# Atomic Beams Probe Surface Vibrations

## *From changes in the energy of helium beams scattered from solid surfaces, scientists can measure the frequencies of surface vibrations*

In the last 2 years, surface scientists have begun trying to obtain the vibrational frequencies of surface atoms in both insulating and metallic crystals from beams of helium atoms that are scattered (reflected) from these materials.

The vibrations of atoms and molecules at solid surfaces are of intense interest to chemists, materials scientists, and physicists who want to understand the details of the chemical reactions that take place there. Such reactions form the basis for heterogeneous catalysis (reactions catalyzed on surfaces), a key process in the multibillion-dollar petrochemical industry and, more recently, in synthetic fuels production. And, as microelectronic devices continue to shrink, careful control of surface reactions is becoming increasingly important in their fabrication.

There is also the promise of laser chemistry. By injecting energy into specific molecular vibrations with an infrared laser, scientists hope to direct reactions along one path to desired product molecules rather than the many paths leading to a multiplicity of products in thermally promoted reactions. Although there is considerable skepticism that this kind of selectivity will ever be practical (whether in gas-phase, liquid-phase, or surface reactions), there is nonetheless much effort devoted to the possibility. At the Third International Conference on Vibrations at Surfaces,* for example, Ingo Hussla and Joachim Heidberg of the University of Hannover, West Germany, reported on their ability to selectively desorb methyl fluoride from a sodium chloride surface covered with both methyl fluoride and ethane. They achieved the selectivity by tuning a carbon dioxide laser to match a particular vibrational frequency in the methyl fluoride. The vibrational energy excited by absorption of the infrared photons is transferred to the chemisorption bond between the methyl fluoride and the sodium chloride and thereby breaks it.

Surface vibrations come in two forms. There are the vibrations of the atoms that happen to be at the surface of a sample rather than deep inside, and there are the vibrations of atoms or molecules adsorbed on the surface. The two main ways to study these vibrations are infrared spectroscopy and electron energy loss spectroscopy, and experimental and theoretical papers devoted to these techniques dominated the surface vibrations conference. It is still too soon to say whether helium atomic beam scattering will be a fad or will join these techniques in the main line of a vast array of surface spectroscopies.

Infrared spectroscopy is the classic method of studying molecular vibrations. As applied to surfaces, the technique involves shining a beam of infrared light onto a surface at a glancing angle and measuring the reflected light. As the frequency of the infrared is scanned, small dips in the reflected intensity occur where light is absorbed by the excitations of vibrations. In the past few years, however, this infrared reflectance-absorption technique has met stiff opposition from high-resolution electron energy loss spectroscopy. Vibrational frequencies of surface species are obtained from the changes in the energy of an electron beam that strikes a surface and is reflected (scattered) back. The two methods are partially complementary. Infrared reflectance-absorption spectroscopy has a high spectral resolution and can be applied to samples in "realistic" environments. But electron energy loss spectroscopy, which may require an ultrahigh vacuum of $10^{-10}$ torr or better, is more sensitive to small concentrations of surface species, can detect lower energy vibrations, and can look at very small surface areas.

Surface-enhanced Raman spectroscopy is a third, highly popular way to examine surface vibrations, but its usefulness is controversial. It is potentially a technique of both high sensitivity and high resolution. However, there seem to be so many mechanisms causing the enhancement (which must be sorted out anew in each experiment) that the technique is not very quantitative. In his summary talk at the surface vibrations conference, Harald Ibach of the Nuclear Research Establishment in Jülich, West Germany, concluded that surface-enhanced Raman scattering would be useful only in special circumstances.

So, how do atomic beams apply to the study of surface vibrations? When a beam of atoms (or molecules) strikes a solid surface, three things can happen: the particles may emerge with no change in their energy (elastic scattering); they may lose some of their energy before returning from the surface (inelastic scattering); or they may stick to the surface (adsorption). It is the inelastic scattering that researchers use to probe surface vibrations. As in electron energy loss spectroscopy, the frequencies of surface vibrations are obtained from the changes in the energy of particles scattered from the surface. The mechanism by which the scattering occurs, however, is not the same for the two techniques. Inelastic atomic beam scattering has only been used to obtain vibrational frequency spectra of clean surfaces. Adsorbate-covered surfaces have yet to be attacked by this method.

