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Akitoshi Shiotari

Reactivity of Nitric Oxide on Copper Surfaces

Elucidated by Direct Observation of Valence
Orbitals

Doctoral Thesis accepted by
Kyoto University, Kyoto, Japan

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Supervisor's Foreword

Scanning tunneling microscopy (STM) is currently routinely used in molecular science studies. In particular, its capability of imaging molecular orbitals has made it an invaluable tool for visualizing quantum chemistry in real space. However, the molecular orbitals are quite commonly hybridized with metallic bands of the substrate, which results in quenching of the localized orbital character. Therefore, a requisite for orbital imaging is that the orbital interaction with the substrate be sufficiently weak. A weaker interaction, however, might cause the molecule to diffuse across the template, making it difficult to image individual molecules. In this context, a copper substrate is ideal, where moderate interactions fix molecules to the surface while their orbitals remain localized on the molecule. A key factor for effective STM measurements is the position of the substrate d-band with respect to the Fermi level.

In his doctoral work, Akitoshi Shiotari imaged the $2\pi^*$ orbital of nitric oxide (NO) using STM. He used three kinds of low-index planes of copper as the substrates and showed that the orbital has either a degenerate (ring) or non-degenerate (dumbbell) character, depending on the structure of the templates. Most notably, in addition to imaging the orbital, the overlap between the molecules could also be controlled. Consequently, in this study, covalent bond formation could be visualized as a function of the intermolecular distance. Furthermore, by applying the full spectrum of STM techniques including scanning tunneling spectroscopy, inelastic electron tunneling spectroscopy, and “action” spectroscopy, he conducted a series of single-molecule chemical and physical surface studies of NO. From these studies, the intermolecular interactions, N–O bond dissociation, and electronic-vibrational coupling were elucidated. The local probe technique proved useful in disentangling the complex chemistry of NO on metal surfaces. This work provides a demonstration of the quantum properties of a molecule and is a useful reference for future single-molecule studies of NO on metal surfaces.

Kyoto, Japan
February 2017

Hiroshi Okuyama

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- A. Shiotari, Y. Kitaguchi, H. Okuyama, S. Hatta, T. Aruga, “Imaging Covalent Bonding between Two NO Molecules on Cu(110),” *Physical Review Letters* **106**, 156104 (2011). Copyright 2011, American Physical Society. Reproduced with permission.
- A. Shiotari, S. Hatta, H. Okuyama, T. Aruga, “Role of hydrogen bonding in the catalytic reduction of nitric oxide,” *Chemical Science* **5**, 922–926 (2014). Reproduced by permission of The Royal Society of Chemistry.
- A. Shiotari, T. Mitsui, H. Okuyama, S. Hatta, T. Aruga, T. Koitaya, J. Yoshinobu, “Configuration change of NO on Cu(110) as a function of temperature,” *The Journal of Chemical Physics* **140**, 214706 (2014). Copyright 2014, American Institute Physics. Reproduced with permission.
- A. Shiotari, S. Hatta, H. Okuyama, T. Aruga, “Formation of unique trimer of nitric oxide on Cu(111),” *The Journal of Chemical Physics* **141**, 134705 (2014). Copyright 2014, American Institute Physics. Reproduced with permission.
- A. Shiotari, H. Okuyama, S. Hatta, T. Aruga, M. Alducin, T. Frederiksen, “Role of valence states of adsorbates in inelastic electron tunneling microscopy: A study of nitric oxide on Cu(110) and Cu(001),” *Phys. Rev. B* **94**, 075442 (2016). Copyright 2016, American Physical Society. Reproduced with permission.

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