sults, although fluctuations in airglow were quite severe.

Finally, Tifft *et al.* (*11*) report observing on several occasions a rise, of somewhat more than 0.5 percent of the night sky intensity, at a point approximately 180 degrees from the parent satellite. The duration of the rise is considerably greater than that of the increase noted near the parent satellite, and, again, some doubt attaches to these observations.

Conclusions

Photographic and photoelectric observations show that the West Ford dipole belt was no brighter than had been predicted. If the needles had been released during the dark of the moon the results might have been better; nevertheless, the surface brightness of the belt seems well established.

Unfortunately, no polarimetric observations were made. At best, they would have been extremely hard to make. I hope that any observations made during the early days of the experiment but not yet reported will be sent me in the near future.

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12. On behalf of the West Ford committees of the Space Science Board and the International Astronomical Union, I thank all astronomers who participated in this effort to measure the optical brightness of the West Ford belt. Many persons, both named and unnamed in this article, contributed to the results reported. Dr. John W. Findlay, chairman, and Dr. E. R. Dyer, secretary of the West Ford Committee, as well as the other members of the committee, helped me greatly in preparing this report. The assistance, on many occasions, of numerous Lincoln Laboratory scientists and technicians is likewise gratefully acknowledged.

Free Radicals and Unstable Molecules

Mass spectrometry and electron spin resonance yield insights on energies, reaction mechanisms, and structure.

S. N. Foner

The study of transient chemical species has fascinated researchers for many years. Aside from satisfying an innate curiosity about the mode of formation and subsequent demise of these normally short-lived chemical entities, such studies yield considerable information on chemical processes and contribute to a deeper insight into atomic and molecular structure.

In discussing unstable chemical species it is important to differentiate between intermediates whose lifetime is limited by chemical reaction (for example, free radicals) and those which are intrinsically unstable (for example, electronically excited atoms or molecules).

Components in the first category can be transferred from their hostile environment into a high-vacuum region, where they may be examined for a short time; or they may, in many cases, be stored for an indefinite period by isolation in an inert matrix, and studied at leisure. On the other hand, there is no available means of preventing the radiative decay of components in the second category, and these have to be studied within a time span dictated by the component rather than chosen by the experimenter. The techniques described here have been applied predominantly to free radicals, although some progress has been made in the study of electronically excited species.

Mass spectrometry and electron spin resonance are particularly useful techniques for studying free radicals in chemical reactions. In reactions the concentration of free radicals is generally quite low, simply because radicals are highly reactive. Both mass spectrometry and electron spin resonance are methods of high sensitivity, and both can give unambiguous identification of radicals and can be used for quantitative analysis. The methods are complementary rather than competitive, since the mass spectrometer can handle only gaseous samples, whereas electron-spin-resonance studies are usually carried out on solid or liquid samples. In addition, the types of information derived by these methods, aside from identification, relate to different characteristics of the free radical. Furthermore, mass spectrometry measures all the chemical compounds present in the sample, while electron spin resonance responds only to species with unpaired electron spins.

Application of Mass Spectrometry

The earliest definitive application of mass spectrometry to the study of free radicals probably was the measurement by Hipple and Stevenson (*1*) of the ionization potentials of the methyl and ethyl radicals produced by pyrolysis of lead tetramethyl and lead tetraethyl in a heated quartz tube inside the mass spectrometer. The study of free radicals formed in gas-phase reactions, particularly combustion and thermal decomposition reactions, was pioneered by

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The author is supervisor of the Electronic Physics Group, Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Md.

Eltenton (2), who used a pinhole in a reaction vessel, at relatively high pressure, to leak a molecular beam of reaction products into the ion source of the mass spectrometer, and employed differential pumping to maintain low pressures in the ionization chamber and analyzer. The experimental techniques for free-radical studies were greatly improved and refined by Lossing and his co-workers (3, 4) and used to investigate a large number of free radicals (4). For the study of very reactive species a mass spectrometer with a modulated-molecular-beam sampling system has been developed (5).

Free radicals and unstable compounds have been observed in (i) heterogeneous reactions, (ii) thermal decomposition reactions, (iii) flame and combustion reactions, (iv) photolytic reactions, and (v) electrical discharges. The objectives of the studies range from detection of a suspected free radical to detailed analysis of the role of a radical in the kinetics of a chemical reaction.

A mass spectrometer with an electron-multiplier detector should be capable of detecting a component producing a partial pressure of about 10^{-15} torr (a torr = 1 mm-Hg) in the ion source (6). Since ion-source pressures of 10^{-5} torr or higher are generally used in analytical work, a component present in a concentration as low as 1 part in 10^{10} should, in principle, be readily detectable.

