ity of the fuel resource either, unless dream cycles are realized. The advantages are chiefly environmental and social ones, but those are not guaranteed. "Several ways that fusion reactors could work would not be cleaner or safer than fission," says John Holdren at the University of California at Berkeley. "My fear is that in the haste to get a machine at all, we will throw away the potential advantages as a matter of engineering expediency."

The national energy plan of ERDA emphasizes that fission, solar energy, and fusion are three long-range energy *options*, which should not all be expected to work. What is not clear at the present time is whether the efforts on behalf of fusion will be directed toward making it the most attractive option, or whether the program planners will settle for an unattractive technology likely to be implemented only if the other options fail.

—WILLIAM D. METZ

Laser Spectroscopy: Illuminating the Dynamics of Collisions

Laser light is characterized by its high intensity, monochromaticity, temporal and spatial coherence, and directionality. In the first half of this decade researchers exploited these properties to develop a panoply of ultrahigh resolution techniques for resolving the details of atomic and molecular spectra. If this collection of techniques constitutes the first wave of laser spectroscopy, then the second wave may comprise ways to apply lasers to the study of atomic and molecular collisions.

The use of lasers to study collisional phenomena conveniently breaks into two categories: steady-state and transient methods. The steady-state techniques are, for the most part, variations of the highly successful "Doppler-free" laser spectroscopies, which depend on the high intensity and monochromaticity of lasers (*Science*, 24 October 1975, p. 344). In addition to these features, the transient techniques also take advantage of the coherence properties of laser light and are optical analogs of Fourier transform nuclear magnetic resonance (NMR) (*Science*, 20 October 1972, p. 247).

Collisions are of fundamental interest to researchers in many fields. For chemists, the study of chemical reactions reduces ultimately to the study of collisions that break the chemical bonds of the reactants and allow product bonds to form. Astrophysicists measuring the spectra of radiation emitted from stars or large interstellar gas clouds need to understand collisional effects in order to extract the physical parameters of the gas from their data. And spectroscopists trying to unravel the details of atomic and molecular structure find that collisions determine the shape of spectral lines.

The latter effect on line shapes has, in fact, provided the principal means of studying collisions since the work of A. A. Michelson, 80 years ago. The width of a spectral line is determined (by way of the uncertainty principle) by the lifetimes of the quantum states involved, which can be limited by several varieties of collisions. In particular, by measuring the detailed dependence of the widths of spectral lines on gas pressure (pressure broadening), spectroscopists have obtained information about the forces between colliding particles.

One problem with this approach is that any measurement is an average over atoms or molecules with a thermal distribution of velocities and quantum states, which are constantly colliding. With the new laser methods, scientists can select specific quantum states and velocities by changing the laser frequency, but a given particle will, in general, suffer many collisions and the resulting spectrum will be averaged over these. The transient optical methods have the additional advantage of being able to distinguish between different collision mechanisms that are simultaneously operative.

A major limitation of spectroscopic methods has been the Doppler effect, whereby gas particles have a distribution of resonant frequencies for absorption or emission of radiation that corresponds to the thermal distribution of particle velocities. The Doppler effect is a considerable nuisance to spectroscopists because a broad band due to the superposition of narrow lines from each velocity group obscures the intrinsic spectrum.

Exploiting the Doppler Effect

At the Massachusetts Institute of Technology (MIT), Ali Javan, Thomas Mattick (now at the University of Washington), and their colleagues took advantage of the Doppler effect to measure the temperature dependence of pressure-broadening of absorption by ammonia molecules. Particles absorbing laser light at frequencies near the center of the Doppler band move slowly in the direction of the laser beam, whereas those in the wings of the band move rapidly. Since the temperature increases with the square of the velocity, the effective absolute temperature of particles in the wings of the Doppler profile may be more than ten times that of the apparatus.

