Observing the Motion of a Single Adsorbed Atom with Picosecond and Subnanometer Resolution

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A new method is described for recording the motion of a single adsorbed atom or molecule in real time, with an ultimate achievable resolution of 10^{-14} s. The time dependence of electron field emission through an atom adsorbed on a metal tip is measured by focusing the electrons into a beam, which is swept across a detector screen. Simultaneous temporal and one-dimensional spatial resolution of the dynamics is possible. The motion of single Cs atoms between sites on atomically characterized W(111) tips is observed at 2 ps resolution.

The physical and chemical properties of matter are determined by atomic motion, which occurs on the length scale of angstroms and on the 10^{-14}–10^{-12} s time scale of vibration. Until recently, temporal information on this scale has been deduced only indirectly from scattering experiments or from spectral data in the frequency domain. Pump-probe laser techniques [1,2] have now been applied to large ensembles of molecules to achieve temporal resolution good enough to resolve molecular vibrations in stable and reacting molecules [1], and time-resolved electron diffraction techniques have achieved somewhat poorer resolution [3]. Optical techniques are generally incapable of continuously observing the motion of single atoms and molecules on picosecond and shorter time scales, because they are insufficiently sensitive and because the optical probes drastically perturb the motion by changing the electronic state. On a much slower microsecond time scale, scanning tunneling microscopy [4] (STM) and field emission microscopy [5–7], which can also be applied to thermal ensembles [8], have been used. The jumping of single atoms can be traced by field ion microscopy (FIM), but with a resolution of only $\simeq 1$ s [9]. STM has been combined with pump-probe laser techniques to monitor electronic relaxation with subnanometer resolution [10].

We have developed a method for continuously observing the motion of single adsorbed atoms or molecules by recording the variation of field emission intensity from a metal tip. The jumping of a Cs atom between adsorption sites on a tungsten tip has been recorded with 2 ps and subnanometer resolution. In our femtosecond field emission camera (FFEC) [11], electrons field emitted from a tip and selected by a lens aperture are focused [12] into a spot which is swept electrostatically across a microchannel plate–phosphor screen detector coupled to a vidicon [Fig. 1(a)]. The spatial variation of the detected intensity along the sweep records the temporal variation of the field emission intensity (1 mm=10–100 ps). To image the tip by field ion or field emission microscopy [13], the lens voltage is turned off or reduced, so that the angular distribution of emitted electrons or ions is projected onto the detector [Fig. 1(b)].

Field emission (FE) is a tunneling process, which occurs when the width of the potential barrier at the surface of a metal tip is reduced by applying a negative potential (Fig. 2) [13]. Electrons originate from the metal interior, but the tunneling rate depends exponentially on the local barrier height, which is determined by the identity and location of surface atoms. FE thus provides a method for monitoring the position of surface atoms without strongly perturbing them by electronic transitions.

Fink [14] showed that the triatomic end of a tungsten tip can continuously emit currents as large as 10^{-5} A, or 6×10^{13} e^-/s, which gives many electrons during the 10^{-13} to 10^{-12} s vibrational period of adsorbed heavy atoms. To begin our experiments, we sputter sharpen a chemically etched $\langle 111 \rangle$ W tip to a $\simeq 300$ Å radius by field emitting in 6×10^{-2} Pa Ne [14]. Annealing briefly at 1100 K forms a corner of three {211} planes [14]. Using FIM [13] to image the tip atoms, we field evaporate
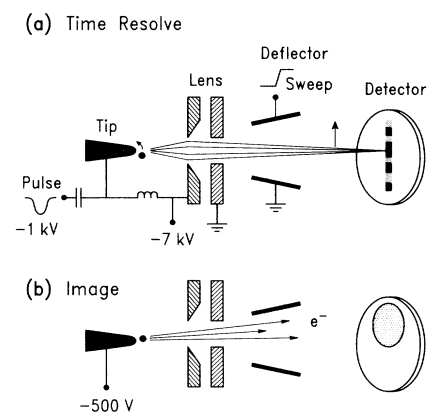

FIG. 1. Femtosecond field emission camera. Not to scale; tip-lens distance, 0.7 cm; total length, 60 cm. (a) Time-resolving mode, in which the electrons are focused and swept across the detector screen. (b) Imaging mode, in which the emitted electrons are projected onto the detector to spatially resolve their emission point on the tip (field emission microscopy). For FIM imaging, the tip voltage is made positive.
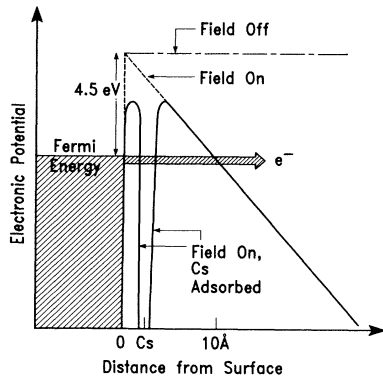
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FIG. 2. Potential energy diagram for electron field emission from a sharp tip, showing the effect of electric field and the adsorption of a Cs atom.

to form an apex lane composed of a triangle of three W atoms [14].

