PERSPECTIVES: SURFACE SCIENCE

Electron Dynamics at Surfaces

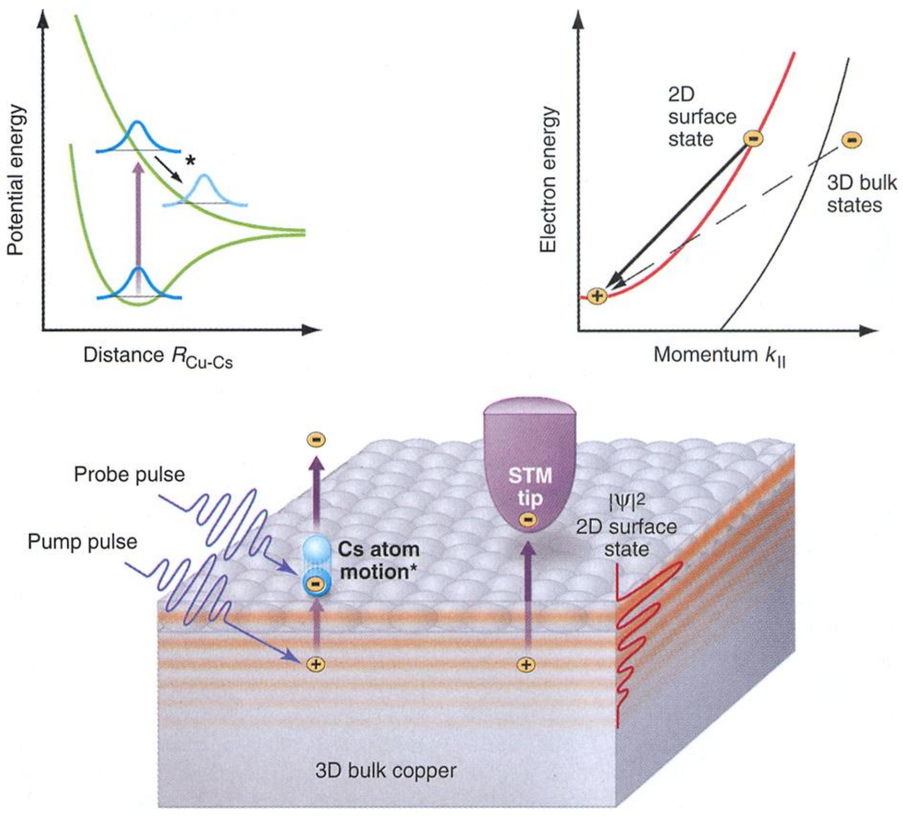
Martin Wolf and Gerhard Ertl

Many processes at surfaces, from chemical reactions to electron transfer, involve the creation and decay of electronically excited states. At metal surfaces, the density of electrons is high, leading to strong interactions and fast electron scattering. As a result, electronic excitations at metal surfaces are extremely short-lived. Surface imperfections and defects, which are always present on real surfaces, often influence or even determine these lifetimes and thus complicate the interpretation of experimental data. On page 1399 of this issue, Kliewer *et al.* (*1*) overcome this obstacle using the unique capabilities of the scanning tunneling microscope (STM). They select a large area on a single-crystal surface in which the atoms are perfectly ordered and probe the response of the electron gas to a well-defined electronic excitation confined to the topmost layers of the crystal (see the figure). On page 1402, Petek *et al.* present another twist to this line of investigation (*2*). They use ultrashort laser pulses to induce a transfer of electrons from the underlying metal to cesium atoms adsorbed on a copper surface, which results in a stretching of the Cs-metal bond. Using time-resolved photoemission spectroscopy (*3*), Petek *et al.* record a real-time "movie" of the Cs atom motion.

