Adsorption and dissociation of O₂ on Ir(111)

Ye Xu and Manos Mavrikakis^{a)}

Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

(Received 21 December 2001; accepted 27 March 2002)

The adsorption and dissociation of dioxygen on the Ir(111) surface have been studied using periodic self-consistent density functional theory (DFT-GGA) calculations. Three di- σ -type chemisorbed molecular precursors are identified: One is located over bridge sites and has a binding energy of -1.3 eV and a bond length of 1.4 Å; the other two are located over threefold hollows and have similar binding energies of *ca.* -1.2 eV and bond lengths of *ca.* 1.5 Å. None are magnetic, suggesting a peroxo (O_2^{2-}) nature for these precursors. The minimum energy path for O₂ dissociation is determined using the nudged elastic band method, and a very small activation energy is found, *ca.* 0.06 eV. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479716]

INTRODUCTION

Like other Group VIII transition metals, iridium has numerous applications in the chemical and petroleum industries. For instance, Ir and Ir alloy catalysts are widely used in reactions that require the activation of the strong C–H bonds in alkanes.¹ Many important and valuable industrial reactions share this requirement. These include the conversion of saturated hydrocarbons in petroleum naphtha fractions to aromatic compounds (dehydrocyclization of alkanes and dehydrogenation of cycloalkanes), which are high-octane components of gasoline;² the conversion of lower alkanes to feedstock chemicals; and the steam reforming of methane as well as the conversion of methane to higher hydrocarbons or methanol.^{3,4} Ir has also been considered in the on-going effort to improve the automobile catalytic converter because of its ability to decompose NO⁵ and to reduce NO_x with hydrocarbons.⁶ Recently, two new homogeneous Ir-based catalysts have further demonstrated the usefulness of iridium. One has improved the production of acetic acid by a methanol carbonylation process,⁷ and the other catalyzes liquid-phase dehydrogenation of cycloalkanes, which could produce hydrogen gas from gasoline to be used as fuel in automobile fuel cells.⁸

Chemisorbed dioxygen species have been detected on a number of transition metal surfaces (see Table I), generally at temperatures below ~ 150 K. Although the exact nature of the molecular precursors cannot be determined with complete confidence, vibrational spectroscopy has suggested the existence of a peroxo form (O_2^{2-}), with an O–O stretching frequency of 610 – 690 cm⁻¹, and a superoxo (O_2^-) form, with a stretching frequency of 810 – 870 cm⁻¹. A third form, with a stretching frequency of 950 cm⁻¹, is observed on the Pd(111) surface.¹³ These precursors generally adopt orientations in which their molecular axes are parallel to the surface (the di- σ configuration).

A significant charge transfer from the substrate to the O₂ π_{2p}^* orbital weakens the O–O bond, causing it to lengthen

by up to 20% of its gas-phase length and reducing its stretching frequency. Such structural changes suggest that these molecular states are likely precursors to O₂ dissociation. Because the existence of molecular O₂ precursors could influence surface reaction kinetics, it is important to ascertain the characteristics and behavior of these precursors.

Different mechanisms for O₂ dissociation have been identified on different metal surfaces.²⁰ These include direct dissociation upon adsorption and precursor-mediated dissociation. In the chemisorbed-precursor mechanism, the incident O₂ molecule initially chemisorbs intact. Subsequent thermally driven kinetics determines the selectivity between desorption and dissociation. It is well known that O₂ molecules readily dissociate on the Ir(111) surface, but there is a hidden level of complexity to the adsorption mechanism. Weinberg *et al.* observed a constant sticking probability of O₂ at 325 K until surface coverage neared saturation²¹ and postulated that O₂ molecules accessed a molecularly adsorbed precursor state on the surface before dissociation and that the precursor could readily diffuse across the surface. In their molecular beam study Davis *et al.*⁹ observed that in the high incident kinetic energy regime (>0.1 eV) O₂ molecules had an initial dissociative chemisorption probability that was dependent on surface temperature. They also observed no increase in saturation coverage with increasing incident kinetic energy. They therefore also suggested that O₂ molecules dissociated after directly accessing a molecular chemisorbed state first.

Direct evidence of the existence of molecularly adsorbed O₂ on Ir(111), however, proved harder to find than on such surfaces as Pt(111),¹⁶ Pd(111),¹¹ and Cu(111).¹⁰ The lifetime of such a species is too short to be observed at room temperature, and even at 180 K Marinova *et al.* did not observe molecular oxygen species with EELS.²² Davis *et al.* captured molecularly adsorbed O₂ on Ir(111) with EELS at ~ 68 K and only at intermediate to high surface coverage ($1/4$ – $1/2$ ML of oxygen atoms). They assigned two loss peaks to molecularly adsorbed O₂, one at 740 cm⁻¹ and the other at 805 cm⁻¹. No molecular oxygen species was detected when the coverage of atomic oxygen was below $1/4$ ML. After a flash to 120 K those two loss features were no longer found.

^{a)} Author to whom correspondence should be addressed: 1415 Engineering Drive, Madison, Wisconsin 53706. Telephone: +1 (608) 262-9053; fax: +1 (608) 262-5434; electronic mail: manos@engr.wisc.edu

TABLE I. Transition metal surfaces on which molecularly adsorbed O₂ has been detected experimentally. O–O stretching frequencies measured with EELS, if available, are shown here to distinguish between different molecular precursor states. As a reference, the vibrational frequency of O_{2(g)} is 1580 cm⁻¹ (Ref. 19).

