High-spin molecular rotation spectra are surprisingly simple

In the past few years enormous experimental and theoretical progress has been made toward the understanding of the vibration–rotation spectra of polyatomic molecules. With a laser spectrometer of unprecedented size and complexity, Christian Bordé and his colleagues at the Université Paris-Nord are now able to resolve hyperfine and "superfine" splittings of less than one part in 10^{10} over a considerable infrared wavelength range in the spectra of such molecules as sulfur hexafluoride. SF_6 is particularly interesting not only because its highly symmetrical configuration produces astonishing spectral patterns that have given impetus to a new level of theoretical understanding; it also serves as a stand-in for UF_6. Much of the support for SF_6 spectroscopy has been impelled by the practical interest in laser separation of uranium isotopes.

Rotational energy surface of a semi-rigid octahedral molecule such as SF_6, for fixed angular momentum $J = 35$. The height of the surface at any point indicates the rotational energy of the molecule if **J** is pointing in that particular direction in the body reference frame. The bands indicate contour lines of constant energy corresponding to Bohr–Sommerfeld quantized trajectories, giving the semiclassical states of the motion of **J** in the molecular body frame.

The great surprise that has come out of the last decade of infrared absorption spectroscopy and brute-force computer analyses of such molecules as SF_6, UF_6, SiF_4, CF_4, and OsO_4 is that the rotational substructure of the vibrational spectra at high angular momentum is far simpler than anticipated. One had expected the rotational dynamics of these molecules to be complicated almost to the point of incomprehensibility, yielding only to very approximate theoretical treatment.

The first indication—in the mid 1970s—of this unexpected spectral simplicity at high angular momentum came not from spectroscopic data, but rather from massive number-crunching programs devised at Los Alamos to diagonalize the vibration–rotation Hamiltonians of these molecules by brute force. Writing down the Hamiltonians with a few adjustable parameters is relatively straightforward, but understanding the eigenvalues the computer spits out after many hours of diagonalization is another matter. The emerging peculiar pattern of "superfine" clustering at high angular momentum was at first more of a puzzle than a source of enlightenment. The standard theoretical approaches of the day offered no obvious explanation.

From the theoretical work of William Harter (now at Georgia Tech) and Chris Patterson (Los Alamos) we now have an appealingly simple theoretical picture[1] that explains the unexpected paucity of rotational fine-structure lines at high angular momentum in terms of a neatly clustered superfine substructure, with intracluster splitting becoming ever finer and harder to resolve as one goes to higher rotational quantum numbers. The theory employs a powerful heuristic device—the molecular rotational energy surface—which makes it easy to visualize the panoply of rotational states, their energies and the transitions between them, and to calculate the transition rates and spectral splittings.

An important prediction of the Harter–Patterson theory is that the superfine rotational splittings eventually become so small that they are comparable to the hyperfine splitting due to magnetic interaction with the nuclear spins. At this level, they point out, one should see the violation of a hitherto sacrosanct selection rule of molecular spectroscopy; different symmetry states will become so mixed that the symmetry species designation is no longer a valid quantum-state label. This widespread breakdown of the point-group symmetry of vibration–rotation states has in fact been observed[2] by the Bordé group in SF_6.

The semiclassical trajectories on the rotational energy surface that describe the quasi-stationary states of molecular rotation afford us an enlightening opportunity to see the correspondence principle in action. At the high angular momenta typical of these molecules, the Heisenberg uncertainty relation $\Delta\phi\Delta J_z \geq \hbar$ is not a very severe restriction. "Usually we see only the two ends of the correspondence-principle road—a few quanta or billions," Harter told us. "Here we can see the whole freeway." The centrifugal distortion of the rapidly spinning symmetrical molecule reduces its resting symmetry, forcing the molecule to spend most of its time in semiclassical rotation states in which the total angular momentum vector is highly localized in the body reference frame. It is the infrequent quantum-mechanical tun-

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neling between symmetrically equivalent trajectories on different parts of the molecule that produces the superfine splitting of the semiclassical trajectories into clustered eigenstates.