Individual Cs atoms can be observed in FE because the partially ionized adatom greatly lowers the local work function [15] (Fig. 2). A Cs atomic beam is directed at very low flux onto a 90 K tip, so that the average time between the arrival of atoms detected in the viewed area ($\simeq 20$ Å diam) is $\simeq 60$ s. To ensure that no more than one Cs atom resides near the apex, frequent positive voltage pulses evaporate Cs atoms from the tip. Deposition is ended when a bright spot [Fig. 1(b)] appears near the image of the apex, increasing the FE by a factor of 5 to $\simeq 10^{-11}$ A, and signaling the arrival of a single Cs within 1 nm of the apex. At 90 K, the atom remains at this site.

A series of alternating sweeping and imaging experiments are now performed, so that the position of the Cs atom is determined after each sweep. To sweep, the tip is pulsed with a negative voltage for several ns, generating a 5 μA e^- beam, which is focused and swept across the screen to record the emission intensity displayed in Figs. 3 and 4. The high current heats the adsorbed Cs to $\simeq 800$ K, presumably by inelastic electron tunneling [6,16] or the Nottingham effect [17], so that during the sweep, it may jump to another site [18]. Following each sweep, FE images the Cs after it has cooled [Fig. 1(b)].

Because the tip pulse is rounded, if no Cs motion occurs, the FE will be bell shaped, as in sweep 6 of Fig. 3. Judging from the FE images (Fig. 3) at 90 K, the Cs occupies one of two sites in these sweeps. (Some other sites were observed in other sweeps.) In sweeps 1, 7, and 8, the Cs jumps between sites. During sweep 1, an abrupt increase in FE is observed, with a rise time within 20 ps. The atom has moved from the position giving lower field FE, occupied in sweep 6 and designated L, to a position designated H, resulting in higher FE. The images indicate that Cs has moved from the upper left-hand portion of the image to the center, increasing in brightness because the field is stronger at the tip apex. Between sweeps 1 and 6, the atom has moved back to position L.
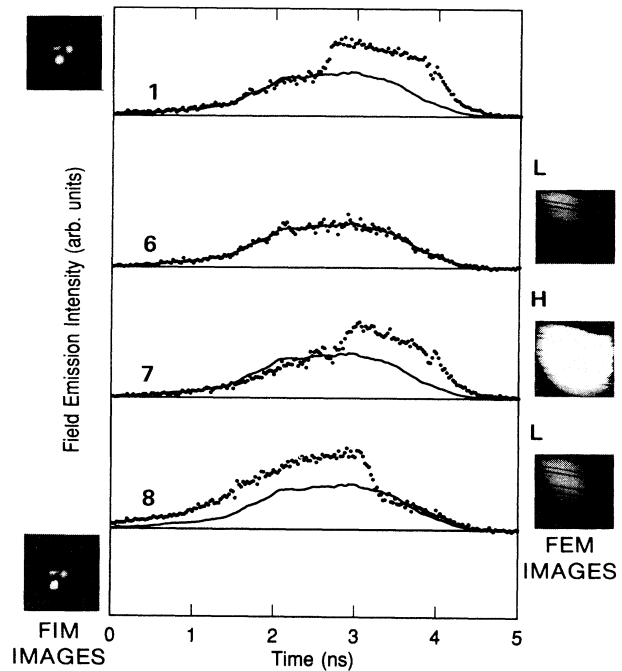

FIG. 3. Series of sweeping and imaging experiments documenting the jumping of a single Cs atom between two adsorption sites on a tungsten tip. The numbered plots present the time-resolved field emission intensity for four of eight consecutive sweeps. The time axis is referenced to the tip voltage pulse, and a smoothed sweep 6 is superimposed on all plots. The field emission images to the right are recorded after each sweep. At the same magnification, FIM images taken before and after the field emission measurements of the three W atoms (spacing, 4.5 Å) of the apex layer of the tip are presented at the upper and lower left, respectively. The upper left atom image is partially blocked by a deflection electrode, and the equilateral geometry of the three atoms is distorted by the focusing optics.

In sweep 7 an $L \rightarrow H$ transition is observed at about the same time as in sweep 1. Although the jumping of the atom is a statistical process, in both sweeps the jump occurs at the time when the FE is sufficiently strong to heat the Cs vibration high enough to activate the atom. During sweep 8, Cs moves $H \rightarrow L$. The FE changes back to the curve of sweep 6 characteristic of the L position, and the FE image correspondingly returns to that after sweep 6. (Compared to the $\times 5$ FE change observed in the images, the change during the sweeps is lower because the barrier is lower at the higher sweeping voltage.) After the experiments, FIM confirmed that the atomic geometry of the W tip was unchanged by either the negative or positive pulses (Fig. 3).

