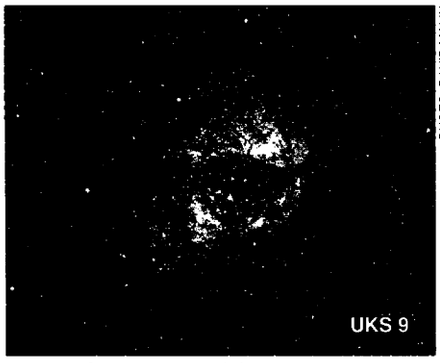


PHOTO: DAVID MALIN

Fig. 2. The Rosette Nebula. A 1° diameter Strömgren Sphere. [Courtesy of Anglo-Australian Observatory]

drogen can exist only in very limited regions of the interstellar medium is quite compelling.

The presence of wide spread ionization (the DIG) in our galaxy and others therefore implies that something is seriously wrong, or at least very incomplete, with this picture. Both pulsar dispersion measurements (*16*) and the subsequent detections of very weak, diffuse H-alpha from the interstellar medium (see Fig. 1) have provided convincing evidence that ionized hydrogen is spread throughout vast regions of the galaxy where the hydrogen was supposed to be completely neutral, regions that are far from O stars and well outside the classical Strömgren Spheres.

So what is going on? The only known source of ionization with sufficient power to produce the DIG is the galactic population of O stars, but their ionizing radiation does not appear capable of permeating the galaxy. Perhaps the Strömgren Sphere argument can somehow be circumvented. For example, it has been shown that certain fractal (*17*) or other distributions (*5*, *6*) of the neutral hydrogen can make the interstellar medium more transparent to an O star's ionizing photons. The alternative—that there is another significant source of ionization in the galaxy that has not yet been identified—is also possible. This source would have to be almost as powerful as the O stars but much more diffusely distributed throughout interstellar space. Although a number of such sources have been proposed (*7*–*9*), none has yet been confirmed. New clues uncovered by the optical emission line studies should soon begin to resolve this long-standing mystery.

References

1. M. Guélin, in *Galactic Radio Astronomy, IAU Symp. No. 60*, F. J. Kerr and S. C. Simonson, Eds. (Reidel, Dordrecht, Germany, 1974), p. 51.
2. R.-J. Dettmar, *Fundam. Cosmic Phys.* **15**, 143 (1992).
3. R. J. Rand, S. R. Kulkarni, J. J. Hester, *Astrophys. J.* **352**, L1 (1990).
4. D. A. Hunter and J. S. Gallagher, *ibid.* **362**, 480 (1990).
5. W. W. Miller and D. P. Cox, *ibid.* **417**, 579 (1993).
6. J. B. Dove and J. M. Shull, *ibid.* **430**, 222 (1994).
7. J. C. Raymond, *ibid.* **384**, 502 (1992).
8. J. G. Skibo and R. Ramaty, *Astron. Astrophys. Suppl.* **97**, 145 (1993).
9. D. W. Sciama, *Astrophys. J.* **409**, L25 (1993).
10. J. E. Gaustad, P. R. McCullough, D. Van Buren, *Publ. Astron. Soc. Pac.* **108**, 351 (1996).
11. B. Dennison, G. A. Topasna, J. H. Simonetti, *Astrophys. J.* **474**, L31 (1997).
12. S. L. Tufte, thesis, University of Wisconsin–Madison, Madison, WI (1997).
13. R. J. Reynolds, S. L. Tufte, L. M. Haffner, K. Jaehnig, J. W. Percival, in preparation.
14. L. M. Haffner, R. J. Reynolds, S. L. Tufte, in preparation.
15. B. Strömgren, *Astrophys. J.* **89**, 526 (1939).
16. J. H. Taylor and J. M. Cordes, *ibid.* **411**, 674 (1993).
17. B. G. Elmegreen, *Astrophys. J.* **477**, 196 (1997).

