

OPTICAL PUMPING

In this new technique of experimental physics light is used to "pump" electrons to higher energy-levels. The method is employed to study the interaction of atoms and radio waves

by Arnold L. Bloom

The rather odd term optical pumping means just what it says. In general "pumping" is a process of raising matter from lower to higher energy; for example, raising the potential energy of water by moving it from an underground well to an elevated tank. In this article we shall be concerned with the pumping of individual atoms from lower to higher states of internal energy. The word optical refers to the light energy that is the source of power for the pump.

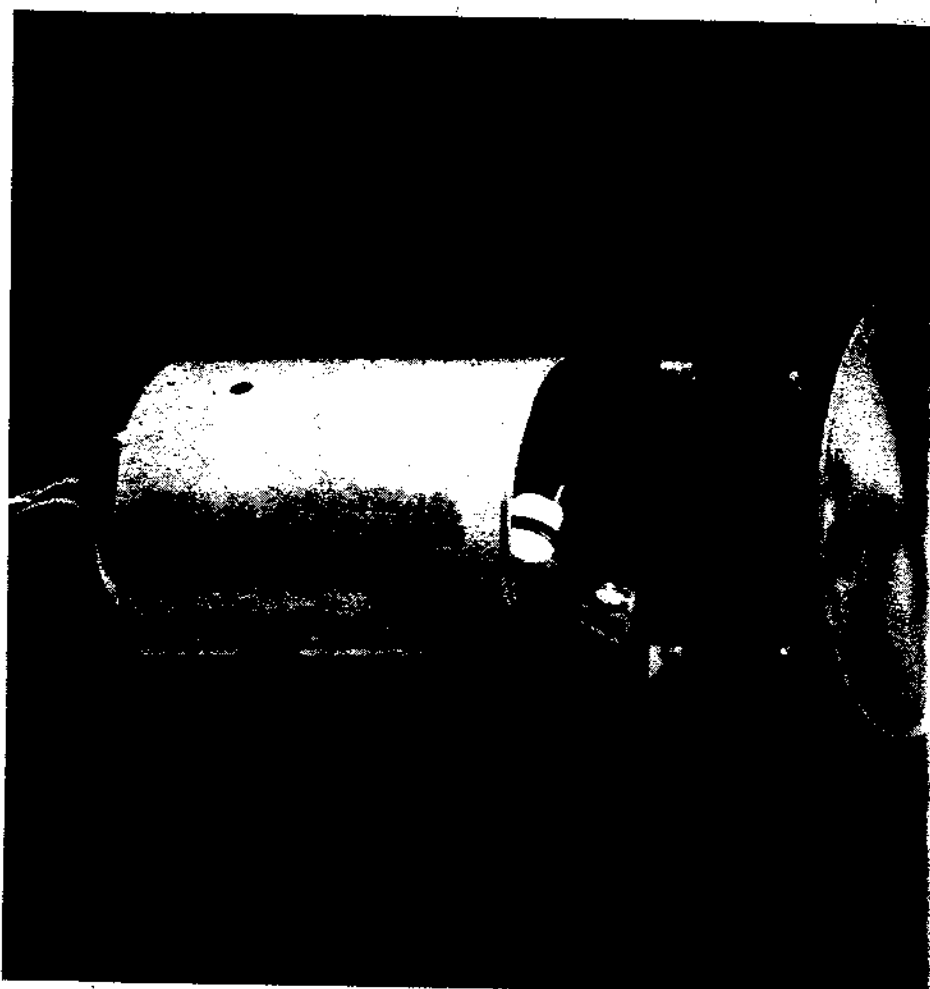
Why pump atoms? The purpose is to prepare them for a special kind of spectroscopic analysis. When we think of a spectrum, we usually visualize bands of color. Actually atomic spectra extend far beyond the wavelengths of visible light (a few hundred thousandths of a centimeter) in both directions. Atoms can emit and absorb electromagnetic radiation ranging from radio waves (whose length is measured in hundreds of meters) to X-rays (a thousandth as long as light waves). The visible spectrum has been intensively studied for a century, and the X-ray spectrum for about 50 years. Among the results of these investigations is the quantum theory of atomic structure. But spectroscopy in the radio-frequency region is a very recent development, in part made possible by the technique of optical pumping, and only now beginning to be exploited. Paradoxically, long-wave studies are now revealing fine detail in the structure of atoms that is invisible at shorter wavelengths. And optical pumping has already led to a number of practical applications.

The reason for both the effectiveness and the difficulty of using radio waves for spectroscopy lies in their low energy. Like all other electromagnetic radiations, radio waves are divided into discrete

packets, or photons, the energy of which varies directly with their frequency, or inversely with wavelength. Having frequencies millions or even billions of times lower than the frequencies of visible light, their energy is less in the same proportion.

When photons are absorbed or emitted by an atom, the atom gains or loses

the energy they contain, changing its physical state in some way. The photons of light, with their comparatively high energy, involve the transition of an electron from one orbit to another. The photons of radio waves merely shift the axes of spinning electrons within an orbit. Since the electrons are tiny magnets with fields aligned along their axes, such a



RUBIDIUM IS PUMPED by beaming light from a rubidium-vapor lamp (far left) through a circular polarizer (square at left center) and a plastic condensing lens into an

shift produces a small change in the magnetic energy of an atom.

The transition between energy states, or levels, is a two-way street: atoms at a higher level tend to fall spontaneously into the lower one; those at the lower level will jump to the higher one if the requisite quanta of energy are available. If a transition is to be detected spectroscopically in a sample of matter, there must be a net excess either of upward or of downward jumps among its atoms. In jumping up, the atoms subtract photons from a transmitted beam of radiation, producing an absorption spectrum; in jumping down, they send out photons, producing an emission, or "bright line," spectrum. Generally speaking, matter must be in the form of a gas or a vapor to exhibit sharp emission or absorption lines. In solids and liquids interactions of neighboring atoms broaden the energy levels, so that the spectra consist not of lines but of wide bands of frequencies.