Surface	$\nu_{(\text{O-O})}$ (cm ⁻¹)		References
Ir(111)	740	805	9
Cu(111)	610	820–870	10
Pd(111)	635	805–850	950–1035
Pt(111)	690	870	11, 12, 13
Ni(111)			14, 15, 16
			17, 18

The structural and electronic properties of the precursors, however, have still not been well understood, and the detailed O₂ dissociation path on Ir(111) has not been studied theoretically. Here we present periodic self-consistent DFT calculations performed to investigate the characteristics of various molecular and atomic oxygen states and to explore the dissociation of O₂ on Ir(111).

METHODS

Periodic self-consistent DFT calculations were performed using DACAPO.²³ Adsorption was allowed on only one of the two surfaces of a (2×2) unit cell used to construct the Ir(111) surface, with the electrostatic potential adjusted accordingly.²⁴ The metal slab consisted of four layers of Ir atoms. Successive slabs were separated by a vacuum equivalent to six layers of Ir. The surface Brillouin zone was sampled at 18 special *k* points. Ionic cores were described by ultrasoft pseudopotentials.²⁵ The Kohn–Sham one-electron valence states were expanded in a basis of plane waves with kinetic energies below 25 Ry. The exchange–correlation energy and potential were described by the generalized gradient approximation (GGA-PW91).^{26,27} Besides PW91, the RPBE functional was also used non-self-consistently for comparison. The self-consistent PW91 density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density.²⁸ All total energies have been extrapolated to $k_B T = 0$ eV. Because, as shown in a recent DFT study on the dissociative adsorption of CH₄ on Ir(111),²⁹ the number of layers in the metal slab may have a pronounced effect on adsorption and dissociation energetics, we verified the convergence of our results with respect to the number of metal layers and with respect to the number of *k* points.

The calculated equilibrium lattice constant for bulk Ir is $a = 3.86$ Å (PW91), in good agreement with the experimental value of $a = 3.84$ Å.³⁰ The calculated bond energy and bond length for gas-phase O₂ are 5.64 eV and 1.24 Å, respectively, in reasonable agreement with the experimental values of 5.25 eV³¹ and 1.21 Å.³² The PW91 bond energy of gas-phase O₂ (5.64 eV) differs from the corresponding number given in Ref. 31 (6.20 eV) probably because the latter result was obtained with the O–O bond fixed at its experimentally determined length.

The adsorption of atomic and molecular oxygen at various sites was studied on an ideal fixed bulk-truncated

Ir(111) surface. The binding energies ($E_b = E_{\text{total}} - E_{\text{substrate}} - E_{\text{gas-phase adsorbate}}$), geometries, and magnetic moments of the adsorbates were calculated with respect to the clean fixed surface. The effect of *surface relaxation* was investigated by relaxing the top two layers of the slab, and the various properties were re-calculated with respect to the clean relaxed surface. The vibrational frequencies of various species were calculated in the harmonic oscillator approximation. Based on the adsorbate structure optimized on a relaxed surface, a series of static calculations were performed for a system, in which the atomic oxygen was displaced up to ±2% from its equilibrium position and for molecular oxygen the O–O bond was varied by ±2% with respect to its equilibrium length while its center was kept fixed. The resultant data points (binding energy vs displacement) were fitted to a parabola $E = k(x - b)^2/2$, where k is related to the vibrational frequency of the harmonic oscillator via $\nu = (\sqrt{k/M})/2\pi$, M being the reduced mass of the vibrating system (an O atom or an O₂ precursor molecule on the Ir slab).

The minimum energy path for O₂ dissociation on Ir(111) was determined using the nudged elastic band (NEB) method.³³ Five intermediate images were used between two fixed end states to discretize the path. The calculations were not spin-polarized in view of the fact that neither the initial state, nor the final state, nor any of the more stable atomic species that we found, carried any remaining magnetic moment. The complete path was interpolated³⁴ by fitting a cubic polynomial through all the images in order to locate the transition state and thereby to determine the activation energy barrier.

RESULTS AND DISCUSSION

Atomic oxygen on Ir(111)

Before presenting our results, we review the interaction of atomic oxygen with Ir(111) as documented in the literature. It has been well established that the exposure of a clean Ir(111) surface to oxygen produces a 2×2 pattern in LEED. At room temperature an exposure of ~20 L is sufficient to produce a very sharp such image.^{35,36} Prolonged exposure (>100 L) results in no new structure,^{35,37} which suggests oxygen saturation. Tucker pointed out that a 2×2 overlayer LEED pattern from an fcc(111) substrate surface could be caused either by a $p(2\times 2)$ surface structure or by three domains of a (1×2) surface structure rotated 120° with respect to one another.³⁸ The $p(2\times 2)$ surface structure corresponds to a coverage of 1/4 ML of oxygen atoms, and the (1×2) surface structure corresponds to a coverage of 1/2 ML. Zhdan *et al.*³⁹ and Marinova *et al.*²² deduced from XPS data that 1/2 ML was the maximum coverage for atomic oxygen. A single loss peak in EELS of 550 cm⁻¹ at saturation coverage was observed by several authors over a wide range of temperature, which they attributed to a unique chemisorbed state for atomic oxygen on Ir(111).^{5,9,22}