Attempts to observe inelastic scattering of atoms by crystal surfaces date to at least 1969. One of the first successful tries at identifying surface vibrations by this means was the 1978 experiment of James Horne and David Miller of the University of California, San Diego. They studied lithium fluoride with a helium atomic beam having an energy of 63 millielectron volts (meV).

Vibrations in a crystalline solid are complex combinations of modes (waves), each characterized by a frequency and a momentum (a vector whose magnitude is the Planck constant divided by the wavelength of the mode). The variation of the vibrational frequency with the momentum up to some maximum momentum is given by a dispersion curve. A given crystalline material will have several dispersion curves corresponding to different vibrational modes. At a surface, atoms may have contributions to their vibrations corresponding to these "bulk" modes and also to certain vibration modes that occur only in the surface layers. The surface vibrational modes may have complete dispersion curves of their own, or they may exist at only one frequency and momentum (or a narrow range). Among the modes occurring only near surfaces that do have a dispersion curve are the acoustic Rayleigh waves, the lowest frequency vibrations on a surface. Horne and Miller measured two points on the dispersion curve for lithium fluoride Rayleigh waves [(001) surface].

But the experiment that once and for all demonstrated the feasibility of the helium atomic beam-scattering tech-

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nique was a complete study of the Rayleigh wave dispersion curve in lithium fluoride that was reported in 1980 and 1981 by G. Brusleylins, R. Bruce Doak, and J. Peter Toennies of the Max Planck Institute for Fluid Dynamics in Göttingen. By expanding high-pressure helium gas cooled to liquid nitrogen temperature into an ultrahigh vacuum chamber, the investigators produced a beam of 20-meV helium atoms having a spread in their velocities of less than 1 percent. This was an improvement of better than a factor of 10 over the earlier experiments of Horne and Miller. They recorded the time it takes for helium atoms to reach a mass spectrometer detector after scattering from the lithium fluoride. Elastically scattered atoms provide a kind of reference time. Time delays with respect to this reference give the losses in energy of the beam due to excitation of surface vibrations, whereas advances give the increases in beam energy due to annihilation of vibrations during the scattering. Either process can be used to deduce vibrational frequencies. To measure a full dispersion curve, it is necessary to make several series of measurements at closely spaced angles of incidence of the helium beam.

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By this means, the German researchers reconstructed the full Rayleigh wave dispersion curve for lithium fluoride [(001) surface]. It would have been difficult to duplicate this by electron energy loss spectroscopy because the light electrons do not carry as much momentum as helium (or other) atoms. Hence, electrons cannot transfer enough momentum to the surface to excite high-momentum vibrations in the dispersion curve. In addition, the best resolution in electron energy loss spectroscopy is about 5 meV, whereas for inelastic helium scattering it is down to almost 0.1 meV.

The German researchers also observed so-called acoustic "bulk" vibrations. The vibrational modes of crystals fall into two classes: acoustic modes, in which the frequency goes to zero as the momentum decreases, and optical modes, in which the frequency remains relatively large. The dominant modes seen in the helium experiments are the acoustic Rayleigh surface vibrations, and it had been thought that the acoustic bulk modes would be too difficult to observe. Even more surprising, Giorgio Benedek of the University of Milan, in his review talk at the surface vibrations conference, reported that the German group recently has observed an optical mode. Theorists' calculations had shown that inelastic scattering from these vibrations should be very small.

Lithium fluoride and other alkali halide crystals that have been studied are natural first examples because the inelastic scattering effect is large and the peaks are well separated from the elastic scattering peak. Recently, however, attention has been shifting to the scientifically more interesting metals. For example, last year B. F. Mason and B. R. Williams of the National Research Council of Canada in Ottawa measured inelastic scattering of helium beams from copper [(100) surface]. The investigators found scattering peaks attributable to both bulk and surface vibrations.

