Translational Energy Selection of Molecular Precursors to Oxygen Adsorption on Pt(111)

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Adsorption intermediates of oxygen on a platinum (111) surface were examined with electron energy-loss spectroscopy (EELS) and molecular beams. Low incident kinetic energies promote initial adsorption into both a superoxolike (870 cm^{-1}) and peroxolike (690 cm^{-1}) molecular surface species at 77 K. High incident energies, however, exclusively populate the more strongly bound peroxolike species, suggesting a close correlation between incident kinetic energy and the reaction coordinate for adsorption. This investigation directly verifies surface intermediates in high kinetic energy adsorption and provides evidence of translational energy affecting adsorption product distribution. [S0031-9007(98)07249-4]

Oxygen adsorption at transition metal surfaces serves as the initial mechanistic step in many industrially important catalytic processes and has thus been studied extensively over the past few decades. The continued development of surface science techniques employing ultrahigh vacuum ($\sim 10^{-10}$ Torr), molecular beams, and surface-specific spectroscopies has contributed significantly to a more detailed comprehension of the physical and chemical interactions between adsorbates and surfaces by permitting investigation of energetically controlled incident gas molecules on well characterized, clean, single-crystal metal surfaces. The adsorption reaction between oxygen and the (111) face of platinum has been examined particularly thoroughly in recent years, due largely to its relevance in environmentally significant oxidation reactions [1]. Additionally, the ability of Pt(111) to adsorb oxygen in both an atomic and molecular state under easily attainable laboratory conditions underscores its potential value as a model system in elucidating microscopic details of dissociative chemisorption.

The notion of dissociation precursors dates back nearly 70 years, when Langmuir recognized that a mobile surface intermediate could explain a coverage independence in the adsorption probability of cesium on a tungsten filament [2,3]. Since this time, the relevance of molecular intermediates has been debated for many adsorption systems under various conditions. At translational energies less than ~ 0.1 eV, dissociative adsorption of oxygen on Pt(111) is well established as proceeding through sequential physically and chemically adsorbed molecular precursors [4–6]. An impinging molecule is thought to initially dissipate sufficient momentum to the surface to bind via van der Waals forces; subsequent conversion to chemically bound molecular and atomic adsorbates likely proceeds through a thermally driven kinetic competition between desorption and reaction. Such a mechanism is often referred to as trapping-mediated chemisorption and has been widely observed in various gas-adsorption reactions.

Conversely, simple direct dissociation—without a surface intermediate—has typically been the explanation of choice for higher incident energy molecules, and such an interpretation appears at least topically intuitive as an energetic molecule may be pictured to fall apart essentially upon surface impact [4,7–9]. However, in an investigation of nitrogen on Fe(111) a decade ago, Rettner and Stein questioned this classical interpretation, suggesting that rather than directly dissociating, hyperthermal molecules chemisorb initially intact and subsequently dissociate due to substrate thermal effects [10]. Recent investigations of oxygen adsorption on several surfaces have implicated similar chemisorbed molecular intermediates for high kinetic energy adsorption as well [11–15]. While kinetic studies [11,12,14,15] and thermal desorption experiments [12] have provided compelling indications of molecularly chemisorbed intermediates in low-coverage, high-energy adsorption, until recently verification of such a mechanism has unfortunately rested on inherently circumstantial evidence [16], as the presence of the dissociation precursor is merely inferred. Investigations of oxygen adsorption on silver surfaces have demonstrated the utility of vibrational spectroscopy in observing molecular species and offered stronger verification of high-energy molecular intermediates [13,17]. Thus, we have employed electron energy-loss spectroscopy (EELS) to probe surface molecularity and demonstrate definitively the applicability of molecular surface intermediates to an adsorption regime once considered purely direct.

We have utilized EELS in combination with molecular beam techniques to verify *directly* and characterize surface species in the initial adsorption reaction of the $O_2/Pt(111)$ system. Experiments were performed in an ultrahigh vacuum apparatus [18] equipped with EELS, an Auger electron spectrometer (AES), a quadrupole mass-spectrometer (QMS), and an ion-sputtering gun. The Pt(111) surface was prepared by argon-ion sputtering and repeated oxygen-anneal cycles until judged clean by the absence of energy-loss peaks in EEL spectra (EELS resolved impurities below the detection limit of Auger

electron spectroscopy). Sample temperatures were maintained through conductive cooling from a liquid nitrogen filled reservoir and resistive heating. Beams of molecular oxygen were generated by supersonic expansion from a stainless-steel nozzle assembly with a 120 μm diameter aperture, and translational energies were selected by dilute seeding in He or Ar and through nozzle temperature control and quantified using standard time-of-flight techniques [19]. Surface coverages were determined by comparing mass-spectrometer signal levels during thermal desorption of doses to that of a saturated surface.

