Spinning to a Subtle Molecular Beat

Finer and finer details illuminating a molecule's most subtle movements are showing up in molecular spectra

By IVARS PETERSON

Nudge a molecule and it dances—twirling, twisting, tumbling and stretching to the beat of a light beam's touch. Each leap from one motion to another, from the wildest gyration to the slowest spin, leaves its mark in the jagged peaks and valleys of a molecular spectrum, the plotted trace that shows how much light energy of a given wavelength a molecule emits or absorbs. Each peak within an absorption spectrum represents light energy that a molecule uses to step into a more lively movement at a higher energy.

When researchers started to look at the details, at the peaks within peaks of these spectra, few expected to see anything more clear than a complicated jumble. Says physicist William G. Harter of the Georgia Institute of Technology in Atlanta, "It was reasonable to suppose that complex molecules would have a complicated spectrum that no one could understand at all, but that has turned out to be untrue."

The most recent spectral measurements actually show a surprising order — hitherto hidden patterns and clusters that seem to illuminate the most subtle movements that a molecule can make. At the same time, tentative theoretical explanations for these clusters are beginning to emerge.

"There is no doubt that we are pushing instrumentation to the point where we're seeing finer and finer details," says molecular spectroscopist Jon T. Hougen of the National Bureau of Standards in Gaithersburg, Md. "At some level, we always expect to see these details, and in our hearts, we believe that we're going to understand them." But Hougen cautions, "Precisely what form that understanding is going to take is a little unclear until one actually does see the spectra."

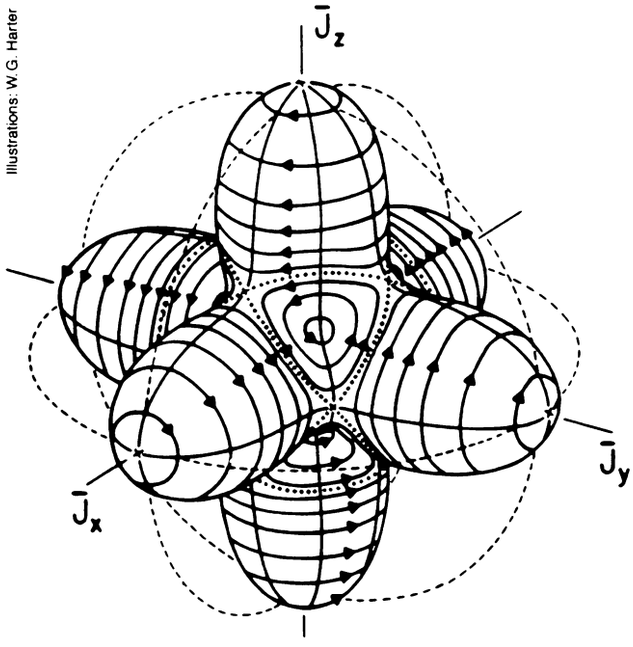
With the help of steadily improving lasers and refined experimental techniques for obtaining molecular spectra, the fine structures present in these spectra are now becoming somewhat clearer. A decade ago, a researcher could get infrared spectra that showed peaks representing transitions of gaseous molecules from one state of vibration to another. With care, it was also possible to detect the lower-energy transitions that revealed changes in a molecule's rotational energy while it was vibrating. These appeared as a collection of spikes on either side of the fundamental vibrational peak.

Around 1976, researchers at the Los Alamos National Laboratory in New Mexico were interested in separating uranium isotopes by tickling molecules of uranium hexafluoride with precisely tuned laser light. Molecules containing the lighter, U-235 isotope would have slightly different, although overlapping, molecular spectra compared with those for molecules containing U-238. "It was thought it was necessary to tune the laser to just one spectral feature," says Harter. "The trouble was that they didn't know what spectral feature to use until they actually took the spectrum and analyzed it."

With the aid of newly invented, tunable semiconductor (diode) lasers, spectroscopists like Robin S. McDowell at Los Alamos began a detailed study of the rotational structure in spectra for uranium and sulfur hexafluoride molecules. They found that each rotational bump resolved into distinctive sets of clusters, now labeled "fine structure."

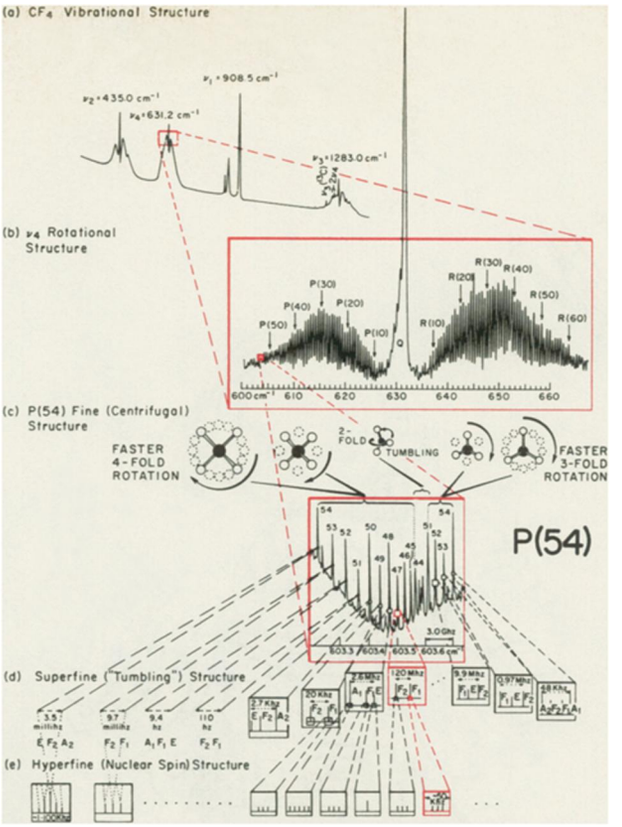
The world's best measurements on heavy, symmetric molecules like sulfur hexafluoride and carbon tetrafluoride are now being made in Paris at the laboratory of Christian J. Bordé and Jacques Bordé. Their results reveal that each fine-structure peak can be resolved further into a set of new peaks that make up a "superfine structure" level, and each one of these in turn shows a "hyperfine structure." The equipment that the Bordés use is sensitive enough to identify features as fine as one part in 10 trillion—something like picking out the bumps on a particle of rock in the midst of a great chain of mountains.