Now the energy associated with a quantum jump can be exchanged through the direct collision of atoms as

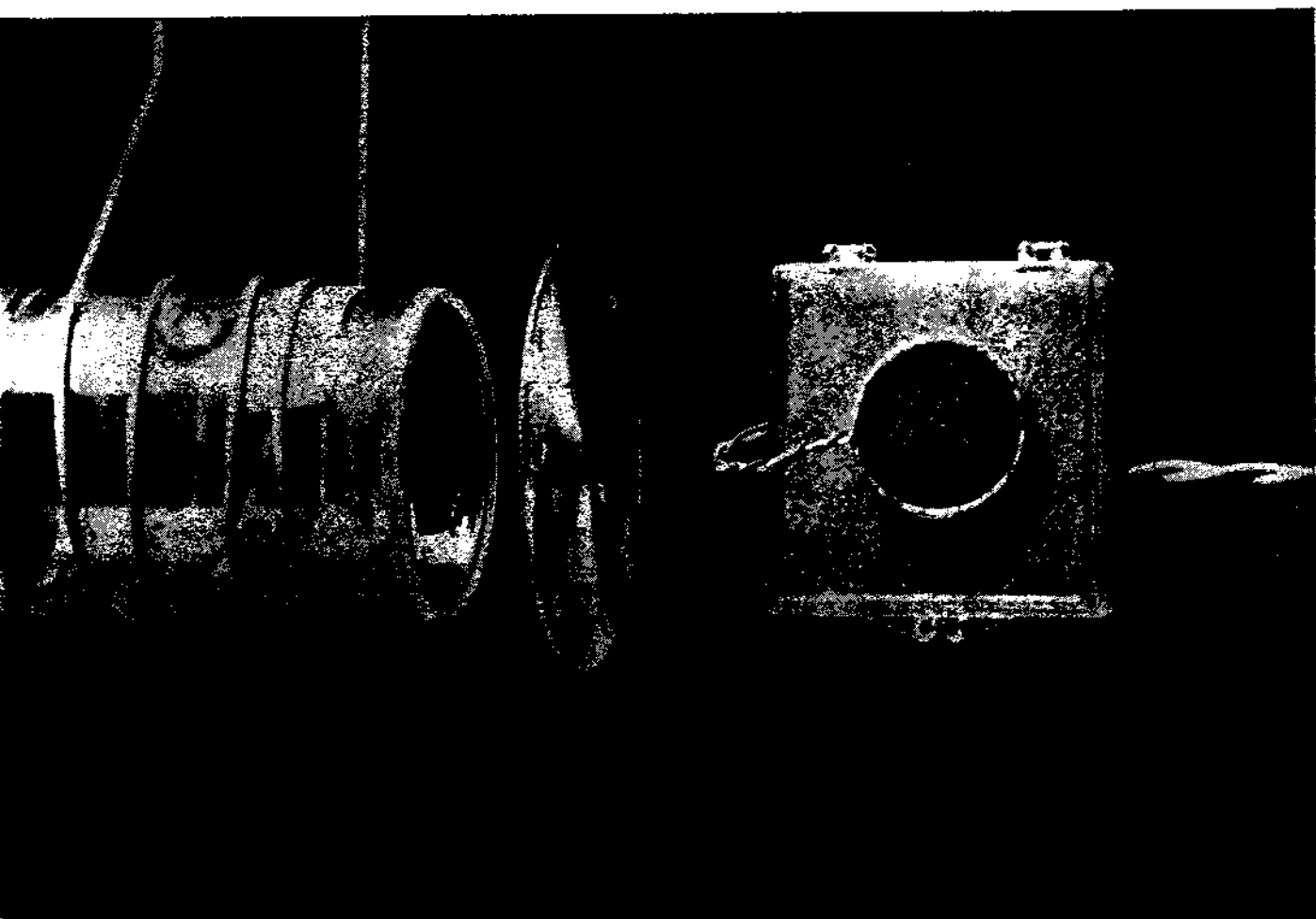
well as by radiation. At room temperature atoms are not moving fast enough to raise one another up to the levels required for the emission of visible light. Therefore they are in a position to absorb energy from an external light source. On the other hand, by raising the temperature of a substance, collisions between its atoms can be made sufficiently energetic to excite them so that they emit light.

The situation is otherwise for the radio-wave spectrum. The minute quantity of energy necessary to shift atoms between the closely spaced levels is available many times over in thermal motion at room temperature. As a result the atoms continually shift back and forth, and those in the emitting state are almost exactly counterbalanced by those in the absorbing state. In order to do spectroscopy some way must be found to put a majority of atoms into one state or the other.

There are a few ways to accomplish this. The most direct is to cool a material to a point where it no longer has enough thermal energy to produce transitions

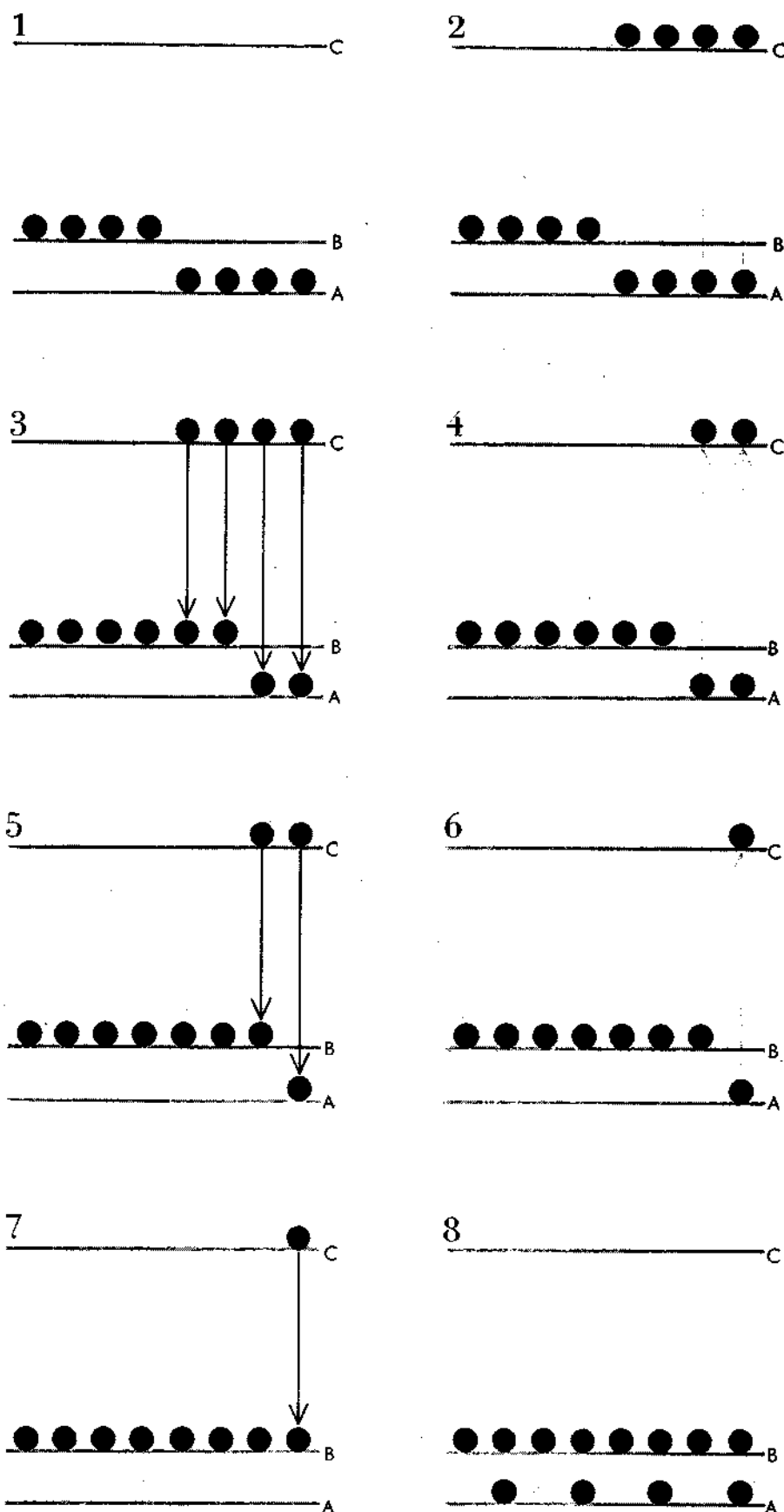
even between closely spaced levels. Normally this means bathing the material in liquid helium. Another rather difficult technique is to pass a beam of atoms through a magnetic field, which separates them according to their energy states. More recently experimenters have been reluctant to use these relatively cumbersome approaches and have developed extremely sensitive radio receivers to detect emissions or absorptions arising out of the tiny differences in energy population (measured in parts per million) that exist naturally.