At near-saturated surface coverages, low incident energies, and temperatures below 130 K, O_2 has been observed to adsorb in two distinct molecular chemically bonded states. EELS and NEXAFS (near edge x-ray absorption fine structure) data indicate predomination of a superoxolike (O_2^-) species formed at bridge sites with an intramolecular vibrational frequency of 870 cm^{-1} [20]. A second, less-populated molecularly chemisorbed state corresponding to a more strongly bound peroxolike (O_2^{2-}) intermediate with a stretching frequency at 690 cm^{-1} has been observed in threefold hollow sites [20]; these assignments are in good agreement with recent theoretical calculations [21,22]. Thermal conversion is thought to occur from the superoxolike through peroxolike state, and upon sufficient heating (surface temperature about 130 K) to an atomic species in threefold hollow sites [23] with a Pt-O bond vibrational frequency of 490 cm^{-1} [6]. Although useful, high-coverage studies provide by nature a

convoluted insight into the fundamental mechanisms of the O_2-Pt adsorption reaction, as interadsorbate effects and significant substrate electronic changes preclude a simple investigation of gas-metal chemisorption. Thus, vibrational spectra taken in the limit of zero substrate coverage are required to probe the initial reaction mechanisms precisely.

Figure 1 shows EEL spectra taken after several low-coverage doses of high translational energy O_2 (0.70 eV) on the Pt(111) surface held at 77 K. Clearly for each coverage shown, the intramolecular bond frequency of the peroxolike species (690 cm^{-1}) is present, indicating unequivocally that high kinetic energy oxygen is capable of adsorbing *associatively* on the metal surface at low surface coverages. The peaks present near 2080 cm^{-1} correspond to a small amount of adsorption from background CO always present in the analysis chamber, and the loss features at 490 cm^{-1} are characteristic of two nearly degenerate vibrational modes—the Pt-O vibration of adsorbed atomic oxygen and the Pt-C stretching mode of adsorbed CO. A presence of atomic oxygen would appear to indicate either a channel to direct dissociation at high energies or fast conversion from the initial molecular state, but the portion of this signal actually due to oxygen is difficult to quantify. To address this question, a series of time and temperature resolved spectra was recorded and is shown in Fig. 2. As the time between dosing and the EELS scan is increased from 2 to 5 and 15 min, the magnitude of the 490 cm^{-1} peak increases relative to that of the molecular species.
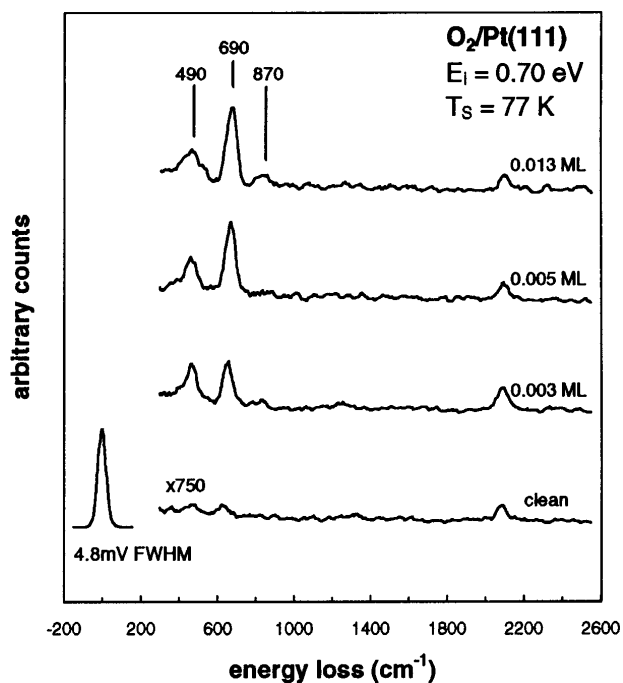

