

of the distortion of the reaction intermediate, that is, the introduction of new patterns of molecular motion in the presence of additional reagent energy. Enhanced vibration permits reaction through a stretched intermediate, whereas enhanced translation gives rise to reaction through more compressed and bent intermediates.

An observation that reactions consuming a substantial amount of energy can be most efficiently accelerated if the reagents are vibrationally rather than translationally excited was linked in Polanyi's study to the existence of a "late barrier crest" for such reactions. In simple terms one would say the energy is optimally employed in stretching the bond under attack, through vibrational excitation, rather than in compressing the reaction intermediate through reagent translation, that is, collision energy.

Infrared chemiluminescence has also revealed families of reactions that give rise to a single reaction product with bimodal distributions over the vibrational, rotational and translational states. In these cases the reaction dynamics exhibits "microscopic branching"—two different, identifiable patterns of molecular motion lead to the formation of the same chemical species. The existence of alternative routes to reaction, dependent on reaction energy, is a phenomenon of general interest in reaction dynamics.

The methods developed by Polanyi, Herschbach and Lee are complementary in describing the details of a chemical reaction. In the laser-induced fluorescence method developed by Zare (see the article by Zare and Bernstein in *PHYSICS TODAY*, November 1980, page 43), one combines crossed molecular beams and lasers to study reaction dynamics.

The study of intermediate products in a reaction is still in its infancy. "Instead of looking at the newborn products or looking at the effect of reagent motions you try to interact with the few actors who, at any given time, are actually on the stage," says Polanyi. His group has done this by looking at chemiluminescence originating from the colliding species, that is, the transition state. Brooks and Robert Curl (Rice) have evidence of laser absorption by reaction intermediates. Only in the last few years have chemists seen indications that these transient intermediates can actually be observed.

In reaction dynamics the interest is not in the overall rate at which reagents form products. That was the earlier focus of research by physical chemists. What engrosses people who work on reaction dynamics is the detailed rate constants for the formation

of products with specified vibration, rotation and translation states and—if possible—from specified states of vibration, rotation and translation in the reagents. This state-to-state chemistry is in fact synonymous with reaction dynamics. The intention nowadays of trying to open up the field of transition state spectroscopy is to provide still another tool for the study of molecular motion in chemical reactions.

The three Nobel Prize winners are currently engaged in a variety of theoretical and experimental research. Herschbach is doing theoretical calculations of electron configurations as well as experiments using coincidence measurements of velocity and rotational angular momentum vectors to undo averaging over initial impact parameters and molecular orientations. In recent years, Lee and his group, using seven molecular beam machines in the laboratory, have been leaders in studying the chemical reactions of large organic molecules such as those significant for combustion chemistry and atmospheric chemistry. Polanyi says of his group that "our current major interest these days is to induce reactions at sub-monolayer coverages on surfaces—single crystal surfaces. We are trying to move our reaction dynamics from the three-dimensional world of gas to the two-dimensional world of the adsorbed state. We have to go back to the classroom to learn about surfaces from the people who have been making great strides in studying them—among

whom are the winners of the 1986 Nobel Prize in Physics" (see *PHYSICS TODAY*, January, page 17).

Vital statistics. Herschbach received his BS in mathematics in 1954 and his MS in chemistry in 1955, both from Stanford. He received a second master's degree in physics in 1956 and his PhD in chemical physics in 1958, both from Harvard. Since then Herschbach has held positions at Harvard, except for the period 1959–63, when he was an assistant and an associate professor at Berkeley. He has been Baird Professor of Science at Harvard since 1976.

Lee received his BS in 1959 from National Taiwan University and his MS in 1961 from National Tsing Hua University (also in Taiwan). He received his PhD in chemistry from Berkeley in 1965. He carried out postdoctoral research beginning in 1965 at both Lawrence Berkeley Laboratory and Harvard prior to his joining the chemistry faculty at the University of Chicago. Since 1974 he has been a professor of chemistry at Berkeley and a principal investigator with the Materials and Molecular Research Division at Lawrence Berkeley.

Polanyi received his BSc (1949), MSc (1950) and PhD (1952) in chemistry from the University of Manchester. After positions at the National Research Council (Ottawa) and at Princeton, Polanyi moved in 1956 to the University of Toronto, where since 1974 he has held the position of University Professor of Chemistry.

