

Orbital specific chemistry: Controlling the pathway in single-molecule dissociation

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A scanning tunneling microscope (STM) was used to control the pathway of the dissociation of single O₂ molecules chemisorbed on Ag(110) at 13 K. Tunneling of electrons from the STM tip into the O₂ caused dissociation of the molecule, giving rise to two adsorbed O atoms separated along the $[1\bar{1}0]$ direction. In contrast, the ejection of electrons from the O₂ molecule produced adsorbed O atoms separated along the $[001]$ direction. These results illustrate that control of the dissociation pathway and product formation are associated with a specific molecular orbital located at the Fermi level. © 2005 American Institute of Physics. [DOI: 10.1063/1.1940007]

An important aspect of the study of chemical dynamics is its potential application to the control of chemical reactions.^{1,2} From a practical viewpoint, an understanding of the reaction dynamics can make it possible to suppress unwanted side products while building new products. Numerous approaches have been taken to the control chemical reactions, including varying the external conditions of the reactants (temperature or pressure) and using a catalyst that selectively lowers the activation barrier of the pathway to the desired reaction products. However, the control of chemical reactions at the single-molecule level has received little attention. The study of chemical reactions at the single-molecule level is a highly challenging area that has the potential to provide fundamental insights into the control of macroscopic-scale reactions as well as into single-molecule chemical dynamics.

The dissociation of a diatomic molecule on a surface is one of the simplest surface chemical reactions. Given that most bimolecular reactions on surfaces involve this type of molecular dissociation, atomic-scale knowledge of the dissociation of diatomic molecules is a prerequisite for understanding more complicated surface reactions. The adsorption of oxygen on a silver surface has been extensively studied on account of its catalytic significance and the different states of the adsorbed oxygen molecule at different temperatures.^{3–13} The O₂ is chemisorbed on the Ag(110) surface between 40 and 150 K and dissociates at higher temperatures. Molecular O₂ chemisorbs parallel to the surface with weakened O–O bond. The dissociation of the O₂ may be an essential process in the partial oxidation of ethylene molecule (epoxidation) over silver catalysis.⁷

Here we report that the dissociation pathway of O₂ on Ag(110), and therefore the product formation, can be controlled at the single-molecule level using a scanning tunneling microscope (STM). The O₂ dissociation pathway depends on the tunneling direction of the electrons, which is

associated with a molecular orbital located at the Fermi level. We show that injection of tunneling electrons into this O₂ orbital induces dissociation into O atoms adsorbed along the $[1\bar{1}0]$ direction, whereas removal of electrons from the O₂ orbital leads to dissociation into O atoms lying along the $[001]$ direction. The ability to control the dissociation pathway in the manner demonstrated in the present work should eventually make possible the selective initiation of individual chemical reactions.

Experiments were conducted using a homebuilt variable temperature STM,¹⁴ housed inside an ultrahigh vacuum chamber with a base pressure of 2×10^{-11} Torr. The Ag(110) sample was cleaned by repeated cycles of 500-eV Ne ion sputtering at room temperature followed by 693-K annealing. During adsorption of the O₂ molecules (<0.01 ML) onto the sample, the temperature was maintained between 40 and 75 K to ensure molecular chemisorption. After adsorption was complete, the sample and the STM were cooled to 13 K to minimize the drift in the tip-sample junction. A very small number of CO molecules (<0.001 ML) were also adsorbed on the surface at 13 K. The transfer of one of these CO molecules to the STM tip apex enables atomically resolved imaging.^{11,15,16}

When exposed to a Ag(110) surface between 40 and 75 K, an O₂ molecule is chemisorbed onto the fourfold hollow site with its molecular axis either along the $[001]$ direction $[O_2(001)]$ or the $[1\bar{1}0]$ direction $[O_2(1\bar{1}0)]$.^{11,17} Topographical images of the O₂(001) are shown in Figs. 1(a) (taken using a bare tip) and 1(b) (taken using a CO-terminated tip). The alignment of the molecular axis was assigned based on the symmetry of the electronic orbital associated with vibrational excitation,¹¹ the dissociation pathway, and theoretical calculations^{8,9} and further confirmed by the theoretical STM image calculation.¹³ The O₂ molecule exhibits negatively charged states (peroxide or superoxide),^{6,9} where electrons flow from the Ag surface into the O₂ $1\pi_g$ (antibonding) orbital.