Adsorbed oxygen desorbs from Ir(111) as molecular oxygen between 800–1200 K, depending on surface coverage.^{5,40} In their XPS study Zhdan *et al.* observed that the surface concentration of oxygen started to decrease quickly

FIG. 1. A top view of adsorption sites for atomic oxygen on an Ir(111) surface. Open circles denote Ir atoms and filled circles denote O atoms.

when the substrate temperature increased to above 600 K in 10^{-7} Torr O_2 .³⁹ They explained this decrease as oxygen atoms diffusing into the bulk Ir lattice and forming a *bulk*-dissolved oxide state. Besides bulk-dissolved oxygen they also found in the *sub-surface* region a different oxide state after extensive oxidation of the surface (more than 10 minutes at 700 K in 10^{-7} Torr O_2). Marinova *et al.* observed two separate loss peaks (~ 800 and 1000 cm^{-1}) in EELS at 600 K and 10^{-5} Pa O_2 and above.²² They attributed them to oxygen in a *surface* oxide state and *sub-surface* diffused state and showed that neither was IrO_2 . In contrast to adsorbed oxygen, oxygen in these various oxide states produced under high temperatures showed no reactivity toward CO or H_2 .^{39,40} Ivanov *et al.*⁴⁰ reported the decomposition of the surface oxide that they discovered at 1270 K. The decomposition temperature led to the hypothesis that the desorbing species was IrO_2 . Zhdan *et al.*³⁹ found that the sub-surface oxide state could be removed by heating the Ir crystal to 1600 K but that 1600 K was not sufficient to remove the dissolved oxygen completely from the crystal. It should be noted that bulk IrO_2 does not form through heating pure Ir in

O_2 , probably because the surface oxide provides an additional diffusion barrier to prevent further uptake of oxygen.⁴¹

As indicated in Fig. 1, in our investigation of the adsorption of atomic oxygen on Ir(111) at $1/4$ ML coverage, we studied four high-symmetry sites. The O atom was allowed to move freely in all directions during energy minimization, except for the calculation of the bridge site on the static surface, where only motion in the z -direction was allowed of the O atom. Results are shown in Table II. As has been discovered on the (111) facets of several other fcc metals, atomic oxygen preferentially adsorbs in threefold hollows on Ir(111). The best site is fcc, with a binding energy of -4.54 eV/O , leading the hcp site by 0.25 eV . The top site is probably a relatively flat minimum in the potential energy surface because an oxygen atom in this configuration is insensitive to small perturbations to its position. Surface relaxation affects binding energies very little. In every case it introduces a gain of less than 3%. The exception is the bridge site, which does not provide a stable adsorption minimum on a relaxed surface. The adsorption height, as measured from the plane of the centers-of-mass of the top-layer Ir atoms in the fixed bulk-truncated positions to the center of mass of the O atom, is changed by 7% at most when surface is relaxed. Compared to a clean relaxed surface, the three Ir atoms in the unit cell that are bound to the O atom adsorbed in a fcc or hcp site relax outward by $\sim 0.07\text{ \AA}$. They also move laterally ($\sim 0.05\text{ \AA}$) away from the O atom to accommodate its presence. The fourth Ir atom in the unit cell, which is not bound to the O atom, relaxes inward by $\sim 0.01\text{ \AA}$. Davis *et al.* reported the vibrational frequency of atomic oxygen to be 550 cm^{-1} at $1/4$ ML surface coverage,⁹ whereas we calculated the frequency of the Ir–O stretch to be 483 cm^{-1} at the same coverage.

TABLE II. Properties of atomic oxygen adsorbed on Ir(111). E_b is the binding energy, calculated as $E_b = E_{\text{total}} - E_{\text{substrate}} - E_{O(g)}$, where E_{total} is the total energy of the system, $E_{\text{substrate}}$ is the energy of either a clean fixed bulk-truncated Ir(111) surface or such a surface with its top two layers relaxed, and $E_{O(g)}$ is the energy of an O atom in the gas phase; z is the height measured from the plane of the centers-of-mass of the top-layer iridium nuclei (fixed bulk-truncated positions) to the center-of-mass of the O atom(s); $d_{(Ir-O)}$ is the distance between O and the nearest Ir atom; $\nu_{(Ir-O)}$ is the frequency of O vibration perpendicular to the surface; μ is the residual magnetic moment; and $\Delta e\phi$ is the change in surface work function with respect to the clean Ir(111) surface. E_b of fcc $\times 2$ is in eV/ O_2 and is calculated as described in Table III.