—PER H. ANDERSEN

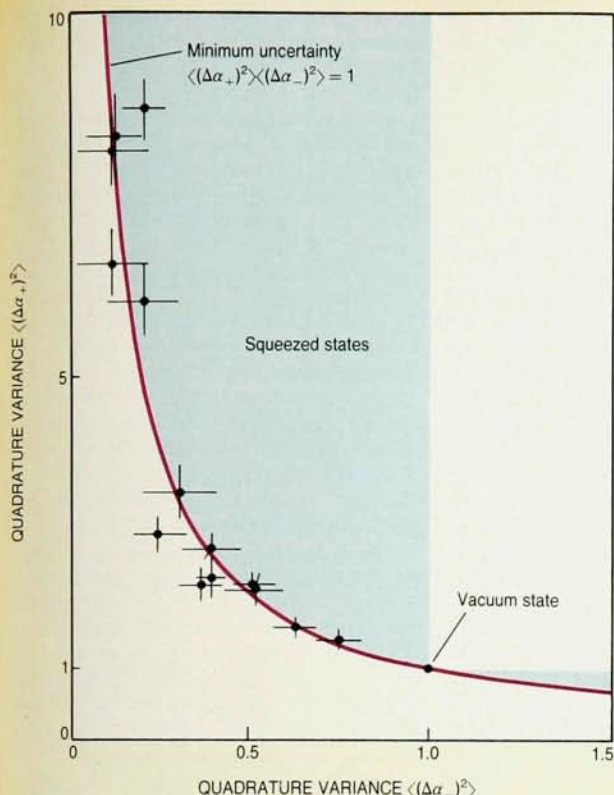
Still more squeezing of optical noise

Quantum optics experimenters have been pushing hard to generate greater "squeezing." This drive was encouraged by last year's milestone demonstration at AT&T Bell Labs that the noise from an optical cavity had been measurably squeezed, that is, that the noise in one phase of the signal had been reduced below the level normally associated with quantum mechanical fluctuations in the vacuum field. Until then, that vacuum noise level had represented the fundamental quantum limit to precision in optical experiments. The Bell Labs experiment reduced the noise by 7–10% below this normal quantum limit (see *PHYSICS TODAY*, March 1986, page 17), and several experiments since then have achieved noise reductions of at least 20%. The most spectacular results to date have been obtained by a team at the University of Texas at Austin consisting of Ling-An Wu, Min Xiao, H. Jeffrey Kimble, John L. Hall (of the

Joint Institute for Laboratory Astrophysics) and Huifa Wu, who have observed noise reductions to more than 60% below the normal level.¹

Furthermore, the Texas team demonstrated the squeezing of light into a minimum-uncertainty state, and they inferred that the state had actually been squeezed by more than a factor of ten. By eliminating some experimental sources of noise that now degrade this large degree of squeezing, they hope to translate it into comparable reductions in the noise levels actually observed. Thus not only did the Texas experiment dispel any doubts that a usable amount of squeezing is available, but it also indicated a viable path to achieve that squeezing.

Squeezed states of light are a macroscopic manifestation of quantum behavior. They are best understood if one writes the electric field vector as the sum of two terms whose time variations are given by sine and cosine functions,



Uncertainty principle is illustrated in these measurements of light produced in a squeezed state. The plotted measurements are the variances in the two quadratures of the squeezed state. They are seen to lie along the hyperbola (the red curve given by $\langle(\Delta\alpha_+)^2\rangle\langle(\Delta\alpha_-)^2\rangle = 1$) predicted for a squeezed state. When either variance is less than 1 (the blue region), the state is said to be squeezed.

cial conversion of the subharmonic back into the pump beam. (Collett and Dan Walls of the University of Waikato have shown that it is also possible to get good squeezing above the oscillation threshold, provided that cavity losses of the pump beam are considerably lower than the losses at the subharmonic, but this may be technically much harder.)

The squeezed light is observed by a technique that permits phase-sensitive detection at the frequency of the optical field. In this "balanced homodyne" detection scheme, the output from the optical parametric oscillator combines at a beam splitter with a local oscillator, which is part of the original 1.06-micron laser beam. When the two waves from the beam splitter illuminate two photodiodes, the difference in photocurrents reveals the fluctuations in the squeezed light. This method allows one to observe the signal fluctuations as a function of the phase angle between the squeezed light and the local oscillator. The Texas team has reported noise levels as much as 63% below the vacuum level.

