

## LETTERS

### Dissociative Adsorption of Br<sub>2</sub> on Pt(111): Hot Atom Dynamics

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Scanning tunneling microscopy was used to study the dissociative adsorption of Br<sub>2</sub> on a Pt(111) surface held at 25 K. At low coverage, Br atoms were observed in correlated pairs with a mean separation of  $9.2 \pm 1$  Å, indicative of substantial repulsive energy release and transient mobility as the nascent Br atoms separate during dissociative adsorption. An upper bound for the friction coefficient of these hot Br atoms on Pt(111) was calculated to be  $\eta \leq 2.2$  ps<sup>-1</sup>. At higher Br<sub>2</sub> exposures, Br atoms were found in chainlike structures, and eventually two-dimensional islands, even though thermal diffusion of Br atoms was quenched at 25 K. The latter observations are consistent with Br<sub>2</sub> adsorption into a transient molecular precursor state and enhanced dissociation in the vicinity of preadsorbed Br atoms.

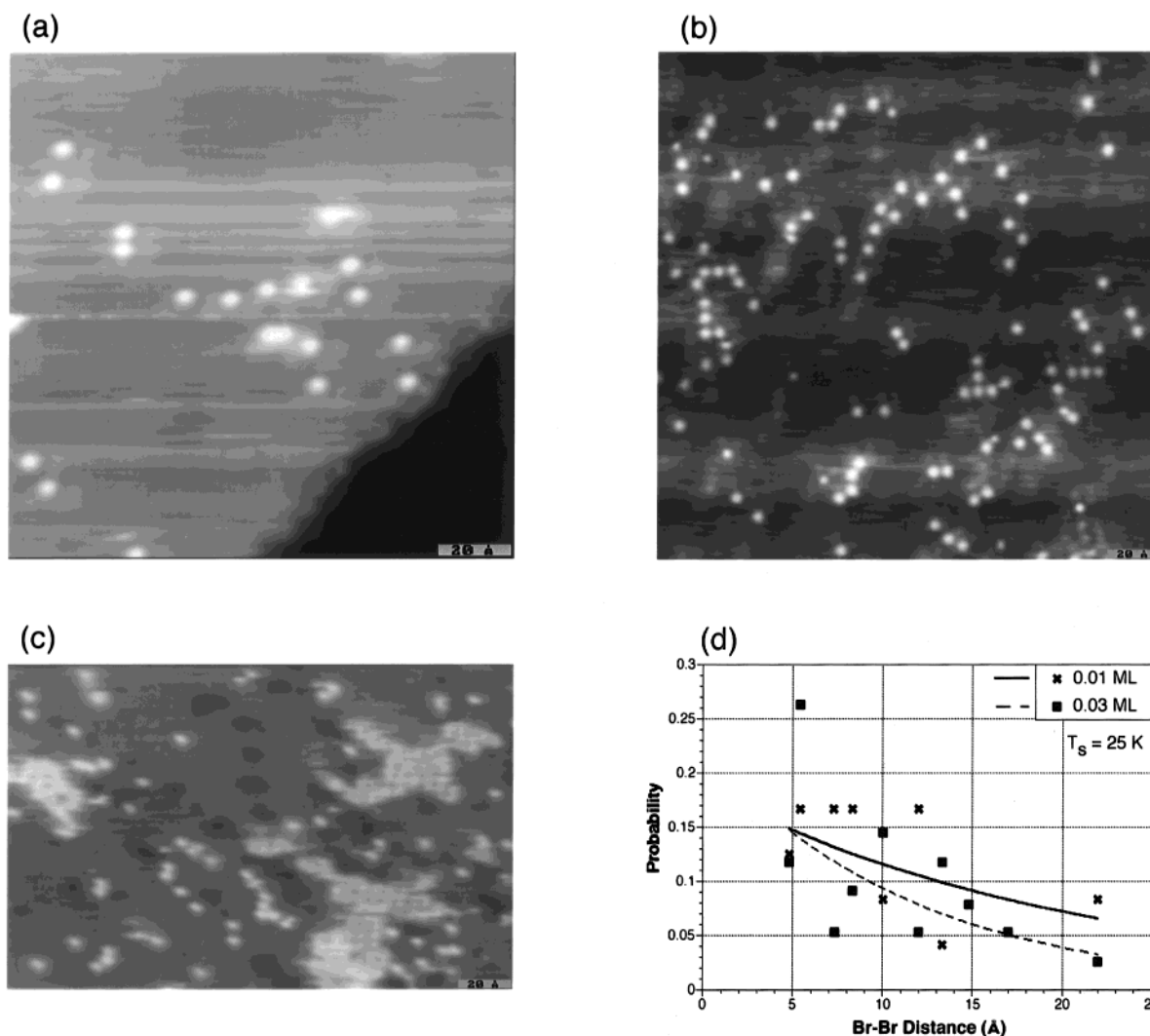
There is considerable scientific and technological interest in driving surface reactions at relatively low temperature using "hot" or hyperthermal atoms or radical fragments derived from adsorbate dissociation.<sup>1</sup> For example, CO<sub>2</sub> is readily produced when molecular O<sub>2</sub> is thermally<sup>2</sup> or photochemically<sup>3</sup> dissociated alongside coadsorbed CO on Pt(111) at surface temperatures less than 150 K. The low coverage activation energy for the oxidation reaction between adsorbed O atoms and CO is 1 eV which amounts to almost all of the 1.1 eV per O atom available from thermal dissociative adsorption of O<sub>2</sub>. Dynamics experiments in which rare gases were collisionally desorbed by hot O atoms produced by photofragmentation of O<sub>2</sub> on Pt(111) indicate that the separating O atoms are repulsed from one another and can develop translational energies in excess of 0.7 eV.<sup>1,4</sup> Further evidence for repulsive energy release during O<sub>2</sub> dissociative adsorption stems from low-temperature scanning tunneling microscopy (STM) experiments which show that both thermal<sup>5</sup> and nonthermal<sup>6</sup> dissociation of O<sub>2</sub> on Pt(111) yield O atom pairs separated by one to three lattice spacings. Given that O<sub>2</sub> dissociation is accomplished by charge transfer from the metal into molecular antibonding orbitals and the O atoms

