RESEARCH: CONDENSED MATTER PHYSICS

Self-Trapping of Electrons at Surfaces

Ulrich Höfer

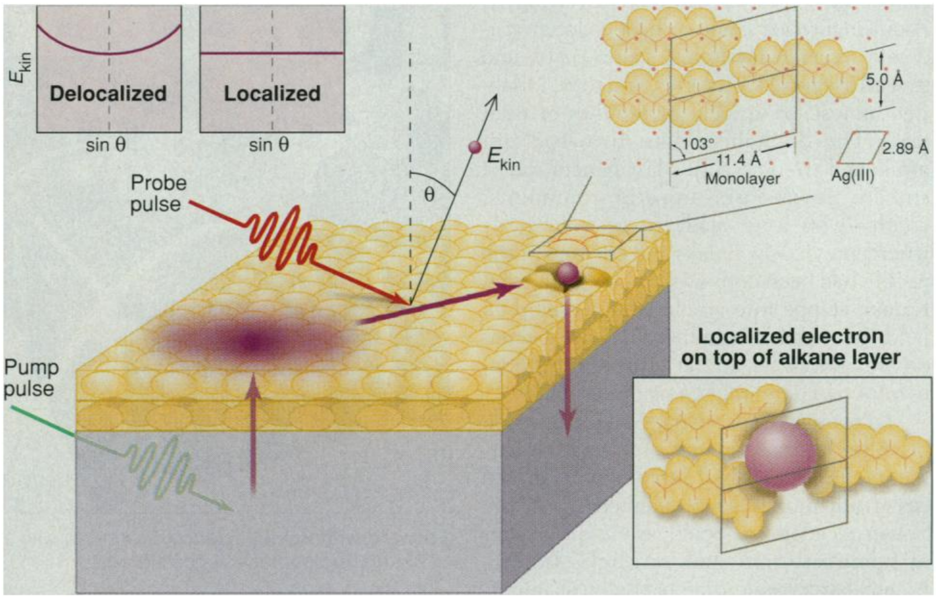
Whether we like it or not, our knowledge about the microscopic properties of solid surfaces and interfaces has generally lagged behind that of bulk crystals. "God created the solids, the devil their surfaces." This comment by Wolfgang Pauli has frequently been quoted to allude to the problems of sample preparation, experimental sensitivity, reduced symmetry, and other difficulties that surface science faces. Yet, on page 202 of this issue, Ge *et al.* (*1*) report an experiment on ultrafast electron dynamics that is an excellent example of exactly the opposite. With a surface experiment, they address a classic question of solid-state physics: the self-trapping of electrons in small polarons. By exploiting the rather unique capabilities of time-resolved photoelectron spectroscopy, they were able to provide information on the dynamics of this process with unprecedented detail and clarity.

What is called a polaron today was considered by Landau in a brief note in 1933 (*2*). Electrons in rigid crystal lattices are delocalized and like free electrons, just as Bloch electrons in metals. In a deformable periodic lattice, slight distortions cause scattering but not trapping of the electrons at specific sites. However, in the case of strong electron-lattice interaction, the electron is able to lower its energy by polarizing and displacing surrounding atoms. "Large" polarons involve moderate lattice deformations extending over several unit cells. The electrons are still able to move rapidly together with the lattice deformation (*3*). Electrons associated with "small" polarons are momentarily confined (trapped) in a self-induced attractive potential with dimensions of a lattice spacing (*4*). Their motion becomes an activated hopping process, a behavior that is observed for charged carriers in many dielectric solids (*5*). Whereas a number of the microscopic properties of small polarons—such as structure, transport, and related phenomena—are reasonably well understood, little precise knowledge exists about the initial process of their formation (*6*). Theoretically, the dynamical coupling of a conduction electron to lattice phonons is a complicated many-body problem even in simple one-dimensional situations (*7*). In two or three dimensions, the interplay of long-range and short-range forces makes self-trapping a highly nonlinear process that is difficult to tackle in quantum dynamical modeling.

In their experiment, Ge *et al.* (*1*) investigate self-trapping in real time at a thin molecular film of ordered alkane layers adsorbed on a silver surface (see figure). A short laser pulse (pump pulse) photoexcites an electron from the conduction band of the metal into an image-potential state (*8–10*). In this state, the electron is localized perpendicular to the surface within a few angstroms at the alkane-vacuum interface. Parallel to the surface the electron initially retains its delocalized character and is able to move almost freely along the surface. Then, within a couple of hundred femtoseconds, it becomes localized, and finally, on a picosecond time scale, it tunnels back into the metal (*1*). The localization of the electron is clearly reflected in the angular dependence of the photoemission signal from a probe laser pulse that follows the pump pulse with variable delay. Because photoemission at surfaces preserves parallel momentum, the kinetic energy of the photoelectron E_{kin} from delocalized free-electron–like states increases with the emission angle θ, whereas localized states are characterized by flat angular dependencies (see figure). Quantitatively, the measured kinetic energy is given by

$$E_{\text{kin}} = \hbar\omega - E_B + \hbar^2 k_{\parallel}^2/2m^* \tag{1}$$

with the photon energy $\hbar\omega$, the binding energy of the electron perpendicular to the surface E_B, the parallel momentum $\hbar k_{\parallel} \propto \sin\theta$, and the effective electron mass m^*.