SURFACE PHYSICS

More Than Skin Deep

Ward Plummer

Electrons are normally not supposed to wander very far from metal surfaces. Yet on page 1480 of this issue, Höfer *et al.* (*1*) report an interdisciplinary investigation that catches surface electrons at their most adventurous. By combining laser techniques used so successfully in atomic, molecular, and semiconductor physics (*2*–*4*) with angle-resolved photoelectron spectroscopy, the workhorse of surface science (*5*), Höfer *et al.* give us a glimpse of the time evolution of electronic states at a metal surface. For the first time, quantum beats between coherently excited states at a clean metal surface have been observed, allowing the authors to resolve high-order states, inaccessible with standard photoelectron spectroscopy. Coherent excitation of higher order Rydberg-like states, selected by the energy in the photoelectron spectrometer, display dramatic time evolution as a consequence of the motion of the wave packet, which travels about 200 Å away from the surface into the vacuum and then returns with a period of 800 fs.

The author is in the Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, USA. E-mail: eplummer@utk.edu

The highly excited states in an atom or molecule are referred to as Rydberg states because their energy separation resembles that predicted by Rydberg for the hydrogen atom. A similar series of excited states exists on many metal surfaces called image potential states (*6*). They are quantum states trapped in the image potential well, where the classical image potential is $V(z) = -e^2/4z$ (z being the perpendicular distance above the surface). In most metals there is no barrier for an electron to return to the metal, but in a few metals there is a band gap near the vacuum level, and an excited electron is trapped in the quantum states of the image potential. The resulting quantized electronic states form a Rydberg-like series with an energy level scheme given by

$$E_n = -0.85\ \text{eV}/(n+a)^2 \qquad (1)$$

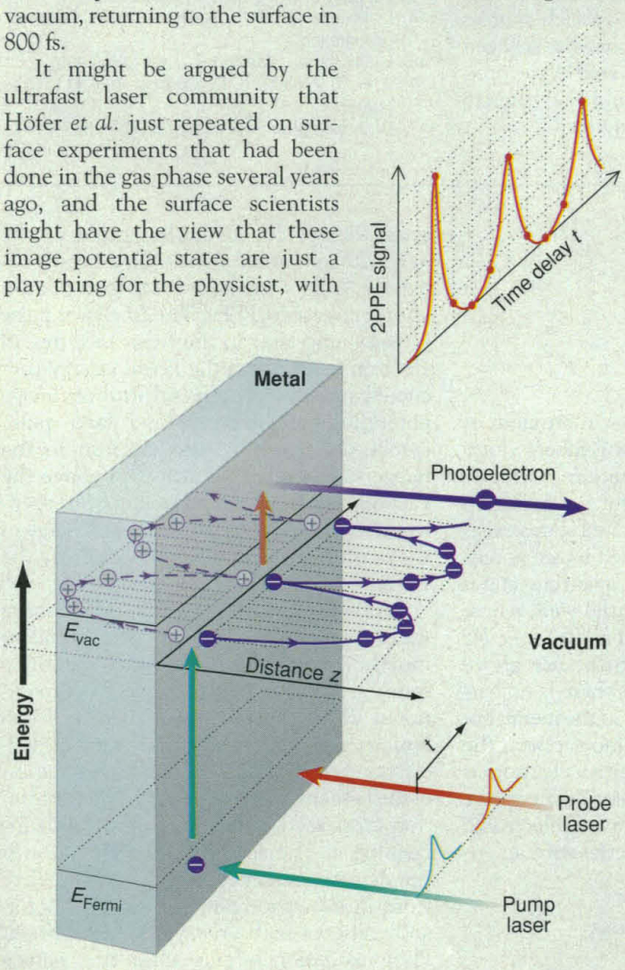
where n is a positive integer and a is a "quantum defect" to account for the nature of the penetration of the electron wave function into the solid, within the band gap.

