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Role of molecular orientation in vibration, hopping, and electronic properties of single pyridine molecules adsorbed on Ag(1 1 0) surface: A combined STM and DFT study

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ABSTRACT

A combination of low-temperature scanning tunneling microscopy and density functional theory calculations was used to determine the adsorption characteristics of single pyridine molecules on Ag(1 1 0) surfaces. Pyridine was chemisorbed onto Ag(1 1 0) surfaces at 13 K in either the stand-up or flat-lying configuration. The fractional ratio of the two configurations depended on the molecular coverage: at very low coverage, the flat-lying pyridine predominated on the surface; however, the molecules stood up with increasing surface coverage until the stand-up configuration was favored. The adsorption configurations were characterized by distinct C–H stretching vibrational energies, hopping barriers, and binding characteristics: (i) The C–H stretching energy for the flat-lying configuration was lower than that of the stand-up configuration. (ii) The hopping barrier for the stand-up configuration along the $[1\bar{1}0]$ direction was the lowest. (iii) The electrostatic interaction was the dominant contribution to the binding of pyridine on Ag surfaces in both configurations, although the interaction was especially strong for the flat-lying configuration.

1. Introduction

Organic molecules adsorbed on metal surfaces have both practical and scientific value. Many molecular systems on metal surfaces have been employed in the construction of organic functional devices such as field-effect transistors [1] or high-density memory circuits [2]. Self-assembled monolayers adsorbed on a specific metallic substrate may be a promising way to manufacture molecular electronic devices. The structures and functions of such organic devices vary, requiring a delicate balance between molecule–molecule and molecule–substrate interactions. Therefore, understanding the binding characteristics of organic molecules on metal surfaces and their coverage-dependency, at the molecular scale, is crucial for developing molecular devices.

Pyridine adsorbed on metal surfaces has received considerable attention over the decades due to its activity as a catalytic poison of heterocyclic molecules [3] and its surface-enhanced Raman effects [4]. Isolated pyridine has two essential features: (i) delocalized π electrons similar to those of benzene and (ii) a nonbonding lone pair associated with the nitrogen atom. The interplay between these two features leads to several possible adsorption modes on metal surfaces. Depending on the relative contributions of the lone-pair and the π electrons, the molecular orientation can range from a configuration in which the plane of the pyridine ring is parallel to the surface (flat-lying configuration) to a configuration in which the molecule stands upright, bound to the surface solely via the nitrogen lone pair (stand-up configuration). These configurations are referred to as π-bonding and *N*-bonding, respectively, and have been reported for pyridine adsorption on several metal surfaces [5–16]. The binding geometry of pyridine on metal surfaces depends on the coverage. For example, on Pt(1 1 1) surfaces, a reflection absorption infrared spectroscopy study [5] has shown that pyridine initially adsorbs in either a tilted conformation or as a mixture of tilted and *N*-bonded species. With increased coverage, the molecule shows a complicated tilting and twisting, presumably due to intermolecular interactions. A similar coverage-dependent transition of the adsorption geometry was characterized on Cu(1 1 1) by two-photon photoemission [6], and on Cu(1 1 0) by temperature programmed desorption observations [6] and scanning tunneling microscopy (STM) [7]. Pyridine adsorption on silver surfaces has been studied by high resolution electron energy loss spectroscopy [8], UV photoemission spectroscopy [8], and analysis of near-edge X-ray absorption fine-structure [9]. These studies have proposed three possible geometries, depending on surface coverage: flat-lying, tilted, and stand-up configurations. In addition, binding through the nitrogen atom was proposed to be dative and weaker than the π-bonded species.

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In the present study, we determined the adsorption characteristics of single pyridine molecules on Ag(1 1 0) using low-temperature STM imaging, STM–inelastic electron tunneling spectroscopy (STM–IETS), and density functional theory (DFT) calculations. We found that pyridine bound to silver in either a flat-lying or a stand-up configuration. A transition was observed from the predominantly flat-lying configuration to stand-up binding, with increased pyridine coverage. The C–H stretching energy and hopping barrier depended on the molecular configuration. It is notable that (i) the negative (positive) charge of the nitrogen (silver) atom of the pyridine/silver system contributed significantly to the bonding for both configurations and (ii) the flat-lying configuration had an additional ring–surface interaction, which resulted in a lower C–H stretching energy and an increased hopping barrier. Our observations are an important addition to the current knowledge of surface binding characteristics that may be particularly relevant to the active fields of organic molecular device research [17].

2. Experimental and calculation methods

STM imaging and STM–IETS of single pyridine molecules was performed using a home-built variable temperature STM housed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-11} Torr [18]. The Ag(1 1 0) sample was prepared by 500 eV neon ion sputtering followed by annealing at 693 K. Polycrystalline tungsten tips were prepared *in situ* by self-sputtering and annealing. Pyridine adsorbates were introduced into the chamber via a microcapillary array doser attached to a variable-leak valve at a substrate temperature of 13 K. A room temperature liquid source of pyridine (Aldrich Chemical) was used, after purification by repeated freeze–pump–thaw cycles. The pyridine coverage was kept low to permit investigation of individual, well-isolated molecules. Coadsorption of CO molecules onto the Ag(1 1 0) surface at a coverage of less than 0.01 ML was also performed at 13 K. Atomically resolved imaging of silver atoms was achieved by transferring a CO [19,20] or pyridine [21] molecule to the tip at 13 K. All experiments described here were performed at 13 K.

