

# A molecular-beam study of the dissociative chemisorption of O<sub>2</sub> on Ir(110)-(1×2)

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The zero-coverage probability of dissociative chemisorption of O<sub>2</sub> on Ir(110)-(1×2) has been measured using molecular-beam techniques for a wide range of incident kinetic energies, incident angles, and surface temperatures. The data indicate that a trapping-mediated mechanism is responsible for dissociative chemisorption at low energies, whereas at high energies a direct mechanism accounts for dissociative adsorption. Total energy scaling approximately describes the dissociative dynamics on the very corrugated Ir(110)-(1×2) surface.

Dissociative chemisorption on transition-metal surfaces is a key step in many industrially important heterogeneous catalytic reactions. The dynamics of dissociative chemisorption are currently poorly understood and an active area of research. In an effort to contribute further to an understanding of dissociative chemisorption, we have conducted a series of experiments to probe the interaction of molecular oxygen with the Ir(110)-(1×2) surface.

Two studies of oxygen chemisorption dynamics employing molecular beams have appeared recently. Rettner *et al.*<sup>1</sup> have studied the interaction of oxygen with a W(110) surface and concluded that the initial probability of adsorption depends strongly on the incident kinetic energy  $E_i$  scaling with the normal energy  $E_n = E_i \cos^2 \theta_i$ , where  $\theta_i$  is the angle of incidence. They also found some evidence for the existence of a weakly bound precursor to dissociative chemisorption at low incident kinetic energies. Williams *et al.*<sup>2</sup> have investigated the dynamics of dissociative adsorption of oxygen on Pt(111). They concluded that trapping-mediated chemisorption occurred for low incident energies and low surface temperatures, whereas at high incident kinetic energies a direct mechanism was likely the mechanism for chemisorption of oxygen. Taylor *et al.*<sup>3</sup> have investigated the interaction of oxygen with Ir(110)-(1×2) previously, and their work provided motivation for this study. They used thermal desorption mass spectrometry, low-energy electron diffraction, and work function measurements, and concluded that the initial probability of chemisorption was independent of surface temperature  $T_s$ . They also concluded for  $T_s$  between 300 and 700 K that the adsorption kinetics could be described by a second-order precursor model.

Zero-coverage dissociative chemisorption measurements have been made using the reflectivity method (of King and Wells<sup>4</sup>) employing an apparatus that will be described in detail elsewhere.<sup>5</sup> Briefly, the apparatus consists of a thrice differentially pumped supersonic molecular-beam source and ultrahigh vacuum scattering chamber. Low-energy electron diffraction optics, Auger electron spectroscopy, and an ion gun are mounted on the scattering chamber for obtaining and checking surface cleanliness and order. A quadrupole mass spectrometer is also mounted on the scattering chamber for thermal desorption mass spectrometry, reflectivity measurements, and beam time-of-flight measure-

ments. The source chambers contain the nozzle, a high-speed shutter, and a chopper for beam modulation as well as apertures for beam collimation. Both the scattering chamber and the third-beam chamber are pumped by turbomolecular pumps. The other two beam chambers are pumped by diffusion pumps. The Ir(110)-(1×2) sample is mounted on a manipulator in the scattering chamber which provides precise alignment of the sample in the beam. The manipulator is liquid nitrogen cooled, providing rapid cooling of the sample to 80 K. The sample temperature is determined from a 0.003-in. W/5% Re-W/26% Re thermocouple spotwelded to the back of the crystal. As mentioned above, the initial probability of adsorption data reported here have been determined by a beam reflectivity method similar to that of King and Wells.<sup>4</sup> The partial pressure of oxygen in the scattering chamber is used as a measure of the flux of O<sub>2</sub> molecules that do not chemisorb. Initial chemisorption probabilities  $S_0$  (corresponding to chemisorption at zero coverage) are thus determined by a comparison of the initial oxygen partial pressure, following the opening of the high-speed shutter, to the oxygen partial pressure from the beam scattering from the saturated surface. Beam energies are varied by a combination of seeding and variation of nozzle temperature, and are measured by time-of-flight techniques.

Figure 1 shows  $S_0$  as a function of incident kinetic energy for an angle of incidence of 15° with respect to the surface normal and surface temperatures of 150 and 300 K. As  $E_i$  is increased from its lowest values,  $S_0$  decreases from a relatively high value to a minimum at ~4 kcal/mol. Note that this occurs for the measurements at 150 K as well as those at 300 K. The data displayed in Fig. 2 support the insensitivity of  $S_0$  to  $T_s$ . This figure shows  $S_0$  vs  $T_s$  for an incident angle of 45° and total incident energy of 980 cal/mol, and an incident angle of 15° and  $E_i$  of 9.1 kcal/mol. A decrease in  $S_0$  with increasing kinetic energy in the low-energy range is associated with a trapping- or precursor-mediated chemisorption mechanism, cf. Fig. 1. A similar decrease in  $S_0$  with  $E_i$  in the low  $E_i$  regime for O<sub>2</sub>/W(110),<sup>1</sup> O<sub>2</sub>/Pt(111),<sup>2</sup> N<sub>2</sub>/W(100),<sup>7</sup> C<sub>3</sub>H<sub>8</sub>/Ir(110)-(1×2),<sup>8</sup> and C<sub>4</sub>H<sub>10</sub>/Ir(110)-(1×2)<sup>8</sup> has been observed before. However these systems displayed a strong sensitivity to surface temperature, with  $S_0$  decreasing with increasing surface temperature. This type of behavior can be interpreted as follows: the trapping proba-