If free radicals could be handled as ordinary molecules are, and if interferences from background or extraneous reactions could be avoided, this sensitivity would also apply to the detection of free radicals. Unfortunately, free radicals are too easily destroyed in conventional gas-handling systems, and interference from background is the rule rather than the exception, so the effective sensitivity of the mass spectrometer is lowered by a few to several orders of magnitude. However, the available sensitivity for gaseous systems is still considerably higher than the sensitivity attainable by other methods.

When the concentration of free radicals is sufficiently high, analysis can be carried out at high electron energy (50 to 75 ev) according to the principle of detailed material balance, the free radical being treated just like any other component. In the cases discussed here, the concentrations are too low for this method to be applicable and extensive use is made of the discriminating action of low-energy electrons.

Appearance Potentials

Measurements of electron energies at which particular ions first appear are called "appearance potentials," and are extremely important in the detection and identification of free radicals. The appearance potential $A(R_1^+)$ of the R_1^+ ion from the molecule R_1R_2 formed by the ionization process

$$\mathrm{R_1R_2} + e \rightarrow R_1^+ + R_2 + 2e \qquad (1)$$

is given by

$$A(R_1^+) \geqq I(R_1) + D(R_1 - R_2) \qquad (2)$$

where $I(R_1)$ is the ionization potential of the R_1 radical; $D(R_1{-}R_2)$ is the dissociation energy of the $R_1{-}R_2$ bond; and the inequality includes the possibility that the fragments may possess excess kinetic or excitation energy, or both. Since bond-dissociation energies are typically of the order of a few electron volts, it is possible, by using electron energies well below the appearance potential of the R_1^+ ion from the dissociative ionization process, to detect the presence of a small concentration of the radical R_1 in a large excess of compounds of the type R_1R_2. In many cases it has been established that excess energy is absent in the ionization process; in these cases relation 2 becomes an equality, and, therefore, a measurement of the ionization potential of a radical subtracted from its appearance potential from the molecule R_1R_2 gives a direct determination of the $R_1{-}R_2$ bond-dissociation energy.

A complicating factor in these measurements arises from the fact that the electrons are emitted from a hot filament and, therefore, do not possess a discrete energy determined by the accelerating potentials but have, additionally, a Boltzmann distribution of energies characteristic of the filament temperature. As a consequence, appearance-potential curves do not show sharp discontinuities at the energy for onset of ionization but, instead, are rounded, and below the appearance potential exhibit an exponential drop-off with decreasing energy. Several methods, some empirical and others highly sophisticated, have been developed for analyzing such data.

A particularly simple example, illustrating detection and determination of the ionization potential of a free radical, is shown in Fig. 1. The hydroxyl radical was produced by an electrical discharge in water vapor. An energy-scale shift of 2.59 electron volts is required to match the ionization curve for OH with the ionization curve for argon, used as an internal standard with spectroscopically known ionization potential, $I(\mathrm{Ar}) = 15.76$ ev; thus we obtain the value $I(\mathrm{OH}) = 13.17$ ev. The appearance potential of the OH^+ ion from $\mathrm{H_2O}$ was also measured in the experiment and found to be 18.19 ev (7). From these values, $D(\mathrm{H{-}OH}) = A(\mathrm{OH}^+) - I(\mathrm{OH})$ may be obtained: 5.02 ± 0.15 ev $= 115.8 \pm 3$ kcal/mole. Combining this result with thermochemical data, one obtains $D(\mathrm{O{-}H}) = 103.1 \pm 3$ kcal/mole, a value which agrees with the more accurate spectroscopic value of $D(\mathrm{O{-}H}) = 101.3 \pm 0.3$ kcal/mole.

Modulated-Molecular-Beam Mass Spectrometry

To solve critical problems in sampling highly reactive free radicals and to discriminate against extraneous background signals, a special mass spectrometer has been designed (5, 8) which employs a modulated collision-free molecular-beam sampling system. The instrument is shown schematically in Fig. 2. Gas from the reaction zone enters through a small circular aperture (typically 0.01 to 0.03 cm in diameter) in a glass or quartz cone ground to a feather edge. Within about 10^{-6} second the gas density is sufficiently reduced to prevent further reaction. Two additional slits collimate the molecular beam and prevent scattered molecules from entering the ion source. The three sections of the molecular-beam system are evacuated by separate high-speed diffusion pumps, so that, in operation, the pressures are typically 10^{-3} torr in the first region, 10^{-5} torr in the second region, and 10^{-7} torr in the ion source. The molecular beam is mechanically modulated at 170 cy/sec by a vibrating reed chopper in the first section, to discriminate against background. The background which concerns us is not only that related to the ultimate vacuum attained by the pumping system, which could be reduced to a very low level by ultrahigh vacuum techniques, but also includes the pressure produced by the molecular beam after scattering, and possibly reacting, in the apparatus. The background is thus a function of the input, and the task of the modulation scheme is to distinguish between incoming-beam molecules and all others.