	Site	E_b (eV/O)	z ($\text{\AA}$)	$d_{(Ir-O)}$ ($\text{\AA}$)	$\nu_{(Ir-O)}$ (cm^{-1})	μ (μ_B)	$\Delta e\phi$ (eV)
Fixed	top	-3.40	1.79	1.79		0.65	+0.87
Substrate	bridge	-3.97	1.45	1.99		0.00	+0.52
(1/4 ML)	hcp	-4.29	1.32	2.05		0.00	+0.27
	fcc	-4.54	1.31	2.05		0.00	+0.28
Relaxed	top	-3.50	1.90	1.77		1.07	+0.89
Substrate	hcp	-4.32	1.23	2.04		0.00	+0.18
(1/4 ML)	fcc	-4.57	1.22	2.04	483	0.00	+0.25
Relaxed	fcc $\times 2$	-3.19	1.26	2.04	482–526	0.00	+0.54
Substrate							
(1/2 ML)							
Experimental							
Saturation (0.5 ML)		3.04 ^a			550 ^b		+0.56 $\pm$ 0.04 ^c
Low coverage (0.02 ML)					525 ^d		

^aReference 35.

^cReference 40.

^bReferences 5, 9, 22.

^dReference 9.

FIG. 2. (a) A top view of adsorption sites for O₂ precursors on an Ir(111) surface, and (b) a schematic showing the definitions of the spherical angles θ and ϕ , as used in Tables III and V. Open circles denote Ir atoms and filled circles denote O atoms.

The adsorption of atomic oxygen at 1/2 ML coverage was also investigated. This was necessary because the final state of the dissociation of an O₂ precursor in a (2×2) unit cell represented 1/2 ML of atomic oxygen and must be determined before the dissociation path could be analyzed. The most stable such configuration turns out to be two oxygen atoms in a set of adjacent fcc sites (fcc×2). When repeated, this gives rise to an ad-layer with a $p(1\times 2)$ unit cell. The $p(1\times 2)$ unit cell has three possible orientations on the (111) surface, and it is conceivable that domains of all three orien-

tations exist at saturation. This would give rise to the 2×2 LEED structure, if interpreted as three domains of the (1×2) surface structure rotated 120° with respect to one another. Several other possible final states for O₂ dissociation in the (2×2) unit cell have also been considered, all of which are considerably less stable than fcc×2. The binding energy for fcc×2 is calculated to be -3.19 eV/O₂ (with respect to gas-phase O₂). Küppers *et al.* estimated the binding energy of oxygen to be about -70 kcal/mol or -3.04 eV/O₂, presumably at the saturation coverage.³⁵ Ivanov *et al.* measured the increase in surface work function at saturation to be 0.56 ± 0.04 eV.⁴⁰ We found 0.54 eV for fcc×2, in good agreement with their result. Because at 1/2 ML there are two O atoms per unit cell, we took the *in-phase* vibration of the two O atoms as the upper limit and the *out-of-phase* vibration as the lower limit when calculating the Ir–O stretching frequency at 1/2 ML. The frequency of the in-phase vibration is determined to be 526 cm⁻¹, and that of the out-of-phase vibration 482 cm⁻¹. The average of the two figures, 504 cm⁻¹, is 46 cm⁻¹ lower than the experimentally observed 550 cm⁻¹.

Molecular oxygen precursors on Ir(111)

Our calculations for molecular oxygen precursors were carried out with one O₂ molecule in each (2×2) cell, amounting to $\theta_{O_2} = 1/4$ ML. We found stable precursor states in the t-b-t, t-h-b, and t-f-b configurations (see Fig. 2 and Table III). The adsorbed O₂ molecule displaces surface Ir atoms to a similar extent as does the oxygen adatom. Although t-f/h-b and t-b-t are located over different sites, their binding energies are identical on the static surface. The t-f/h-b precursors gain ~ 0.05 eV in binding energy upon surface relaxation, whereas the t-b-t precursor gains a larger ~ 0.15 eV to -1.27 eV/O₂, thus distinguishing itself from the t-f/h-b precursors. The O–O bond lengths of the precursor states vary slightly between 1.43 – 1.50 Å (compared to the calculated gas-phase O–O bond length of 1.24 Å). Self-

TABLE III. Properties of molecular O₂ precursors on Ir(111). Coverage of O₂ is 1/4 ML. E_b is the binding energy, calculated as $E_b = E_{\text{total}} - E_{\text{substrate}} - E_{O_2(g)}$, where E_{total} is the total energy of the system, $E_{\text{substrate}}$ is the energy of either a clean fixed bulk-truncated Ir(111) surface or such a surface with its top two layers relaxed, and $E_{O_2(g)}$ is the energy of an O₂ molecule in the gas phase; z is the height measured from the plane of the centers-of-mass of the top-layer iridium nuclei (fixed bulk-truncated positions) to the center-of-mass of the O₂ molecule; θ and ϕ are the spherical angles as defined in Fig. 2(b); $d_{(O-O)}$ is the O–O bond length; $\nu_{(O-O)}$ is the O–O stretching frequency; μ is the residual magnetic moment; and $\Delta e\phi$ is the change in surface work function with respect to the clean Ir(111) surface. DFT calculations have been performed to obtain the properties of O₂ in the gas phase, shown in the first entry as a reference.

