

Theoretical study on aryl isocyanides adsorbed on the Pt(111) surface

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Introduction

For searching the favorable self-assembled monolayers (SAMs) which can be used as a part of molecular electronic devices, appropriate organic molecules and metal electrode surface are required. In this study, natural bond orbital (NBO) theory implemented in a periodic density functional theory scheme has been applied to the aryl isocyanide molecules adsorbed on the Pt(111) surface. Various aryl isocyanide molecules with different substituent groups that have respective electron donating or withdrawing ability are used to elucidate the mechanism of electron transport between molecule and the surface. We demonstrate the capability of our computational approach for the aryl isocyanide molecules adsorbed on the Pt surface. Such a comprehensive theoretical research can examine the substituent group effect on the electron transport properties.

Results and discussion

Firstly, we carried out the geometry optimization and vibrational frequency calculations for the isolated aryl isocyanide molecules ($X-C_6H_4-NC$; $X = -N(CH_3)_2, -NH_2, -OCH_3, -CH_3, -H, -Cl, -CF_3, -CN, -NO_2$). Then, we examined the bonding nature of NC anchor group based on the NBO analyses, and found the strong correlation between the NC stretching frequency ν_{NC} and the NC bond order. The NC bond order can be analyzed by separating contributions from σ and π orbitals. Detailed information generated from the NBO analyses reveals the dominant sources for the electron transfer between NC and the substituent groups.

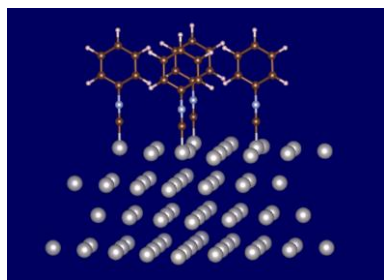


Fig. 1. Optimized configuration of the aryl isocyanide molecule adsorbed on Pt(111) surface, in case of $H-C_6H_4-NC$ molecule adsorption model.

Then, we shifted our attention to the aryl isocyanide molecule adsorbed on Pt surface, and examined the surface effect on the correlation of the vibrational frequency (ν_{NCPt}) and electron donating and withdrawing ability of the substitution group. **Figure 1** shows the optimized geometry of the molecule ($H-C_6H_4-NC$, as an example) adsorbed on the Pt surface. In comparison to the isolated molecules, the NC stretching frequency in the adsorbed molecule increases by 50 cm^{-1} , which is consistent with the experimental results ^[1]. The charge transfer between the molecule and the surface contributes to the change in ν_{NCPt} . Interaction and electron transfer between the lone pair orbital of C atom in NC and the partially occupied Pt d-states as well as the π^* anti-bonding orbitals of NC account for the change in ν_{NCPt} . The analyses of NC bond length indicate that the Pt surface enhances the NC bond length variation. The NC bond

strength in the surface environment has also been characterized by the bond order model.

Finally, we expand our calculation into the specific occupancy change in some typical bonding and anti-bonding orbitals. Role of each bonding and anti-bonding orbitals on the electron transfer (σ donation and π^* back-donation) between NC group and Pt surface has been clarified through the quantitative calculation explicitly.

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