Ions produced by electron impact in the ion source are accelerated, pass through a magnetic analyzer, are accelerated by a few thousand electron volts, and then impinge on a 13-stage beryllium-copper electron-multiplier detector which has a current gain of about 10^6. Pulses from the electron multiplier are amplified, shaped, and sent through an electronic switch which is synchronized with the beam chopper. The electronic switch directs the pulses to two electronic counters, one of which records ions, N_1, when the beam chopper is open, the other of which counts ions, N_2, when the beam chopper is closed. The difference between the two ion counts, $N_1 - N_2$, is the signal produced by the molecular beam, while $(N_1 + N_2)^{1/2} = \sigma$ is approximately the standard deviation of the measurement. The deleterious effect of a high background is evident from the expression for σ. With a high background count the integration time necessary to raise the net count above the fluctuation level of the background may become inconveniently long. For example, with an input beam corresponding to 10 ions per second in a background of 100 ions per second, it would require 1 second for probable detection and 100 seconds to get a value reliable to within 10 percent. If the background were increased to 10,000 ions per second, the times would become 100 seconds for probable detection and 10,000 seconds, or almost 3 hours, for a measurement with an uncertainty of 10 percent. This illustration also emphasizes the advantage of working at low electron energies, since this results in a large reduction in background intensity.

Under favorable conditions this instrument has measured ion intensities as low as 0.01 ion per second, an intensity which corresponds to a partial pressure of about 10^{-16} torr in the ion source. The lowest reported concentration at which a free radical has been observed is about 1 part in 10^7, attained in the case of the hydrazino (N_2H_3) radical (*9*).

Hydrogen-Oxygen System

The hydrogen-oxygen system has been the subject of several thousand investigations by diverse methods. Although there are only nine known neutral chemical entities in this system—namely, H, H_2, O, OH, H_2O, O_2, HO_2, H_2O_2, and O_3—their study presents severe challenges to mass spectrometry. In contrast to organic free radicals such as CH_3 or C_2H_5, which can survive many wall collisions in a mass spectrometer, the oxygen-containing radicals O, OH, and HO_2 may be destroyed by single, or perhaps only a few, collisions with the walls of the ion source. This does not imply that these radicals are intrinsically much more reactive than organic free radicals, but implies simply that metal surfaces comprising the ion-source electrode structure are excellent catalysts for the destruction of simple oxygen-containing radicals. Indeed, until recently (*10*), even the mass spectrum of hydrogen peroxide was quite uncertain because of serious interferences from its own decomposition products.

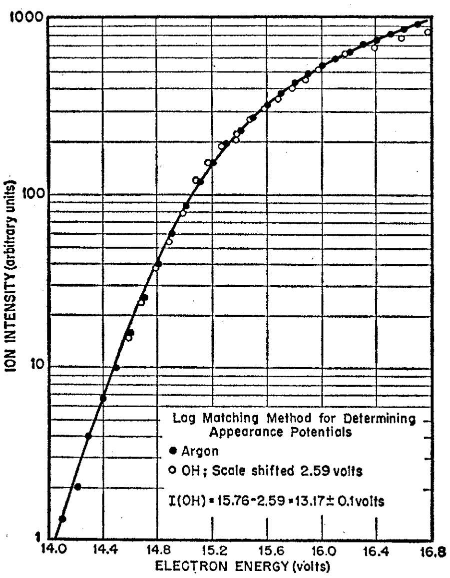


Fig. 1. Determination of the ionization potential of the hydroxyl free radical by electron impact.

The hydroperoxo (HO_2) radical, an important intermediate in theories of oxidation, combustion, and explosions, has been the target of investigations by mass spectrometry, optical spectroscopy, microwave spectroscopy, and electron spin resonance. Although the HO_2 radical has been detected in mass-spectrometer studies by at least three independent groups (*11*) and its ionization potential and relevant thermochemical energies have been measured (*8*), it has successfully eluded positive identification by other methods. Several reactions were found (*8*) to produce hydroperoxo radicals: (i) reaction of H atoms with O_2; (ii) reaction of H atoms with H_2O_2; (iii) reaction of O atoms with H_2O_2; (iv) reaction of OH radicals with H_2O_2; (v) ultraviolet photolysis of H_2O_2; and (vi) electrical discharge in H_2O_2.