Kimble told us that the basic interaction involved in their experiment is well represented by the same transformation that generates minimum-uncertainty states (in which the product of the variances in quadrature equals the smallest allowed value). Indeed, the quadrature variances determined from their experiment lie along the hyperbola that defines the class of minimum-uncertainty states, as shown in the figure on this page. The data points are pairs of experimentally determined quantities, $\langle(\Delta\alpha_+)^2\rangle$ and $\langle(\Delta\alpha_-)^2\rangle$, which play the role of variances for the orthogonal set of quadrature phases. These points lie along the line defined by the equation

$$\langle(\Delta\alpha_+)^2\rangle\langle(\Delta\alpha_-)^2\rangle = 1$$

as would be expected for a minimum-uncertainty state. The figure provides a striking demonstration of the Heisenberg uncertainty principle as applied to the electromagnetic field.

For a given frequency ω , the variables $\langle(\Delta\alpha_+)^2\rangle$ and $\langle(\Delta\alpha_-)^2\rangle$ describe the degree of squeezing for a frequency pair located at $\pm\omega$ about the carrier frequency. For a vacuum state and for a coherent state, both variables equal 1, but for a perfectly squeezed state, one variable goes to 0 while the other goes to infinity. One can derive a theoretical expression that relates the values of these variances from an ideal single-ended cavity to the rms voltage actually observed as a function of the ratio of the pump power to the threshold power for parametric oscillation. Such theoretical values agree well with the values of these squeezing parameters

respectively. For a single-mode field, the quadrature operators α_+ and α_- for these two terms form a pair of canonically conjugate variables analogous to the position and momentum operators for a harmonic oscillator. Like the uncertainties in the position and momentum, the variances associated with two quadrature operators must obey the uncertainty principle. Coherent states, which represent the classical limit, have equal variances, whose value constitutes the zero-point fluctuation of the vacuum state. More generally, however, quantum theory allows the light to be squeezed into states with unequal variances: The variance is reduced in one quadrature phase provided it is correspondingly increased in the other phase. Thus, in a squeezed state, the quantum noise fluctuations are redistributed in a phase-dependent way.

Generation of a squeezed state of light requires a phase-sensitive amplification process to increase and decrease the quadratures selectively. This can be done with a variety of nonlinear optical interactions that generate pairs of highly correlated photons.

The University of Texas experiment used a technique called parametric downconversion to take photons from a pump beam and generate pairs of photons of half the frequency. The pump beam, at ω_2 , is converted to the subharmonic, at ω_1 , in an optical cavity

containing a crystal of lithium niobate, which has a large, second-order nonlinear susceptibility. The operation of this optical parametric oscillator can be likened to the action of a periodic force on a pendulum whose natural frequency is half that of the driving force: The pump field amplifies a coherent subharmonic field when the two are in step, and it deamplifies the subharmonic when they are 90° out of step. The associated fluctuations at the subharmonic are amplified and deamplified in the same way. Thus the light at frequency ω_1 emerges from the cavity in a squeezed state. Bernard Yurke² of Bell Labs, as well as Matthew Collett and Crispin Gardiner³ of the University of Waikato, New Zealand, predicted that the field emitted by an optical parametric oscillator would be nearly perfectly squeezed, that is, that the variance in one quadrature phase would be reduced almost to zero.

The Texas experimenters use a 0.53-micron pump beam obtained by doubling the frequency of light from a frequency-stabilized neodymium-doped YAG laser at 1.06 microns. The 0.53-micron light enters the optical parametric oscillator through a mirror at one end, and the squeezed light at 1.06 microns is preferentially transmitted through a mirror at the far end. The experiment is conducted at a power level below the 30-mW threshold for parametric oscillation, to avoid appre-

determined from separate measurements of the noise voltages and sources of loss.

Kimble and his colleagues infer from their data that the field was actually squeezed more than tenfold, and they believe that they can translate this squeezing into comparably reduced noise levels by straightforward improvements in cavity design and detection efficiency. They are already implementing these improvements. More importantly, Kimble expects that increased precision in the measurement of loss mechanisms may enable them to infer degrees of squeezing higher than the present factor of ten.

Still, a tenfold noise reduction begins to attract attention for such applications as precision interferometry, including the detection of gravity waves. If practical applications require that noise be reduced by more than a factor of ten, Kimble notes, the photodetector efficiency will have to be increased above the 90% level typical today.