Rotational substructure. With a spectral resolution of a few GHz—considered pretty good for infrared absorption spectroscopy in the 1960s—the ν_4 line of SF_6, a principal vibrational excitation of the molecule at 16.3 microns, resolves into a central peak, corresponding to no change in the total angular momentum J, flanked by two sequences of finer lines, corresponding to the angular-momentum transitions $J \rightarrow J \pm 1$ for J up to almost 100. With tunable diode lasers and fast-Fourier-transform spectroscopy providing resolutions down to 10 MHz by the mid 1970s, each of the $J \pm 1$ transitions lines at large J was seen to have a fine structure of several dozen lines. The big surprise, however, was that there were far fewer such fine-structure lines "than anyone had ever dreamed," Harter told us. For the $J = 88 \rightarrow 87$ line of ν_4, for example, diode spectroscopy shows only a few dozen fine-structure lines. Standard symmetry analysis of the octahedal molecule had led one to expect $2J + 1 = 177$ rotational transitions, grouped into 74 perfectly degenerate multiplets (singlets, doublets and triplets).

The whereabouts of the missing fine-structure lines finally emerged from the Los Alamos computer diagonalization of the SF_6 Hamiltonian in 1976. Instead of the expected anarchic distribution of 74 resolvable fine-structure lines, the diagonalization yields an orderly array of about two dozen tightly bound clusters of nearly degenerate lines, with superfine spacings far too small to be resolved by laser diode spectroscopy. Whereas the spacing between clusters (the fine-structure splitting) is on the order of 10 to 100 MHz, the intracluster (superfine) splitting is very much smaller, except near the center of the fine-structure spectrum. Decreasing exponentially with distance from the center, the superfine splitting ranged from 10 MHz down to fantastically small splittings on the order of 10^{-11} Hz—one cycle in 5000 years! The center from which the superfine splittings decrease in both directions (Harter and Patterson call it the separatrix) is also a watershed in another sense. To its right (toward higher frequencies) all the superfine clusters have a multiplicity (degenerate plus nearly degenerate) of eight; to the left the cluster multiplicity is always six. Neither the clustering nor its orderly division by the separatrix had been anticipated. With Doppler-free infrared saturation spectroscopy now providing resolution down to a kilohertz, these peculiar spectra calculated at Los Alamos have been verified wherever the limited tunability of the lasers has provided access.

Theory. Instead of this surprisingly tidy Russian-doll pattern of clusters within clusters, one had expected the complex ro-vibrational dynamics of these symmetrical polyatomic molecules to yield a far more disorderly pattern at high J. "What in the world are these clusters?" was the question posed by the Los Alamos computer group—Harold Galbraith, Burton Krohn, James Louck and Kenneth Fox—when they presented their first results in 1976. Seeing the high multiplicities—six and eight—of the nearly-degenerate superfine clusters in the SF_6 spectrum, people tried unsuccessfully to interpret them in terms of a Zeeman-like splitting of some previously unsuspected higher symmetry, much as particle theorists look to gather elementary particles into representations of ever higher symmetry groups.

Harter and Patterson followed a rather different path. They eventually concluded that the superfine splittings were in fact spontaneous symmetry breakings associated with the lowering of molecular symmetry by centrifugal distortion at high rotation rates. Unlike Zeeman and other such splittings, which result from an external symmetry-breaking term in the Hamiltonian, spontaneous symmetry breaking results when a system must choose arbitrarily between rigorously equivalent alternatives. Quantum tunneling between these alternatives provides the coupling that determines the splitting. Similar ideas had been put forward in 1972 by A. J. Dorney and J. R. G. Watson at the University of Reading in England to explain the spectrum of CH_4.