	Site	E_b (eV/O ₂)	z (Å)	θ (°)	ϕ (°)	$d_{(O-O)}$ (Å)	$\nu_{(O-O)}$ (cm ⁻¹)	μ (μ_B)	$\Delta e\phi$ (eV)
O _{2(g)} (bond energy)		5.64				1.24	1607	2.00	
Experimental		5.25 ^a				1.21 ^b	1580 ^c		
Fixed substrate	t-b-t	-1.13	1.88	0.0	30.0	1.42		0.00	+0.90
	t-h-b	-1.13	1.77	7.5	0.0	1.47		0.00	+0.80
	t-f-b	-1.13	1.76	8.4	0.0	1.49		0.00	+0.83
Relaxed substrate	t-b-t	-1.27	1.90	0.0	30.0	1.43	679	0.00	+0.93
	t-h-b	-1.18	1.74	8.0	0.0	1.50		0.00	+0.87
	t-f-b	-1.17	1.75	8.0	0.1	1.48	513	0.00	+0.92
Experimental							740,805 ^d		

^aReference 31.

^bReference 32.

^cReference 19.

^dReference 9.

TABLE IV. Molecular O₂ precursors identified on several metal surfaces in DFT studies. The PW91 functional is used. The properties, in the order listed, are configuration; binding energy; O–O bond length; adsorption height; residual magnetic moment; and O–O stretching frequency, where available. Pt, Ni, and Pd results are obtained on fixed substrates. Cu and Ir results are obtained on relaxed substrates.

Surface	Precursor species	Properties	Precursor Species	Properties	Precursor species	Properties
Pt(111) ^a	Chemisorbed in threefold hollow	top–fcc–bridge –0.68 eV 1.43 Å 1.78 Å 0.0 μ _B 690 cm ^{–1}	Chemisorbed in threefold hollow	top–hcp–bridge –0.58 eV 1.42 Å 1.81 Å 0.0 μ _B 710 cm ^{–1}	Chemisorbed at bridge site	top–bridge–top –0.72 eV 1.39 Å 1.92 Å 0.4 μ _B 850 cm ^{–1}
Ni(111) ^a	Chemisorbed in threefold hollow	top–fcc–bridge –1.65 eV 1.47 Å 1.62 Å 0.2 μ _B	Chemisorbed in threefold hollow	top–hcp–bridge –1.67 eV 1.46 Å 1.62 Å 0.2 μ _B	Chemisorbed at bridge site	top–bridge–top –1.41 eV 1.42 Å 1.77 Å 0.4 μ _B
Pd(111) ^a	Chemisorbed in threefold hollow	top–fcc–bridge –1.01 eV 1.39 Å 1.75 Å 0.0 μ _B 890 cm ^{–1}	Chemisorbed in threefold hollow	top–hcp–bridge –0.92 eV 1.41 Å 1.79 Å 0.0 μ _B 830 cm ^{–1}	Chemisorbed at bridge site	top–bridge–top –0.89 eV 1.36 Å 1.91 Å 0.3 μ _B 960 cm ^{–1}
Cu(111) ^b	Chemisorbed in threefold hollow	bridge–hcp–bridge –0.56 eV 1.48 Å 1.55 Å 0.0 μ _B 729 cm ^{–1}	Chemisorbed in threefold hollow	top–hcp–bridge –0.52 eV 1.44 Å 1.65 Å 0.0 μ _B 789 cm ^{–1}	Chemisorbed at bridge site	top–bridge–top –0.45 eV 1.35 Å 1.88 Å 0.99 μ _B 954 cm ^{–1}
Ir(111) (This study)	Chemisorbed in threefold hollow	top–fcc–bridge –1.17 eV 1.48 Å 1.75 Å 0.0 μ _B 513 cm ^{–1}	Chemisorbed in threefold hollow	top–hcp–bridge –1.18 eV 1.50 Å 1.74 Å 0.0 μ _B	Chemisorbed at bridge site	top–bridge–top –1.27 eV 1.43 Å 1.90 Å 0.0 μ _B 679 cm ^{–1}

^aReference 42.

^bReference 43.

consistent DFT calculations have been used recently to investigate O₂ precursors on metal surfaces such as Ni(111),⁴² Pt(111),⁴² Pd(111),⁴² and Cu(111)⁴³ (see Table IV). The O₂/Ir(111) system bears similarity to those previously studied systems, with one important difference: None of the three precursors has any remaining magnetic moment, which is in accord with the significant charge transfer from Ir as indicated by the commensurate increase of ~0.9 eV of the surface work function. In that sense, the *superoxo* precursor state, as has been discovered on surfaces such as Cu(111) and Pt(111), does not exist on Ir(111). We found only peroxo-like (O₂^{2–}) precursors on Ir(111).

As mentioned before, Davis *et al.* detected two loss peaks at 740 and 805 cm^{–1} that they assigned to molecular O₂ precursor states.⁹ We calculated the O–O stretching frequencies for the t–f–b and t–b–t states and found 513 and 679 cm^{–1}, respectively. It should be noted that the intensity of the loss peaks that Davis *et al.* observed is appreciable only when the surface coverage of oxygen atoms is well above 1/4 ML. Those detected molecular states clearly must co-exist with atomic oxygen, whereas we have analyzed the vibrational frequencies of the precursor states at an O₂ coverage of 1/4 ML *without* the presence of oxygen atoms. The co-existence of atomic and molecular oxygen in the experiments may be responsible for a large fraction of the differ-

ence between experimental and theoretical O_{2(a)}/Ir(111) vibrational frequencies.