ultimately acquire considerable negative charge on the surface, Coulombic interaction likely dominates the interatomic repulsion.<sup>7</sup> In this Letter, we use STM to report on a similar system, Br<sub>2</sub> dissociative adsorption on Pt(111), which produces hot atom pairs which separate considerably further. An upper bound for the friction coefficient of Br atoms on Pt(111) is derived and discussed in relationship to theoretical models for adsorbate mobility.

Although physisorbed and chemisorbed O<sub>2</sub> precursor states to dissociative adsorption have been isolated on Pt(111) at temperatures less than 40 and 150 K, respectively, there are no reports of similarly stable Br<sub>2</sub> precursors to dissociative adsorption on metals.<sup>8</sup> Nevertheless, the dissociative sticking probabilities for halogen molecules on metals often show characteristics, such as coverage independence and decreasing sticking with increasing surface temperature, which are signatures of precursor-mediated sticking. In consequence, we should not discount the possibility that Br<sub>2</sub> may exist in a short-lived, mobile precursor state prior to its dissociation on Pt(111).

Experiments were performed using an ultrahigh vacuum chamber ( $P_{\text{base}} < 1 \times 10^{-10}$  Torr) equipped for surface studies and variable temperature scanning tunneling microscopy.<sup>9</sup> The Pt(111) surface was initially prepared by repeated cycles of Ar<sup>+</sup>

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**Figure 1.** STM images recorded after exposing a Pt(111) surface held at 25 K to varying exposures of  $\text{Br}_2$ . (a) A  $140 \times 140 \text{ \AA}^2$  image at an accumulated Br coverage of  $\theta_{\text{Br}} = 0.01 \text{ ML}$ . (b) A  $160 \times 160 \text{ \AA}^2$  image at  $\theta_{\text{Br}} = 0.03 \text{ ML}$ . (c) A  $160 \times 100 \text{ \AA}^2$  image at  $\theta_{\text{Br}} = 0.07 \text{ ML}$  which shows Br island formation at a surface temperature where thermal diffusion of Br atoms is quenched. (d) Probabilities for specific Br atom pair separations at accumulated Br coverages of 0.01 and 0.03 ML. The data derive from 100 Br atom pairs identified from Figure 1a and b.