FIG. 1. EEL spectra of several low coverages of oxygen following exposure to a 0.7 eV molecular beam indicate that high-energy molecules adsorb in a molecular precursor state. The peroxolike species at 690 cm^{-1} appears to be the favored molecular intermediate for high translational energies.
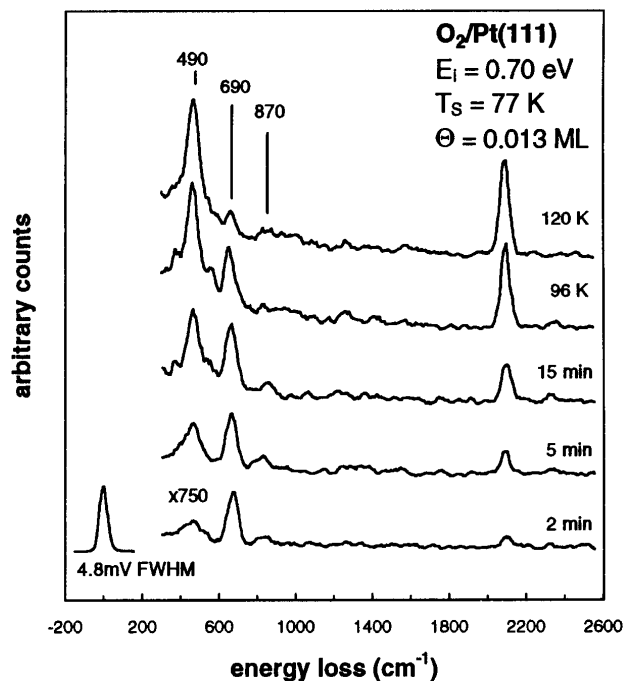

FIG. 2. Time and temperature resolved EEL spectra for a 0.013 ML coverage of oxygen following exposure to a 0.7 eV molecular beam suggest rapid conversion from the peroxolike species to the dissociated product (490 cm^{-1}), even at 77 K. The observed atomic peak in the 2 min scan is likely a result of conversion—not direct dissociative adsorption.

The Pt-C stretch in CO is known to exhibit an EELS intensity approximately half that due to the C-O vibration [24], indicating that a substantial portion of this combined peak is likely due to CO—judging by the rapid increase in the 2080 cm^{-1} feature with each successive scan. Electron beam-induced dissociation of oxygen is negligible, as no difference was observed in time-resolved spectra with the electron gun on and off. Further, since the molecular oxygen loss feature at 690 cm^{-1} shows no attenuation over the 15 min period, substantial dissociation from the molecular state at 77 K seems unlikely. The rather significant uncertainties associated with EELS intensities preclude an accurate quantification of atomically adsorbed oxygen, but the preponderance of molecular adsorption over a potential direct dissociative channel seems clear. Mild substrate heating offers strong evidence of dissociation from the molecular precursor state, as the drop in 690 cm^{-1} peak intensity is dramatic in heating ramps to 96 and 120 K.

Figure 3 shows low coverages of oxygen dosed at the highest kinetic energy (1.3 eV) available with our apparatus. As observed with an incident energy of 0.70 eV, the peroxolike molecular state predominates, with some potential atomic conversion. The combination of Figs. 1–3 yields strong evidence that, even for very high translational energies, molecularly bound oxygen is the species first accessed by the gas phase, and any channel to simple direct dissociation appears minimal.

Of particular interest is the observation that high kinetic energy oxygen appears to populate exclusively the peroxolike molecular species at the lowest coverages on Pt(111). As the surface coverage increases (Fig. 3), an energy-loss peak characteristic of the superoxolike state develops at 870 cm^{-1}, an effect likely representative of local work function elevation due to near-neighbor coadsorbates. This preferential filling of the peroxolike 690 cm^{-1} state is in stark contrast to the EEL spectra shown in Fig. 4, which were obtained after dosing *low* kinetic energy oxygen (0.055 eV) on the 77 K platinum surface. For all coverages shown, the superoxolike species at 870 cm^{-1} is present in concentrations comparable to the more advanced peroxolike state. Thus, *we demonstrate the ability of translational kinetic energy to affect the initial adsorption reaction product.*