SF_6 is a regular octahedral molecule, with a fluorine atom at each of the six apexes and a sulfur at the center. Because the S–F bonds are much stronger than the the binding between adjacent fluorine atoms, the molecule is less centrifugally distended when it spins about one of the three axes (with 4-fold rotational symmetry) that connect opposite apexes than when it spins about one of the four (3-fold-symmetric) axes whose ends are centered in opposing triangular faces. Because the rotational energy for a given J varies inversely with the moment of inertia, and hence the centrifugal distension, the rotational kinetic energy of the molecule is greatest when it spins about one of the 4-fold axes.

To visualize this dependence of the rotational energy on the direction of the angular momentum vector in the molecular body frame of reference, Harter and Patterson have devised the rotational energy (RE) surface. With cartesian axes fixed in the molecule, the radial distance from the origin to the RE surface in any particular direction (for fixed J) is given by the rotational energy when $\mathbf{J}$ points in that direction. Thus the RE surface for SF_6 at high J will look somewhat like the molecule itself, with six peaks corresponding to the high spin energies (clockwise or counterclockwise) about the three four-fold axes, and eight depressions, corresponding to the four low-energy, three-fold axes. Angular momentum conservation requires that $\mathbf{J}$ be fixed in space, but not necessarily in the body of the molecule, which can precess, nutate and tumble.

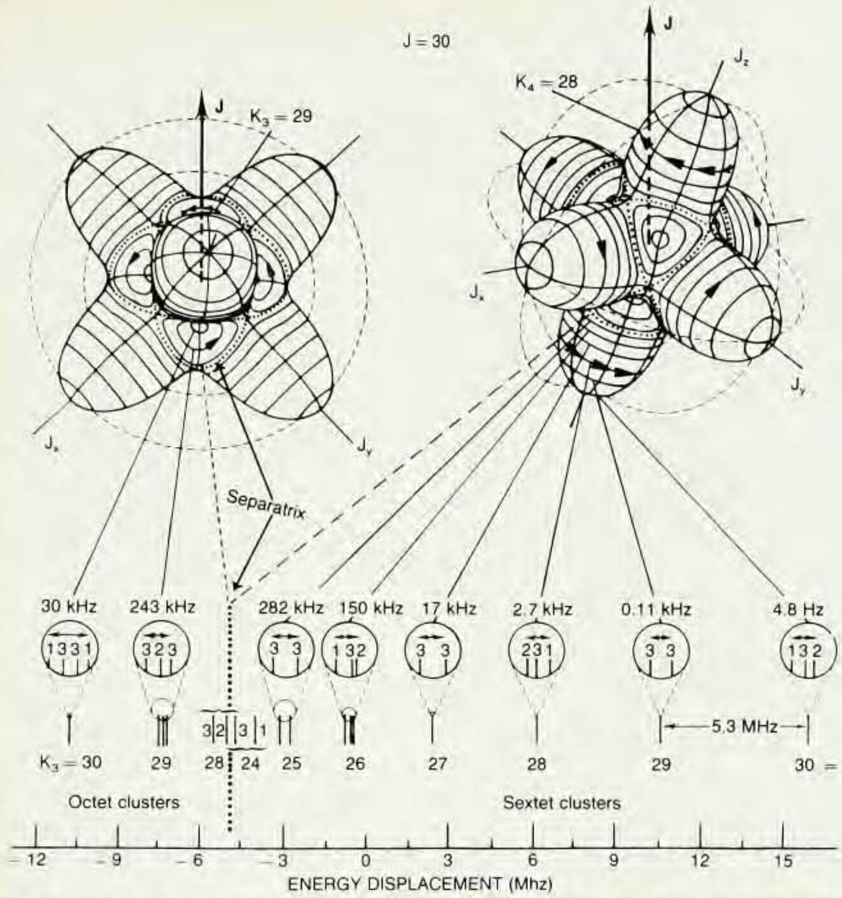
Regarding the SF_6 molecule as a classical, semi-rigid octahedral top, conservation of energy requires that $\mathbf{J}$ move only along contour lines on the RE surface—trajectories of constant distance from the origin. These contour trajectories then describe the classical motion of the molecular top, its instantaneous rotation axis precessing and nutating about a $\mathbf{J}$ fixed in space. Because high-angular-momentum RE surfaces of such symmetrical molecules are strongly featured with peaks and valleys as a result of centrifugal distortion, the contour trajectories are in general quite localized, circling a particular summit or depression; they do not circumnavigate the RE surface, as they might for a more rigid or less highly symmetrical molecule.