A key point is that the scattering peaks were each due to a single vibrational mode. This need not always be the case, as scattering events in which several modes participate are theoretically possible. For example, Berndt Feuerbacher of the European Space Research and Technology Center in Noordwijk, the Netherlands, and R. F. Willis of the University of Cambridge reported a year ago on the scattering of neon atoms from nickel [(111) surface]. Neon is a considerably larger atom than helium, and the increased atomic diameter played a significant role. Feuerbacher and Willis found that they could measure the Rayleigh wave dispersion curve only up to a critical momentum less than the allowed maximum—that is, the entire dispersion curve could not be observed. For energy transfers larger than that corresponding to the most energetic Rayleigh wave, the investigators found only peaks of increasing energy but always zero momentum, which they attributed to multiple vibrational modes.

Their explanation relied on the large number of free electrons that abound in metals but not in insulators like the alkali halides. The electrons act to distribute the impact of the incident atomic beam over several surface nickel atoms, effectively increasing the size of the bombarding particles. Surface Rayleigh waves can be excited only if their wavelengths are longer than the effective particle size. The large initial size of the neon atom and the distributing effect of the electrons limit the Rayleigh waves to long wavelengths (low momenta) so that the full dispersion curve is not accessible.

From the point of view of studying surface vibrations, the conclusion is that it is best to use the lighter, smaller helium atom as a probe. For example, at the surface vibrations conference, Michael Cates and Miller at San Diego reported on their study of surface vibrations on gold by means of inelastic scattering of helium beams. They obtained nearly the full dispersion curve for one surface vibrational mode [(111) surface].

To make the technique fully quantitative, surface scientists must make more refined analyses than simply calculating vibrational frequencies from the positions of scattering peaks. For example, the shapes of scattering peaks depend on the shape of the dispersion curve of the vibrations being probed. If the curve is flat, so that over a wide momentum range the vibrations have nearly the same frequency, the scattering peaks will be different than if the curve is steep. Taking all this into account requires a scattering theory.

Interestingly, because the helium atoms never penetrate beyond the first layer of a surface, the scattering calculations are relatively straightforward. It is the potential energy that gives rise to the scattering that is the problem. The theory starts with the Lennard-Jones– or Morse-type potential energy curves that exist between two atoms approaching one another. As they get closer, the energy drops, and there is a "well" in which the atoms are bound together. If they get closer still, the energy rises rapidly. In the scattering experiment the incoming atom is not bound because its kinetic energy keeps it above the well. Instead, it is reflected from the steeply rising, repulsive part of the potential energy curve. All the theoretical work has been devoted to calculating the reflection process with various approximations to a realistic potential energy curve. In fact, it is also possible to turn the process around and use the scattering to determine the true potential energy curve.

Most of the theoretical activity has been for the case of elastic scattering. This case is of great interest because, just as x-rays and electrons can elastically scatter from crystals and give rise to diffraction patterns that characterize the atomic structure of the scattering medium, so too can atomic beams diffract. To quantitatively obtain the positions of the surface atoms giving rise to the diffraction pattern, accurate calculations based on realistic potential energy curves are required. Surface scientists are studying both clean and adsorbate-covered materials in this way.

In the case of inelastic scattering, Benedek and Nicolàs García of the Autonomous University of Madrid showed last year that the shapes and intensities of the main peaks in the scattering data from lithium fluoride of Brusdeylins, Doak, and Toennies could be explained by the so-called hard corrugated surface approximation. A hard surface is one in which the repulsive part of the potential curve is approximated as a vertical line (that is, the potential rises infinitely fast). Corrugation refers to the fact that the surface is not smooth because the surface atoms occupy discrete sites. The potential energy between the atoms is slightly lower than it is over an atom.