O₂ dissociation on Ir(111)

After investigating the adsorption of atomic and molecular oxygen on a (2×2) unit cell, we discuss the dissociation of O₂ on the relaxed Ir(111) surface using the most strongly

FIG. 3. Selected states along the O₂ dissociation path from t–b–t to fcc×2 on a relaxed Ir(111) surface. Shown here are (a) the initial state (t–b–t), (b) the first intermediate image in the NEB calculations (Image 1), (c) the third intermediate image (Image 3), and (d) the final state (fcc×2). The coverage is 1/4 ML of O₂ initially, corresponding to 1/2 ML of O at the end of the dissociation process. The upper row of panels show the side views, and the lower row of panels show the top views. For clarity, periodically repeated images of adsorbates have been omitted so that only one O₂ molecule is shown in each image.

FIG. 4. Minimum energy path for O₂ dissociation from t-b-t to fcc×2 on a relaxed Ir(111) surface, determined by NEB calculations in a (2×2) unit cell. The binding energy of O₂ is calculated as $E_b = E_{\text{total}} - E_{\text{substrate}} - E_{\text{O}_2(\text{g})}$, where the substrate is a clean bulk-truncated Ir(111) surface with its top two layers relaxed. The binding energy of the final point on the path (F.S., i.e., two O atoms at infinite separation) marked by the circle at the lower right corner of the graph is calculated as $E_b = 2 \times E_{b,\text{O}(\text{fcc})} - BE_{\text{O}_2(\text{g})}$, where $E_{b,\text{O}(\text{fcc})}$ is the adsorption energy of an O atom in the fcc site and $BE_{\text{O}_2(\text{g})}$ is the calculated bond energy of an O₂ molecule in the gas phase. The zero of the energy axis corresponds to the total energy of an O₂ molecule in the gas phase plus the total energy of the clean relaxed slab at infinite separation from each other. The seven circles on the line mark the positions of the initial and final states and of the five intermediate images in the NEB calculations. The line connecting these images is the result of interpolation, in which the force tangent to the reaction coordinate on each image is used to fit a cubic polynomial through all the images in order to approximate the minimum energy path. The calculated dissociation barrier (E_a) and heat of reaction (ΔE) are indicated. Horizontal lines are drawn only as a guide for the eye.

bound initial and final states, t-b-t and fcc×2, respectively. Figure 3 shows snapshots of the initial and final states and of two intermediate images along the calculated minimum energy reaction path, and Fig. 4 shows the energetics of the entire calculated minimum energy path. The properties of all the images in the NEB calculations are listed in Table V. With the interpolation scheme described in the Methods section, we estimated the barrier to O₂ dissociation to be 0.06 eV/O₂. The reaction is exothermic, yielding 2.2 eV/O₂ when both reaction products, O adatoms, have diffused away from each other on the Ir(111) surface. The entire path is located beneath the gas-phase zero. These characteristics

TABLE V. Properties of the initial, intermediate, and final states in the NEB calculations for O₂ dissociation on the relaxed Ir(111) surface. Images are as labeled in Fig. 4. Coverage of O₂ is 1/4 ML. E_b is the binding energy, calculated as $E_b = E_{\text{total}} - E_{\text{substrate}} - E_{\text{O}_2(\text{g})}$, where E_{total} is the total energy of the system, $E_{\text{substrate}}$ is the energy of a clean bulk-truncated Ir(111) surface with its top two layers relaxed, and $E_{\text{O}_2(\text{g})}$ is the energy of an O₂ molecule in the gas phase; z is the height measured from the plane of the centers-of-mass of the top-layer iridium nuclei (fixed bulk-truncated positions) to the center-of-mass of the O₂ molecule; θ and ϕ are the spherical angles as defined in Fig. 2(b); and $d_{(\text{O}-\text{O})}$ is the O-O bond length.

Image	$E_b(\text{eV/O}_2)$	z (Å)	θ (°)	ϕ (°)	$d_{(\text{O}-\text{O})}$ (Å)
t-b-t	-1.27	1.90	0.0	30.0	1.43
#1	-1.23	1.83	0.0	31.5	2.34
#2	-1.34	1.76	2.7	40.3	2.70
#3	-2.20	1.62	9.6	54.8	3.01
#4	-2.39	1.48	10.8	48.8	2.93
#5	-2.83	1.32	4.6	37.2	2.76
fcc×2	-3.19	1.26	0.0	30.0	2.73

FIG. 5. Evolution of the density of states (DOS) in the O₂ dissociation process on a relaxed Ir(111) surface. ε_F denotes the energy of the Fermi level. Darker lines represent local d -DOS projected onto an Ir atom in the top layer that is bound to the O₂ precursor or O atom; lighter lines represent local s - and p -DOS projected onto one of the two O atoms. Panel (a) corresponds to the clean surface and gas-phase O₂ (discrete states) serving as a reference. Panel (b) corresponds to the initial state (t-b-t). Panel (c) corresponds to the transition state (approximated by Image 1). Panel (d) corresponds to the final state (fcc×2) of the calculated minimum energy path.

combined indicate that O₂ should dissociate very readily on the Ir(111) surface, which is entirely in agreement with experimental observations.