ion sputtering at 850 K, oxidation at 750 K, and annealing to 1200 K. Afterward, the surface was typically prepared by performing repeated oxygen thermal programmed desorption (TPD) runs until a TPD spectrum characteristic of the clean surface was attained. A solid-state electrochemical cell<sup>10</sup> working at 373 K was used to generate  $\text{Br}_2$  and direct the gas toward the Pt(111) surface. The  $\text{Br}_2$  surface exposure was proportional to the integrated cell current. During operation, the cell increased the chamber pressure by less than  $2 \times 10^{-11}$  Torr. Auger electron spectroscopy (AES), TPD, and STM indicated that only  $\text{Br}_2$  was dosed onto the surface. Calibration of the Br surface coverage was accomplished by TPD and low-energy electron diffraction (LEED). After annealing to 300 K, a saturated layer of Br on Pt(111) produced a sharp  $(3 \times 3)$  LEED pattern indicative of a coverage of 0.44 ML (where 1 ML is the Pt(111) atom density of  $1.5 \times 10^{15} \text{ cm}^{-2}$ ).<sup>9</sup> STM imaging of Br atoms was done at 1 nA current and a W tip-sample bias of less than  $\pm 1 \text{ V}$ . These conditions were adequate to image Br atoms without moving them, but did not allow for simultaneous visualization of the underlying Pt(111) lattice.

Figure 1 displays several STM images acquired after dosing  $\text{Br}_2$  on Pt(111) at a surface temperature of 25 K. Isolated Br atoms appear as bright round disks of  $6 \pm 1 \text{ \AA}$  diameter and  $0.7 \pm 0.1 \text{ \AA}$  height in good accord with theoretical expectations

and practical experience for single atom imaging of other elements.<sup>11</sup> The Br atoms were immobile during extended STM observation and we conclude that Br thermal diffusion was quenched at 25 K and that interactions with the STM tip were negligible.

At the 0.01 ML Br coverage of Figure 1a, Br atoms were found in correlated pairs separated by several lattice constants. We assume that the atoms were transiently mobile following dissociation of a  $\text{Br}_2$  molecule. There does not appear to be preferential dissociation of the  $\text{Br}_2$  at the Pt step edge in the lower right-hand corner of the image. However, Figure 1b at a Br coverage of 0.03 ML shows a tendency for the Br atoms to locate near other atoms to form loose chainlike structures. The relative orientation of these chains appears to be influenced by the underlying 3-fold (and more locally 6-fold) symmetry of the Pt(111) fcc lattice. Figure 1c shows that some of the Br atom chains evolve into islands by a coverage of 0.07 ML. Given that Br atoms are immobile at the surface temperature of 25 K and have only limited transient mobility following dissociation of  $\text{Br}_2$ , the Br atom clustering is likely to arise from the existence of a mobile, weakly bound, molecular adsorption state of  $\text{Br}_2$  which is a precursor to dissociation. If such a species existed long enough to explore the surface over a length scale on the order of six lattice constants (i.e.,  $\theta^{-1/2}$  at  $\theta = 0.03 \text{ ML}$

which is roughly the mean distance between Br atoms in 1-D when chain growth begins) and was preferentially dissociated at preadsorbed Br atoms the atom clustering can be broadly rationalized. Very similar clustering phenomena has already been observed for O atoms on Pt(111) at relatively high temperatures where the O<sub>2</sub> precursor states are rendered thermally unstable and exist only transiently.<sup>12</sup>

Although most Br atoms could be assigned in pairs following dissociation of Br<sub>2</sub> molecules, a few relatively isolated Br atoms can be observed in Figure 1 ( $8 \pm 3\%$  of the total Br atoms). These isolated Br atoms have no nearby neighbors (within 25 Å) which can be easily assigned as a pair atom from the dissociation of a common parent molecule. The surface energetics support the possibility of abstractive adsorption in which Br<sub>2</sub> dissociates to produce one atom on the surface and the other in the gas phase. Given the 2.3 eV adsorption energy for Br atoms on Pt(111) and the 2 eV bond dissociation energy of gaseous Br<sub>2</sub>, abstractive adsorption of Br<sub>2</sub> is exothermic by 0.3 eV, while complete dissociative adsorption is exothermic by 2.6 eV.<sup>9</sup> If we assume that each isolated Br atom derives from an adsorbing Br<sub>2</sub>, then 15% of the adsorbing molecules undergo abstractive adsorption. This value is relatively small compared to the 30% abstractive adsorption rate for Br<sub>2</sub> (incident with  $E_{\text{trans}} = 0.5$  eV) and 75% abstraction rate for F<sub>2</sub> ( $E_{\text{trans}} = 0.03$  eV) on Si(111) surfaces.<sup>13</sup> The abstractive adsorption probabilities increase with the net exothermicity of the process;  $\Delta H = -0.3, -2.0$ , and  $-4.8$  eV, respectively, for the examples cited above.

