprints for its chemical identification and thus can reflect the nature of its interactions with the environment. 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.<sup>[4]</sup> It is shown that isocyanide molecule adsorbs on the atop site on gold, silver, and platinum surfaces, while it adsorbs at a bridge site on palladium surfaces. 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 and BLYP functionals and double- $\zeta$  plus polarization (DZP) basis set, using the SIESTA 4.0 package. The core electrons for gold, silver, platinum and palladium metal atoms were replaced with the Troullier – Martins norm-conserving pseudo-potentials. A common energy shift of 50 meV was employed. All calculations were performed accounting for spin polarization. The energy cutoff of 200 Ry was chosen to guarantee a convergence of the energies and forces. The unit cell was relaxed for optimization of metal surfaces, and was fixed during optimization of isocyanide adsorbed on the metal surfaces. Four different adsorption sites (atop, bridge, two hollow sites) have been examined. The basis set superposition error (BSSE) was corrected by a counterpoise method, free energy was calculated by including zero-point energy (ZPE) corrections.

### [Results and Discussion]

We examined the adsorption of alyl isocyanides on different metal surfaces such as gold, silver, platinum and palladium by DFT calculations. For each selected metal surface, atop, bridge and hollow sites have been generated for alyl isocyanides adsorption, and the adsorption configurations, adsorption energies, and vibrational frequencies as well as the substituent effects are determined and compared with the available experimental data.

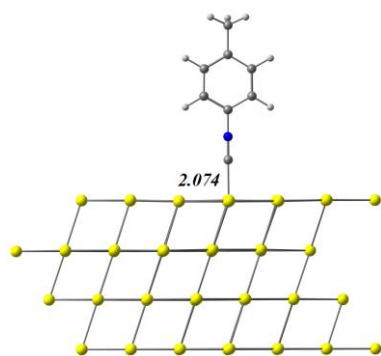


Figure. MPI adsorbed on Au (111)

Until now, two typical organic molecules, MPI and 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. For gas-phase free organic molecule, the full vibrational spectra were computed, while for the adsorbate systems, the partial vibrational spectra (phonon spectra) where only the organic molecules and adsorbed metal atoms were displaced from their equilibrium positions, other metal atoms were all fixed, accounting for the computational efficiency. The computed frequencies agree well with the available experimental values. The surface effect on electronic structure of adsorbed molecules are 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)