resources that are publicly owned, citing giveaways of more than 22 billion tons of coal and plans for rapid and probably uneconomical leasing of offshore gas and oil lands. Federal R & D programs should give more emphasis to solar and other renewable energy technologies and to pollution control, while federal participation in funding demonstration plants, such as in the breeder reactor program, should be greatly reduced.

Clearly, the most controversial aspect of the Project's recommendations is their heavy reliance on federal intervention. The Advisory Board generally agreed that more emphasis should be given nationally to conservation, that the federal government needs to put its own house in order in the area of managing energy resources, and that the report gave inadequate attention to the finite nature of fossil fuels, especially oil and natural gas. But they disagreed on nearly everything else, from the effectiveness of conservation measures to the federal government's role.

Predictably, the industry representatives on the Board largely viewed a reliance on government action as naive and impractical in the light of past performance and vouchsafed a free market faith with little charity toward slowing energy growth. D. C. Burnham of Westinghouse, for example, said the report is misleading in asserting that decisions on commercial development of new energy sources can be delayed a decade or more and that conservation will not affect economic well-being. He criticized the report's estimates of future demand because, among other

things, they made no provision for new energy-consuming devices. Minor Jameson, a consultant to the Independent Petroleum Association of America, criticized the report for anti-industry bias. And William Tavoulareas of Mobil Oil called the report "an unabashed primer for regimentation." He characterized the conservation approach as risky and attacked Freeman for public statements that prefigured the main outline of the report before the studies on which it was supposed to be based were even completed.

In contrast, the Sierra Club's Michael McCloskey defended the report, noting that industrial critics are selective in their opposition to government intervention, since they still want special tax concessions and a host of existing government policies that encourage energy consumption. Harvey Brooks of Harvard University and Karl Kaysen of the Institute for Advanced Study, Princeton, agreed that relying chiefly on the workings of the marketplace is not an adequate way to deal with the energy problem. But they found the report unsophisticated in dealing with political issues, and McCloskey faulted it for hedging its critique of unrestrained energy growth. Dean Abrahamson of the University of Minnesota found the report timid and too defensive in discussing reductions in energy consumption. Despite a variety of objections to specific points, many of the academics and environmentalists, and some of the industrialists, on the 21member Board seemed to credit the report with having successfully accomplished its main objective-outlining a

coherent set of alternative policies to deal with the energy problem.

It is fair to note that some of the report's recommendations (such as that government should encourage builders to use energy-saving designs) are vague and provided with no persuasive evidence that they can be put into effect. There may be, moreover, some substance to the criticism that Freeman has used the Project as a launching pad for his own ambitions, which seem to include becoming Mr. Energy in any Democratic Administration. [He is now a consultant to the Senate Commerce Committee at the behest of Senator Magnuson (D-Wash.)]. But the main thrust of the report-that conservation is not only feasible but an essential and still unrealized component of national policy-does not depend on the details of its recommendations or on the ambitions of its authors.

The disagreement over conservation and how to put it into practice is evidence that the major debate and the major decisions on the energy future of the United States are still to come. The Energy Policy Project would appear to have made a significant contribution to that debate. Overall, it will amount to 20 volumes, and the six that have already been published, although of varied quality, include some landmark studies (such as Mason Willrich and Theodore Taylor's analysis of nuclear safeguards). In view of the relative neglect of energy conservation in federal energy planning and the leisurely pace of that planning, the Freeman report and its sense of urgency are very timely.—Allen L. HAMMOND (Continued on page 461)

### RESEARCH NEWS

# Laser Spectroscopy: A New High Resolution Technique

A new high resolution spectroscopic technique based on the simultaneous absorption of one photon from each of two oppositely directed, highly monochromatic, tunable dye laser beams has been demonstrated by scientists at several laboratories in the United States and France. The application of this two-photon absorption method is expected to yield new and highly detailed information on the electronic structure of atoms and on the electronic, vibrational, and rotational structure of molecules. Such information was heretofore either unavailable or obtainable only with great difficulty. The new laser technique may also find application in such diverse fields as metrology and photochemistry.