About 10 years ago A. Kastler and J. Brossel of the Ecole Normale Supérieure in Paris and Francis Bitter of the Massachusetts Institute of Technology hit upon a better idea, which Kastler named optical pumping. To understand the principle, consider a simplified atom with only three energy levels, which we shall call A, B and C [see illustration on next page]. Levels A and B are low-lying and very close together; the energy difference between them corresponds to a radio-frequency spectrum line, and ini-



absorption cell (center). Coil around cell sets up a fluctuating magnetic field. Some of the energy of the light beam is absorbed to

pump atoms in cell to higher energy-levels; the rest passes through the absorption cell and is measured by the photocell at far right.



PUMPING PROCESS is depicted schematically in this diagram of the energy states of atoms. Before pumping, the atoms are divided evenly between energy levels A and B, as in 1. After absorbing photons from a beam of light (2) and being raised to energy level C, atoms drop back in equal numbers to energy levels A and B (3). As the process continues, only one atom is left in level A (5); finally it, too, ends up in level B (7). The atoms are then completely pumped. Pumping can be removed by a radio-frequency signal (8).

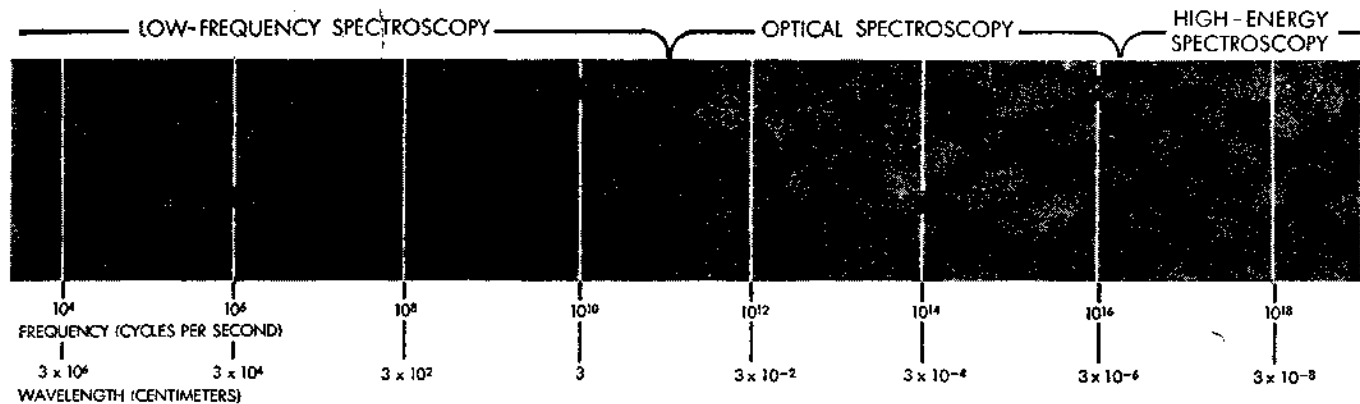
tially all the atoms are distributed equally between them. Level C is much higher; the transitions A-C and B-C correspond to lines in the optical part of the spectrum. Suppose we irradiate a sample of these atoms with a light beam from which the spectral line BC has been filtered. The beam contains photons that can excite atoms in level A but not in level B. Atoms excited out of A absorb energy and rise to C. They will remain there for a short time (as little as a ten millionth of a second) and then emit energy, dropping back either to the A or B state.

The proportion going to each state depends on the structure of the atoms, but the important thing is that occasionally an atom drops into B. When it does, it can no longer be excited by the incident light. If it returns to A, the light will raise it to the C state again, and again it will have some probability of dropping to B. Given enough time, every atom must end up in the B state, and the material is then completely pumped.

Once this condition has been attained, there are a number of ways to detect it. The simplest and most effective is the method developed by H. G. Dehmelt of the University of Washington. It depends on the fact that the transparency of the sample to the light beam varies with the degree of pumping. As atoms are removed from the A state, the material can absorb less and less of the pumping light, and more of it passes through, reaching a maximum when pumping is complete. Now if some atoms are suddenly returned to the A state, light will again be absorbed, and the brightness of the transmitted beam will drop sharply.