By imposing Bohr–Sommerfeld quantization on these classical trajectories, Harter and Patterson obtain the semiclassical quasi-stationary rotation states of the molecule. Because each of these quantized trajectories is localized around one of the symmetry axes of the RE surface, the projection of $\mathbf{J}$ on that axis is an approximately conserved quantum number that labels the individual fine-structure lines associated with a given $J \rightarrow J \pm 1$ transition.

No constant-energy trajectory connects one peak or depression of the RE surface with another, but $\mathbf{J}$ *can* switch allegiance between symmetry axes by quantum tunneling. It is this tunneling that explains the superfine clustering. Because there are six equivalent high-energy peaks on the RE surface of SF_6, there must be six equivalent semiclassical trajectories for each fine-structure line. The possibility of tunneling between them breaks this six-fold degeneracy. The six nonlocalized eigenstates that result are appropriate linear superpositions of the localized trajectories that represent distinct representations of the molecular symmetry group. The superfine energy splitting between these almost degenerate symmetry states is determined by the tunneling integral. The semiclassical trajectories closest to their associated peaks (or nadirs) require the longest tunneling distance to their equivalent trajectories elsewhere on the RE surface. This explains why the superfine splitting decreases exponentially with distance from the separatrix; the larger the projection quantum number, the weaker the tunnel coupling. The separatrix that divides the fine-structure spectrum corresponds to the boundary curve that separates hills from adjacent depressions on the RE surface. No semiclassical trajectory crosses the separatrix.

In like manner we understand the eightfold degeneracy of the superfine clusters on the other side of separatrix. These are associated with the trajectories that circle the eight equivalent low-energy depressions of the RE surface. Near the separatrix the tunneling distances between equivalent trajectories are so short that cluster splittings become comparable to the fine-structure splitting. Superfine clusters in this central region of the spectrum are no longer well defined.

A major triumph of the Harter–Patterson theory is that it explains the observed simple ratios of energy splittings between different symmetry species within a given superfine cluster. To the extent that one can neglect magnetic interaction with nuclear spins, the mixing between different symmetry species is strictly forbidden. But as the superfine splitting decreases exponentially toward the wings of the fine-structure spectrum, hyperfine interaction can no longer be neglected. As Harter puts it, the molecule spends so much time on a given semiclassical trajectory in these regions of weakest tunneling that it has the leisure to sense the nuclear spin state. The result is the symmetry-species mixing first observed by Bordé's group in 1980.



Rotational substructure of the $J = 30$ energy level (2.54×10^{12} Hz) of SF_6, calculated from the Harter–Patterson theory with fitted inertial parameters. Naively one expects to see 20 perfectly degenerate multiplets (singlets, doublets and triplets, labeled 1,2,3) representing the $2J + 1 = 61$ rotation states. But these 20 fine-structure lines are surprisingly gathered into only 9 superfine clusters, most of which are difficult or impossible to resolve, with superfine splittings as small as 4.8 Hz. By contrast, the splitting between clusters is on the order of 5 MHz. Each cluster corresponds to one of the semiclassical **J** trajectories (solid) circling a peak or depression on the RE surface. Each is labeled by K, the projection of **J** on the symmetry axis of its peak (K_4) or depression (K_3). The K_4 (K_3) clusters have multiplicity six (eight) because there are six (eight) equivalent peaks (depressions) on the RE surface of the octahedral SF_6 molecule. The superfine splittings are determined by quantum tunneling (dashed) between equivalent trajectories. Near the separatrix (dotted) between peak and depression states the superfine splitting is large because tunneling distances are short.

