# Theoretical study on aryl isocyanide molecules adsorbed on the Pt(111) surface

○Ben Wang[1], Min Gao[2,3], Tetsuya Taketsugu[1,2,3]

[1] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan
[2] Department of Chemistry, Faculty of Science, Hokkaido University, Japan
[3] Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Japan

[Introduction] As an essential component of molecular electronic devices, self-assembled monolayers (SAMs) can vastly determine the transport properties and conjunction behavior of the electronic devices. [1] In order to find the favorable monolayers, both organic molecules and metal electrode surfaces should be considered. Uosaki et al. studied the vibrational properties of isocyanide monolayers, trying to measure the transport behavior occurring at the interface of molecule and gold, silver, platinum and palladium surfaces. [2] Although spectroscopic properties of molecule-metal interface have been investigated experimentally, the interaction between isocyanide molecules and metal surfaces is still not clearly understood. It is crucial to clarify the interaction between the molecule and surface, and the conjunction behavior for different types of electronic devices. The aim of this study is to clarify the detailed mechanism of the effect of different substituent groups on the vibrational spectra, electronic structure and chemical bonds in the adsorbed molecules adsorbed on the Pt surface. Adsorption of aryl isocyanide molecules ($R-C_6H_4-NC$) with different para substituent groups while the donating and withdrawing ability of them can be quantified by Hammett constant ($R=N(CH_3)_2$, $NH_2$, $OH$, $OCH_3$, $CH_3$, $H$, $F$, $Cl$, $CF_3$, $CN$, $NO_2$) on the Pt(111) surface has been modeled using the plane-wave DFT method.

[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. Spin polarization has been included into our calculations. 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.

[Results] Main contents of this study cover three points. Firstly, NBO analysis and normal mode analysis are carried out for aryl isocyanide molecules adsorbed on the Pt(111) surface, and the correlation between the NBO bond order and vibrational frequency, as well as bond length each of which is treated as a function of Hammett constant is discussed. It is shown that the dependency of the CN bond order on the substituent group entirely comes from the $\pi$ component. Then, electron transfer mechanism between aryl isocyanide molecules and Pt surface has been studied explicitly. The donation from the CN $\sigma$ orbital to the metal $d_{z2}$ orbital and back-donation from the metal $d_{yz}$ and $d_{xz}$ orbitals to the CN $\pi^*$ orbital have been quantitatively estimated by the occupancy in Pt-C $\sigma^*$ orbital and CN $\pi^*$ orbitals consisting of $\pi^*_\perp$ and $\pi^*_\parallel$, respectively. Concomitantly, the relation between the electron transfer and donating ability of different molecules has also been exemplified. Finally, the difference of Pt atom, Pt cluster and Pt(111) surface has been validated from the point of view of the vibrational frequency and NBO occupancy. The rationale for this difference has also been presented.

## References

[1] W. Y. Wang, T. Lee, and M. A. Reed, *Rep. Prog. Phys*. **68**, 523 (2005).

[2] M. Ito, H. Noguchi, K. Ikeda, and K. Uosaki, *Phys. Chem. Chem. Phys*. **12**, 3156 (2010).