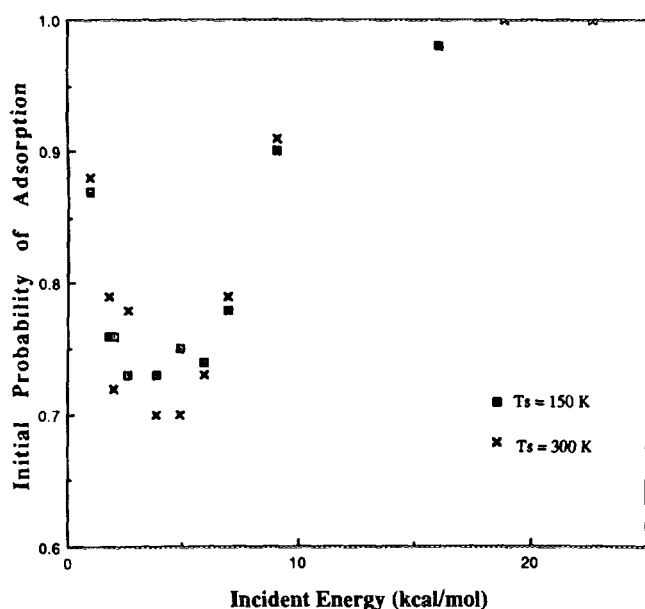


FIG. 1. The initial probability of dissociative chemisorption  $S_0$  as a function of incident kinetic energy for  $T_s = 150$  and  $300$  K, and incident angle of  $15^\circ$ .

bility into the precursor state is a strong function of  $E_i$ , decreasing with increasing  $E_i$ , but weakly influenced by  $T_s$ .<sup>9</sup> Once a particle is in the precursor state it either desorbs or chemisorbs dissociatively, the temperature dependence of which depends on the kinetic parameters for desorption and dissociation.<sup>10</sup> For the system under discussion, O<sub>2</sub>/Ir(110)-(1×2), the relative insensitivity of  $S_0$  to  $T_s$  at low  $E_i$  suggests that the activation energy for dissociation is nearly equal to the activation energy for desorption from the precursor or trapped state. The slight decrease in  $S_0$  observed from 400 to 600 K is probably due to a decrease in the trapping probability.<sup>9</sup> The insensitivity of  $S_0$  to  $T_s$  at high  $E_i$  supports the assignment of a direct mechanism to dissociative chemisorption in this regime. Behavior of this type has been observed previously,<sup>1,7,8</sup> but one should note that in the study by Williams *et al.*<sup>2</sup>  $S_0$  was found to have a surface temperature dependence even at high  $E_i$ . The previous study of O<sub>2</sub>/Ir(110)-(1×2) by Taylor *et al.*<sup>3</sup> supports these conclusions in that  $S_0$  was determined to be insensitive to  $T_s$  from 300 to 700 K. The fact that  $S_0$  for the O<sub>2</sub>/Ir(110)-(1×2) system is nearly insensitive to incident angle suggests near total energy scaling for the chemisorption dynamics of this system. This is not too surprising considering that the surface reconstructs into a very corrugated geometrical structure, providing a corrugated potential energy surface. Total energy scaling in dissociative chemisorption of a diatomic has been reported previously for the N<sub>2</sub>/W(110) system<sup>6</sup> and the N<sub>2</sub>/W(100) system.<sup>7</sup> Chemisorption probabi-

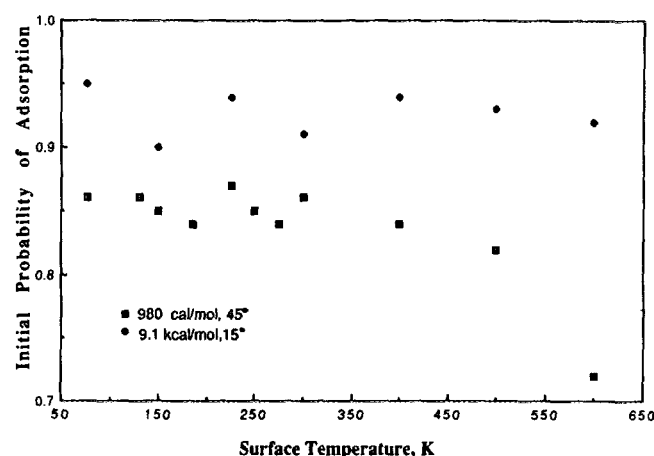


FIG. 2. The initial probability of dissociative chemisorption  $S_0$  as a function of surface temperature for  $E_i = 980$  cal/mol and  $\theta_i = 45^\circ$ , and for  $E_i = 9.1$  kcal/mol and  $\theta_i = 15^\circ$ .

lities  $S$  have also been determined as a function of coverage over a wide range of conditions. At low incident kinetic energies and low surface temperatures,  $S$  remains constant or decreases slowly for low coverages. This provides further supporting evidence for our assignment of a trapping-mediated chemisorption mechanism for the low  $E_i$  regime. A more complete description of the coverage dependence of the probability of dissociative chemisorption, as well as other details, will appear in a future publication.<sup>5</sup>

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