Tunneling of electrons into the O₂(001) causes it to rotate. Application of a positive voltage pulse between 450 and

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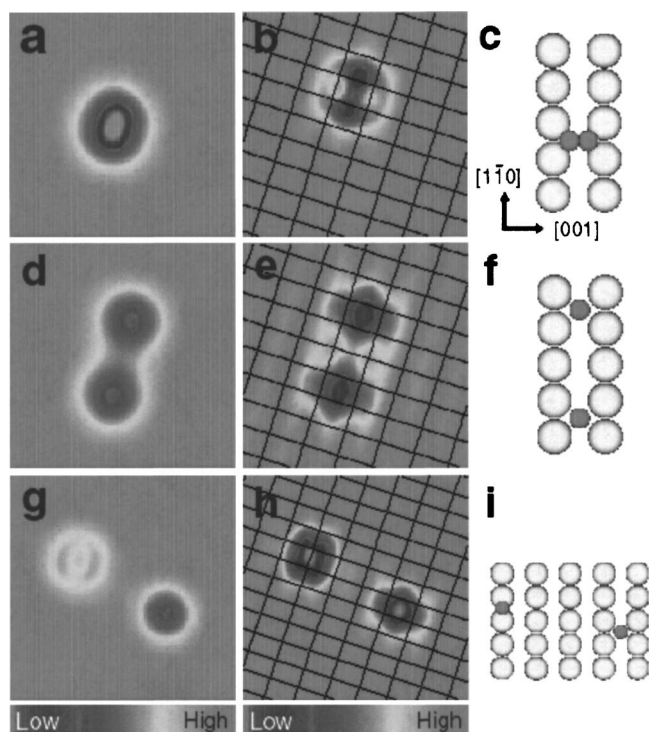


FIG. 1. Dissociation of O_2 chemisorbed on $Ag(110)$ at 13 K. The left column shows topographical images obtained using a bare tip at a sample bias voltage of 70 mV and a tunneling current of 1 nA [(a), (d), and (g)]. The center column shows the atomically resolved topographical images obtained using a CO-terminated tip at a sample bias voltage of 70 mV and a tunneling current of 1 nA [(b), (e), and (h)]. The grid lines are drawn through the Ag surface atoms. Schematic diagrams of the adsorption sites are shown in the right column [(c), (f), and (i)]. The small circles represent O atoms and the large circles represent Ag atoms. The sizes of the circles are scaled to the atomic covalent radii. (a)–(c) An O_2 molecule chemisorbed on the fourfold hollow site with its molecular axis aligned along the $[001]$ direction. The scan area of images (a) and (b) is $25 \times 25 \text{ \AA}^2$. (d)–(f) The O_2 molecule is dissociated along the $[1\bar{1}0]$ direction by a +480-mV voltage pulse applied to the sample with the feedback off. The dissociated O atoms are adsorbed on fourfold hollow sites. The scan area of images (d) and (e) is $25 \times 25 \text{ \AA}^2$. (g)–(i) Two O atoms dissociated along the $[001]$ direction by a –390-mV voltage pulse applied to the sample with the feedback off. One O atom is adsorbed on the fourfold hollow site and the other is bonded onto the short bridge site. The scan area of images (g) and (h) is $31 \times 31 \text{ \AA}^2$.

470 mV with a duration of 25 s over the $O_2(001)$ (voltage pulse applied to the sample with the feedback off after positioning the STM tip over the molecule at a tunneling current of 1 nA) causes the molecule to rotate by 90° ; that is, the molecular axis changes to the $[1\bar{1}0]$ direction.¹⁸ This rotation is irreversible and occurs only with a positive sample voltage pulse.