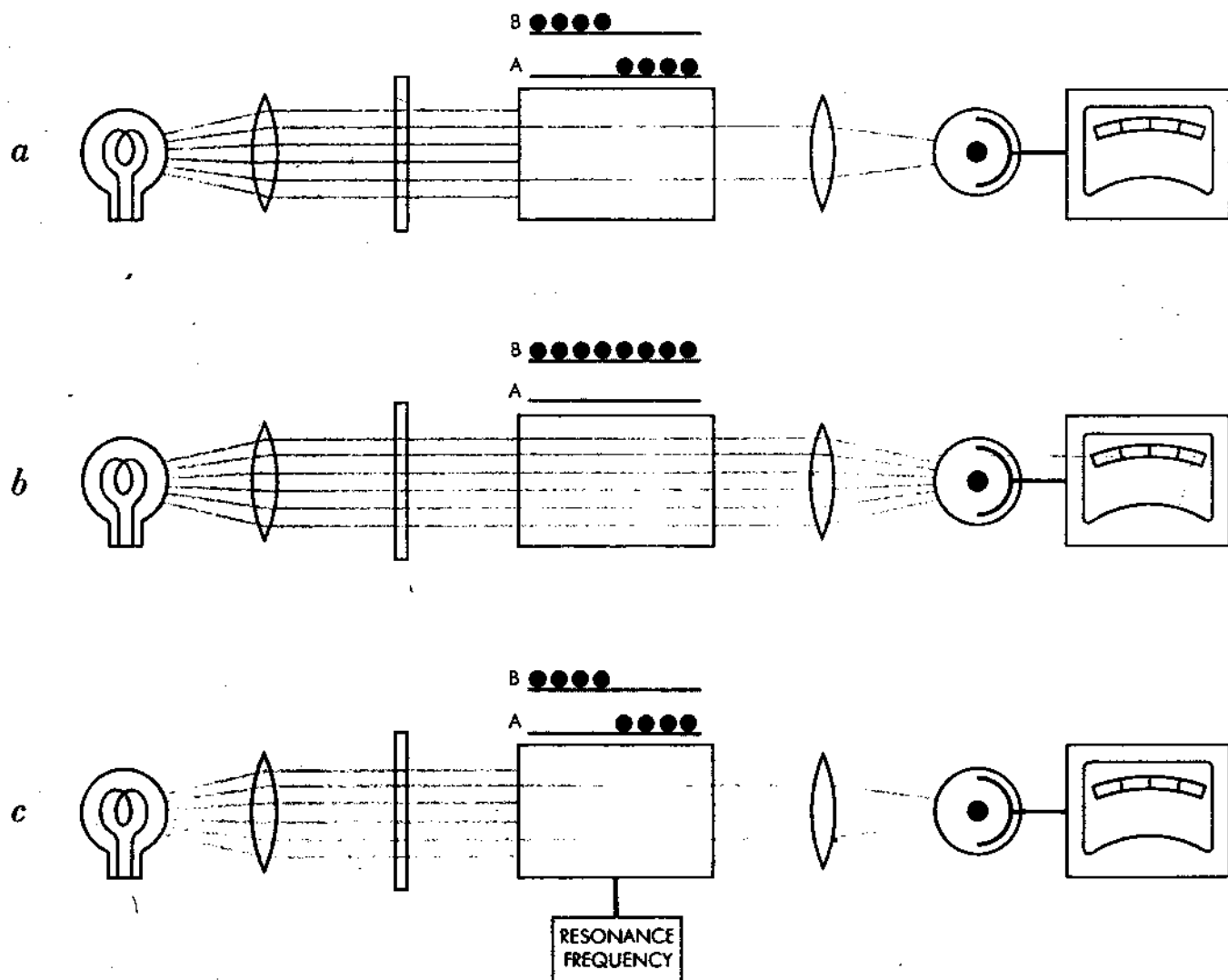
This can be accomplished by irradiating the atoms with radio waves at the frequency corresponding to the energy of transition between levels A and B. The effect is rather complicated in its details, but roughly speaking the radio-frequency photons cause the atoms to shuttle back and forth between the two states, thus effectively transferring some of them from B to A.

The technique is extraordinarily sensitive. A sample of vapor at a pressure of a ten millionth of a millimeter of mercury can reduce the transmitted light intensity by as much as 20 per cent when the correct radio frequency is applied. In effect every photon of radio-frequency energy undoes the pumping of at least one optical photon. Since the latter's energy is perhaps a billion times greater than that of the radio-frequency



ELECTROMAGNETIC SPECTRUM ranges from low-frequency radio waves (left) to high-frequency gamma rays (right). Vertical

black lines show three spectral lines of sodium; labels on lines indicate corresponding transitions in energy levels of an electron.



EFFECT OF PUMPING on the transmission of a beam of pumping light is depicted schematically. Rectangles at center represent absorption cells; circles above them show energy levels of atoms within them. Little light gets through unpumped cell in row a,

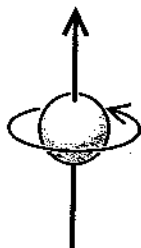
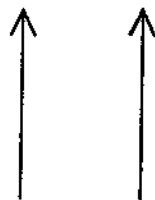
as is shown by the reading on meter connected to photocell at right. Completely pumped cell in row b is optically transparent; when pumping is removed by applying magnetic field that fluctuates at radio frequency, cell again becomes almost opaque (c).

MAGNETIC FIELD

LIGHT

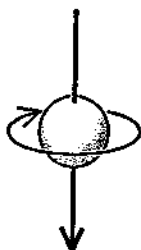
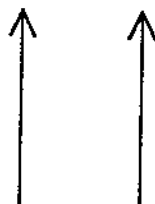
SPIN

a



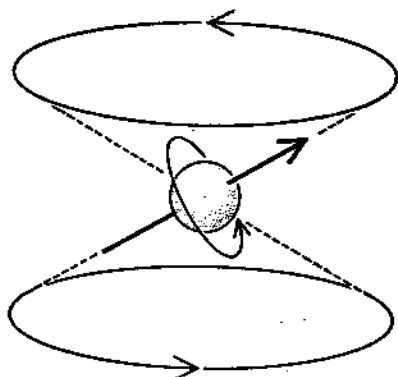
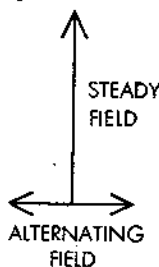
OPEN SHUTTER

b



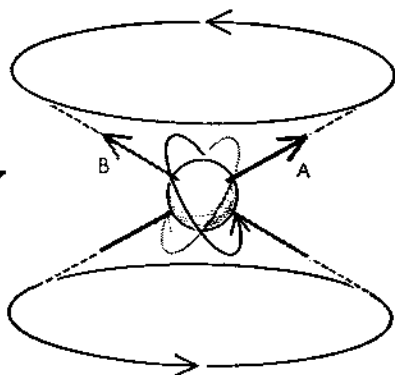
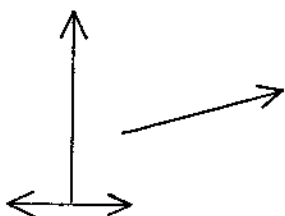
CLOSED SHUTTER

c



PARTIALLY OPEN SHUTTER

d



A



B



FLUCTUATING SHUTTER

photon, we have in effect an amplifier whose gain is a billion!

Our description thus far has glossed over a complication that accounts for the fact that this basically simple effect was not discovered long ago. When atoms arrive in the B state, they are not firmly caught there, but "leak" back into the A state through collisions with one another or with the walls of the container. To be effective, pumping must be faster than the leaks. Even in extremely dilute gases, where collisions between atoms are infrequent, each atom will bump into the walls of the container perhaps 10,000 times a second. Since an atom can absorb no more than about 1,000 photons per second from existing spectral lamps, the leak is clearly much too fast. Successful optical pumping had to await the discovery of methods for slowing down the leak.