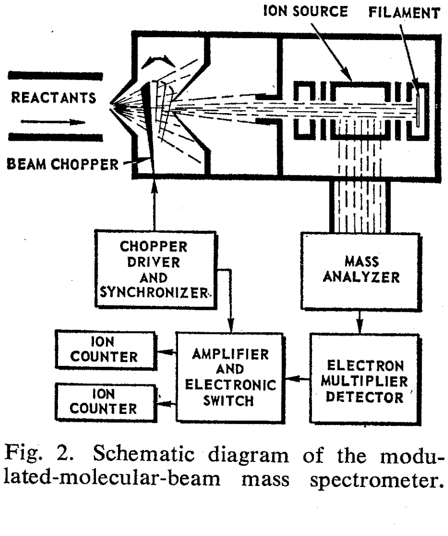


Fig. 2. Schematic diagram of the modulated-molecular-beam mass spectrometer.

An electrodeless electrical discharge of low power in a high-speed stream of H_2O_2 vapor was found to be an excellent source of HO_2 radicals. The technique is one of rather general applicability to the generation of free radicals and other unstable intermediates. The apparatus is extremely simple, consisting of a quartz or glass tube around which are wrapped two wire-loop electrodes, spaced perhaps a centimeter apart, which are connected to a radio-frequency generator (5 to 10 Mcy/sec is a convenient frequency range). The idea here is to set up a miniature "chemical factory" in which the electrical discharge decomposes some of the input gas to produce an assortment of ions, radicals, and excited molecules which can react immediately with the undecomposed parent compound, and by using high-speed gas flow to get any interesting products out of the reactor before they are destroyed.

The electrical discharge products from H_2O_2 observed within 1 millisecond of H_2O_2 decomposition are H, H_2, O, OH, H_2O, O_2, HO_2, H_2O_2, and O_3; they comprise a complete catalog of the known components in the hydrogen-oxygen system. Within a few milliseconds the system becomes considerably simplified, the predominant radical component being the hydroperoxo radical. The concentration of HO_2 as a function of H_2O_2 decomposition at 0.003 and 0.006 second is shown in Fig. 3. The production of HO_2 is seen to be an insensitive function of H_2O_2 decomposition over the range from 5 to 30 percent. The principal reactions involved in HO_2 production are

$$H_2O_2 \rightsquigarrow 2OH$$

and

$$OH + H_2O_2 \rightarrow HO_2 + H_2O.$$

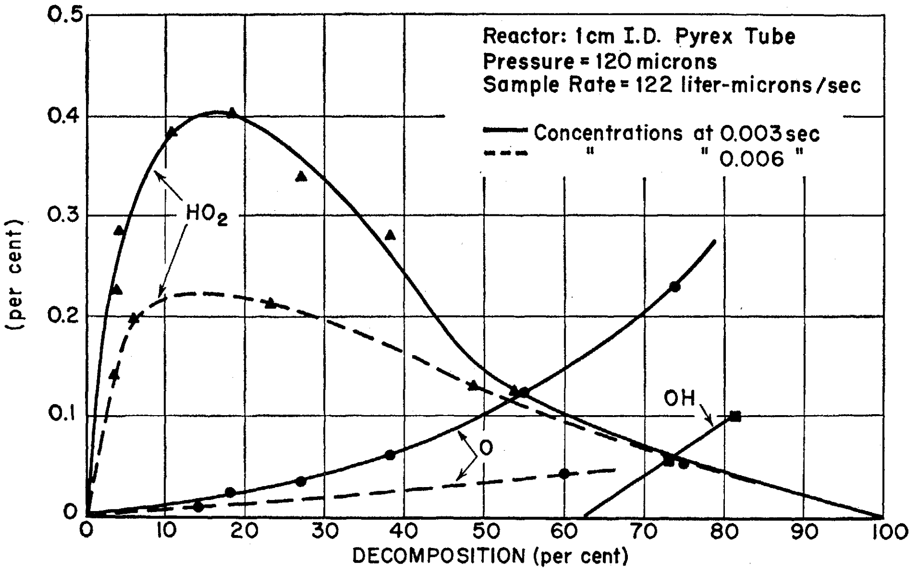


Fig. 3. Production of HO_2 by an electrical discharge in hydrogen peroxide.