Unraveling the details of the quantum mechanical structure of atoms and molecules has been hindered both by the limited resolving power of the best spectrometers and by effects within the atomic or molecular system itself which tend to broaden spectral lines. An important example of the latter is the Doppler effect, whereby the frequency of light seen by a moving atom or molecule is shifted by an amount proportional to its longitudinal velocity (the velocity component in the direction of propagation of the light). Thus, the frequency of light that can be absorbed or emitted is dependent on the velocity of the particle. Since the particles in a gaseous sample will have a statistical distribution of velocities, the spectroscopist will see a broadened line made up of a superposition of narrower lines (one for each velocity in the distribution) rather than the details of the transition of interest. In addition, the Doppler-broadened line may be wider than the separation between the frequencies of adjacent absorptions or emissions so that the separate lines become blurred and overlap. In both cases, information important to the spectroscopist is lost.

The advent of tunable dye lasers in the visible region of the spectrum has helped to ameliorate both the limited instrumental resolution and Doppler broadening (Science, 18 February 1972, p. 739). For example, tunable dye lasers with resolutions up to 1 part in 10<sup>8</sup> (as compared with 1 part in 10<sup>6</sup> for the best grating spectrometers) have been built in recent years and are becoming commercially available. (The highest resolution-a few parts in 1010-tunable dye laser has been constructed by S. Ezekiel and his associates at Massachusetts Institute of Technology, Cambridge.) Moreover, because of the high power densities (in watts per square centimeter) obtainable, these lasers have been used in a technique, known as saturation spectroscopy, which greatly lessens the Doppler effect.

### **Two Lasers Reduce Doppler Effect**

The technique is based on two laser beams (an intense, saturation beam and a weaker, probe beam) each with the same frequency. The beams are passed through a cell containing the atoms or molecules of interest (in the form of a gas), but in opposite directions. Because of the opposite Doppler shifts for a particle with a particular longitudinal velocity, each beam is absorbed by a separate group of gas particles. However, when the laser is tuned exactly to the frequency of the transition, both beams are seen by the same particles (those with zero longitudinal velocity and hence with no Doppler shift). Now the probe beam is less strongly absorbed because the saturation beam has already excited most of the possible absorbing particles. Thus, by measuring the absorption of the probe beam, one finds a narrow dip in the center of a Doppler-broadened absorption line. This dip is the Doppler-free line.

However, there are quantum mechanical selection rules (arising from symmetry considerations and conservation of angular momentum) that govern which quantum states of an atom or molecule may be connected via radiative transitions. In particular, some excited states cannot be reached when only a single photon is absorbed by a single particle, as in saturation spectroscopy. However, if two photons are simultaneously absorbed, each with a frequency equal to one half of that needed to excite the particle (in the simplest case), then the selection rules are different. In this respect saturation spectroscopy and two-photon absorption are complementary techniques, because each probes a different set of quantum states. Such two-photon effects, in which two photons are absorbed from a single light source, have been known in theory for decades and have been observed in a variety of materials since lasers have become available.

In its basic operation, the high resolution, two-photon absorption technique that made its appearance this spring combines the Doppler-free capability of saturation spectroscopy with the accessibility to heretofore forbidden excited states of two-photon absorption. Moreover, it superficially resembles saturation spectroscopy in that two laser beams pass in opposite directions through a gas cell, but with the important difference that a single particle absorbs two photons, one from each of the equally intense beams. The effect of taking one photon from each of the two beams (rather than two from the same beam as in previous two-photon studies) is that, whatever the velocity of the particle in the gas, the Doppler effects for the two photons cancel. Thus, the entire sample absorbs the laser light at the same time and only when the sum frequency is equal to that of a transition within the particle. And the absorption observed has the narrow line characteristic of the transition itself (although phenomena other than the Doppler effect may still cause some line broadening).

