surfaces dictate the confinement or departure of the nuclei, and thus the outcome of the chemical process. For his development of computational techniques that greatly facilitate the calculation of molecular potential-energy surfaces, Northwestern University theorist John Pople shared last year's chemistry Nobel Prize. (See PHYSICS TODAY, December 1998, page 20.)

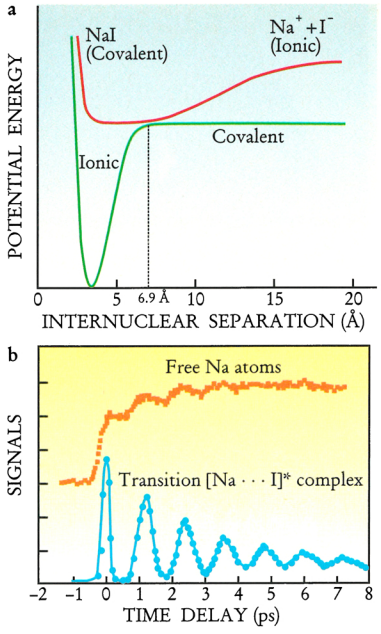
When the potential energy of a diatomic molecule, at a given electronic excitation level, depends only on the distance between the two nuclei, the potential-energy surfaces are simply curves, as we see in the figure at right. For NaI, a prototypical alkali halide molecule, the figure shows the theoretically calculated ground-state potential curve, with a deep ionic-bonding well at an equilibrium nuclear separation of 2.8 Å, and a nearby excited-state potential curve with a broad, shallow well.

In a 1988 experiment,[3] Zewail and coworkers gave a striking demonstration of how femtochemistry can elucidate the dynamics of such a fundamental molecular system. The two NaI potential energy curves come very close to each other when the nuclei are 6.9 Å apart. At this point there's a bonding role reversal, as is often the case at such "avoided crossings": The strong ground-state bond, which is ionic at small separations, becomes covalent, and thus weaker, at separations beyond 6.9 Å. Conversely, the short-distance covalent bond of the excited state becomes ionic, and thus stronger, beyond 6.9 Å. This long-distance creation of an ionic bond in the exited state has been described as harpooning the iodine atom from afar with the sodium atom's valence electron.

The Caltech group's experiment began with a pump pulse that raised NaI molecules in the beam to the excited state. That was followed, at 50 fs intervals for the next 10 ps, by probe pulses at wavelengths chosen to reveal the creation of free Na atoms and of a putative short-lived transition complex of bonding and antibonding states, denoted $[Na\cdots I]^*$. The experimental results, shown in part b of the figure, exhibit a remarkably clear and persistent oscillation, with a period of 1.25 ps. The upper data curve signals the liberation of Na atoms, while the lower curve signals the fleeting appearance of the elusive transition complex.

The 1.25 ps periodicity manifests the oscillation period of the NaI molecule in the excited state's broad potential well. Every time the separation approached the 6.9 Å avoided-crossing point, the $[Na\cdots I]^*$ transition state would form, and there was a roughly 10% chance that the molecule would jump down to the covalent branch of the ground-state curve and thus finally dissociate.

But—if the experimental signal is a sum over millions of independent molecules—why don't the oscillations wash out? The answer is that, in such a femtochemistry experiment, the pump pulse catches all the ground-state molecules at once, all of them very close to the equilibrium 2.8 Å separation at the bottom of the deep potential well. Thus they all start to oscillate in the excited well almost in lockstep, giving us an unprecedented "movie," with angstrom resolution, of a prototypical molecular disintegration in progress.



MOLECULAR DYNAMICS of NaI at femtosecond resolution.[3] (**a**) Potential energy curves for the ground state (green curve) and the experiment's excited state (red) come very close to each other at 6.9 Å and trade bonding characteristics. (**b**) Probe laser pulses at 50 fs intervals detect 1.25 ps oscillations in the population of liberated Na atoms (orange data points) and a short-lived transition complex (blue).

Femtosecond diffraction

"Now we're looking at biological systems and other very complex processes," Zewail told us, "and we're hoping to apply electron diffraction techniques on a femtosecond scale. Kent Wilson's [University of California, San Diego] group has recently managed to do lattice-dynamics diffraction experiments with picosecond x-ray pulses."[4] As these diffraction techniques evolve, they should make possible the structural study of crystals and complex molecules on the timescale of their formation.