Both studies involve a two-dimensional (2D) electronic state, in which the electrons are confined within the top few layers at the surface but can move freely in the direction parallel to it (*4*). In Kliewer *et al.*'s experiment, an electron tunnels out of this state to the STM tip, leaving behind a positive hole that is subsequently filled by electrons from energetically higher lying states (see the figure). Using a line width analysis, Kliewer *et al.* determine the time scale of this relaxation process with very high accuracy (*5*). They find substantially longer lifetimes than previous photoemission studies, which were strongly influenced by defects (*4*). Theoretical analysis shows that the hole is filled predominantly by 2D surface state electrons and not by the three-dimensional (3D) electron gas of the bulk crystal. However, the 3D bulk electrons are not just spectators: They soften ("screen") the interactions within the 2D surface state. Kliewer *et al.* thus obtain a complete understanding of an elementary excitation at a metal surface.

In Petek *et al.*'s experiment, a short laser pulse (a "pump pulse") excites an electron from the same 2D surface state to an unoccupied orbital of a Cs atom adsorbed on copper (*6*). Because the resulting excited state is antibonding with respect to the Cs-metal bond, the Cs atom is accelerated away from the surface (see the figure). This stretching of the Cu-Cs bond lowers the energy of the Cs orbital. Petek *et al.* investigate the changes in the electronic structure in response to the nuclear motion in real time by measuring the photoemission of the electron in the antibonding state. To do so, they use a second probe laser pulse that follows the pump pulse with a variable delay. Analysis of the changing kinetic energy of the photoelectrons as a function of time yields the forces acting on the Cs atom. This allows a potential energy curve for the nuclear motion in the excited state to be derived.

As pointed out by Born and Oppenheimer in 1927, electrons move much faster than the heavier nuclei, and the electronic motion can therefore be treated separately from the much slower nuclear dynamics (*7*). The Born-Oppenheimer approximation provides the backbone of modern quantum chemistry and leads to the concept of an adiabatic potential energy surface on which the nuclei move (*8*). However, for excited electronic states, the concept of a single potential energy surface is only justified if the lifetime of the excited state is long compared with the time scale of nuclear motion. This is the case for reactions in the gas phase but not for systems with fast energy relaxation. The work by Petek *et al.* is of fundamental importance, because it analyzes the energy transfer between electronic and nuclear degrees of freedom on the time



Dynamics of excited electronic states at a metal surface. The dynamics are analyzed with time-resolved photoemission spectroscopy (left) and STM (right). Electrons in the 2D surface state with charge density $|\Psi|^2$ are confined to a few layers at the surface. **(Left)** After excitation of an electron from the 2D surface state to an adsorbed Cs atom, the Cs copper bond, R_{Cu-Cs}, begins to stretch on a repulsive potential energy curve. Subsequently, the electron is photoemitted by a time-delayed probe pulse. From its kinetic energy, one can calculate the amount of energy transferred into the nuclear motion. **(Right)** An electron tunnels from the 2D surface state to the STM tip, leaving behind a positive hole, which is filled by electrons from the 2D surface state that have higher energy and momentum $k_{\parallel}$ (velocity) parallel to the surface.

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scale of electronic relaxation and provides a test of the Born-Oppenheimer approximation for short-lived electronic states.

Many chemists are trying to control the rates and branching ratios of reactions by manipulating the quantum mechanical properties of the system with light (*9*, *10*). Progress has recently been made with controlling gas phase reactions in this way (*11*), but at metal surfaces, quantum control remains a daunting task, because coherence is lost on an extremely short time scale. To date, control of branching ratios in surface photoreactions has been achieved only incoherently by exploiting different mechanisms for energy transfer (*12*). Given the recent advances in laser technology with pulse durations below 10 femtoseconds, the study of Petek *et al.* may well mark the point at which quantum control of surface reactions becomes feasible.