The absence of OH radicals at 0.003 second for less than 60-percent decomposition indicates that the reaction of OH with H_2O_2 is extremely rapid. Oxygen atoms formed in the discharge are at least 100 times less reactive than OH radicals, a finding confirmed by observation of O atoms long after OH has disappeared. At low decomposition (5 to 10 percent), the system is a relatively pure source of HO_2 radicals flowing in a stream of nonreactive gas consisting of H_2O_2 with small amounts of H_2, O_2, and H_2O.

The collisional efficiency for the recombination of HO_2 radicals in the gas phase by the reaction

$$2HO_2 \rightarrow H_2O_2 + O_2$$

has been indirectly inferred from various experiments. The spread in estimates is considerable, ranging from 10^{-6} to unity. This reaction, which is of interest in theories of explosion limits, has been studied in a flow system by means of mass spectrometry, and although there are some complications caused by heterogeneous reactions and the study has not been completed, it is clear that neither of the extreme estimates is valid and that the collisional efficiency of the reaction is actually about 1 percent.

Unstable Compounds

A few years ago, while attempting to generate the imine (NH) radical in the decomposition of hydrazoic acid (HN_3), we discovered diimide (N_2H_2), the parent molecule of the azo-compounds (*12*). This was surprising in two respects; first, we would not, a priori, have attempted to synthesize N_2H_2 from HN_3; second, it was known (*13*) that this compound, if it existed, was quite unstable, and all previous attempts to prepare it had given nitrogen and ammonia. One thing that this and subsequent experiments accomplished was the filling in of a number of disturbing blank spaces in the chemical catalog of nitrogen compounds. Positive identifications were made of the previously unobserved compounds diimide (N_2H_2), triazene (N_3H_3), tetrazene (N_4H_4), and methylimide (HN_2-CH_3).

The electrodeless-electrical-discharge, "chemical-factory" system, used so successfully in the HO_2 work, was also used in most of these studies. The production of diimide and triazene by an electrical discharge in hydrazine is plotted in Fig. 4. There is an obvious similarity between the curves for production of these compounds and that for production of HO_2 from H_2O_2, shown in Fig. 3. A noteworthy feature is the high conversion efficiency of N_2H_4 into N_2H_2 at low decomposition—approximately 30-percent conversion at 5-percent hydrazine decomposition. In addition to the unstable molecules, the electrical discharge generated a number of free radicals. In the case of hydrazine, the radicals observed were H, NH_2, and N_2H_3 (*14*). The hydrazino (N_2H_3) radical is very easily detected at low concentrations (as noted earlier) because it has a low ionization potential (7.88 ± 0.1 ev) and at this energy there is virtually no background to contend with.

In view of the current feverish investigation of compounds of the rare gases, it would be remiss not to comment on this subject, even though there may be a question as to whether these compounds are sufficiently unstable to fall within the scope of this article. Some of these compounds are so stable that they can be crystallized and stored indefinitely at room temperature (*15*). Mass spectrometric studies (*15, 16*) carried out with a conventional time-of-flight mass spectrometer confirmed the existence of the compound XeF_4 and gave the first indication of the existence of the compound XeF_2; in these studies the presence of xenon oxyfluorides was noted and some evidence of the presence of XeF_6 was obtained. A mass spectrum of krypton fluoride (KrF_2) has also been reported (*17*). Thus far, no studies of fluorine-rare gas systems by means of free-radical mass spectrometers, in a search for

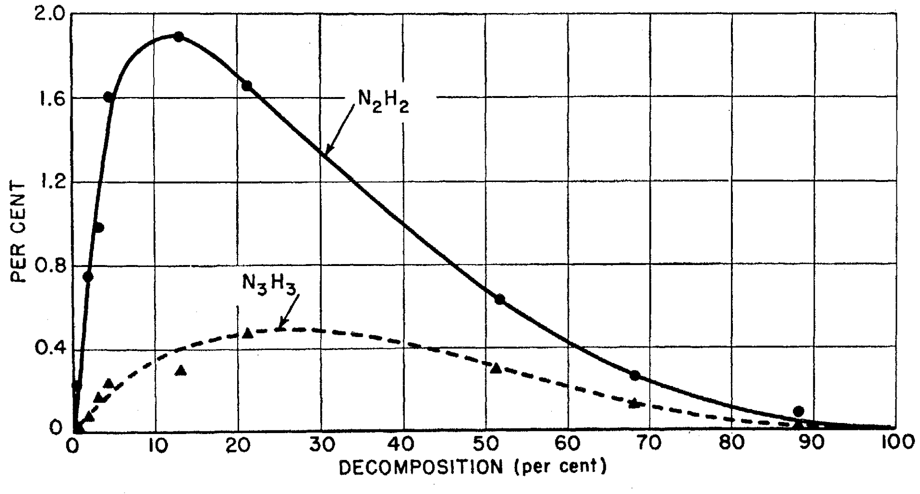


Fig. 4. Production of diimide and triazene by an electrical discharge in hydrazine.

highly unstable rare-gas compounds, have been reported. This is an area of research which clearly should be explored (*18*).