Formation of a small polaron at a layer of alkane molecules, and detection with time- and angle-resolved two-photon photoemission. After the excitation of a metal electron by the pump laser, the electron is delocalized over many alkane molecules and able to move freely above the surface. It localizes as a small polaron by creating itself a potential well in the alkane layer. The time-delayed probe pulse reveals a parabolic angular dependence of the kinetic energy of emitted photoelectrons for the free delocalized state and no angular dependence for the trapped small-polaron state. The rate at which localization occurs is reflected in the decay time of the signal from the dispersing feature and the rise time of the flat feature.

With this capability, Ge *et al.* are not only able to determine the time scale of the transition from a well-defined, delocalized state to a localized state: The most exciting aspect of their experiment is rather the possibility to investigate the localization time as a function of the parallel momentum of the initially delocalized electron. This is accomplished simply by recording the rise time of the flat feature and the decay time of the dispersing feature in the photoelectron spectrum for different emission angles. Because small fluctuations of the atomic positions cannot cause electron localization in

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small polarons, there is a barrier to their formation. Electrons with finite parallel momentum can help to overcome this barrier. On the other hand, fast-moving electrons will be more difficult to trap at specific sites. From these classical arguments, one intuitively expects an optimum parallel momentum to facilitate localization. The experiment suggests that this effect is present but that there is an additional strong quantum contribution from resonant tunneling into intramolecular vibrational modes that are involved in the formation of the polaron state. The determination of the time scales and energetics as well as the identification of the relevant phonon modes surely provide an excellent basis for further in-depth theoretical studies of the localization dynamics for this system.

Such detailed experimental information is hardly accessible with transient absorption or other purely optical techniques that have been used to time-resolve electron dynamics in bulk materials (*11*, *12*). It is one of the great virtues of time-resolved photoelectron spectroscopy from two-dimensional systems that by measuring the kinetic energy, the emission angle and possibly also the spin of the emitted photoelectron, one is able to completely determine the time evolution of its quantum state before ejection. On the picosecond time scale, these capabilities have been applied most successfully at semiconductor surfaces (*13*, *14*). Recent progress toward a time resolution of 10 fs and the investigation of coherence phenomena have opened up many possibilities (*10*, *15*, *16*). The work by Ge *et al.* might very well mark the point where this powerful probe for ultrafast electron dynamics is applied to areas of research that are not directly connected to the physics and chemistry of surfaces.

In chemistry and biology, for example, the interplay between localization and delocalization of weakly bound electrons is crucial for electron transfer reactions in large molecules such as photosynthetic reaction centers. Furthermore, self-trapping phenomena are important in the dynamics of solvated electrons (that is, excess electrons in liquids that are used as models for studying the chemical physics of solvation). And, quite generally, there is a close relation between the theory of polarons and the electron transfer theory of Marcus (*17*). In terms of technological applications, small polarons are believed to play an essential role in recently discovered materials, such as high-temperature superconductors and manganates with giant magnetoresistance, as well as in conductive polymers, organic light-emitting diodes, and other devices in the rapidly expanding field of molecular electronics.

Certainly, the preparation and characterization of surface layers of some of these materials will not always be simple or even possible. There are obvious differences in the physics of electron localization in two dimensions and in three dimensions. The presence of a conducting substrate, which is highly desirable for photoemission experiments, may lead to undesired coupling effects. However, over the years, surface scientists have learned how to master many of the preparative difficulties. Coupling effects, for instance, can easily be eliminated or controlled by using oxidized surfaces or spacer layers (*18*, *19*). To this end, the fact that solids have well-defined surfaces might very well prove to be a blessing for future investigations of electron dynamics in many areas of science.

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SIGNAL TRANSDUCTION

Calcium Signaling: Up, Down, Up, Down.... What's the Point?

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The simple, ionized form of the element calcium belies its value as a key carrier of information in cells. Just over a decade ago, this messenger was first seen: Calcium-sensitive photoproteins and fluorescent dyes allowed scientists to track calcium concentrations in the cytoplasm of single, living cells in real time and as they responded to outside cues (*1*). In neurons and other excitable cells, where calcium channels are opened by membrane depolarization, it was not surprising that intracellular calcium concentrations rose and fell along with the cyclical depolarizations associated with action potentials. However, it came as something of a shock that, even in nonexcitable cells, hormone stimulation triggered a series of pulses of calcium inside cells, superimposed on a baseline level (*2*).

Two fundamental questions remain: How do these oscillations arise? And what is their function (*3*)? From years of research, something is known about the answer to the first question, but the answer to the second—what the oscillations are actually doing—has remained a mystery. Now, an elegant and creative experimental approach to understanding how molecules decode intracellular calcium oscillations is described in a report by De Koninck and Schulman on page 227 of this issue (*4*).

Calmodulin-dependent protein kinase II (CaM kinase II) is a ubiquitous enzyme target of calcium signaling pathways. It is not directly activated by calcium, but rather responds to another ubiquitous molecule, calmodulin, but only when in its calcium-bound form (calcium-calmodulin). The kinetics of this interaction are complex. In addition to acute activation of the enzyme resulting in phosphorylation of appropriate protein substrates, association of calcium-calmodulin also catalyzes the autophosphorylation of CaM kinase II (*5*), with the result that the enzyme "traps" calmodulin and continues to be active even after calcium levels decline (*6*). In this state, the enzyme becomes au-

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