If the voltage pulse is increased slightly to +480 mV (at a tunneling current of 1 nA), the $O_2(001)$ dissociates into O atoms that are separated along the $[1\bar{1}0]$ direction [Figs. 1(d) and 1(e)]. In all 148 $O_2(001)$ molecules examined in this study, every O atom formed by dissociation under the positive voltage pulse lay in the fourfold hollow site along the $[1\bar{1}0]$ direction. These dissociated O atoms were separated by up to two empty sites, forming either a nearest-neighbor (not shown), next-nearest neighbor (not shown), or next-next-nearest neighbor [Figs. 1(d) and 1(e)] configuration.

The details of the dissociation pathway were determined by controlling the duration of the voltage pulse. By monitor-

ing the tunneling current during application of the voltage pulse, we can identify the sudden increase or decrease of tunneling current associated with changes in the adsorbed molecule. If the voltage pulse is stopped upon detecting this sudden change in the tunneling current, intermediate states can be probed. Using this approach, we found that $O_2(001)$ is rotated to $O_2(1\bar{1}0)$ before the dissociation with a positive voltage pulse. The threshold voltage for the dissociation was determined to be +470 mV (± 10 mV) (with the pulse duration of 25 s at the tunneling current of 1 nA). This is slightly higher than the observed barrier for the rotation (+450 mV).

The $O_2(001)$ molecule is also dissociated by negative voltage pulses, although different products are formed.¹⁹ Intriguingly, one O atom occupies the fourfold hollow site (O_{fhh}) while the other is bonded on the short-bridge site (O_{sb}) [Figs. 1(g) and 1(h)]. In addition, they are separated not along the $[1\bar{1}0]$ direction but along the $[001]$ direction. Imaging the same area before and after the dissociation allowed us to probe the trajectory of the O atoms during dissociation. We found that the O_{fhh} remains in the position of the original $O_2(001)$ while the O_{sb} moves away along the $[001]$ direction, a distance of more than 10 \AA . The threshold voltage for dissociation was determined to be –390 mV (± 10 mV) under application of a negative voltage pulse (with a pulse duration of 25 s at a tunneling current of 1 nA).

Such difference in the dissociation pathway with the negative voltage pulse from the positive voltage is induced by the different alignment of the molecular axis before the dissociation because the O_2 preferentially dissociates by extending the O–O bond in the chemisorbed state. When a positive voltage pulse is applied, the $O_2(001)$ rotates before the dissociation occurs. In contrast, when a negative voltage pulse is applied, the $O_2(001)$ molecule rotates at most only slightly.²⁰ Interestingly, the $O_2(1\bar{1}0)$ dissociation pathway is the same for positive and negative voltage pulses, with the two O atoms always separating along the $[1\bar{1}0]$ direction. This is in line with the fact that the O_2 rotation is irreversible.

The observation of an O atom on the short-bridge site [Figs. 1(g) and 1(h)] was unexpected and has not been previously reported in the thermal dissociation literature.¹² In contrast, O_{fhh} has been experimentally observed and proposed as the most stable O species on the basis of theoretical calculations.⁸ O_{fhh} is highly stable even under 1-V voltage pulse. On the other hand, O_{sb} undergoes thermal diffusive motion; for example, it moves up to two lattice spacings within a few tens of minutes at 13 K. According to the calculations of Gravil *et al.*,⁸ the binding energies of O_{fhh} and O_{sb} are 3.14 and 2.75 eV, respectively, at the low coverage limit. We found that O_{sb} atoms always diffused to other short-bridge sites, even if they could diffuse along either the $[001]$ or $[1\bar{1}0]$ direction. This observation indicates that the O_{sb} atoms have a higher barrier for diffusion to a fourfold hollow site than to another short-bridge site. When the O_{sb} diffuses along the $[001]$ direction its pathway may bypass the fourfold hollow site. In addition, we observed that O_{sb} did not react with CO molecule whereas the O_{fhh} easily reacted with an adsorbed CO molecule.²¹