Metastable Atoms and Molecules

The same instrumentation that is used for studying free radicals is used for studying excited-state atoms and molecules. The time needed for a typical molecule, such as N_2, to traverse the 10 centimeters from the entrance slit to the ionization chamber is about 200 microseconds. Only electronically excited species whose transitions to lower states are highly forbidden will not have decayed in transit. The examination of these metastable species by mass spectrometry is useful as a complement to optical spectroscopic studies, which are very insensitive in this application because of the low transition probabilities.

Electrical discharges in nitrogen and nitrogen-helium mixtures have been used to generate significant concentrations of metastable nitrogen atoms and molecules (*19*). Consider the case of the N atom, whose energy-level diagram, given in Fig. 5, shows the two long-lived metastable states, ^{2}D and ^{2}P, whose transitions to the ^{4}S ground state are strictly forbidden for dipole radiation but are slightly permissible for electric-quadrupole and magnetic-dipole radiation. The radiative lifetimes of the ^{2}P and ^{2}D states are 12 seconds and 9.4×10^4 seconds, respectively. Atoms in these states have different ionization potentials, and this difference is used as the key in analyzing the data. If a mixture of about 1 percent of N_2 in helium is observed within 10^{-3} seconds after leaving an electrical discharge of high power, the nitrogen ionization curve shown in Fig. 6 is obtained. The dashed curve gives the ion current for the unexcited N(^{4}S) atoms. The synthetic curve, which fits the data rather well, was calculated on the assumption that the numbers of N atoms in the ^{2}D and ^{2}P states were, respectively, 17 and 6 percent of the ^{4}S concentration. In a pure N_2 discharge the relative concentrations of metastable atoms were lower by a factor of about 25. These metastable atoms are observed only within a millisecond or so after production, a finding which indicates that they are rapidly deactivated by wall collisions.

Metastable N_2 molecules are also produced in these electrical discharges. The situation is considerably more complicated than in the case of N atoms and involves vibrational excitation of ground-state molecules, electronic excitation of molecules, and vibrational excitation of electronically excited molecules. The data clearly indicate that, among other things, a substantial number of the N_2 molecules are in the $A^3\Sigma_u^+$ state, which is 6.169 electron volts above the ground state, and that several of the vibrational levels of this state are populated to a significant extent. This is not surprising, since radiative emissions involving these levels have been observed in the nitrogen afterglow.

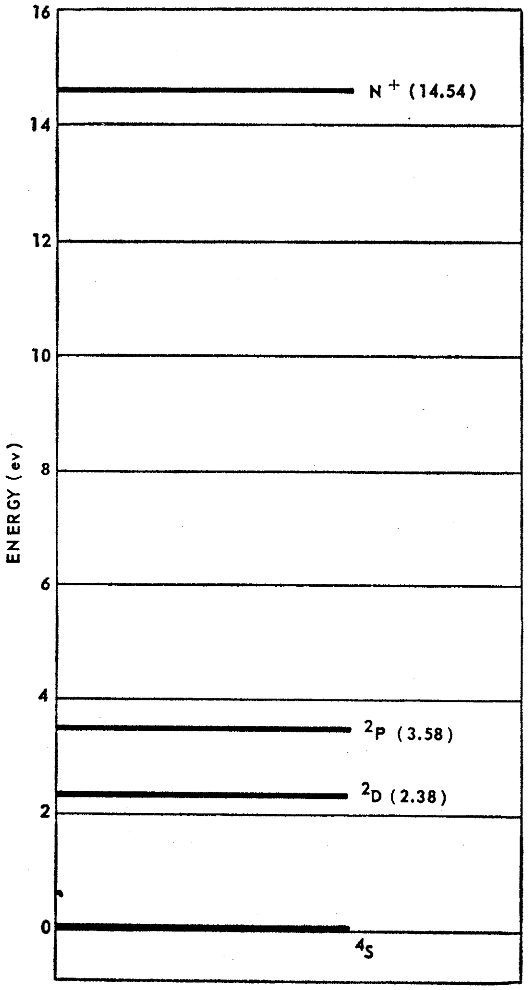


Fig. 5. Diagram of energy levels of atomic nitrogen, showing locations of metastable states.