The interpolated dissociation path has a very small peak in the vicinity of Image 1 (Fig. 4), where the O₂ precursor appears already to be undergoing a bond breaking event. The O-O bond is stretched to 2.34 Å, a length well beyond that of any O₂ molecular state. Therefore, dissociation happens *very early* in the reaction path. After the two oxygen atoms are sufficiently apart they start to fall off the t-b-t position. However, as Image 3 shows, this does not happen in a symmetric manner. It turns out to be more stable for the two oxygen atoms to adopt a top+fcc configuration, which requires a rotation of the O-O axis. There appears to be no barrier to this rotation. To break free of the top+fcc configuration and occupy the two adjacent fcc sites, the two O atoms

TABLE VI. A comparison of the binding energies of key states on the relaxed Ir(111) surface, in the PW91 functional versus the RPBE functional. Zero of the energy-scale corresponds to $O_{2(g)}$ and the clean relaxed Ir(111) slab at infinite separation. PW91 values are self-consistent and RPBE values are not (see the text for details). Bond energy for $O_{2(g)}$ is calculated to be 5.64 eV (PW91) and 5.20 eV (RPBE), respectively.

State	E_b (eV) PW91	E_b (eV) RPBE
Atomic—O/fcc	−4.57	−4.00
Precursor—t–b–t	−1.27	−0.75
Transition state	−1.21	−0.73
Final state—fcc×2	−3.19	−2.49

must rotate about the O–O axis again, and this time the existence of a small barrier of ~ 0.04 eV/ O_2 is evident around Image 4. During the entire process the surface Ir atoms show appreciable movement, to an extent (largest rms displacement being ~ 0.22 Å) close to what we discovered in our study on O_2 dissociation on Cu(111) but much less than what Henkelman *et al.* found in their DFT study of CH_4 dissociation on Ir(111).²⁹

Davis *et al.*⁹ found in their molecular beam study on O_2 /Ir(111) that in the high kinetic energy regime an increase in substrate temperature decrease the initial dissociative chemisorption probability (S_0), although the effect is moderate: Over a range of 800 K they observed only a $\sim 10\%$ decrease. We have calculated an activation energy that is substantially less than the desorption barrier of the O_2 precursor (i.e., the binding energy of the precursor). This would produce the observed negative dependence of the sticking coefficient on substrate temperature, and, given the large difference between the dissociation and desorption barriers, as the entire calculated dissociation path lies well beneath the gas-phase zero, even a substantial rise in temperature cannot increase desorption and reduce dissociation rates sufficiently to alter the sticking probability appreciably. Therefore we believe that our results are consistent with their findings.

Figure 5 shows the distribution of the density of d -states of the Ir(111) surface as well as the s - and p -states of the O atoms. The center of the d -band of a clean Ir(111) slab is -2.85 eV [Fig. 5(a)]. The adsorption of O_2 in the t–b–t state lowers it to -3.17 eV [Fig. 5(b)]. The center of the d -band is further lowered to -3.69 eV at the transition state [Fig. 5(c)] and remains mostly at that position to the end of the dissociation path [Fig. 5(d)].

As mentioned earlier, we have also calculated binding energies using the RPBE functional non-self-consistently. Table VI compares the RPBE energy values for key oxygen states on Ir(111) with those obtained with the PW91 functional. We find that the PW91 results are consistently lower in energy than their RPBE counterparts, with the differences in the range of 0.5–0.7 eV. This finding is in agreement with previous reports that indicate that RPBE predicts decreased binding energy for various adsorbates on a number of transition metal surfaces.²³ We note here that our calculated gas-phase O_2 bond energy in RPBE is 5.20 eV, much closer to the experimental value (5.25 eV) than the PW91 result (5.64 eV).

SUMMARY

Periodic self-consistent density functional calculations have been performed to study the adsorption and dissociation of dioxygen on an Ir(111) surface. Atomic oxygen is found to adsorb preferentially in threefold hollows, with the fcc site being the most favorable ($E_b \approx -4.6$ eV/O) at $\theta_O = 1/4$ ML. Molecular O_2 binds to Ir(111) in several energetically quasi-degenerate states of the di- σ type, of which t–b–t is the most stable on the relaxed surface with $E_b \approx -1.3$ eV/ O_2 at $\theta_{O_2} = 1/4$ ML. None of the precursor states have any residual magnetic moment and are therefore all considered to be of the peroxo type (O_2^{2-}). The dissociation of O_2 on Ir(111) is nearly spontaneous. Its activation energy is found to be a very small 0.06 eV/ O_2 , in agreement with available experimental data. This suggests that molecular O_2 precursors can exist on Ir(111) only at very low temperatures.

ACKNOWLEDGMENTS

The authors thank Graeme Henkelman and Professor Hannes Jónsson for insightful discussions on employing the NEB method. Professor C. B. Mullins is acknowledged for inspiring discussions on Ir surface chemistry. M.M. acknowledges financial support from a NSF-CAREER award (CTS-0134561). This research was supported in part by a National Science Foundation cooperative agreement through computing resources provided by the National Partnership for Advanced Computational Infrastructure. Part of the calculations was performed on Department of Energy supercomputing facilities (NERSC). Y.X. gratefully acknowledges partial financial support from a NSF-GRT grant. M.M. thanks the Shell Oil Company Foundation for a Faculty Career Initiation Award and BP–Amoco for an equipment grant.