The MIT investigators used a variation of a Doppler-free method known as saturation spectroscopy. The researchers directed two beams from a nitrous oxide infrared laser in opposite directions through a gas-filled cell. They tuned the frequencies of the two beams symmetrically about the center of the Doppler profile, one to a higher frequency and one to a lower frequency. Under these circumstances, the velocity group that absorbs light from both beams must have a nonzero velocity along the direction of the laser, and the greater the frequency shift, or detuning, the greater the velocity selected.

The experiment consists of measuring the difference in the absorption of a weak probe beam with and without a strong counterpropagating beam. The latter, termed a saturating beam, excites a large fraction of the particles in the selected velocity group, so that the excited particles do not absorb light from the probe beam. As the laser frequencies are tuned through the resonance condition (symmetric detunings), the difference in the probe absorption displays the pressure-broadened line shape.

By comparing their results with certain theorectical models for pressure-broadening, the MIT group determined that collisions between ammonia molecules are predominantly inelastic collisions—that is, collisions that change the quantum states of one or more or the colliding particles. Collisions between ammonia and xenon, however, were found to be governed by elastic interactions that changed the velocities of the particles, but not their quantum states. The MIT group was also able to estimate the forms of the force laws governing these collisions.

Charles Rhodes and William Bischel of the Lawrence Livermore Laboratory, Livermore, California, using a technique called optical double resonance, were able to measure velocity changes due to collisions. (Both researchers are now at the Stanford Research Institute, Menlo Park, California.) Optical double resonance is another Doppler-free laser spectroscopy. Two lasers of different frequencies excite two different transitions in an atom or molecule; usually both

transitions have one quantum state in common. The first laser selects a particular velocity group and saturates the transition for which it is tuned. As the second laser is tuned to excite a different transition in the same velocity group, absorption of its light drops sharply because of the change in the population of the quantum state in common between the two transitions caused by the saturating laser.

The Livermore investigators excited a transition from a given vibrational-rotational state in a lower vibrational band of carbon dioxide to a state in a higher vibrational band with a carbon dioxide laser. A second carbon dioxide laser excited the same vibrational transition, but involving different vibrational-rotational states. Collisions can cause transitions between vibrational-rotational states within a vibration band, a phenomenon called collision redistribution.

Thus, even though the two transitions do not have a common quantum state, the effect of collisions is to give rise to an optical double resonance effect. Collisions of this type are known as rotationally inelastic because they change the rotational quantum numbers of states within a vibrational band. The resulting spectrum is not completely Doppler-free, but its width is a measure of the effectiveness of the collisions in changing the velocity, and its height is a measure of the effectiveness in changing the rotational quantum number.

Collisional Transfer of Energy

The investigators measured the difference in the fluorescence emitted from the upper vibrational band with and without the saturating beam. With a synchronous detection technique, they could single out that part of the fluorescence due to excitation by the probe beam. By fitting the observed line shape to their theory, Rhodes and Bischel were able to determine the average velocity change imparted by rotationally inelastic collisions of carbon dioxide with itself, molecular hydrogen, neon, ammonia, or methyl fluoride. The magnitudes of the velocity changes were all less than 10 percent of the average thermal velocity.

In the progression of collision partners from molecular hydrogen to methyl fluoride, the interaction forces become increasingly longer range ones, and the Livermore investigators found that the collisions became increasingly effective in changing rotational quantum numbers, but less effective in changing the velocity as the range of the forces increased.

Recently, William Phillips and David Pritchard of MIT proposed a method of measuring cross sections for collisional processes that takes advantage of the Doppler effect and of fluorescence detection (which is more sensitive than absorption) and uses only one laser beam.

Jay Apt and Pritchard have demonstrated this method at MIT in studies of collisional redistribution of energy in excited sodium atoms, when the sodium collided with xenon, argon, or rubidium. A tunable dye laser boosted the sodium from its ground state to an excited state with a nonzero angular momentum ($3P$). Actually, there are two very closely spaced such states (fine structure), and the frequencies of the fluorescence emitted when these decay to the ground state differ by a small amount (1 part in 10^3).