High-resolution spectroscopy. To achieve kilohertz resolution in infrared molecular absorption spectroscopy one must go to gas lasers. But one must find a way to circumvent the Doppler broadening of spectral lines due to thermal motion of the gas in both the laser medium and the molecular gas sample under study. The saturation–absorption technique developed in the late 1960s points the way. (See PHYSICS TODAY, December 1982, page 46.) If one sends a sufficiently intense laser beam through a gas at a wavelength slightly detuned from the absorption transition of interest, a subpopulation of molecules whose thermal velocity component in the beam direction provides just the right correcting Doppler shift will be elevated to the excited state. If one then reflects the laser beam back through the sample cell, this velocity-selective population depletion of the ground state will have no effect on the absorption of the returning beam because that velocity provides the wrong Doppler shift for the *oppositely* directed beam. Only when the laser wavelength is tuned precisely to the molecular transition will both beams address the same velocity subpopulation—those molecules with *zero* velocity component in the beam direction. In that case the returning beam will experience reduced absorption because the incident beam has significantly depleted the ground state of the same velocity subpopulation. With this saturation–absorption effect one can get extremely narrow, Doppler-free absorption dips measuring the precise position of a particular molecular transition.

One can also exploit this same "Lamb-dip" (named for Willis Lamb, now at the University of Arizona) to obtain laser beams with very narrow bandwidths by incorporating a saturation–absorption cell in the laser cavity. In the early 1970s John Hall and his colleagues at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado, were able to achieve a resolution of 0.5 MHz with a He–Ne laser incorporating a CH_4 saturation–absorption cell. The molecular gas has a number of narrow absorbing transitions within the 300-MHz Doppler-broadened bandwidth of the 3.39-micron neon lasing transition.

For higher resolution it is not enough simply to get rid of Doppler broadening. One must also increase the size of the system—the beam diameter and the length of the sample cell. The saturation technique constrains the *longitudinal* velocity of the gas molecules under study, eliminating Doppler broadening, but their *transverse* motion is also a problem. The uncertainty principle tells us that the energy of the transition is broadened in inverse proportion to the transit time of the molecule across the laser beam. Thus one wants the largest possible beam diameter. Unfortunately, the noise-to-signal ratio of the system grows as the fifth power of the diameter. To compensate, one wants the longest possible sample chamber. Size is also important because the velocity selection greatly reduces the absorbing population, as do the low pressure and low beam intensity required to minimize pressure broadening and the "saturation broadening" that comes with too high an excitation rate.

Bordé came to JILA in 1973 to work with Hall on expanding the size of his He–Ne system. Increased size presents difficult optical problems. The optics that expand the laser beam and reflect it through the system must be diffraction limited because excessive divergence destroys the precise definition of beam direction upon which the Doppler-free technique depends. As apertures become larger, the tolerable angular content of the beam decreases. By 1975 Hall and Bordé had a He–Ne laser system large enough to study the hyperfine structure of CH_4 at 3.39 microns with a resolution of less than a kilohertz. Comparable advances in spectroscopic technique were being achieved at about the same time by Veniamin Chebetayev at Novosibirsk.

These He–Ne laser spectroscopy systems have the virtue of great stability, but they can only be tuned over a very narrow range around 3.39 microns. In quest of a more broadly tunable system, Bordé returned to Paris in 1975 to build a high-pressure CO_2 laser system. CO_2 has about a hundred lasing transitions in the 10-micron region of particular interest to molecular spectroscopists. Exploiting the Doppler and high-pressure broadening of the lasing gas, one can tune the laser over 300-MHz-wide bandwidths around each of these CO_2 lines. If one can afford to fill the laser with isotopic variants of CO_2, one gets enough 300-MHz windows to get 50% tuning coverage of the infrared regime from 9.6 to 11 microns. With so broadly tunable a laser one can study significant portions of the SF_6 ro-vibrational spectrum in detail.