Many authors have reported in the past year, however, that satisfactory fits to elastic, diffractive scattering require more accurate potential energy curves than the hard wall. There is considerable experimental evidence for a softer (that is, not infinitely fast rising) wall. At the surface vibrations conference, García and John Barker and Inder Batra of the IBM San Jose Research Laboratory discussed realistic potentials for helium scattering from nickel, copper, and gold. In his conference summary talk, theorist Thomas Grimley of the University of Liverpool urged his colleagues to begin a first-principles calculation of the potential energy curve and its coupling to surface vibrations, although "it may take years." The theory is only semiquantitative until this is accomplished.

Grimley also asked whether it would be possible to use atomic beam inelastic scattering to observe vibrations in adsorbed molecules. It should be feasible, he said, and could become a competitive technique with electron energy loss spectroscopy. However, in his summary talk, experimentalist Ibach, who is regarded as the father of electron energy loss spectroscopy, pointed out that the rather low energies of the atomic beams used so far (less than 100 meV) could prevent researchers from using atomic beams to look at high-energy surface vibrations. In general, vibrations in adsorbed molecules have much higher energies than the vibrations on clean surfaces.—ARTHUR L. ROBINSON

# Extinction Leaves Its Mark on Ecology

## *In addition to energetic considerations, selective extinction helps shape the composition of living communities*

Nineteenth-century naturalists argued about the most appropriate way in which to analyze the causal factors in community structure and dynamics. Today's ecologists continue the debate in vigorous manner, with a currently popular emphasis on features such as coevolution, resource partitioning, and thermodynamics. James MacMahon of Utah State University and Charles Fowler of the National Marine Mammal Laboratory, Seattle, suggest in a recent paper* that in addition to these processes ecologists should also take note of important historical effects, specifically selective extinction and speciation, both in geological and ecological time frames.

As a group, ecologists represent a broad range of scientific backgrounds, some of which embody the kind of historical perspective urged by MacMahon and Fowler. However, the main thrust of contemporary thinking, brilliantly pioneered by such figures as G. Evelyn Hutchinson and Robert MacArthur, concentrates on current ecological processes. "Historical processes are very difficult to deal with," comments Robert Ricklefs of the University of Pennsylvania. "Nevertheless, it is an important consideration to which ecologists in general have not paid sufficient attention." Peter Grant of the University of Michigan agrees that "The temporal dimension has been somewhat neglected."

Any ecological community will comprise a range of organisms of different size, habits, and abundance. Thermodynamic considerations will determine the total biomass a given area might support, but, say MacMahon and Fowler, they are less helpful in explaining the overall composition of species. Their suggestion is that since certain properties of species, such as body size, geographic range, and evolutionary plasticity affect probabilities of extinction, community composition will in part at least reflect these probabilities.

For instance, one of the substantive problems of ecology is the shape of the trophic pyramid, which goes rapidly from an abundance of primary producers at its base to a sparsity of carnivores at its apex. Why is the number of trophic levels so limited? And why is the pyramid generally so broadly based?

"There are many contending explanations," says Robert May of Princeton University. "One of them is the inefficiency of energy transfer from level to level. In this case you'd expect to see longer food chains among cold-blooded animals, which are more energy efficient than endotherms. But this is not the observed case."

MacMahon and Fowler point out that the probability of extinction of a species in a food chain is the sum of its own inherent probability and that of the levels below upon which it depends. Extinction probabilities therefore tend to increase as one climbs the trophic pyramid. The concepts of selective extinction "produces a rather simple explanation of the rather short nature of most trophic chains," write MacMahon and Fowler.

The argument can be taken further, in examining species' habits in the food chain. A specialist feeder which depends on a single food source is more vulnerable to extinction than one which has a broader resource base, for obvious reasons. This being the case, "there will be more trophic levels in communities comprised of generalist than in communities where specialization . . . [is] characteristic of the species . . . involved," predict MacMahon and Fowler.

A second property of species, but not of individuals, that bears on extinction probability is geographic range. A species with a very limited geographic range is clearly more vulnerable to extinction through local catastrophe than is a widespread species. A corollary of this is that the density of species will increase with increase in the total area of a particular environment being examined. Both these points are borne out by observation.

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