Figure 1d gives the relative frequency of the separation distance between Br atom pairs for accumulated Br atom coverages of 0.01 and 0.03 ML. At the higher coverage there was a tendency to form Br atom pairs at 2 lattice spacings, which relates to the appearance of the chainlike structures in Figure 1b. The mean distance between Br atom pairs was  $\langle \Delta x_{\text{Br-Br}} \rangle = 9.2 \pm 0.1$  Å for the 100 pairs analyzed from Figure 1a and b.

Previous STM observations of Br on Pt(111) at 85–300 K<sup>9</sup> showed that Br atoms could be found in both ( $\sqrt{3} \times \sqrt{3}$ ) and ( $3 \times 3$ ) islands which place Br atoms at 3-fold hollow, and 2-fold bridge and atop sites, respectively. Individual Br atoms on the Pt(111) terraces were mobile at 80 K and could not be seen by STM. The activation energy for Br atom diffusion can be estimated as  $\sim 10\%$  of the Br desorption energy of 2.3 eV. Assuming a preexponential for hop diffusion of  $10^{13} \text{ s}^{-1}$ , this leads to  $10^{-33}$  hops per second at 25 K and 0.2 hops per second at 85 K, in broad accord with the STM results. It should be noted that since Br can coexist in ( $\sqrt{3} \times \sqrt{3}$ ) and ( $3 \times 3$ ) islands, at least metastably after brief annealing to 300 K, the corrugation of the surface potential is probably relatively modest because all the high-symmetry adsorption sites can be simultaneously populated. The Br atoms in the high-temperature islands imaged with a vertical heights of 0.6, 0.3, and 0.2 Å for atoms in atop, bridge, and hollow sites, respectively.<sup>9</sup> These heights are somewhat low in comparison to the 0.7 Å value reported here for isolated Br atoms at 25 K. However, UPS data show that halogens in islands develop an electronic band structure which should smooth and reduce the electronic corrugation imaged by STM.<sup>8</sup> Accordingly, we see reduced Br atom corrugation ( $0.6 \pm 0.2$  Å to the Pt(111) lattice floor) within the islands of Figure 1c. Nevertheless, our data suggest that Br<sub>2</sub> dissociative adsorption produces Br atoms that come to rest at atop sites, even when metastable island structures are formed. If true, this would be a somewhat surprising result because

atomic adsorbates in thermal equilibrium on metal surfaces are usually assumed to bind at the highest coordination sites available.<sup>14</sup>

Analysis of the Br atom pair separations following Br<sub>2</sub> dissociative adsorption can provide an upper bound for the friction coefficient of Br atoms on the Pt(111) surface. Hot adatom motion has been addressed theoretically by Wahnström and co-workers<sup>15</sup> beginning with

$$m \frac{d\mathbf{v}}{dt} = -\nabla V(\mathbf{r}) + m\eta \mathbf{v} + \mathbf{F}^{\text{st}}(t) \quad (1)$$

where  $V(\mathbf{r})$  is the adatom–surface potential for a rigid surface lattice,  $m$ ,  $\mathbf{v}$ , and  $\eta$  are the adatom mass, velocity, and friction coefficient, and  $\mathbf{F}^{\text{st}}(t)$  represents a stochastic force which satisfies the fluctuation–dissipation theorem. In molecular-dynamics modeling of the O<sub>2</sub> dissociative adsorption on Al(111), Wahnström found that most of the O atom pair separation occurred during the first 0.2 ps after dissociation. Scattering on the corrugated adatom–surface potential served to rapidly equilibrate the translational degrees of freedom so that there was negligible net increase in the O atom pair separations after the initial 0.2 ps of ballistic motion. The later random hopping motion that occurred as the energy finally dissipated was simply much less efficient at increasing the pair separation. For the low-temperature Br/Pt(111) system, an upper bound for the friction coefficient defined in eq 1 can be roughly estimated by neglecting  $V(\mathbf{r})$  and  $\mathbf{F}^{\text{st}}(t)$ , and assuming that the Br<sub>2</sub> heat of adsorption is shared equally, instantaneously, and repulsively between the nascent adatoms. The distance between the Br atom pairs will then evolve as