"Again and again, Zewail's group has shown us how much one can learn by resolving the dynamics of chemical systems on femtosecond scales," says Herschbach. "This inspirational impact is an important aspect of Zewail's contribution."

BERTRAM SCHWARZSCHILD

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A New Way to Guide Light in Optical Fibers

A novel form of fiber optics, featuring a hollow core rather than one made of glass, holds promise for communications systems or other applications.

Many of our phone conversations and e-mail communications race to their destinations over optical communication links that rely on total internal reflection to guide pulses of light down hair-width fibers of glass. Despite their prodigious bandwidth, these glass fibers will be hard pressed to meet the heavy traffic demands being placed on them by the exploding use of the Internet. Recently, researchers from the US and UK have demonstrated another way to transmit light waves though narrow channels: By surrounding a hollow core with photonic bandgap structure.[1] Their achievement opens the way for guiding light with little or no loss through an evacuated channel. That's important because the interaction of light with glass now limits the maximum power that one can transmit with today's glass-core fibers. It's not possible to have hollow cores with fibers that rely on total internal reflection because the core must have a larger index of refraction than the cladding, and there's no solid material that has an index of refraction less than one.

The recent demonstration is thus

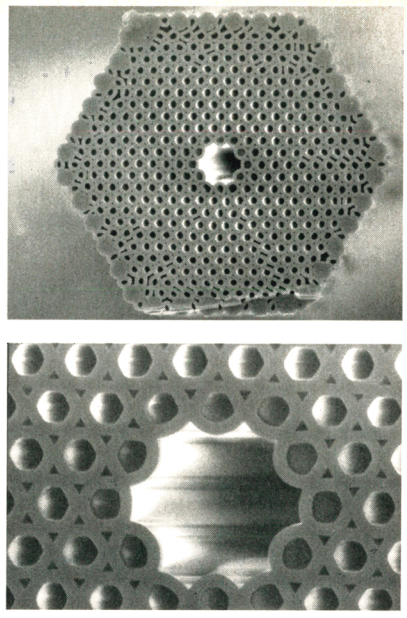
an important step, although so far propagation has been shown only for fibers a few tens of centimeters long. If the technique can be scaled up to long distances, it may help communications companies better keep up with the growing demand on their fiber networks (which is currently met by lightguides, microwaves, and satellite-based systems). Higher power is needed to carry more information in fibers, but the power levels in conventional fiber-optic systems are limited by the nonlinearities of the medium.

Short of replacing conventional fibers, however, photonic bandgap fibers may find niche markets because they have different properties from fibers based on total internal reflection. They allow greater flexibility in the nature of the core, for example, because the index of refraction for the core does not have to be lower than that of the cladding. But they are more restricted in the range of wavelengths they can carry without loss. Aside from lightwave applications, they might be used to guide atoms or small particles down capillary tubes.

The guiding principle

What serves as the cladding in the new photonic bandgap fibers? As shown in cross section in the figure above, it is a lattice of silica penetrated by a hexagonal close-pack array of holes that surrounds a large central hole (the core). Such arrays of contrasting dielectric materials (in this case, silica and air or vacuum) strongly scatter light rays passing through them. Thanks to their regularity, the structures can have a photonic energy spectrum analogous to that of electrons in a crystal. For certain geometries, the spectrum can even feature a bandgap—that is, a band of wavelengths that cannot propagate within the material. Photonic bandgap materials are attracting increasing interest for applications such as lasers, optical cavities, and couplers (see the news story in PHYSICS TODAY, January 1999, page 17, and the article by Sajeev John in PHYSICS TODAY, May 1991, page 32).

If a fiber has a photonic bandgap structure as its cladding, light whose wavelength falls within the bandgap cannot leak into the cladding, but must remain within the core. That idea has motivated the team that did the recent demonstration: Philip Russell, Timothy Birks, Jonathan Knight, and their postdocs and students at the University of Bath in the UK, along with John Roberts of the Defence Evaluation and Research Agency in Malvern, England, and Douglas Allan of Corning Inc in Corning, New York. Russell told us that, when he started out toward this goal in 1992, many in the field felt that success would require a bigger contrast in the two indexes of refraction than that between silica and air (1.46 to 1) to get a full bandgap. Nevertheless, Russell's group has shown that it's possible to get a two-dimensional bandgap using these structures.[2]



PHOTONIC BANDGAP FIBER. This scanning electron micrograph of the cleaved end face of a light-guiding fiber shows the overall shape (top) and a closeup (bottom) of the honeycomb array of holes in silica. Light is guided down the large central core, which is 14.8 μm in diameter. (Adapted from ref. 1.)