The discovery came through one of those happy accidents that every scientist hopes for. Kastler and his associates did their early experiments on sodium vapor contained in highly evacuated glass bulbs. They were barely able to keep ahead of the leaking, but they did observe a very small pumping effect. Then one day in 1955 a defective vacuum system filled one of the bulbs with hydrogen instead of evacuating it. When this bulb was tested, it was found, to everyone's amazement, to show a much larger pumping effect. The investigators had known that a foreign gas could act as a buffer and slow the drift of sodium atoms to the walls. What they had failed to realize was that collisions between the sodium atoms and the buffer atoms would not undo the pumping. The reason is that the shapes of the electron orbits of the sodium atoms and the buffer atoms prevent the magnetic interaction of their electrons. And it is by this interaction that pumped atoms leak back to the unpumped state.

Capitalizing on the lucky error, Kastler began to try hydrogen and helium as buffers, and was able to use them at pressures as high as one millimeter of mercury. Further he could not go, because the buffer interfered with the process by which he detected the pumping effect. At about that time Dehmelt was developing his method of monitoring transmitted light, which is much less sensitive to the presence of buffer gas. Thus he was able to work at much higher pressures. In a sodium experiment with an argon buffer at 40 millimeters of mercury, he found that the time required for the pumping to leak away

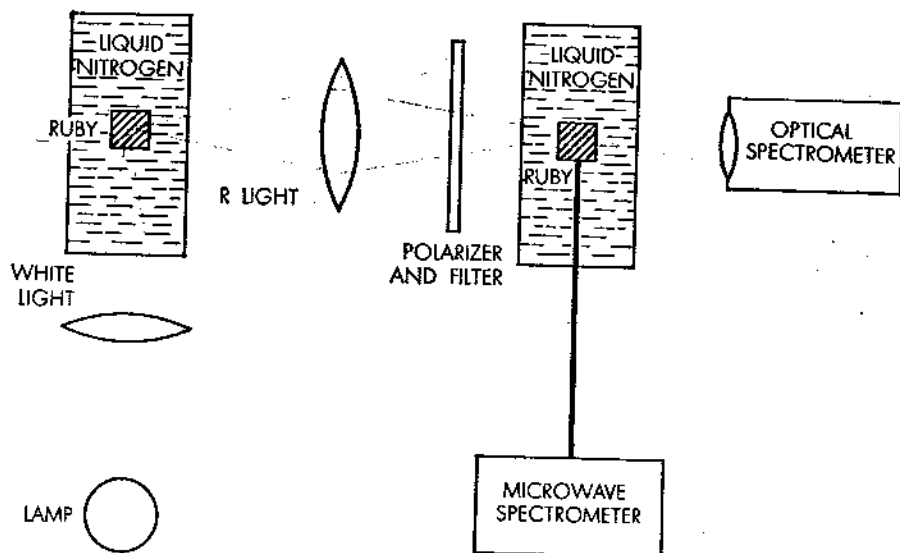
ELECTRON SPIN determines whether absorption cell will act as an "open shutter" that transmits pumping light or as a "closed shutter" that blocks it. When spin axis of electron is parallel to that of magnetic field across cell, and to the polarization of the light, as in diagram a, electron acts as a miniature open shutter. When spin is reversed, electron acts as closed shutter (b). When an alternating magnetic field is applied (c), electron precesses and acts as partially open shutter. When polarization of light is changed, the presence of the alternating field causes electron to act as a fluctuating shutter (d).

could be made as long as a 10th of a second. Thus he had achieved a "relaxation time" 100 times longer than the time between photon absorptions.

This was a remarkable result, but Dehmelt then proceeded to do even better without the buffer gas! He reasoned that, since the gas does not completely stop atoms from hitting the walls, a better solution would be to coat the walls themselves with a buffer. The coating should resemble argon in its electronic structure, but should remain solid near 130 degrees centigrade, the temperature at which sodium is pumped. Dehmelt concluded that the requirements could best be met by hydrocarbons with long, straight-chain molecules. Using substances with as many as 40 carbon atoms per molecule, Dehmelt and others have obtained relaxation times as long as two seconds. These experiments are performed with rubidium and cesium, which behave like sodium but which can be pumped at lower temperatures. Apparently, the only reason relaxation occurs at all is that once in every 20,000 collisions or so an atom hits the tiny spot of rubidium or cesium metal placed in the vessel to maintain the vapor.

The actual pattern of energy states in sodium, cesium and rubidium that makes them suitable for optical pumping is a bit more complicated than that of our example. Their atoms contain a single, unpaired electron in their outermost electron shells. According to the rules of quantum mechanics the magnetic field of the electron (and therefore its spin axis) can take only two directions with respect to an external field: parallel or antiparallel. The two conditions correspond to our levels A and B. They are distinguished not only magnetically, but also in terms of the "angular momentum" associated with the spin. When the electron's axis points one way (the B state, say) the atom as a whole has one more quantum unit of angular momentum than when the direction is reversed (the A state). In many of their excited states the atoms can have still greater angular momentum than in the B state. The important point, as we shall see in a moment, is that at least one level (our level C) can have no more angular momentum than the B state.

It is important because light photons also have one unit of spin or angular momentum. In an ordinary light beam the spins take on all directions. However, it is possible to restrict them to a single direction, in which case the light is said to be circularly polarized. When atoms absorb photons from a polarized



RUBY IS PUMPED by red light from another ruby. First ruby (*left*) fluoresces in the red (R) region of the spectrum when illuminated by intense white light. Pumping effect was detected by the optical spectrometer at right, but not by the microwave spectrometer at bottom.

beam, their angular momentum necessarily changes by one unit, increasing or decreasing depending on the direction of polarization.

Suppose we have a mixture of atoms in the A and B states and illuminate them with light of the proper wavelength to raise them to C. If the light is polarized so as to increase angular momentum, then the atoms in A can absorb it. They move up to C, gaining one unit of angular momentum in the process. But the atoms in B already have as much angular momentum as the maximum allowable in state C. Hence they cannot absorb the light. This is precisely the condition for optical pumping.

In Dehmelt's classic sodium experiment [see top illustration on next two pages] pumping light is obtained from a sodium-vapor lamp. Its beam is directed parallel to the earth's magnetic field, which serves as the external field to distinguish the A and B states. After passing through a circular polarizer, the light enters the sample cell: a glass bulb containing sodium metal and a trace of vapor plus argon as a buffer gas. Around the bulb are two sets of coils, one to feed in radio waves and the other to vary the strength of the earth's field slightly. Light transmitted by the bulb falls on a photocell, the output of which is amplified and displayed on an oscilloscope.