In addition to its relative experimental simplicity, as compared with other techniques that can give the same information, two-photon spectroscopy has another advantage. Because it does use two photons, there is a frequency doubling effect that permits those excited states to be probed with a visible laser that normally would require ultraviolet frequencies. The use of a visible laser is a considerable advantage, as no tunable ultraviolet lasers which have both high power and high resolution are now available.

The parentage of the Doppler-free,

two-photon absorption technique seems to be traceable to V. P. Chebotaev and his colleagues at the Institute of the Physics of Semiconductors, Novosibirsk, who treated the subject theoretically in 1970. Perhaps because of a lack of suitable lasers to do the experiment, the idea was not picked up at the time. Later on, a group at the Ecole Normale Supérieure, Université de Paris, headed by B. Cagnac, began a theoretical and experimental attack on the problem.

The French group used a rhodamine 6G dye laser pumped by a flashlamp to excite atoms in a cell filled with sodium vapor. Rather than measuring the absorption of the laser light directly, Cagnac and his associates used the fluorescence given off when the excited sodium atoms decayed to less energetic states to determine when two-photon absorption was occurring. Thus, by monitoring the intensity of the fluorescence as a function of the frequency of the laser light, an absorption line free from the Doppler effect could be observed. In this way, the French scientists could barely resolve hyperfine structure-which is due to an interaction between the spin of the outer electron and the spin of the nucleus-in the absorption spectrum resulting from a transition from sodium 3s to 5s states. But, because of an unstable laser, they could not make quantitative measurements.

## Hyperfine Splitting Measured

M. D. Levenson and N. Bloembergen at Harvard University, Cambridge, Massachusetts, independently carried out a very similar experiment. The pulsed dye laser used by the Harvard researchers was pumped by a nitrogen gas laser rather than a flashlamp and was sufficiently stable that a numerical value for the hyperfine splitting of the excited sodium 5s state could be obtained. The resolution of the experiment (about 3 parts in 107) was mainly limited by the short pulse length of the laser, since, by the Heisenberg uncertainty principle, there is a reciprocal relation between the minimum duration of a light pulse and the precision with which its frequency (or energy) can be fixed. Levenson and Bloembergen have also carried out experiments with applied magnetic fields (Zeeman effect), in which the shift in the position of energy levels with the magnitude of the applied field was observed.

At Stanford University, Stanford, California, a third group headed by T. W. Hänsch has also studied two-photon

absorption in sodium vapor. The Stanford group, however, used a continuous wave tunable dye laser (referred to usually as a cw laser), rather than a pulsed laser. In general, cw dye lasers have a potentially higher resolution than pulsed lasers, because a continuous wave is effectively an infinitely long pulse and the resolution ceases to be limited solely by the uncertainty principle. However, cw lasers are lower power light sources (less than 100 milliwatts as compared with more than 10 kilowatts). Since two-photon absorption is a second-order, and hence weak, effect, powerful lasers are usually necessary for the experiment to succeed. Hänsch and his associates focused the laser beam to a high power density in order to overcome this difficulty. The resolution obtained in the Stanford experiment was about 2 parts in 10<sup>8</sup>, the improvement over the previous experiments being due to the more stable laser, which was more than sufficient to resolve the fine structure (which results from an interaction between the electron spin and the orbital angular momentum) in the sodium 4d states.

In the most general case, the two photons to be absorbed need not have the same frequency, so long as the sum of their individual frequencies adds up to the transition frequency. In this case, there is a residual Doppler effect, but it can be negligible as compared with other sources of spectral broadening, provided that the two laser frequencies are not too different. The flexibility added by the ability to vary the laser frequencies in this way can help to overcome one limitation of two-photon absorption: its intrinsic weakness (often several orders of magnitude less strong than first-order single photon absorption). If one of the lasers is tuned close to the frequency appropriate for a single photon transition to an excited state with less energy than the excited state being probed by two-photon absorption, then the probability of the two-photon transition is increased by a process called resonant enhancement. The effect of this third state is to increase the electric polarization induced in the gas by one of the two photons being absorbed. The polarization could be viewed as providing a kind of resting place or foothold for the particle as it is being excited, except that the excitation process is simultaneous rather than sequential.