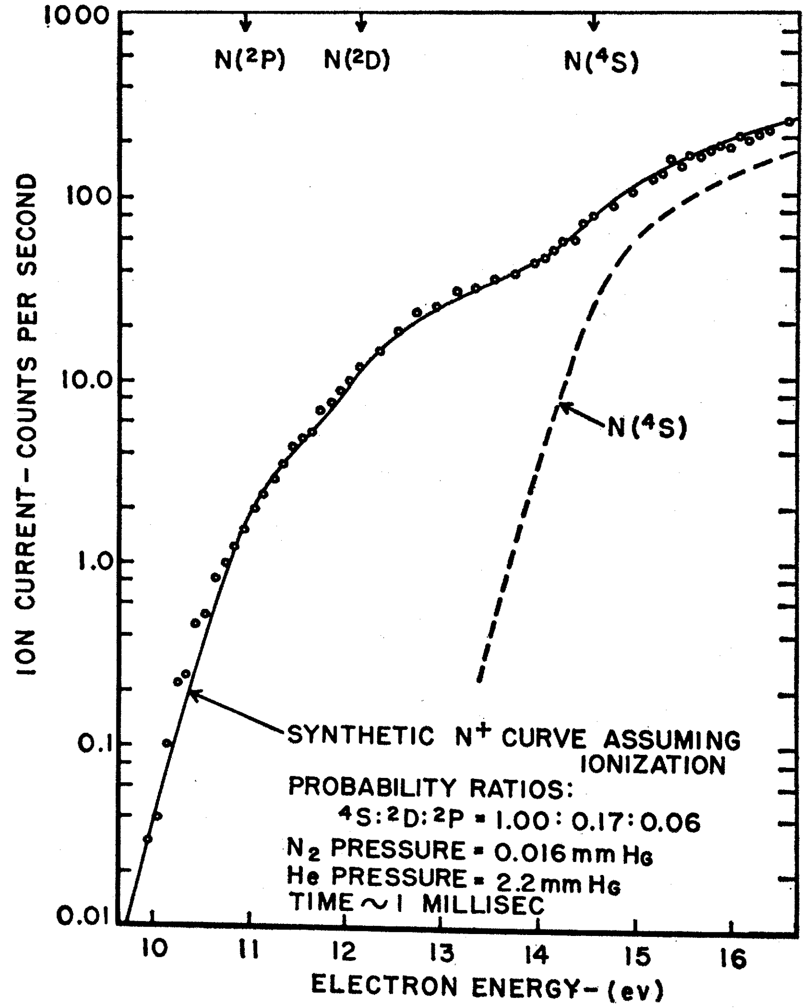


Fig. 6. Plot of N(^{4}S), N(^{2}D), and N(^{2}P) atoms from an electrical discharge in a nitrogen-helium mixture.

Electron Spin Resonance

A free radical may be defined as a molecular fragment formed by rupture of a covalent bond in a stable molecule; it is characterized by the presence of one or more unpaired electrons. An electron possesses a spin, and associated with the spin there is a magnetic moment. In the electron-spin-resonance method, a free radical is examined by studying the energy absorption which depends on the electron spin of the free radical.

In a uniform magnetic field the electron spin is allowed only two orientations, parallel or antiparallel to the field, and, neglecting for the moment interactions with atomic nuclei and other electrons in the radical, the energy separation of the corresponding energy levels is $g\beta H$, where β is the Bohr magneton, H is the magnetic field, and g is a proportionality constant called the electronic g-factor which, for a completely free electron, has the value 2.0023. Transitions between the two states can be induced by electromagnetic radiation at the ferquency ν (or energy $h\nu$, where h is Planck's constant), given by the resonance condition

$$h\nu = g\beta H \tag{3}$$

If magnetic nuclei are also present (as is usually the case), there is an interaction between the electron spin and the nuclear spins, giving rise to what is called hyperfine splitting of the electronic energy levels. Since nuclear magnetic moments are about a thousand times smaller than the electronic moment, the hyperfine splittings are ordinarily a small fraction of the electronic splitting. A nucleus with spin I can assume $2I + 1$ orientations in a magnetic field, giving rise to $2I + 1$ resonance lines. A schematic representation of the energy-level splittings and the allowed transitions for a single nucleus with spin $I = 3/2$ is shown in Fig. 7. Here the allowed electron-spin-resonance transitions ($\Delta M_I = 0$, $\Delta M_S = \pm 1$) are given by