Ostensibly, higher energies facilitate adsorption into the more strongly bound peroxolike state—characterized by a higher degree of charge transfer from the metal to the molecule's $\pi*$ antibonding orbital. An experimental artifact of rapid conversion of the high-energy species from the 870 cm^{-1} state to the 690 cm^{-1} state (on a time scale shorter than the ~2 min necessary to acquire a vibrational spectrum) appears unlikely, as such an effect would be expected, but is not witnessed, for low-energy adsorption as well (Fig. 5). EEL spectra of low-energy adsorption in Figs. 4 and 5 apparently depict a "snapshot" of trapping-mediated chemisorption; upon evolution from the physically adsorbed species, both molecularly chemisorbed intermediates are sampled en route to dissociation.
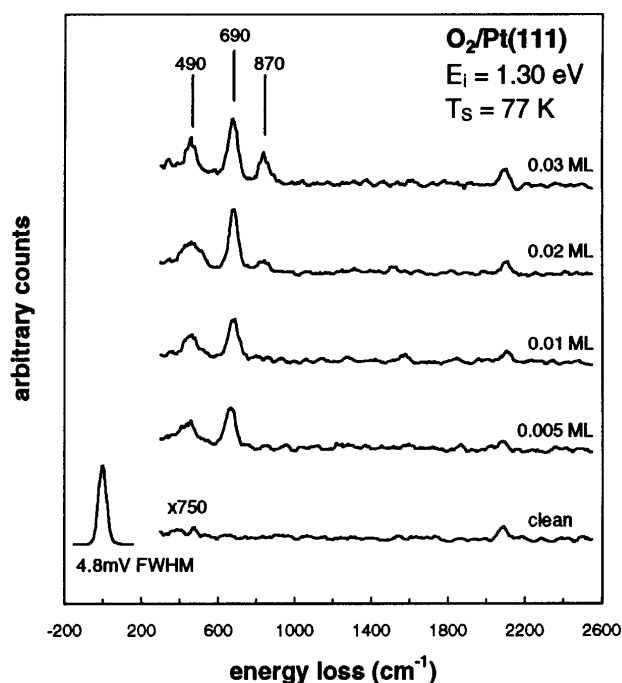

FIG. 3. EEL spectra of low-coverage exposures to a 1.3 eV (the highest energy attainable in our apparatus) molecular oxygen beam mirror results from a 0.70 eV beam (Fig. 1). An emergence of a superoxolike species at 870 cm^{-1} at higher coverages likely results from local work function elevation.
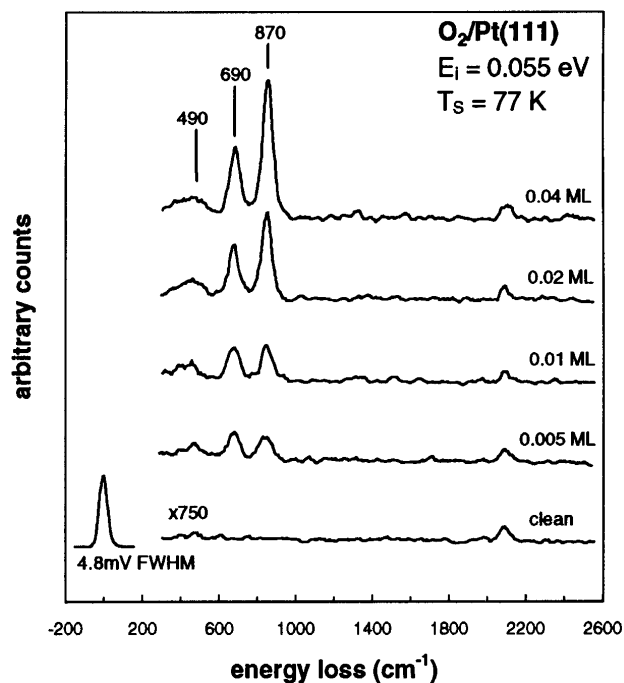
FIG. 4. EEL spectra of low coverage doses of 0.055 eV oxygen indicate filling of both superoxolike (870 cm^{-1}) and peroxolike (690 cm^{-1}) molecular surface species. These spectra differ significantly from those taken after high-energy adsorption (Figs. 1 and 3), which indicate near-exclusive population of the peroxolike state.
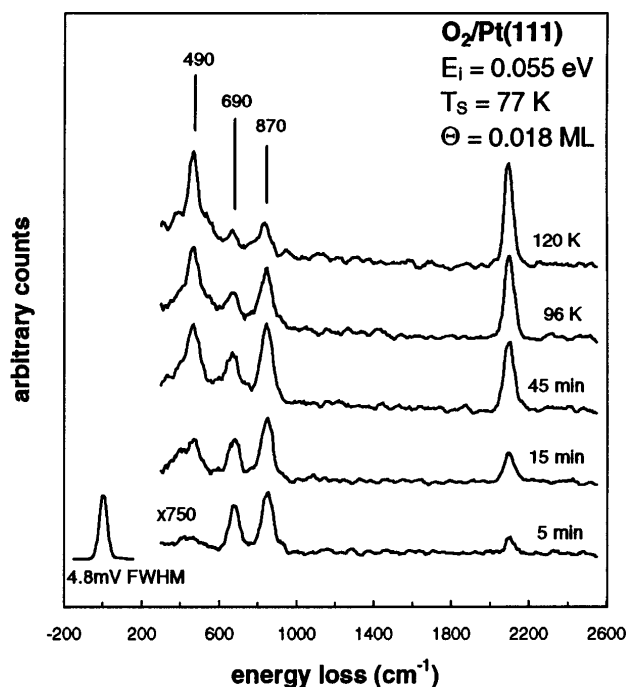
FIG. 5.   Time and temperature resolved EEL spectra for a 0.018 ML coverage of 0.055 eV oxygen depicting conversion through molecular intermediates to the atomically adsorbed state. Conversion from the 870 cm^{-1} to the 690 cm^{-1} molecular state does not appear rapid at 77 K.