The studies of Kliewer *et al.* and Petek *et al.* demonstrate the insights into electron dynamics at surfaces that can be gained from high spatial and temporal resolution studies. The controlled manipulation of atoms and molecules by STM has been demonstrated with great success (*13*). Such manipulation processes often involve the formation of short-lived electronic states localized on single molecules (*14*). However, the unique spatial resolution of the STM can also be exploited to study the interactions of electrons with well-defined defects and structures at the atomic level, such as single atom impurities (*15*, *16*), step edges (*17*), or quantum corrals (*18*). Such studies promise new insights in the microscopic characteristics of the electron dynamics at surfaces and may open the way to their controlled manipulation.

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PERSPECTIVES: PALEOCLIMATE

1000 Years of Climate Change

Ray Bradley

The exceptional warmth of the 1990s—the warmest decade since instrumental records began—has sharpened concern over the nature of anthropogenic influences on climate. However, the causes of 20th century climate variability are difficult to resolve, because the period of instrumental records coincides with the time during which the atmosphere has increasingly been contaminated by greenhouse gases. What are the "natural" variations that preceded the observed warming of the 20th century? To the casual observer, it might seem that this question has a simple answer—20th century warming was preceded by the "Little Ice Age" and before that by a "Medieval Warm Period." But to those who have looked into this question in depth, the answer is not so simple, as was apparent at a recent workshop (*1*). Many questions remain regarding the climatic changes that occurred over the last millennium.

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Lamb was the first to argue for the existence of a "Medieval Warm Epoch" from around A.D. 1000 to 1300, but his evidence was highly anecdotal and largely qualitative (*2*). Furthermore, his reconstruction of the mild winters and dry summers that led him to characterize the epoch as he did was based on records from western Europe only. Nevertheless, the concept of a Medieval Warm Period (MWP) has taken on a life of its own, with the implicit assumption that it was a global phenomenon and that temperatures were warmer than in recent decades.

There is little evidence that this was so. Hughes and Diaz (*3*) argued a few years ago that the available evidence allowed nothing more significant to be concluded "than the fact that in some areas of the globe, for some part of the year, relatively warm conditions may have prevailed" (p. 28). Subsequent research has not altered that conclusion (*4*–*6*). But we cannot entirely rule out the possibility of a globally extensive warm episode (or episodes) for at least part of the period from A.D. 1000 to 1300, because of the paucity of high-resolution records (especially from the oceans and the Southern Hemisphere) spanning that interval. High-precision borehole temperature measurements from Greenland (*7*), and some from Antarctica, do point to warmer conditions around A.D. 1000 than in recent decades, but other paleoclimate records provide a different picture. For example, tree ring data from the Southern Hemisphere do not provide support for a warmer period ~1000 years ago. By contrast, high-latitude tree ring data from the Northern Hemisphere show evidence of strong warming at that time, at least in the summer months, and some marine records from the North Atlantic also suggest warmer conditions (*8*).

Whether there really were warm episodes of global extent in medieval times (though perhaps not as warm as the past few decades) thus deserves further scrutiny. Until a more extensive set of data is available, the absence of evidence does not necessarily mean evidence of absence. This is unfortunate, because the MWP is often pointed to as "proof" that there were periods in the recent past when conditions were "naturally" warm, without anthropogenic influences. Cosmogenic isotope data (^{10}Be and ^{14}C) point to relatively high levels of solar activity (and hence perhaps higher irradiance) around A.D. 1000; orbital considerations also suggest that, at least in boreal summers, insolation was slightly higher at that time (*9*, *10*). Solar activity levels were generally lower than in medieval times for most of the last millennium, only reaching comparable levels in the latter half of the 20th century, and this issue is therefore very important for understanding our current climate state.

Do we have any better ideas about climatic conditions after the purported MWP? As we move forward in time, the amount of information increases rapidly, and the temporal and geographical patterns of climate change come increasingly into focus as the 20th century is approached. By the mid-16th century, global temperatures were colder than in previous centuries, and alpine glaciers around the world—a sensitive bellwether of temperature change—generally advanced. This period of more extensive glacierization, called the Little Ice Age (LIA), lasted until the mid to late 19th century in most regions. But even within this period, there were warmer episodes; for example, the 18th century was warmer than the preceding

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