

Nondissociative adsorption of O₂ on the Si(111)-7×7 surface

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Using first-principles energy minimization calculations, we find that an O₂ molecule is stably adsorbed atop the Si adatom in a tilted grif configuration. The O–O bond is a single bond with a length 0.3 Å longer than the double bond of a free O₂ molecule. The O-derived partial density of states agrees well with ultraviolet photoemission spectroscopy data. The contour plot of the local charge density of the filled states within 2 eV from the Fermi level shows that the observed scanning tunneling microscopy single bright spot is the image of the O–O bond charge.

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The adsorption and reaction of molecules on crystalline surface are important subjects of technological and fundamental interest. Chemisorption of oxygen on the Si(111)-(7×7) surface has received great attention because fundamental understanding of this system can provide insight into the very early stage of the oxidation of Si surfaces. However, despite many experimental and theoretical studies^{1–29} over the past three decades, confusion and controversy remain concerning whether individual oxygen molecules adsorb nondissociatively or dissociatively on the surface at very low coverage.

The first observation of O₂ species was reported by Ibach *et al.* using electron-energy-loss spectroscopy (EELS).¹ Later, other experimental studies also reported existence of the molecular states.^{2–12} It was generally believed that molecular states existed only at low oxygen coverage and low substrate temperatures (including room temperature). Ultraviolet photoemission spectroscopy (UPS) measurements also indicated that O₂ first reacted with a Si adatom dangling bond.^{3,7,8,10,11,13–15} Several scanning tunneling microscope (STM) studies found that at room temperature and very low coverage, mostly bright species at the adatom sites were observed.^{13,14,16–21} Dujardin *et al.*, based on STM and UPS measurements, argued that the bright species was the molecular state.¹⁴ However, Avouris *et al.*, based on earlier calculations,²² which showed that an O₂ molecule bonded on top of a Si adatom gave rise to a dark site, argued that the bright species was an atomic O inserted at the backbond of Si adatoms (the ins configuration).^{13,16,18} A recent variable-temperature STM observation by Hwang *et al.* indicated that the bright species was very stable and could hop on the surface via two intermediate states at temperatures above ~280 °C.^{19,20} These dynamic observations strongly favor a molecular adsorption state for the bright species.

On the theoretical side, Schubert *et al.* proposed para, paul, and grif configurations for the molecular species and performed approximate extended Hückel tight-binding calculations.²² The calculated electronic structures could account for some earlier experimental data. However, the molecular species would appear dark in STM images. Recently, Lee and Kang carried out first-principles pseudopotential cal-

culations and concluded that O₂ dissociated directly upon adsorption on the Si(111) surface.^{23,24} They claimed that a metastable ad-ins configuration could explain the UPS and EELS spectra. This configuration appeared dark, but it would later transform into a stable ins-ins structure, which can explain the bright species observed in STM images. However, if ad-ins has a lifetime long enough for UPS and EELS measurements, it should also be observed with STM. In fact, no evidence of transformation from a dark species to a bright species has been found. Besides, the dynamic observations by Hwang *et al.*^{19,20} could not be explained by the ad-ins or ins-ins structure. In this Rapid Communication, we report a first-principles energy minimization and electronic structure calculations, which not only provide a much better agreement with UPS data, but also satisfactorily explain the STM observations. Our results may resolve the long-standing confusion and controversy about the adsorption of individual oxygen molecules on the Si(111) surface.

The method used in this study^{30–32} is a molecular-dynamics (MD) method based on a real-space norm-conserving pseudopotential method^{33,34} implemented with the Ceperley-Alder exchange-correlation potentials.³⁵ The basis set is composed of Bloch sums of s , p_x , p_y , and p_z pseudoatom orbitals. To accurately treat charge densities and potentials in the interstitial region and the nonspherical parts inside the atoms, we use plane-wave expansions and the fast-Fourier-transform technique to obtain the interstitial part of matrix elements. This method efficiently calculates forces acting on every atom and then predicts the equilibrium atomic positions iteratively until the magnitudes of the forces are smaller than 0.1 eV/Å, which has been shown to work well for semiconductors.^{36–41} The pseudofunction (PSF) method⁴² was used to perform electronic structure calculations. The PSF method adopts the linear theory of Andersen⁴³ for solving the Schrödinger equations inside the muffin-tin spheres. The basis set used contains two sets of Bloch sums of muffin-tin orbitals with exponentially decaying and oscillating tail functions. It uses the Hedin-Lundqvist⁴⁴ form of the local density approximation for the exchange-correlation potential.