When the experiment begins, comparatively little light reaches the photocell because half the sodium atoms are in the light-absorbing state. As pumping proceeds, the vapor rapidly increases in transparency, giving rise to a sharp upward curve on the oscilloscope. The

trace soon levels off, showing that pumping is complete. Now the pumping can be undone by applying radio-frequency energy to flip the electrons over. The exact energy, and hence frequency, required to do this depends on the strength of the magnetic field; in a field of one half gauss, typical of the earth's magnetism at middle latitudes, the frequency at which sodium resonates between the A and B states is about 350 kilocycles per second. The most convenient way to observe the resonance is by varying the earth's field a little in recurrent cycles, or "sweeps." Each time the field passes through the correct value for the radio frequency the brightness of the transmitted light drops sharply, and the drop registers as a dip in the oscilloscope trace. If the field strength is known, the resonance serves as a measure of the radio frequency. Conversely, if the frequency is known, the experiment can be used to determine the earth's magnetic field with high accuracy.

A still more sensitive method of measuring the geomagnetic field takes advantage of an auxiliary resonance-effect. Dehmelt had predicted that, under certain conditions, resonance would not only decrease the over-all intensity of the transmitted light, but would also make it flicker at the radio frequency. The effect was soon observed experimentally by W. E. Bell and the author at Varian Associates in Palo Alto, Calif. It can best be understood in terms of the classical picture of electrons in a magnetic field. On this view the radio waves do not flip the electrons back and forth, but cause them to wobble, or

process, around the field direction at the radio frequency, much as a top precesses around the gravitational field. With respect to the pumping light, the wobbling electrons act as a shutter that is open widest when the axes tip one way and almost closed when they tip the other way [see illustration on page 76]. Since the shutter opens and closes about 350,000 times a second, it produces a flicker at the same rate in the transmitted light. This flicker allows us to "watch" the electrons precess in more than a figurative sense.

When the flickering light strikes the photocell, the electrical output pulsates at the same frequency. Suppose this oscillation is suitably amplified and fed back into the radio-frequency coils around the bulb. Now the circuit can produce its own radio waves. In other words, it is an atomic oscillator. As we have said, the resonant frequency of the electrons depends on the strength of the external field. Hence the frequency of our oscillator, which can be determined very accurately, is a direct measure of the earth's magnetic field.

Magnetometers using pumped rubidium as an atomic oscillator have been built in the author's laboratory. They are more sensitive than any previous instrument, and yet the entire electronic circuit, aside from the lamp, consists of one amplifier. Installed in satellites and rockets, they should be able to measure fields in outer space as weak as a hundred thousandth of a gauss.

The second important application of optical pumping to appear thus far is in atomic clocks and frequency standards. Here the magnetic field that distinguishes the energy levels is supplied not from the outside, but by the nucleus of the atom itself. Until this point in the discussion we have been able to ignore the fact that the nucleus has a spin and a magnetic field. In an alkali atom, such as that of sodium or rubidium, the magnetism of the nucleus and of the outer electron are strongly coupled, and the two precess about an external magnetic field as though they were a single particle. By exciting the atom with microwaves, however, it is possible to uncouple them and make the electron precess about the nucleus. Since the strength of the nuclear magnet is a constant of nature, the frequency at which the electron resonates is precisely determined.

Atomic clocks employing cesium atoms in a beam had been in existence for several years when it occurred to

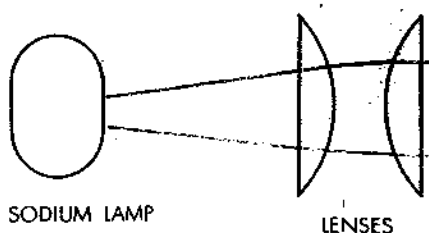
Robert H. Dicke of Princeton University that pumped rubidium vapor in a glass bulb might provide a more convenient and stable standard. However, if the container held only rubidium atoms, their irregular thermal motion would cause Doppler effects, shifting the resonant frequency by a different amount for each atom, and thus smearing out the resonance line. Dicke proposed that the effect might be reduced by adding a buffer gas. (At the time the effectiveness of a buffer in enhancing optical pumping had not been discovered.)

Trying out various gases and using the monitoring technique that Dehmelt had recently developed, a number of workers soon discovered that a buffer did sharpen the resonance line, and that it also shifted the resonant frequency by a small amount. The shift turned out to be directly proportional to the pressure of the buffer gas, and to be upward in light gases such as hydrogen or helium, and downward in heavy gases such as krypton. Because of the pressure shift, an optically pumped atomic clock is not an absolute standard, as is an atomic beam. Instead it is a highly accurate secondary standard that can be precisely tuned, within a narrow range, by adjusting the gas pressure.

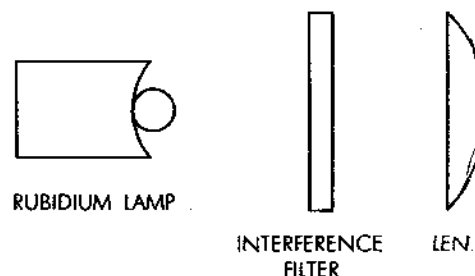
In the past few years a number of workers, notably Peter L. Bender of the National Bureau of Standards, have built optically pumped atomic clocks. Bender's rubidium cell, pumped with light from a rubidium lamp, resonates to a microwave-resonance signal at about 6,834 megacycles per second that is stable to within one part in 100 billion. The device is sufficiently compact to be carried in a satellite, where it could be used to check the gravitational red-shift predicted by the general theory of relativity.