When the scientists tuned the laser to excite one of the $3P$ states, they saw fluorescence emitted at the laser's frequency, as expected. But, in addition, the researchers also observed fluorescence of the frequency corresponding to decay of the neighboring $3P$ state. The ratio of the latter fluorescence to the former is measure of the efficiency of collisions in transferring sodium from one state to the other. By tuning the laser across the Doppler profile for sodium absorption, the MIT investigators were also able to deduce the values of the cross section for collisional energy transfer as a function of velocity.

An altogether different collisional process occurs when a particle absorbs light at the same time that it is undergoing a collision. An example of this type, known as an optical collision, was found by John Carlsten and Abraham Szöke of the Joint Institute for Laboratory Astrophysics (JILA), Boulder, Colorado, in their investigation of light scattering in mixtures of strontium vapor and argon.

When laser light from a tunable dye laser having a frequency slightly different from a resonant frequency of strontium passes through the gas mixture, the spectrum of scattered light contains several components. One component has the same frequency as the laser and is the well-known Rayleigh scattering. A second component, which has the resonant frequency, is produced when the sum of the energy of a laser photon and the energy imparted in an inelastic collision matches this resonant frequency.

When the investigators measured the ratio of the intensity of collision-induced fluorescence to the Rayleigh scattering as a function of the difference between the laser and resonant frequencies, they found a complicated variation with maxima and minima. This result indicates that collisional transfer of energy occurs preferentially at certain energies and constitutes a measurement of the redistribution function for the energy transfer. In principle, scientists could extract information on the operative force laws from this kind of experiment, as has been done for the inverse process (absorption at the resonant frequency and emission in the wings of the Doppler profile) by Alan Gallagher and his colleagues at JILA.

At Stanford University, Derek Lidow, Stephen Harris, and their associates are looking for what they call laser-induced inelastic collisions of strontium with calcium, also known as radiative collisions. The process is somewhat similar to that occurring in optical collisions. Energy stored in an excited state of one atom is transferred to a second atom during a collision when laser radiation is simultaneously present.

Fourier Transform Optical Spectroscopy

The Stanford researchers use a tunable dye laser to prepare strontium in an excited state. For efficient energy transfer during a collision, the energy of the strontium state should match a resonant frequency of the calcium, which is not usually the case. But, when the energy stored in the strontium together with the energy of a photon from a second tunable dye laser correspond to a calcium resonant frequency, energy is transferred and the calcium ends up in an excited state, while the strontium returns to its ground state.

Since the transfer occurs only when the two atoms are close together in a collision, Harris believes that by varying the frequency and intensity of the second laser, it should be possible to probe the force law governing the collisions. Meanwhile, several theorists are busy devising models for these kinds of laser-induced inelastic collisions. Interest in them is great, in part because the inverse process whereby light is emitted during collisions in which energy is transferred from one atom to another might be relevant to making a short-wavelength laser.

All the methods discussed so far are steady-state techniques. A category of transient phenomena known as coherent optical transients provides a way to measure the separate contributions of various collisional processes in a single set of experiments when two or more collision mechanisms are simultaneously operative with comparable strengths.

The observance of coherent spin transients in NMR has led to the development of pulsed or Fourier transform NMR, a technique that has greatly increased the resolution and sensitivity of NMR, while decreasing the time needed to gather

(Continued on page 1367)

RESEARCH NEWS

(Continued from page 1324)

data. The same sort of impact on optical spectroscopy is forecast by adherents of coherent optical transients. Recently, in fact, Richard Brewer and Stephen Grossman of the IBM Research Laboratory, San Jose, California, have obtained Doppler-free spectra with the aid of an on-line computer with a fast Fourier transform algorithm to convert transient signals from the time domain to normal spectra in the frequency domain. The experimenters were able to simultaneously resolve several closely spaced spectral lines and map out coherent transients for each line.

There is a wide variety of coherent transient effects whose ability to distinguish between collisional processes derives from the fact that each decays at a different rate because each is sensitive to a different dephasing process that disrupts the perfect coherence induced in the gas by the coherent laser light.