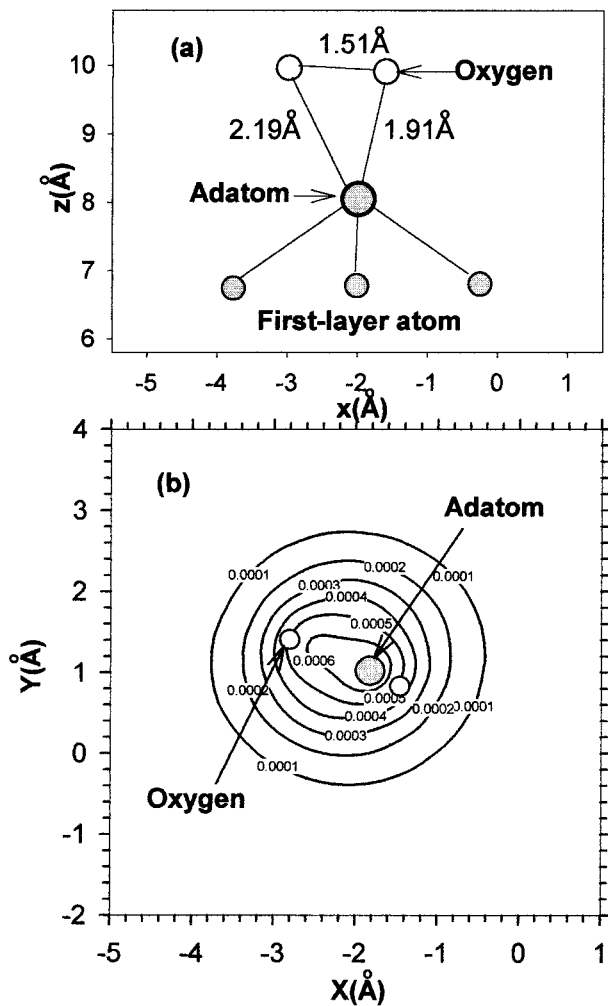


FIG. 1. (a) Side view of O_2 adsorbed atop the adatom in the tilted grif configuration and (b) the contour plot of the local charge density at 2 Å above O_2 .

Limited by the complexity of the surface structure, we follow Vittadini and Selloni⁴⁵ and Lee and Kang^{23,24} to employ the (4×2) surface model for the real (7×7) surface. We use repeated six-layer-slab supercell models with the bottom-layer atoms attached with hydrogen atoms to saturate their dangling bonds. There are 61 atoms per unit cell. The vacuum region between slabs is chosen to be about 10 Å. The optimized atomic positions determined by MD calculations are used for PSF calculations to obtain electronic structures. In energy minimization calculations, we sample only the Γ point, which has been shown to be adequate for semiconductor systems.^{36–41} We used the Monkhorst-Pack special \mathbf{k} -point scheme⁴⁶ with $q=2$ to obtain self-consistent charge densities and potentials in the PSF calculations. The O-derived partial densities of states are obtained by sampling a uniform mesh of 45 \mathbf{k} points in the reduced wedge of the first Brillouin zone.

Starting from the paul configuration atop the Si adatom,²² our calculation results in a tilted grif configuration for the O_2 molecule [Fig. 1(a)]. Our result agrees with recent electron spin resonance (ESR) observation²⁵ and UPS measurements,^{3,7,8,10,11,13–15} which showed that O_2 adsorp-

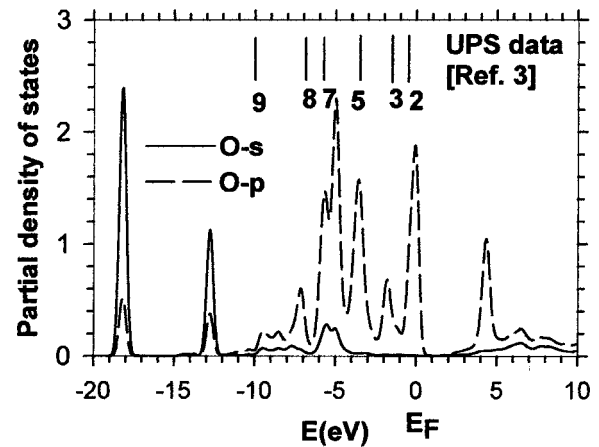


FIG. 2. O-derived partial densities of s and p states for O_2 adsorbed atop the adatom. The numbers under the vertical bars are those used by Höfer *et al.* to assign the O-derived features in the UPS spectra.