The figure shows a semiclassical picture of the motion of an electron in an image potential state (filled circles), accompanied by its image charge (open circle) inside of the metal. Image potential states have been studied for years with laser-based two-photon photoemission (2PPE). The first laser pulse (green pump laser in the figure) excites an electron from below the Fermi energy (occupied states) in the metal into an image potential state. The second laser pulse (probe laser) excites the electron in the image state into the continuum above the vacuum level. The photoelectron spectrometer is used to determine the energy of the emitted electron and consequently the energy of the image state.

Undoubtedly, the most interesting image states are the high n states, which extend far into the vacuum (200 Å for $n = 7$), but these states are not easily accessible to conventional 2PPE spectroscopy. There are two limitations: (i) the spacing of the energy levels soon becomes smaller than the resolution of the best analyzer, and (ii) the photoionization cross section dies off rapidly with increasing n. The decrease in cross section is simply a consequence of the fact that electrons in free space cannot absorb a photon and conserve both energy and momentum. Photoexcitation occurs near the surface where the rapid gradient in potential serves as a source of momentum (*7*). The highest resolution at present is 15 meV in measurements by Padowitz *et al.*, where the first four image states were observed (*8*). Höfer *et al.* were able to determine the energy of the fourth, fifth, and sixth image potential state

on Cu(100) by coherently exciting these three states with a 95-fs laser (14 meV full width at half maximum) and observing the quantum beats in the photoionization as a function of the time delay in the probe laser. The acceptance energy and window of the analyzer were chosen for looking at these states. A by-product of these measurements was the lifetimes of the fourth, fifth, and sixth image state. These are the longest lifetimes ever measured for an electronic state on a clean metal surface (2 ps for $n = 6$) and agree remarkably well with theoretical predictions (6). In a second experiment, they set the analyzer to sample states 15 meV (centered around $n = 7$) below the vacuum level and observed the time evolution of the photoionization signal as a function of the delay time of the probe. These measurements clearly showed the orbital time of the wave packet created near the surface. This semiclassical "particle" moved ~200 Å out into the vacuum, returning to the surface in 800 fs.

It might be argued by the ultrafast laser community that Höfer *et al.* just repeated on surface experiments that had been done in the gas phase several years ago, and the surface scientists might have the view that these image potential states are just a play thing for the physicist, with no real practical importance. I would argue that both would be wrong; in my view Höfer *et al.* have just "scratched the surface." First of all, image-potential states, because of their simplicity, provide an extremely useful model to study the interaction of excited surface electronic states with the underlying substrate directly in the time domain (9). This coupling in turn governs the cross sections and branching ratios of practically all electronically induced adsorbate reactions at metal surfaces (*10*). Second, there are numerous applications and extensions that come to mind. A distinct advantage of the surface experiment compared with the gas phase analog is the fact that the sample is oriented and the angle-resolved detector picks out the velocity of the wave packet or state parallel to the surface. One can really probe the entire wave function. For example, consider the trajectory of the electron shown in the figure. If this is the $n = 7$ image state, the wave packet starts at the surface, goes about 200 Å into the vacuum, and returns to the surface, traveling a distance of about 120 Å along the surface at a velocity of 1.5×10^4 m/s. This specific state is picked out by setting the angle-resolved analyzer at an angle of 1.1° off of the normal. This could become very useful for future detailed studies of dynamics and the control of chemical reactions (*11*). Today, the unique properties of oriented and well-ordered molecular adsorbate layers on insulating substrates are already exploited in investigations of desorbing fragments of photochemical processes (*12*). By the combination of this so-called "surface-aligned photochemistry" with coherent laser excitation and photoelectron detection, it appears possible to completely map the temporal evolution of a system during a chemical reaction.