Finding the right geometric pattern of holes in silica was not straightforward, however, largely because it's not easy to calculate what kinds of structures will give a sufficiently large bandgap in the desired wavelength region. Possible structures differ in the geometrical arrangement of the holes, the size of the holes, and the distances between them. Last year, Knight, Birks, and Russell, together with J. Broeng from the Technical University of Denmark, reported another structure that guided light by a photonic bandgap mechanism, but most of the light traveled through the silica surrounding the central hole, rather than within the hollow core, thus defeating the hoped-for transmission in air that the researchers have now achieved with the new design. One key to their recent success was fabricating a structure with a larger volume fraction of air (around 30%).

To make the fibers, the researchers bundle several hundred hollow capillary rods of silica in a hexagonal close-pack array, each about a millimeter in diameter. They then remove enough rods from the center to leave a hole the size of seven unit cells. The Bath–Corning team then heats this sheaf of rods and draws it out to form long fibers tens of micrometers in diameter. The process introduces additional, small interstitial holes into the gaps between the rods, which have a small effect on the bandgap wavelengths.

Transmission bands

When Russell and his coworkers shone white light through short lengths of these fibers, they found that the core transmitted colored light—presumably those wavelengths in the bandgap of the cladding—while the cladding transported white light, presumably a mix of all allowed wavelengths. The transmission spectrum showed low-loss peaks in several wavelength bands in the visible and infrared bands of the spectrum. Laser light whose frequencies lay within those bands could be guided through sections of fiber up to 40 cm in length, while maintaining a high degree of spatial coherence. The biggest limitation on the length of transmission is the fluctuation of the fiber parameters down the length of the fiber. That problem should be surmountable with efforts to attain a very evenly drawn fiber, so that the bandgap spectrum remains stable down the fiber's full length.

The Bath–Corning researchers would like to compare the observed transmission bands to the bandgaps predicted theoretically for their structure, but so far the calculations have not been done; the computations are just too difficult, especially for the high frequencies involved.

Photonic crystal fibers

Several other groups are working with fibers that have solid cores surrounded with periodic dielectric structures (generally called photonic crystals) that do not have bandgaps (typically the volume fraction of air is smaller than in bandgap fibers). Without the bandgap, a photonic crystal cladding must confine light by the conventional method of total internal reflection; the effective index of refraction of the cladding is a volume average of the silica and air.

The earliest photonic crystal fibers studied by Russell and his colleagues had solid cores and they guided light by total internal reflection (TIR).[4]

These photonic crystal TIR fibers exhibit some behavior that's quite distinct from conventional TIR fibers. For instance, the photonic crystal fibers can support single-mode transmission over a wide range of wavelengths, whereas few conventional fibers can transmit at a single transverse mode over a frequency range greater than one octave. Furthermore, Russell commented to us, the photonic crystal cladding allows one to make the core area about ten times larger than that of a conventional fiber, thereby allowing higher power transmission.[5] These differences suggest that the photonic crystal fibers may find some niche markets.

Several other research teams are exploring the properties of photonic crystal fibers. For example, a group from Bell Laboratories, Lucent Technologies, recently made a structure that has a fiber grating in the core and a photonic crystal as its cladding.[6] (A fiber grating is a periodic variation in index of refraction over the length of the fiber.) The grating, which reflects certain wavelengths back on themselves, helps to couple the single modes in the core of the fiber (doped germanium, in this case) with the higher-order leaky modes—those modes that propagate in the cladding. The Bell Labs group is interested in the application of photonic crystal fibers to optical devices as well as to transmission lines. By studying the transmission of various wavelengths through such fibers, the researchers can deduce which modes of the core couple to the cladding. This technique has enabled them to characterize the cladding modes as a first step toward understanding their potential for lightguide devices.

Innovations in fibers are not limited to those with periodic arrays of holes in the cladding: Benjamin Eggleston of Bell Labs told us that he and his colleagues, and similarly a group at the University of Southampton in the UK, are studying yet other types of fibers. **BARBARA GOSS LEVI**

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