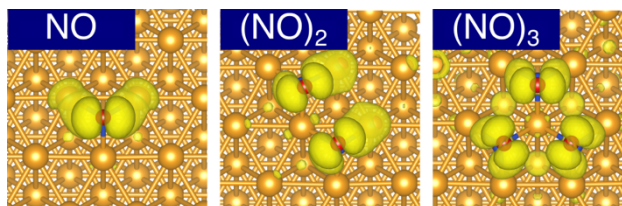


## Density functional theory study on dimeric and trimeric adsorption of NO on Cu(111)

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NO adsorption on metal surfaces has been studied intensively due to its importance in various catalytic processes. It is recognized that NO adsorbs molecularly on noble metal (111) surfaces, i.e., Cu(111), Ag(111), Au(111), at low temperature followed by the formations of dimeric (NO)<sub>2</sub> and N<sub>2</sub>O with further gas exposure. Recently, by using scanning tunneling microscopy, Shiotari *et al.* observed NO unexpectedly adsorbs in a trimeric configuration on Cu(111) [1,2]. To provide the origin of the peculiar formation of NO trimer on Cu(111), we study the adsorption of small NO clusters on Cu(111) [3] using van der Waals density functional method as implemented in STATE package. We found that the NO monomer preferably adsorbs in an upright configuration at the fcc-hollow site, whereas all NO molecules of the NO dimer and trimer are in inclined configurations towards the neighboring NO at fcc-hollow sites due to short-range attractions between molecules. The NO trimer is the most stable regardless of lateral periodicities, which is consistent with the experiment [1,2]. The vibrational analysis also reveals that the N-O stretching mode shifts upward from 182 meV of NO monomer to 193 meV of NO trimer, and the latter mode agrees much better with the EELS data (190 meV). The origin of the preferable formation of the NO trimer on Cu(111) is attributed to a subtle interplay between intermolecular and molecule – substrate interactions.



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