When the sweeping e^- beam is not perfectly focused, the location at which an electron strikes the detector screen will depend on the position of its emission from the tip. This spatial information is lost along the sweeping direction, but, using an astigmatic focus, the time depen-

3612

dence of the spatial distribution of the emitted electrons perpendicular to the sweep direction can be recorded. Figure 4 shows such a measurement at increased sweep speed. Four traces from adjacent detector pixels are presented, each displaying a distinct time dependence from a portion of a 20 Å diam region of the tip. The two upper traces from the upper portion of the tip show a sudden increase in the FE at about 300 ps, while the two lower traces, representing the bottom, show no increase. The sudden increase between two successive pixels separated by 2 ps is consistent with a Cs atom moving suddenly from the edge to the upper portion of the viewed region of the tip.

Compared to photoabsorption, which switches atomic motion to a new potential surface, perturbation of the atomic trajectories by a single field-emitted electron is weak, because the electron mass is so small compared to the Cs mass. Yet the net result of many such interactions over many vibrational periods is substantial heating.

The FFEC is essentially an electronic streak camera [19] in which the photoemitting electron source has been replaced by a field emitter, which is itself the sample of interest. The time resolution achievable by our instrument is in principle limited by four factors. The most obvious is the ratio a/v involving the sweep speed v and the
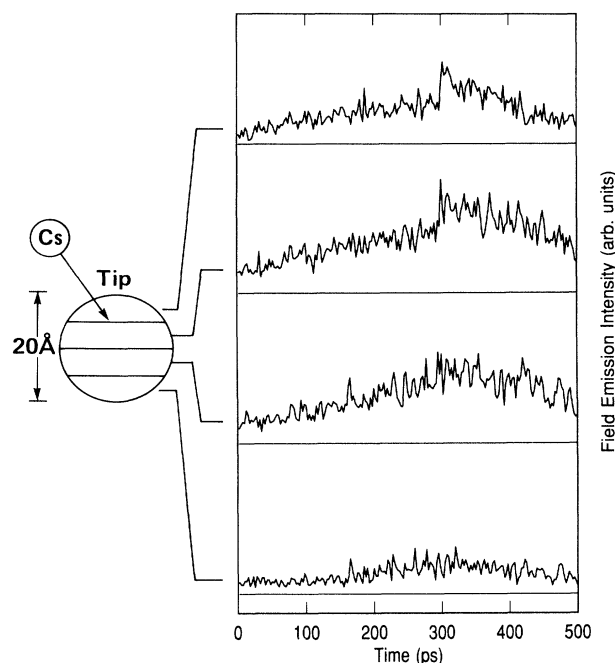

FIG. 4. Simultaneous temporal and one-dimensional spatial resolution of field emission, showing the jumping of a single Cs atom. The four plots, recorded simultaneously, present field emission from four adjacent regions of the tip. Consecutive data points, separated by 2 ps, are connected by a straight line. The schematic indicates a possible motion of the adsorbed Cs atom consistent with the field emission.

size a of the focus spot at the detector. In practice this effect is not limiting, because the tip is a nearly perfect point source for sharp achieveable focusing, and high sweep rates of 10 kV/ns are readily achieveable [20].

A fundamental resolution limit is the distribution of the time of flight (TOF) between the tip and deflecting field caused by the $\simeq 0.5$ eV [21] kinetic energy spread of the emitted electrons. In a spatially uniform accelerating field, most of the TOF spread occurs just after the electrons are emitted, when the electrons are moving slowly and the transit time is strongly affected by the energy. But in field emission from a point, most of the potential drop between tip and lens occurs within 0.5 mm of the tip, and the accelerating field at the tip is so strong ($\simeq 1$ V/Å) that the TOF spread contribution due to initial acceleration is only 1×10^{-14} s. In our instrument, most of the effect of the energy spread on the TOF occurs after the region of strong initial acceleration, but before the lens, where the electron kinetic energy is $\simeq 1000$ eV. This region is traversed in 370 ps, so a $\simeq 0.5$ eV energy spread causes a TOF spread of $(\frac{1}{2}) \times 370 \times 0.5/1000 = 0.090$ ps, while between the lens and deflecting field the TOF spreads 0.050 ps. The spread from the dependence of the flight time on the off-axis angle is estimated from the path length difference to be 0.3 ps.

The net result of these effects is that, at the highest sweep rates, the time resolution of our instrument is $\simeq 0.3$ ps, a number which can be reduced by a factor of 10 by scaling down the size of conventionally manufactured electron optics. By shortening the path length, microfabricated optics [22] could enable achievement of the 10^{-14} s resolution limit imposed by the initial acceleration.

Our measurements exceed by a factor of 10^6 the speed of the fastest previous continuous measurements of single atom motion [4,7]. In addition, one-dimensional spatial resolution has been demonstrated and with more complex electron optics full temporal and two-dimensional spatial resolution can be achieved. Although our method is not completely general, ultrasharp tips can undoubtedly be manufactured from other materials, and other alkalis [15], alkaline earths [21], transition metals [23], and even substrate atoms [15] can be detected. Individual oxygen [24] and organic molecules [5] have been detected by field emission. In future experiments, our instrument will be used to time resolve the trajectories, including the vibrational motion of individual atoms and molecules undergoing diffusion, adsorption, desorption, and reaction.

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