$$\Delta x_{\text{Br-Br}}(t) = \frac{2v_i}{\eta} (1 - e^{-\eta t}) = \frac{2}{\eta} \sqrt{\frac{2E_i}{m}} \left( 1 - \sqrt{\frac{E_f}{E_i}} \right) \quad (2)$$

where  $v_i$  is the initial velocity of the hot Br atoms, and  $E_i$  and  $E_f$  are the initial and final hot atom energies. The energy available to the nascent Br atoms from dissociative adsorption of Br<sub>2</sub> is no more than  $E_i = 1.3$  eV per atom based on the 2.3 eV desorption energy of Br atoms from Pt(111) and the 2 eV bond dissociation energy of Br<sub>2</sub> molecules. Hot Br atoms will ultimately be trapped by the adsorption potential so a minimum value for  $E_f$  is the diffusion barrier of 0.23 eV. With these approximations, the mean separation between Br atom pairs of  $\langle \Delta x_{\text{Br-Br}} \rangle = 9.2$  Å, yields a friction coefficient of  $\eta \leq 2.2 \text{ ps}^{-1}$  and a time constant for hot adatom motion of  $\tau \geq 0.45 \text{ ps}$ .

The same analysis applied to O atom motion following O<sub>2</sub> dissociative adsorption on Pt(111) where  $E_i = 1.1$  eV,  $E_f = 0.58$  eV,<sup>16</sup> and  $\langle \Delta x_{\text{O-O}} \rangle = 5.5$  Å<sup>5,6</sup> leads to a higher bound on the friction with  $\eta \leq 3.6 \text{ ps}^{-1}$  and  $\tau \geq 0.28 \text{ ps}$ . Certainly, with similar initial energies available, the dissociating Br<sub>2</sub> atom pairs separate further than the O<sub>2</sub> atom pairs. These findings provide experimental support for Wahnström's conclusion that hot atom mobility on metal surfaces is limited primarily by rapid 3-D randomization of the initial energy through scattering on the corrugated interaction potential, rather than by dissipative friction. Reduced potential corrugation and increased initial energy should favor longer hot atom travel for Br during the initial ballistic motion which occurs on a time scale short in comparison to frictional energy dissipation. The O/Pt(111) interaction potential with minima only at 3-fold hollow sites is considerably deeper ( $E_{\text{ad}}(\text{O}) = 3.7$  eV;<sup>5</sup>  $E_{\text{ad}}(\text{Br}) = 2.3$  eV) and must be more corrugated than the Br/Pt(111) potential which experimentally exhibits Br atoms at top, bridge, and hollow sites.<sup>9</sup> If dissipative frictional damping was important in

determining the hot atom pair separations, eq 2 explicitly indicates that the separations should scale as  $m^{-1/2}$ , favoring longer O atom travel. Furthermore, for relatively heavy chemisorbed atoms such as O and Br, frictional coupling to the substrate should be overwhelmingly dominated by energy transfer to phonons rather than to substrate electron-hole pairs.<sup>15</sup> The simplest model for the phonon friction is based on impulsive adsorbate-substrate collisions for which energy transfer can be roughly estimated in Baule fashion such that the friction coefficient diminishes with the mass mismatch between the adsorbate and substrate, again favoring longer O atom travel. Hence, we surmise that energy randomization due to corrugation of the adsorbate-surface potential is the primary factor which limits the hot atom travel following O<sub>2</sub> and Br<sub>2</sub> dissociative adsorption on Pt(111).

In conclusion, the adsorption dynamics of Br<sub>2</sub> on Pt(111) were investigated by low and variable temperature STM. At low coverage, roughly 15% of the adsorbing Br<sub>2</sub> underwent abstractive adsorption. Dissociative adsorption of Br<sub>2</sub> at 25 K produced correlated pairs of Br atoms which came to rest with a mean separation of  $\langle x_{\text{Br-Br}} \rangle = 9.2 \text{ \AA}$ . An upper bound for the friction coefficient of hot Br atoms on Pt(111) was estimated as  $\eta \leq 2.2 \text{ ps}^{-1}$ . Corrugation of the adsorbate-substrate potential was identified as the key factor limiting hot atom motion. Islanding of Br atoms following dissociative adsorption of Br<sub>2</sub> at a surface temperature of 25 K, where thermal diffusion should be quenched, was interpreted as evidence for the transient existence

of a molecular precursor state of Br<sub>2</sub> which preferentially dissociated in the vicinity of preadsorbed Br atoms.

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