Other squeezing experiments are proceeding both at the University of Texas and at other laboratories around the world. Together with Mark G. Raizen, Luis A. Orozco, Min Xiao and Tim L. Boyd, Kimble is working on a system of two-level sodium atoms in a cavity. When the cavity is sufficiently small (900 microns in the Texas experiment), the coupling of atoms to the cavity produces a splitting of the cavity modes known as the vacuum-field Rabi splitting. These splittings occur for an arbitrarily weak pump field, in contrast to those of the traditional ac Stark effect employed in four-wave mixing experiments such as that at Bell Labs. Thus, the Texas experimenters operate with a much weaker pump beam, use lower atomic densities and work closer to resonance. So far they have measured noise reduced by 20% below the quantum limit, but their calculations suggest the potential for significantly larger squeezing in this system. Gardiner has pointed out that the squeezed output from such a system might be useful for atomic spectroscopy.⁴

Stephen Perlmutter, Robert Shelby and Marc Levenson at IBM, in collaboration with Bonny Schumaker of the Jet Propulsion Laboratory, are generating squeezed states in an optical fiber. They use a variation of the basic technique called two-mode squeezing, in which a pump beam enters a nonlinear medium at a single frequency and generates pairs of correlated photons. Schumaker has studied the states that result when one pumps a nonlinear medium at two (or more) frequencies to generate groups of four (or more) correlated photons, which correspond to modes symmetrically displaced above

and below each of the pump frequencies.⁵ She has shown theoretically that such four-mode (or higher-mode) squeezing can potentially produce a greater noise reduction in four-wave mixing than can ordinary squeezing for a given total pump power. However, it is more complicated than two-mode squeezing to implement experimentally, requiring multiple pump frequencies for its production and multiple homodynings for its detection. In the optical fiber experiments, the acoustic noise sources are sufficiently severe that this tradeoff between experimental complexity and degree of squeezing appears favorable. Another benefit, Levenson says, is the ability to vary the ratio of gains on two detectors so that the correlated noise subtracts while the uncorrelated noise does not add very much. The initial experiments have produced a noise level 20% below the quantum limit.⁶

Levenson and Shelby, together with Walls and Margaret Reid of the University of Waikato, have varied this four-mode scheme to make "quantum nondemolition" measurements.⁷ Such measurements circumvent the limitations on precision imposed by the uncertainty principle for repeated measurements of the same quantity by feeding the uncertainty introduced by measurements of the variable of interest back into a decoupled variable. In the optical fiber experiment, the variable of interest is the quadrature phase that describes the amplitude fluctuation in one of the output waves. To determine its value, the experimenters sample the quadrature describing the phase fluctuations in the second wave. The Hamiltonian governing the four-mode squeezing interaction relates these two quadrature phases. The uncertainty, or back-action, that results from the measurement feeds back into the other quadrature phase of the second output wave, not into the variable of interest. The IBM-New Zealand collaborators feel they have demonstrated that their scheme works as a quantum nondemolition detector, although its signal-to-noise ratio is too small to be of practical utility.

The pioneering Bell Labs experiment used a technique of squeezing known as four-wave mixing, in which a nonlinear medium couples two pump beams with two weaker beams to yield correlated photon pairs. The Bell team directed the two pump beams in opposite directions through an atomic beam in a cavity. Using a similar scheme but with pump beams directed forward through a cell of sodium vapor, Mari Maeda and Jeffrey Shapiro of MIT, together with Prem Kumar (now at Northwestern University), have mea-

sured a 4% noise reduction.⁸ Their measurement shows that squeezing can be produced even with a Doppler-broadened medium.

All the experiments described so far use nonlinear optical processes to reduce the fluctuations in one of the quadratures of a coherent state once that state is produced. Another approach to squeezing was suggested a few years ago by Malvin Teich (Columbia University), Bahaa Saleh (University of Wisconsin) and David Stoler (Bell Labs). They showed that light with reduced fluctuations in photon number could be produced by an optical system driven with a quiet (sub-Poisson) pump source. Even a linear (one-photon) process gives rise to a squeezed photon number provided the spacing of the excitations is regularized.⁹

Teich and Saleh succeeded in producing broadband squeezing of the photon number by using a space-charge-limited electron beam in a Franck-Hertz experiment.¹⁰ They are currently carrying out a solid-state version of the experiment. Direct detection suffices for observing this kind of squeezing, so a local oscillator and homodyning or heterodyning are not required.

In Japan, a group from Nippon Telegraph and Telephone has recently followed a similar approach to reduce noise in the light from a semiconductor laser by 20%, after correction for quantum detector efficiency. The NTT researchers squeeze the laser emission directly by suppressing the pump amplitude fluctuations in the injection current. Yoshihisa Yamamoto presented the results on behalf of his colleagues, Susumu Machida and Nobuyuki Imoto, at the 1986 International Symposium on the Foundations of Quantum Mechanics in Tokyo.

—BARBARA GOSS LEVI

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