In addition to its practical usefulness, optical pumping offers considerable promise as a research tool. Studies of the pressure shift itself, which is not too well understood, should tell a good deal about the forces between atoms when they collide. A variety of substances other than the alkali metals can be pumped. Experiments on mercury vapor, applying the combined techniques of optical and radio-frequency resonance, have yielded information about details in the optical spectrum that are too fine to be resolved by the best optical spectrograph. Helium atoms, although they do not have the proper structure for optical pumping in their normal state, can be raised to a long-lived, or

metastable, excited state that is amenable to pumping. As shown by Peter Franken of the University of Michigan, low-frequency spectroscopy can then be used to measure the lifetime of the metastable state. Here again, as with sodium, the frequency of the resonance is directly



SODIUM IS PUMPED by light from a sodium-vapor lamp (left). Absorption cell



RUBIDIUM MAGNETOMETER is actually an atomic oscillator. Feedback circuit that

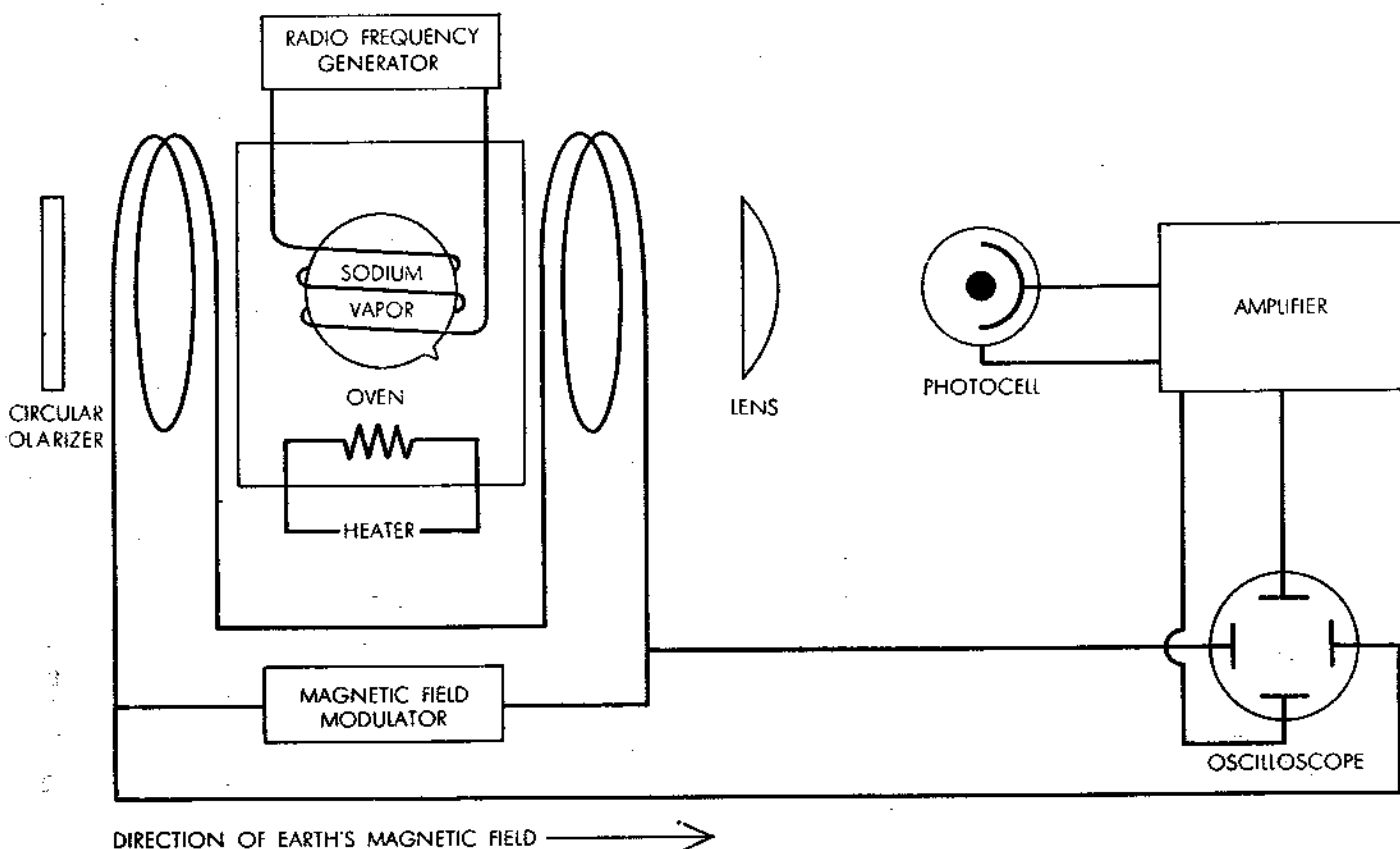
proportional to the strength of the applied magnetic field, and very sensitive measurements of the earth's field can be made in this way.

It is also possible to do low-frequency spectroscopy on vapors that cannot themselves be optically pumped. This is

accomplished by mixing them with atoms of a pumpable substance and taking advantage of a process known as "spin exchange," in which angular momentum is transferred between the materials. Nitrogen and hydrogen have already been investigated, and there is no

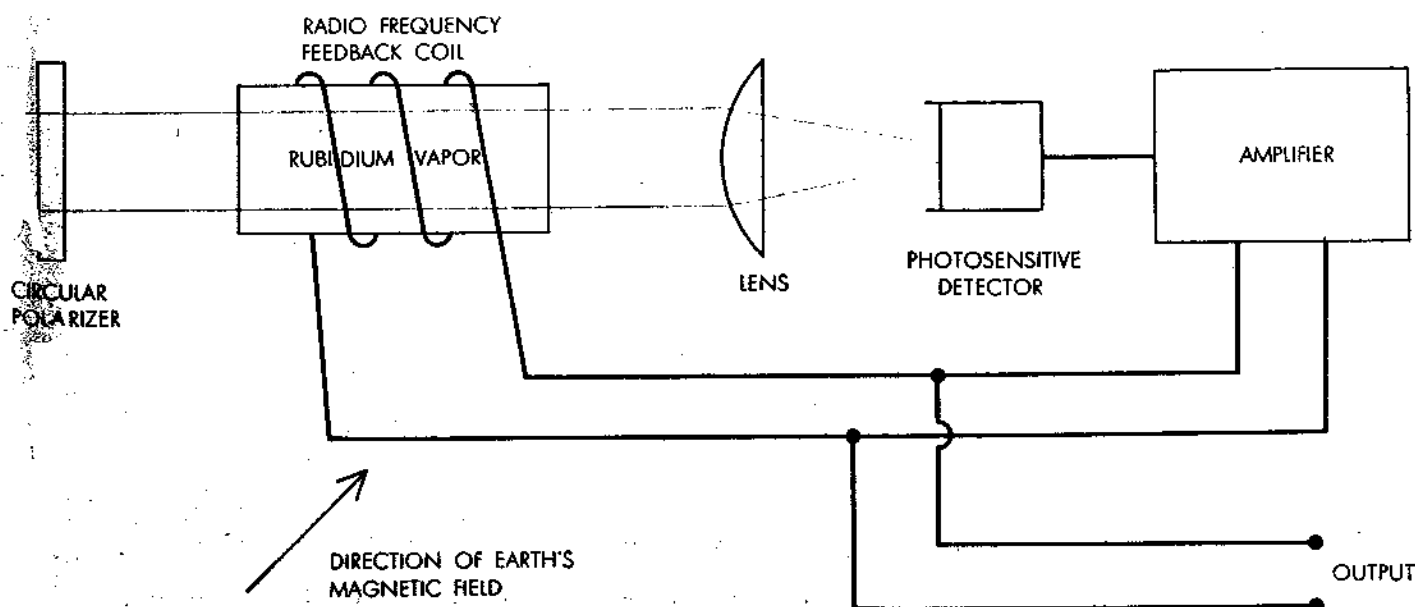
reason why the method cannot be extended to many other vapors.