For example, when coherent light from a laser at the frequency for resonant absorption is suddenly turned on, the quantum mechanical wave functions of each particle in a collection of atoms or molecules evolve together in time—that is, in phase. They change gradually from the wave function of the lower state to that of the upper state of the transition (absorption) and back again (stimulated emission) at a rate that increases with the intensity of the laser. In between, the wave functions are a combination of both upper and lower state waves. Thus, when all the wave functions evolve together in step, the observer sees an oscillating absorption and emission known as optical nutation.

The oscillation would persist in time if it were not for collisions. Both elastic and inelastic collisions interrupt the evolution of the wave functions with time thus forcing them out of step with each other and causing a destructive interference effect owing to their now different phases. The magnitude of the optical nutation therefore decays with time, and the nature of the decay carries information about the collisions causing it.

A special optical nutation experiment, called delayed nutation, depends only on inelastic collisions. To obtain information about elastic collisions, researchers need to measure a phenomenon called a photon echo, which depends on both types of collisions. The two experiments together, therefore, are able to separate the inelastic from the elastic collisions and give information on each separately.

In photon echoes, a very short, intense

laser pulse is applied to the sample; a certain short time passes; a second pulse is applied; another short time equal to the time between pulses passes, at which point the sample spontaneously emits a pulse of light in the direction of the previously applied laser pulses—the echo.

Collisions enter the picture during the time between laser pulses. Because of the previously described dephasing effects due to collisions, the strength of the echo becomes progressively smaller the longer the waiting time between pulses. The decay in the intensity of the photon echo that occurs with different time between pulses thus contains information about the collisions involved.

Although pulsed laser light can be used to observe some coherent transient effects, many researchers feel that the experiments have been generally difficult and some effects not even observable. About 5 years ago at IBM, Brewer and Richard Shoemaker (now at the University of Arizona) introduced a technique called Stark switching that solved some of the difficulties for infrared transients. Molecules with a permanent electric dipole moment, when subjected to an electric field, experience a shift in the energies of their quantum states (Stark shift).

Thus, instead of pulsing a laser, researchers can elicit any of the coherent transient effects by using a continuous wave (cw) laser. The proper sequence of voltage pulses, which are easier to control than laser pulses, applied to the sample shifts the energy levels into and out of resonance with the laser. Since the intensity of the laser does not change, the only transient effect present is that due to the coherent effect under study. And because light emitted by particles after a voltage pulse has a different frequency than the laser, a vastly increased sensitivity can be obtained by means of frequency mixing (heterodyning) the laser light and the frequency-shifted light produced in certain transient effects, such as the photon echo.

Not all molecules have permanent electric dipole moments, however. Recently, Brewer and Azriel Genack at IBM reported on a technique called frequency switching, which will make experiments with coherent optical transients much easier and enlarge their range of applicability. The researchers used a tunable dye laser with an electrooptic crystal in the laser cavity. An electric field applied to the crystal determines its index of refraction, which in turn controls the frequency of the laser. With a sequence of low voltage pulses applied to the electrooptic crystal, the laser can be driven into and out of resonance with the atoms or molecules in the sample.

Certain results on methyl fluoride, which has a large electric dipole moment and therefore is well suited to study by the Stark-switching technique, illustrate the usefulness of the coherent transient techniques. Brewer and Joel Levy at IBM in collaboration with Paul Berman of New York University found that elastic collisions of methyl fluoride with itself are due to velocity-changing collisions in which the characteristic velocity jump is only 85 centimeters per second, or about 0.2 percent of the average thermal velocity! They also found the total elastic cross section to be large and comparable to that for inelastic collisions. And Brewer and Grossman, with the Fourier transform technique, were able to measure the velocity dependence of the photon echo decay rate by Stark-switching different velocity groups from the Doppler profile into resonance with their carbon dioxide laser. With this information, the researchers were able to deduce the form of the intermolecular force law (such as dipole-dipole or van der Waals interaction) for each type of collision.—ARTHUR L. ROBINSON