Succession of precursor species from superoxolike to peroxolike is implied in the absence of "reverse" conversion from the 690 to the 870 cm^{-1} state in the high-energy spectra in Fig. 2. An intuitive argument of sequential charge transfer further corroborates the peroxolike species as the more immediate dissociation precursor. Specifically, a superoxolike adsorbate is formed with the effective donation of one electron to the oxygen molecule, and the peroxolike species results with the addition of a second.

The initial adsorption state of the $O_2/Pt(111)$ system appears largely dependent on the translational energy of the impinging molecule. For low incident energies, an impinging molecule may physically adsorb to the surface and subsequently progress through spectroscopically observable superoxolike and peroxolike precursor states before dissociating. Adsorption directly into the superoxolike state also cannot be ruled out from 77 K measurements. At higher incident energies, however, this sequential mechanism appears abbreviated, and a direct channel of adsorption into the peroxolike dissociation precursor dominates; no evidence is seen for direct dissociation at high incident energies. The physical basis for distinct low- and high-energy dissociation pathways may be correlated with the physical proximity of the newly adsorbed molecules and the surface. The more highly energetic molecules may force a closer orbital overlap, assisting charge transfer to the adsorbate and effectively

surmounting any activation barrier to the more advanced peroxolike state. The implied integral correlation between kinetic energy and reaction coordinate for an adsorption event manifests itself clearly in this model system with two defined adsorption precursors, but likely provides a basis for explaining adsorption trends in other gas-surface systems as well.

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[1] A. Bielanski and J. Haber, *Oxygen in Catalysis* (Marcel Dekker, Inc., New York, 1991), p. 67.
[2] I. Langmuir, Chem. Rev. **6**, 451 (1929).
[3] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).
[4] A. C. Luntz, M. D. Williams, and D. S. Bethune, J. Chem. Phys. **89**, 4381 (1988).
[5] A. C. Luntz, J. Grimblot, and D. E. Fowler, Phys. Rev. B **39**, 12 903 (1989).
[6] N. R. Avery, Chem. Phys. Lett. **96**, 371 (1983).
[7] C. T. Rettner, L. A. DeLouise, and D. J. Auerbach, J. Chem. Phys. **85**, 1131 (1986).
[8] A. Hodgson, A. K. Lewin, and A. Nesbitt, Surf. Sci. **293**, 211 (1993).
[9] X.-C. Guo, J. M. Bradley, A. Hopkinson, and D. A. King, Surf. Sci. **310**, 163 (1994).
[10] C. T. Rettner and H. Stein, Phys. Rev. Lett. **59**, 2768 (1987).
[11] J. E. Davis, P. D. Nolan, S. G. Karseboom, and C. B. Mullins, J. Chem. Phys. **107**, 943 (1997).
[12] C. T. Rettner and C. B. Mullins, J. Chem. Phys. **94**, 1626 (1991).
[13] L. Vattuone, M. Rocca, C. Boragno, and U. Valbusa, J. Chem. Phys. **101**, 713 (1994).
[14] D. Kelly, R. W. Verhoef, and W. H. Weinberg, J. Chem. Phys. **102**, 3440 (1995).
[15] P. Sjovall and P. Uvdal, Chem. Phys. Lett. **282**, 355 (1998).
[16] J. E. Davis and C. B. Mullins, Surf. Sci. **380**, L513 (1997).
[17] F. Buatier de Mongeot, M. Rocca, and U. Valbusa, Surf. Sci. **363**, 68 (1996).
[18] J. E. Davis, S. G. Karseboom, P. D. Nolan, and C. B. Mullins, J. Chem. Phys. **105**, 8362 (1996).
[19] D. J. Auerbach, in *Atomic and Molecular Beam Methods,* edited by G. Scoles (Oxford University Press, New York, 1988), Vol. 1.
[20] C. Puglia *et al.,* Surf. Sci. **342**, 119 (1995).
[21] I. Panas and P. Siegbahn, Chem. Phys. Lett. **153**, 458 (1988).
[22] A. Eichler and J. Hafner, Phys. Rev. Lett. **79**, 4481 (1997).
[23] H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 1 (1982).
[24] W. D. Mieher, L. J. Whitman, and W. Ho, J. Chem. Phys. **91**, 3228 (1989).