The higher mobility of O_{sb} atoms may explain the larger atomic separation by negative voltage pulse than by positive voltage pulse. The average atomic separation induced by a positive (negative) voltage pulse is 4.3 Å (11.7 Å). This is about 1.5 (2.9) times the lattice spacing along the $[1\bar{1}0]$ ($[001]$) direction. The formation of O_{sb} may be related to the more corrugated surface potential and larger lattice spacing along the $[001]$ direction in comparison with the $[1\bar{1}0]$ direction. The dissociation barrier for the $O_2(001)$ molecule along the $[001]$ direction (0.76 eV) is higher than that along the other direction (0.62 eV).⁹ This higher-energy barrier indicates that the dissociation process involves a larger extension of the O–O bond along the $[001]$ direction, enabling the formation of the O_{sb} species. The atomic separation for thermal dissociation of O_2 on Ag(110),¹² Pt(111),²² Cu(110),²³ and Rh(001) (Ref. 24) is usually more than one lattice constant, and is similar to that of tunneling-electron induced dissociation.^{25,26} To account for this finding, which is contrary to expectations based on the high diffusion barriers, it has been suggested that hot atoms are produced by the transfer of adsorption energy into kinetic energy. Similarly, in the system considered here, the chemical energy released from the dissociation may be partially transformed into kinetic energy as well as directly dissipated into the substrate.

In the case of the $O_2(001)$ on Ag(110), the $1\pi_g^\perp$ resonance is located at the Fermi level.¹³ This resonance is involved in the STM imaging¹³ and vibrations¹¹ of the $O_2(001)$ such as the O–O stretch and the antisymmetric O_2 –Ag stretch. Such orbital resonance will also favor dissociation of $O_2(001)$. The temporary removal of electrons from the $1\pi_g^\perp$ orbital or the temporary injection of electrons into this orbital induces elongation of the O–O bond, which is similar to the O_2 chemisorption results.^{3,9} The threshold voltages that resulted in dissociation in the present work (–390 and 470 mV) correspond to the energy of the highest projected density of states on the $O_2(001)$ $1\pi_g^\perp$ orbital.¹³ The observation of distinct dissociation pathways under positive and negative voltage polarities can be due to (i) the higher efficiency of energy transfer to the rotational mode of $O_2(001)$ in the case of electron injection compared to electron removal, or (ii) the fact that, under a negative voltage pulse, the barrier to dissociation becomes lower than the barrier to rotation.

In conclusion, we have demonstrated that the reaction pathway and product formation in the dissociation of a single O_2 chemisorbed on a Ag(110) surface can be controlled by changing the tunneling direction of electrons using STM. A resonant orbital located at the Fermi level is associated with

such distinct pathways, which is stimulating theoretical calculations. The approach proposed here could potentially be used to elucidate the energy-transfer process during other chemical reactions and to understand the chemical dynamics of those systems at the single-molecule level.

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- ¹⁸The image of the $O_2(1\bar{1}0)$ molecule obtained using a bare tip exhibits a deeper oval-shaped depression than is observed in the image of the $O_2(001)$ molecule in Fig. 1(a). The two protrusions observed in the image of $O_2(001)$ in Fig. 1(b) (taken using a CO-terminated tip) are not observed in the image of $O_2(1\bar{1}0)$.
- ¹⁹Under the negative voltage pulse, 15% of the 138 $O_2(001)$ molecules examined showed a dissociation pathway the same as that found under a positive voltage pulse and 85% showed a different dissociation pathway.
- ²⁰In the dissociation, 12% of the O_{sb} atoms were found along the O–O bond direction of the parent $O_2(001)$. In contrast, O_{sb} can be shifted along the $[1\bar{1}0]$ direction, e.g., up by one lattice site as shown in Figs. 1(g)–1(i).
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