Bordé and his Paris colleagues have built a high-pressure CO_2 laser spectroscopy system that is, by previous standards, enormous. The saturation–absorption cell that contains the low-pressure (10 microtorr) molecular gas under study is 18 m long and 70 cm across. The length of the cell is traversed by laser beams expanded by telescopes to a diameter of 30 cm. With beam diameters so large, the diffraction limit of angular tolerance is less than an arcsecond. The Bordé group has therefore had to devise reflecting corner cubes and other large optical elements within these demanding tolerances. All this is particularly difficult in the infrared, where the eye is of little use in making adjustments.

It is not enough that the bandwidth of the laser source be narrow. It must also be extremely stable. This is a particular problem for CO_2 lasers, which are inherently much less stable than He–Ne lasers. Bordé stabilizes the frequency of his CO_2 laser spectrometer by exploiting a technique pioneered by Hall at JILA. In place of a single laser the Paris group has two CO_2 lasers in tandem, one of which is optimized by stability. This laser is kept at a fixed frequency corresponding to a convenient absorption line of the molecular gas in its saturation cell, thus serving as a stable reference for the second laser, which is optimized for spectroscopy. As the second laser is tuned through the region of spectroscopic interest, its output is mixed with that of the reference laser in an optical heterodyne mixer. The resulting beat frequency is converted to an electronic signal by a photodetector, providing a feedback signal for a piezoelectric transducer that adjusts the length of the spectroscopic laser cavity.

The present resolution of the Paris spectrometer is better than a kilohertz over a broad wavelength region around 10 microns. At the 38th Symposium on Molecular Spectroscopy, held last summer at Ohio State University, Jacques Bordé, Christian's younger brother and the group's theorist, reported that he and his colleagues had confirmed the Harter–Patterson theory (and the computer diagonalizations) for all parts of the SF_6 spectrum where their many 300-MHz-wide windows and resolution limits have thus far permitted them to look. The high-pressure CO_2 laser bandwidth also overlaps with interesting spectral regions of many other molecules. The Paris group has, for example, been investigating the spectrum of OsO_4. Aside from its purely academic interest, OsO_4 holds out the promise of being a spectacularly good saturation-absorption stabilizing gas for CO_2 lasers.

With the current state of spectroscopic precision and theoretical understanding of molecular ro-vibrational dynamics comes the promise of what Harter calls "clockwork molecules." By exciting a molecule with just the right frequency of laser light, he forsees, one should be able to nudge it into any state one chooses. —BMS

References

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New tandem mirror machine starts operation at MIT

The Tara tandem mirror experimental fusion device began operation at the MIT Plasma Fusion Center's new Nabisco Laboratory at the end of March. In recent testing, rf heating has raised the ratio of plasma pressure to magnetic pressure in Tara's central solenoid to 2%, indicating an average ion energy of 2 keV (20 million kelvin), much hotter than the temperature at which the device will ultimately run.

The plasma is confined in the central solenoid of the 25-meter-long device by magnetic mirrors at both ends, each consisting of a quadrupole magnet to provide overall magnetohydrodynamic stability and an axisymmetric magnet set that augments confinement by generating an electrostatic barrier. Tara is similar in size to Livermore's two-year-old upgrade of its Tandem Mirror Experiment. The principal difference between Tara and the upgraded TMX is that the new device is designed to achieve an axially symmetric magnetic field in the central solenoid. The asymmetry of the quadrupole magnets produces asymmetrically twisted field lines in the center of the TMX. This is avoided in the Tara design by physically separating the quadrupoles from the electrostatic barrier plugs, removing the quadrupoles further from the central plasma region. Tara was designed to test theoretical predictions that plasma confinement in a tandem mirror machine will be significantly improved by making the confining field axially symmetric.

Richard S. Post, head of the MIT Plasma Fusion Center's mirror-confinement division (and no relation to Livermore's Richard F. Post), told us that these tests of new design concepts are going forward in conjunction with work on Livermore's much larger tandem-mirror machine, the MFTF-B, scheduled for completion in 1986 (PHYSICS TODAY, September 1981, page 22). Tara was built at a cost of $15 million. The building housing the experiment is an old Cambridge baking plant, donated by Nabisco.