The adsorption characteristics of pyridine on Ag(1 1 0) were determined by total energy calculations, which were performed using the Vienna *ab initio* simulation package (VASP) [22]. Electron–ion interactions were described by the projected augmented wave (PAW) method [23], which is a frozen-core all-electron calculation. Exchange–correlation effects were treated within the local density approximation (LDA). All valence electrons, as well as the 5d electrons of the Ag atom, were explicitly considered in the KS equation. The Ag(1 1 0) surface was constructed on the *XY* plane based on the optimized lattice constant of the *fcc* Ag crystal. Five layers of the 3×4 surface were built along the [0 0 1] and $[1\,\bar{1}\,0]$ directions in a supercell, in which the three bottom layers were fixed at the bulk geometry. k-space sampling was performed with the $4 \times 4 \times 1$ Monkhorst–Pack scheme on the surface Brillouin zone (SBZ). In doing this, we used large supercells along the [1 1 0] direction in a way that guaranteed that the interatomic distances between the closest atoms in neighboring cells were greater than 15.00 Å. The cutoff energy was set sufficiently high (400 eV) to ensure accurate results, and the conjugate gradient method was employed to optimize the geometry with the convergence criterion that the Hellmann–Feynman force exerted on each atom was less than 0.03 eV/Å.

3. Results and discussion

3.1. Adsorption configurations

Pyridine molecules were adsorbed onto the Ag(1 1 0) surface at a sample temperature of 13 K, and the resulting surface was investigated using STM. Fig. 1a and b shows topographical images obtained from single pyridine molecules. The pyridine molecules appeared as protrusions and were classified into two different configurations according to their appearance (***a*** and ***b***). These features increased with the number of exposures to pyridine, verifying that they were due to adsorbed molecules. Feature ***a*** in Fig. 1a appears as an oval-shaped protrusion elongated along the [0 0 1] direction of the Ag(1 1 0) surface. The atomic-scale image of the Ag(1 1 0) surface [19–21] shows that each isolated pyridine molecule of feature ***a*** was bound to a surface silver atom. Feature ***b*** in Fig. 1b is in the shape of a heart and appears asymmetric with respect to the [0 0 1] direction. Its main symmetry axis is near the $[1\,\bar{1}\,0]$ direction. The adsorption position of feature ***b*** (the center of the feature) was determined to be near the fourfold hollow site. The topographical height of ***b*** was slightly lower than that of ***a*** [24], due to the flat binding geometry.

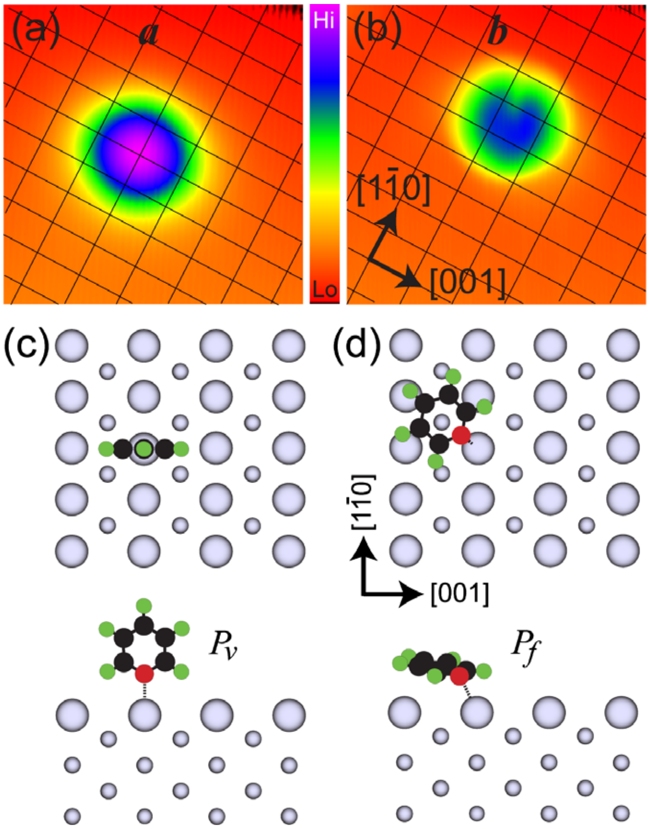

Fig. 1. (a) and (b) STM topographical images of two types of single pyridine molecules adsorbed on Ag(1 1 0) at 13 K. The scan area was 2.5 × 2.5 nm^2. Both images were obtained with a bare metallic tip at a sample bias of 70 mV and a tunneling current of 1 nA. Grid lines in the images were drawn through the silver surface atoms, the positions of which were determined by imaging using a CO- or pyridine-terminated tip. (c) and (d) Equilibrium atomic structures of pyridine molecules adsorbed on Ag(1 1 0) surfaces. (c) Vertically upright (stand-up) configuration (P_v). (d) Flat-lying configuration (P_f). Top views of the two topmost layers and cross-section views of the four topmost layers of the 3×4 Ag(1 1 0) surface in a supercell are shown in each configuration. Larger gray spheres represent Ag atoms on the surface layer, while smaller gray spheres represent those on a layer below it. The black, green, and red circles represent carbon, hydrogen, and nitrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 1c and d shows the two most stable configurations calculated for the pyridine molecule on the Ag(1 1 0) surface. To find the most stable structures, we relaxed the geometry of the system, starting from various initial configurations of the pyridine molecule. The first one (P_v in Fig. 1c), which had a binding energy of 0.98 eV, corresponded to a pyridine molecule located on top of a