tion eliminated the adatom dangling bond. The axis of the O_2 molecule is approximately parallel with the surface, in agreement with near-edge x-ray-absorption fine-structure (NEXAFS) measurements.²⁶ The calculated O–O bond length of 1.51 Å is slightly larger than the O–O single-bond length 1.48 Å of a peroxide (H_2O_2) molecule.⁴⁷ The Si–O bond lengths of 2.19 and 1.91 Å are larger than the sum of Si and O covalent radii, 1.84 Å.⁴⁸ This shows that the two Si–O bonds are weakened or shared. Figure 1(b) shows the contour plot of the local charge density of the filled states within 1.7 eV from the Fermi level E_F at a height of 2 Å above the O atoms. O_2 appears as a single bright spot above the Si adatom, in agreement with STM observations.^{13,14,16–21} The result of a dark O_2 STM image obtained by Schubert *et al.*²² might arise from a lack of self-consistency in Si to O electron transfer in their calculations. This rendered the O–O bonding states to be too deep below E_F . Figure 2 shows the calculated O-derived partial densities of s and p states, which have six distinctive features below E_F that can account for the UPS spectra obtained by Höfer *et al.*,² if the inflection point of the leading edge of the spectra is interpreted as E_F to take into account experimental broadening. More recent UPS measurements by several different groups^{3,7,8,10,11,13–15} also resembled those by Höfer *et al.*

Hwang *et al.* observed a metastable state with a STM image spot lying between the adatom and rest atom sites.^{19,20} Starting from the peroxy configuration proposed by them, we obtain the relaxed atomic arrangement shown in Fig. 3(a). The peroxy lies between the adatom and rest atom with adatom–O–O and O–O–rest-atom bond angles of 114° and 113°, respectively. They are close to the bond angle of O–O–H of 100° in the peroxide molecule and of Cl–O–O of 107° in the covalent compound SO_2Cl_2 .⁴⁷ The O–O, adatom–O, and O–rest-atom bond lengths are 1.48, 2.69, and 2.38 Å, respectively. The elongation of the Si–O bonds results from the constraint of the adatom–rest-atom distance and the tendency for the O ions to conserve their bond angles. Though the Si–O bonds are elongated, the bonding is still significant because the negative O ion has an increased

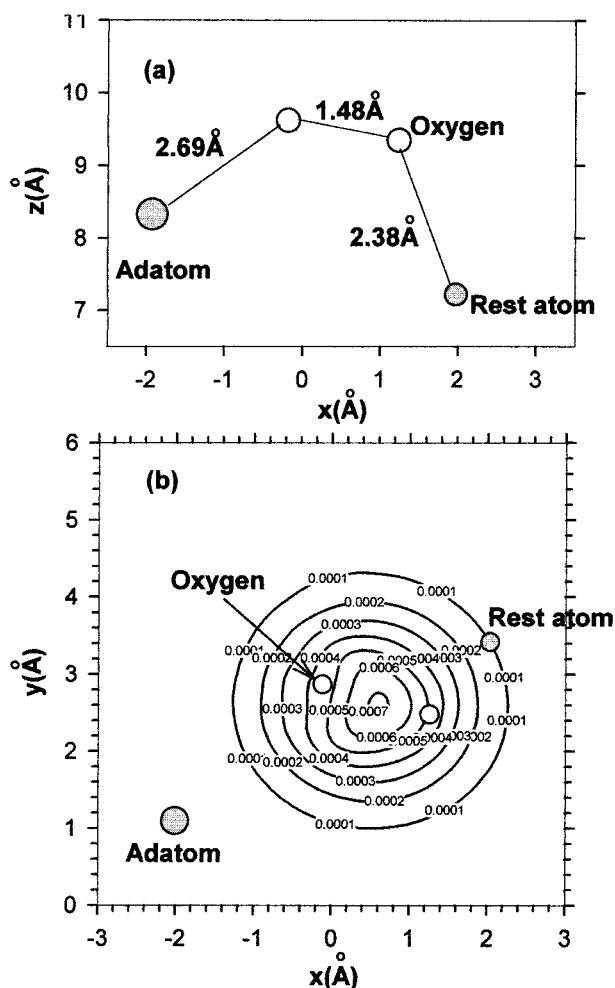


FIG. 3. (a) Side view of the peroxy in the intermediate state and (b) the contour plot of the local charge density at 2 Å above the peroxy. Only the adatom and rest atom bonded with the peroxy are shown.