Wandering electrons. Schematic representation of an electron (filled circles) moving outside of a surface in an image potential state. The image inside the metal is shown by the open circles. The image state is occupied by exciting an electron from below the Fermi energy with the pump laser. A second, time-delayed probe laser excites the electron in bound image potential state into the continuum where it is detected. (**Inset**) The ionization cross section as a function of the time delay.

For a molecular chemist the image states look like a one-dimensional hydrogen atom, but for a physicist these are states in a quantum well, confined in the direction normal to the surface. This perspective opens up many new avenues of investigation. Fabrication of well-characterized quantum wires and quantum dots of metals on semiconductor surfaces is progressing rapidly. Coherent excitation of these quantum wires and dots could be used to measure the energy level spacings, and the angle-resolved analyzer could be used to probe the anisotropic states in a wire. Finally, it seems possible to explore the transition from quantum mechanics to classical mechanics by using image potential states in the same way as Rydberg states in atoms have been used (*13*). With higher resolution analyzers, more powerful lasers, and interferrometric pump-probe schemes (*14*), the detection limit will certainly be pushed to higher quantum numbers than that of $n = 7$ achieved currently by Höfer *et al.* For example, already the 10th image state extends ~425 A into the vacuum, which is the equivalent radius of the $n = 28$ Bohr orbit in an atom. The reduced dimensionality of the surface hydrogenic system coupled with the straightforward capability of velocity selection parallel to the surface offers a new frontier for angle-resolved photoemission.

References and Notes

1. U. Höfer *et al.*, *Science* **277**, 1480 (1997).
2. W. Kaiser, Ed., *Ultrashort Laser Pulses*, vol. 60 of *Topics in Applied Physics* (Springer, Berlin, ed. 2 1993).
3. *Ultrafast Phenomena IX; Proceedings of the Ninth International Conference*, Dana Point, CA, 2 to 6 May 1994; vol. 60 of *Springer Series in Chemical Physics*, P. F. Barbara, W. H. Knox, G. A. Mourou, A. H. Zewail, Eds. (Springer, Berlin, 1994).
4. J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*, vol. 115 of *Springer Series in Solid-State Sciences* (Springer, Berlin, 1996).
5. S. D. Kevan, Ed., *Angle-Resolved Photoemission*, (Elsevier, Amsterdam, 1992).
6. P. M. Echenique and J. B. Bendry, *Progr. Surf. Sci.* **32**, 111 (1990).
7. This is the same argument used in excitation of Rydberg states in atoms, that is, "ionization take place predominately close to the atomic core." A. ten Wolde, L. D. Norrdam, A. Lagendijk, H. B. van Linden van den Heuvell, *Phys. Rev. Lett.* **61**, 2099 (1988).
8. D. F. Padowitz, W. R. Merry, R. E. Jordan, C. B. Harris, *ibid.* **69**, 3583 (1992).
9. M. Wolf, *Surf. Sci.* **377–379**, 343 (1997).
10. The lifetime of the excited state is the most important "unknown" in the Menzel-Gomer-Readhead model that is commonly used to describe electronically induced desorption and dissociation processes at surfaces. D. Menzel and R. Gomer, *J. Chem. Phys.* **40**, 1164 (1964); P. A. Readhead, *Can. J. Phys.* **42**, 886 (1964).
11. A. H. Zewail, *J. Phys. Chem.* **100**, 12701 (1996); J. Manz and L. Wöste, Eds., *Femtosecond Chemistry* (VCH Verlag, Weinheim, 1995), vols. 1 and 2.
12. J. C. Polanyi and H. Rieley, in *Dynamics of Gas-Surface Interactions*, C. T. Rettner and M. N. R. Ashfold, Eds. (Royal Society of Chemistry, London, 1991), pp. 329–363.
13. M. Nauenberg, C. Stroud, J. Yeazell, *Sci. Am.* **270**, 24 (June 1994).
14. S. Ogawa, H. Nagano, H. Petek, A. P. Heberle, *Phys. Rev. Lett.* **78**, 1339 (1997).