- D. F. Johnson and W. H. Weinberg, *Science* **261**, 76 (1993).
- J. H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts, and Applications* (Wiley, New York, 1983).
- D. C. Seets, M. C. Wheeler, and C. B. Mullins, *Chem. Phys. Lett.* **266**, 431 (1997).
- D. C. Seets, C. T. Reeves, B. A. Ferguson, M. C. Wheeler, and C. B. Mullins, *J. Chem. Phys.* **107**, 10229 (1997).
- J. C. L. Cornish and N. R. Avery, *Surf. Sci.* **235**, 209 (1990).
- C. Wögerbauer, M. Maciejewski, and A. Baiker, *J. Appl. Catal. B* **34**, 11 (2001).
- A. Haynes, J. M. Pearson, P. W. Vickers, J. P. H. Charmant, and P. M. Maitlis, *Inorg. Chim. Acta* **270**, 382 (1998).
- D. Morales-Morales, D. W. Lee, Z. H. Wang, and C. M. Jensen, *Organometallics* **20**, 1144 (2001).
- J. E. Davis, P. D. Nolan, S. G. Karseboom, and C. B. Mullins, *J. Chem. Phys.* **107**, 943 (1997).
- T. Sueyoshi, T. Sasaki, and Y. Iwasawa, *Surf. Sci.* **365**, 310 (1996).
- R. Imbihl and J. E. Demuth, *Surf. Sci.* **173**, 395 (1986).
- P. Sjövall and P. Uvdal, *Chem. Phys. Lett.* **282**, 355 (1998).
- P. D. Nolan, B. R. Lutz, P. L. Tanaka, and C. B. Mullins, *Surf. Sci.* **419**, L107 (1998).
- C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *Surf. Sci.* **107**, 220 (1981).
- P. D. Nolan, B. R. Lutz, P. L. Tanaka, J. E. Davis, and C. B. Mullins, *J. Chem. Phys.* **111**, 3696 (1999).
- J. L. Gland, B. A. Sexton, and G. B. Fisher, *Surf. Sci.* **95**, 587 (1980).
- J. T. Stuckless, C. E. Wartnaby, N. Al-Sarraf, St. J. B. Dixon-Warren, M. Kovar, and D. A. King, *J. Chem. Phys.* **106**, 2012 (1997).

- ¹⁸M. Beutl, K. D. Rendulic, and G. R. Castro, *Surf. Sci.* **385**, 97 (1997).
- ¹⁹K. P. Huber and G. Herzberg, in *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1979).
- ²⁰P. D. Nolan, M. C. Wheeler, J. E. Davis, and C. B. Mullins, *Acc. Chem. Res.* **31**, 798 (1998).
- ²¹W. H. Weinberg, W. F. Egelhoff, Jr., V. P. Ivanov, V. L. Tataurov, and G. K. Boreskov, in *Proceedings of the 7th International Vacuum Congress and the 3rd International Conference of Solid Surfaces*, edited by R. Dobrozemsky, F. Rüdenauer, and F. P. Viehböck, Vienna, 1977, Vol. 2, p. 1151.
- ²²Ts. S. Marinova and K. L. Kostov, *Surf. Sci.* **185**, 203 (1987).
- ²³B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- ²⁴J. Neugebauer and M. Scheffler, *Phys. Rev. B* **46**, 16067 (1992).
- ²⁵D. H. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ²⁶J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ²⁷J. A. White and D. M. Bird, *Phys. Rev. B* **50**, 4954 (1994).
- ²⁸G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ²⁹G. Henkelman and H. Jónsson, *Phys. Rev. Lett.* **86**, 664 (2001).
- ³⁰J. Donohue, in *The Structures of the Elements* (Wiley, New York, 1974), p. 218.
- ³¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ³²*CRC Handbook of Chemistry and Physics*, 76th ed. (CRC, Boca Raton, FL, 1995).
- ³³H. Jónsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.
- ³⁴G. Henkelman and H. Jónsson, *J. Chem. Phys.* **113**, 9978 (2000).
- ³⁵J. Küppers and A. Plagge, *J. Vac. Sci. Technol.* **13**, 259 (1976).
- ³⁶C.-M. Chan and W. H. Weinberg, *J. Chem. Phys.* **71**, 2788 (1979).
- ³⁷D. I. Hagen, B. E. Nieuwenhuys, G. Rovida, and G. A. Somorjai, *Surf. Sci.* **57**, 632 (1976).
- ³⁸C. W. Tucker, *J. Appl. Phys.* **35**, 1897 (1964).
- ³⁹P. A. Zhdan, G. K. Boreskov, A. I. Boronin, W. F. Egelhoff, Jr., and W. H. Weinberg, *Surf. Sci.* **61**, 25 (1976).
- ⁴⁰V. P. Ivanov, G. K. Boreskov, V. I. Savchenko, W. F. Egelhoff, Jr., and W. H. Weinberg, *Surf. Sci.* **61**, 207 (1976).
- ⁴¹H. Conrad, J. Küppers, F. Nitschké, and A. Plagge, *Surf. Sci.* **69**, 668 (1977).
- ⁴²A. Eichler, F. Mittendorfer, and J. Hafner, *Phys. Rev. B* **62**, 4744 (2000).
- ⁴³Y. Xu and M. Mavrikakis, *Surf. Sci.* **494**, 131 (2001).