radius. (The ionic radius of the O⁻¹ ion is 1.76 Å,⁴⁷ while the atomic radius of a neutral O atom is 0.65 Å.⁴⁸) The calculated total energy of this configuration is 1.4 eV/(1 × 1) cell larger than that of the grif configuration. Thus this indeed is an intermediate state. In this state, both O–Si bonds are elongated and weakened, which not only explains why it has a larger total energy, but also why O₂ can hop to atop a nearby Si adatom so easily. The local charge density contour plot of the filled states within 2 eV from E_F [Fig. 3(b)] shows a round O–O bond charge lying between the adatom and rest atom and the absence of the adatom dangling bond charge, in good agreement with STM images.^{19,20}

Using pseudopotential calculations, Lee and Kang concluded that O₂ dissociated spontaneously into ad-ins and then ins-ins configurations.²³ Our calculations starting from these two configurations result in an elongated peroxy bridge bonded between an adatom and a first-layer atom and a pair of first-layer atoms, respectively. The instability of these two configurations is due to the bond angle of the inserted O ion, ~79°, which differs too much from the typical O bond angle in a covalent compound: e.g., the bond angles are 110°, 128°,

and 124° for C–O–C, As–O–As, and P–O–P, respectively.⁴⁷ Therefore the O ion moves to restore its bond angle. Since Lee and Kang used an energy cutoff of 20 Ry, the shortest wavelength of the plane-wave basis set was 0.74 Å. This basis set may not be sufficient for the O–O and Si–O directional covalent bond charges, whose sizes are expected to be fractions of the covalent radius of O, 0.73 Å.⁴⁷ Besides, Lee and Kang's conclusion was based on a comparison of total energies. However, the total energy of the (4 × 2) unit cell contains substantial contributions from long-range electrostatic couplings among negative O ions and compensating positive charges on Si atoms, which strongly depends on the arrangement of O ions or configuration. In contrast, these contributions will be much less significant for the real (7 × 7) surface with low oxygen coverages. Thus Lee and Kang did not compare total energies on the same footing.

STM studies showed that the bright species can react with an incoming oxygen molecule to become a dark species.^{17,18} The reaction cross section was estimated to be ~73 Å² at room temperature.¹⁸ Since the O₂ axis is parallel to the surface, O⁻ has an increased radius, and most importantly the Si–O bonds are weakened, O₂ in the tilted grif configuration is likely to have a large effective cross section due to thermal vibration, bending, and rotation at finite temperatures. In contrast, it is unlikely for the ins-ins or ins configuration to have such a large cross section. In addition, Hwang *et al.* observed that two bright species at neighboring 7 × 7 half-cells exhibited strong interactions across the dimer row.²⁰ One or two oxygen atoms are often transferred from one half-cell to another. This would be possible if they are O₂ molecules, but very unlikely for the dissociated states, such as ins-ins or ins.

Direct evidence of molecular states has been provided by Sakamoto *et al.* with their detection of the O₂⁺ ion at room temperature in electron-stimulated desorption (ESD) measurements.⁴ Recently, Matsui *et al.*, based on NEXAFS measurements, claimed that there was no molecular state at room temperature, but there was a metastable molecular species at temperatures below 220 K for exposures above 0.4 L.²⁷ We believe this molecular state is related to physisorbed O₂ molecules, which retained the double O=O bond, because the peak they measured closely resembles the π_g^* state of the O₂ molecule in the condensed O₂ multilayer. The O=O bond might later become an O–O bond which is chemisorbed on top of an adatom and thus broadened and shifted the O₂-derived bands. There were two other studies that claimed no molecular state. Kim *et al.* carried out Cs⁺ reactive scattering experiments²⁸ and did not find CsO₂⁺ and secondary O₂⁺ ions at temperatures between 140 and 300 K and for exposures up to 3 L. A neutral Cs atom is highly reactive because of its 6s electron. However, a Cs⁺ ion has already lost its 6s electron; it is no longer reactive and primarily forms bond through electrostatic attraction. Thus it is doubtful that this technique was suitable for O₂ or peroxy on the Si surface. Besides, if the O₂ molecule escapes as a secondary species, it is not necessary to be positively charged. Ion photodesorption measurements by Comtet *et al.* also did not detect O₂⁺ ions at temperatures above 30 K for exposures

up to 0.5 L.¹⁵ However, the high-energy photon they used (in the 90–130 eV range, much larger than the strength of the single O-O bond) might cause the dissociation of the adsorbed molecular O₂. Thus this study also cannot exclude the existence of molecular states.

In summary, our first-principles calculations provide a good understanding of the adsorption of individual O₂ molecules. The calculations show quantitative agreement with

UPS measurements and also confirm the existence of molecular states. Most importantly, they provide a good explanation of STM observations of the image contrasts of two molecular states and various detailed dynamic behaviors of individual molecular species.

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