

**Theoretical study on aryl isocyanides adsorbed on the metal surface**

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**[Abstract]**

The aim of this study is to clarify the detailed mechanism of the effect of different metal substrates and different substituent groups on the vibrational spectra, electronic structure and chemical bonding in the adsorbed molecules. Adsorption of aromatic molecules on metal surface has been modeled using plane-wave DFT. Vibrational frequencies are then calculated from finite differences of energy gradients. Using the natural bond orbital (NBO) theory, chemical bonding has also been analyzed. We demonstrated the capability of our approach with the benchmark computations on aryl isocyanide molecules with different para substituent groups adsorbed on Pt adatom, Pt<sub>4</sub> cluster and Pt(111) surface. Of the several selected geometries that have been compared to the databases, we found adatom and cluster provides a relatively poor chemical model for the metal system.

**[Introduction]**

In the field of molecular electronic devices, search for appropriate self-assembled monolayers (SAMs) with prominent transport properties is an indispensable step <sup>[1]</sup>. In order to find the favorable SAM which can be used as a part of molecular electronic devices, appropriate organic molecules and metal electrode surface should be considered. The biggest challenge is how one can describe the conducting behavior at the electrode interface. Both spectroscopic measurement and computational method have been employed to reach this target. For aryl isocyanide molecule, it is known that C≡N triple bond and  $\pi$ -conjugated benzene ring can lower the electron transport barrier, due to electron delocalization. Uosaki et al. concentrated on determining the vibrational properties of isocyanide self-assembled monolayer using sum frequency generation spectroscopy and tried to measure the transport behavior that occurs at the interface of aryl isocyanide molecules and gold, silver, platinum and palladium surfaces, respectively <sup>[2]</sup>. Although spectroscopic properties of the isocyanides-metal interface have been investigated experimentally, effect of substituent groups on vibrational spectra, electronic structure, and charge transfer mechanism in the adsorbed molecule have not been clarified yet.

**[Methods]**

All calculations were performed using plane-wave DFT implemented in the Vienna

ab-initio Simulation Package (VASP), version 5.4.4. The ion-electron interactions were described using projector-augmented wave (PAW) pseudopotential from the VASP database, and the electron-electron exchange and correlation energies were computed using the PBE density functionals. The plane wave cutoff energies have been set to 680 eV for optimization and 816 eV for SCF calculations. Spin polarization has been included into our calculations. In all cases, the Brillouin zone was sampled with a  $\Gamma$ -centered Monkhorst-Pack grid. Vibrational frequencies of aryl isocyanides on Pt(111) were calculated using the method of finite difference. Delocalization and occupancy have been quantified within the natural bond orbital (NBO) analysis which can provide the localized real space representations of bonding interactions and chemical insights into bonding and reactivity. Geometry and orbital visualizations were prepared using Chemcraft, GaussView, VESTA and P4VASP. **Figure 1** shows the computational model for aryl isocyanide molecule adsorbed on the Pt(111) surface.

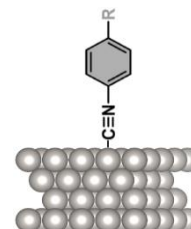


Figure 1. Computational model

### [Results and Discussion]

At first, vibrational frequency for the C $\equiv$ N stretching of the adsorbed aryl isocyanide molecules was calculated, and then substituent group effect on vibrational frequency at the interface was also investigated. In comparison to free molecule, only Pt<sub>4</sub> case gives the lower frequency than free molecule, and there are different trends for Pt adatom and Pt(111) surface.

Then, based on NBO analysis for aryl isocyanide molecules adsorbed on metal adatom and small clusters, we calculated the occupancy and orbital energy of lone pair, bonding and anti-bonding orbitals, and derived the relation between vibrational frequency shift and NBO occupancy. In the case of Pt adatom, trend of vibrational frequency of CN stretching is extremely consistent with bond order of CN bond.

Next, we applied NBO analysis to aryl isocyanide molecules with different para substituent groups adsorbed on Pt adatom, Pt<sub>4</sub> cluster and Pt(111) surfaces. The relation between bonding order of CN and Hammett constant which can quantitatively represent donating and back-donating ability of substituent groups. Difference of Pt adatom, Pt<sub>4</sub> cluster and Pt(111) surface has been found.

Finally, donation and back-donation between CN and Pt(111) surface *d*-states have been quantified by the occupancies of the corresponding NBOs, and these are the highlight parts of this study.

### [References]

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