A particularly interesting development is the recent discovery that optical pumping can be applied to certain solids. It has been known for some time that a ruby, stimulated by a strong white



at center contains sodium that is vaporized by a heater. Light (colored lines) transmitted by cell reaches photocell at right.

Amplified signal from photocell is fed to oscilloscope. Coils at center are used to vary the magnetic field across absorption cell.



connects the photosensitive detector to the amplifier and the coil. The frequency of output signal at terminals at bottom depends on the strength of the earth's magnetic field.

light, will emit a red glow, known as R light, in a very narrow band of wavelengths. Irwin Wieder of the Westinghouse Research Laboratories has successfully used the R light to pump a second ruby in a conventional radio-frequency resonance experiment.

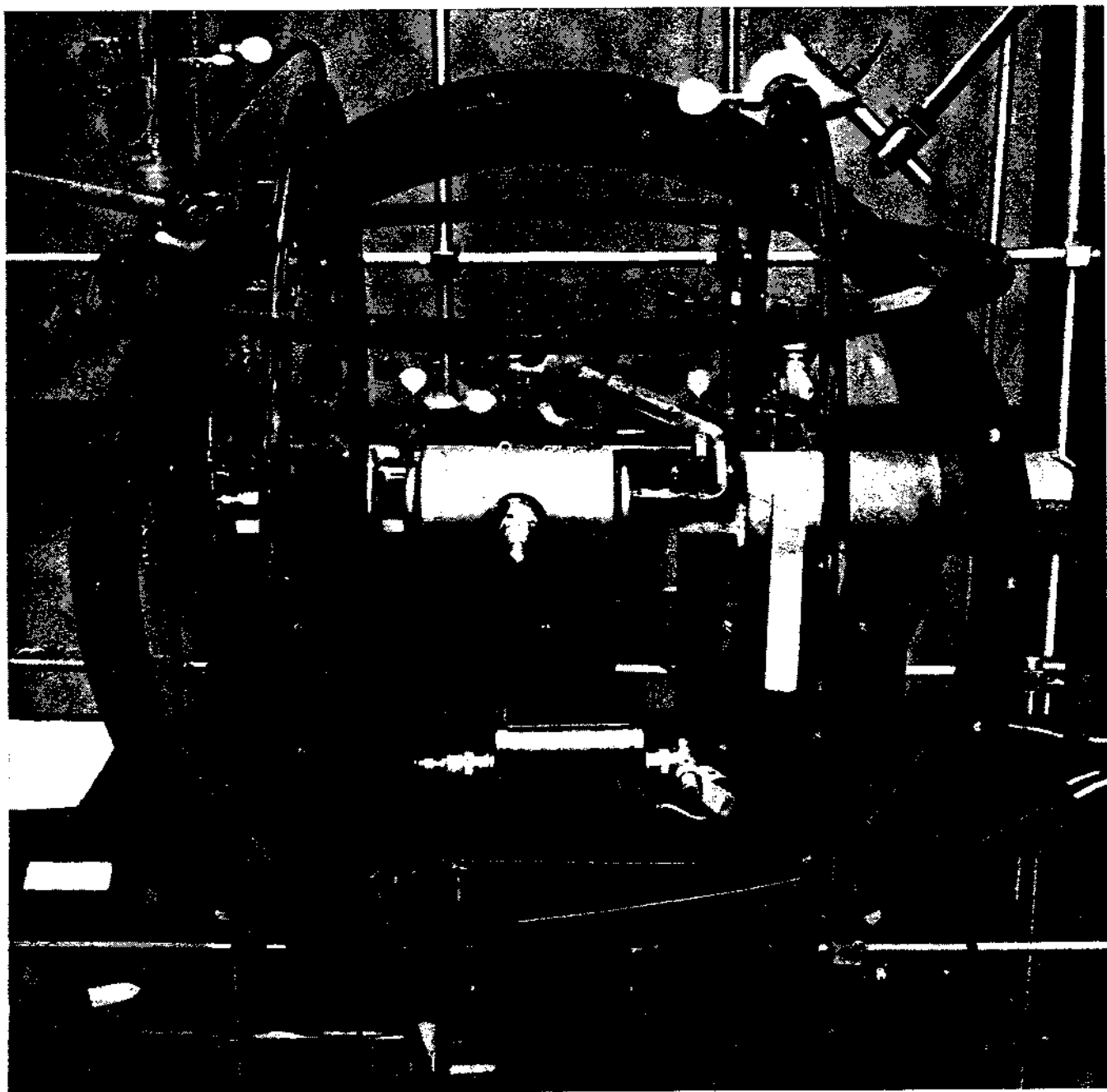
Of much greater potential importance is the first step, in which white light is converted to R light. Again we can picture the process in terms of three energy-levels, but now the large gap is between A and B rather than B and C. Furthermore, C is not a single energy but a rather broad band. Thus the atoms in A can absorb photons of various energies in the white light, and move up to the C band. Thermal motions then cause them

to leak, or rather spill, into the B level almost immediately. From here they fall to the A level far below, emitting light photons of sharply defined energy and frequency.

In this way the energy spread over a wide range of frequencies has been channeled into a narrow band. In effect the energy in this band has been enormously amplified. Moreover if the white light is applied in extremely powerful pulses, then *all* the atoms are pumped at once to level B and fall back to A almost simultaneously. When this happens, a co-operative effect can take place between the atoms that causes them to emit their R photons in unison, or coherently. It is as if the atoms, emit-

ting light waves, are so engulfed by the waves produced by their neighbors that they are forced to radiate synchronously with them. Such coherent radiation in the visible range, now available for the first time, makes possible light devices of unprecedented efficiency. For example, coherent light can be focused into a pencil beam that will not spread more than five feet in 12 miles.

T. H. Maiman at the Hughes Aircraft Company has already observed some degree of coherent emission from a ruby, and he as well as workers at several other laboratories are trying to put R light to practical use. Although a working light amplifier may still be some time away, its prospects now seem excellent.



FREQUENCY STANDARD is tuned by regulating the pressure of buffer gas in a rubidium vapor cell (*inside aluminum cylinder*

at center) while it is still connected to the vacuum system. Rubidium lamp is in tube at right. Large coils control magnetic field.