"Molecular spectra turn out to be filled with all kinds of structure that can be understood if you're careful," says Harter. From the time that he first saw the Los Alamos results in 1977, Harter has been one of perhaps three persons in the world devoting all their time to trying to understand the meaning of the orderly array of peaks within peaks within peaks that show



Illustrations: W.G. Harter

Rotational energy surfaces like the one shown aid in interpreting the details of molecular spectra. Solid lines correspond to allowed angular momentum "orbits," and dashed lines indicate a few of many potential tunneling paths.



This sequence of spectra for gaseous carbon tetrafluoride (CF_4) shows the organized hierarchy of structure (like the one outlined in color) that appears when spectroscopists probe deeper into the details of molecular motions.

up in the molecular spectra of heavy, symmetric molecules.

These distinctive spectral patterns reflect the underlying rules of quantum mechanics. The rules allow molecules to emit or absorb light only in well-defined packages. This means that only certain molecular movements can occur. For example, unlike a spinning toy top, which can rotate at any rate while tilted at an arbitrary angle, a molecule spins at particular frequencies and specific angles. In both cases, this rotational property is measured by a quantity labeled "angular momentum." The most interesting patterns occur at high values of angular momentum where the abrupt jumps of quantum mechanics shade into the smooth motions of classical spinning tops.

Harter was among the first to notice that the clusters found at the fine-structure level appear to be related to the rotation of molecules around various axes. A molecule like carbon tetrafluoride, which can be pictured as a tetrahedron with fluoride atoms at the four corners and a carbon atom in the center, can spin on a point or an edge. Because the two types of spin occur at different rates, their effects show up in slightly different parts of the molecule's spectrum.

"You can look at these clusters and imagine what the molecule is doing for each one," says Harter. To visualize better what is happening, Harter invented the idea of a rotational energy surface. "For each direction of the rotation axis, you figure out what would be the energy of the molecule," Harter says. "Then you simply plot that region as though you were plotting the [gravitational] potential energy of some planet. But it's not potential energy you're plotting here; it's kinetic energy."

Harter likens the procedure to sticking a molecule on a gimbal, spinning it and seeing how it distorts. From the molecule's movements, an energy value for the chosen axis can be determined. Then the process is repeated for other axes until a whole surface of energy values is generated. Harter notes that rotational energy surfaces often have a shape that is roughly similar to that of the molecule they represent.

As a molecule tilts and rotates, much like a spinning top, the angular momentum representing this motion moves from point to point on the molecule's rotational energy surface. The rules of quantum mechanics restrict that motion to particular orbits or rings on the surface. "What's happening is that the rotational axis is slowly precessing — making a loop along those rings. ... The spacing between the clusters [in the spectrum] is roughly the frequency with which the axis runs around the loop," says Harter. "The idea is that molecules are getting stuck on these axes, or these 'mountains' on the rotational energy surface, and behaving more classically than quantum mechanically."

However, occasionally a molecule will "tumble" or flip over, shifting abruptly from one axis of rotation to another. This involves a kind of quantum mechanical tunneling (just as electrons have a probability of leaking out of an electrical-potential well) from one orbit on the rotational energy surface to another orbit. This dynamic tunneling shows up in a molecular spectrum's superfine structure. The chances for a molecular tumble vary considerably — from perhaps once in 50,000 years to once every microsecond — depending on where the orbits are located on the rotational energy surface.

Harter says that hyperfine structure arises from the interactions between spinning atomic nuclei and the rotation of a molecule. "You can think of a molecule as doing a [nuclear magnetic resonance] experiment on itself," says Harter. When a molecule tumbles quickly, the motion is so fast that the tiny nuclear spin doesn't notice what is happening around it. "But once a molecule gets into one of these classical orbits where the angular momentum can be thought of as pinned for long periods, then even the smallest nuclei will finally realize there's something there," Harter says. The nuclear spins pay attention to the molecule's motion and act like little gyroscopes. They line up with the molecule's spin and stabilize its rotation. Harter predicted the existence of the hyperfine spectral structure that represents this effect, and recently, he says, the Bordé laboratory obtained physical evidence of its presence.

Hougen says, "There's a lot of neat stuff in what Harter is doing." His work is leading to new predictions and new ways of looking at molecular spectra and molecular motions, which are going to be very helpful, Hougen adds.

Harter says, "A whole new class of molecular effects is emerging." With the help of constructs like rotational energy surfaces, Harter expects that it will be possible to predict and understand rotational superfine structure in virtually all polyatomic molecules. This may have important applications in the study of how lasers interact with gaseous molecules and how lasers can be used to speed up or slow chemical reactions.

Harter accepts that although his explanations seem to work, better ones may come along later. He says, "I've been working on this full time ever since I discovered it. It's just like a great toy." □