J. E. Bjorkholm and P. F. Liao of Bell Laboratories, Holmdel, New Jersey, have successfully tested such a scheme, again in sodium vapor, by observing the effect on the fluorescence, due to decaying excited 4d states, as one of the lasers was tuned to frequencies near the 3s to 3p transitions (there are two 3p states in sodium). The Bell Laboratories researchers observed that the probability of exciting the twophoton transition could be varied over about seven orders of magnitude, according to how closely the laser was tuned to one of the 3p intermediate states.

Some two-photon experiments related to those already discussed but making use of atomic beams of sodium have also been carried out recently. Atomic (or molecular) beams is another decades-old technique of high resolution spectroscopists based on a highly collimated (parallel) and high speed stream of particles emerging from an oven. Doppler-free single photon spectroscopy has been observed by shining the light beam perpendicularly across the beam of particles, so that none of the particles moves in the direction of the light beam.

#### **Atomic Beam Spectroscopy**

D. Pritchard and his associates at MIT have combined atomic beams and two-photon absorption, but the two photons were from a single laser beam, rather than from two oppositely directed beams. In this experiment, there was no cancellation of the Doppler effect, so that the atomic beam was necessary for high resolution work. And scientists at the Centre National de la Recherche Scientifique, Orsay, combined atomic beams and two-photon absorption, but the two photons were absorbed sequentially rather than simultaneously.

Chemists involved in molecular spectroscopy have become interested in two-photon absorption because of the possibility of studying heretofore inaccessible excited states, but these experiments had been limited to so-called medium or low resolution spectroscopy in which only a single laser beam is used. Now that the opposing beam, high resolution technique has been demonstrated in atomic sodium, researchers at several institutions are rushing to apply it to various molecular systems. For example, a group headed by C. Rhodes at the Lawrence Livermore Laboratory, Livermore, California, has already demonstrated Doppler-free twophoton absorption in methyl fluoride  $(CH_3F).$ 

The Doppler-free two-photon tech-

nique may eventually be applied to the determination of fundamental constants and frequency standards. For example, E. V. Baklanov and Chebotaev have outlined the considerations involved in making a precision measurement of the 1s to 2s transition in atomic hydrogen (which is a forbidden single photon transition). Such a measurement would lead to an improved value for the Rydberg constant (ionization energy of atomic hydrogen, which is one of the fundamental constants) and perhaps eventually to a more accurate frequency or time standard. Hänsch's group at Stanford is reportedly now trying to make such a measurement in order to determine the Rydberg value.

Atomic hydrogen is especially interesting because of the long lifetime of the hydrogen 2s state. The long time before the 2s state decays means that the frequency of the transition can be extremely accurately fixed. In principle, when experimental techniques become available to do the measurements, a frequency standard several orders of magnitude more accurate than the present cesium beam oscillator standard could be constructed.

Photochemistry and, in particular, isotope separation (of which uranium isotopes for nuclear fuels would be the most interesting) have been suggested by many, including P. L. Kelley of MIT's Lincoln Laboratory, Lexington, and his associates, as a possible industrial application for high resolution, two-photon absorption. And D. E. Roberts and E. N. Fortson of the University of Washington, Seattle, have succeeded in selectively exciting (but not separating, which they did not try to do) isotopes of rubidium (85Rb and <sup>87</sup>Rb). However, as no one has as yet sat down and looked at a specific separation scheme in sufficient detail to evaluate its validity, isotope separation is, for the moment at least, problematical.

One manufacturer of high resolution, tunable dye lasers has sold several such instruments to customers interested in the new Doppler-free technique. Interest in this spectroscopic method seems to be picking up some steam, but it will probably be necessary to wait for a second round of experiments to see if the Doppler-free two-photon absorption technique lives up to the billing given it by one enthusiastic supporter: one of the two greatest advances in high resolution spectroscopy since the invention of the laser itself.

-ARTHUR L. ROBINSON

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