$$h\nu = g\beta H + AM_I \tag{4}$$

where A is the hyperfine interaction constant and M_I, the magnetic quantum number, takes the $2I + 1$ allowed values $I, I - 1, \ldots, -I$. If several magnetic nuclei are present, the situation is somewhat more complicated, since the electron experiences an interaction with each nucleus (the magnitude of which is proportional to the product of the electron density at the nucleus and the nuclear moment) and the spectrum is the result of a superposition of the hyperfine splittings for each nucleus. The complexity of such a spectrum is not necessarily undesirable since it often affords one of the best and most definitive means of identifying the radical. If the lines are well resolved, the spectrum can be used as the radical's fingerprint.

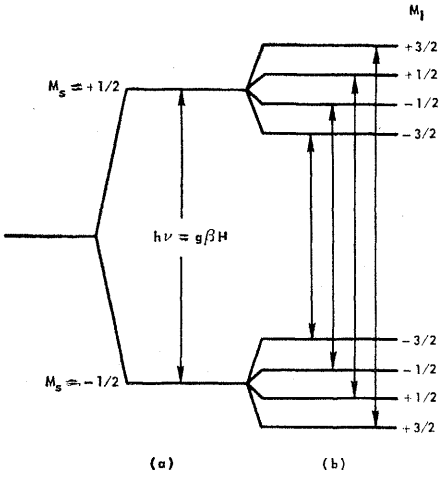


Fig. 7. Splitting of electron energy levels by a magnetic field. (*a*) Effect of electron spin only; (*b*) effect of adding a nucleus with spin $I = 3/2$. Allowed transitions are indicated by arrows.

In addition to the isotropic interactions (interactions independent of the orientation of the radical) thus far considered, there are also anisotropic interactions, which play important roles for radicals trapped in solids or highly viscous media. The hyperfine splitting for a radical that is not spherically symmetric will depend on the orientation of the radical with respect to the magnetic field. For the case of a radical with electron charge distribution axially symmetric with respect to the symmetry axis of the radical (a situation characteristic of a large class of radicals), the electron-spin-resonance transition frequencies for a single nucleus are given approximately by the expression

$$h\nu = g\beta H + AM_I + BM_I\,(3\cos^2\theta - 1) \tag{5}$$

where A is the isotropic hyperfine interaction constant, B is the anisotropic hyperfine interaction constant, and θ is the angle between the magnetic field and the symmetry axis. In the case of radicals in gases or liquids, the radicals can average out the anisotropic term by rapid reorientation, such as tumbling, so that sharp-line spectra are obtained. Spherically symmetric atoms and small radicals that can execute free rotation in solids do not suffer from anisotropy, and their spectra are relatively simple. However, in the case of polyatomic radicals randomly oriented in rigid solids, anisotropy often produces considerable broadening and distortion of the resonance lines (in some cases the broadening exceeds the line separation), and interpretation of the spectra requires extremely careful analysis.

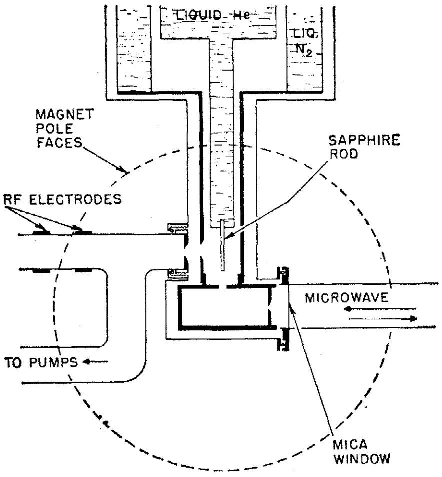


Fig. 8. Schematic diagram of low-temperature cell for experiments on trapped free radicals. The cell can be converted for use in photolytic experiments by replacing the slit at the end of the radio-frequency discharge tube with a suitable window.

In electron-spin-resonance experiments the spectrum is actually observed by sweeping the magnetic field while keeping the microwave frequency ν constant (that is, locked to the cavity resonance). From Eqs. 3, 4, and 5 it may be seen that this procedure is equivalent to sweeping the frequency at constant field. Also, the modulation scheme generally used for detection results in presentation of the resonance lines as derivatives of the absorption.

Electron-spin-resonance studies have been made of a diverse assortment of free-radical systems, including radicals in low-temperature solids, in solutions, in electrolytic reactions, in single crystals, in glasses, and in biological tissue. The observations furnish information on many facets of the subject, including the identity of the radicals, the molecular geometry or structure of radicals, interactions of radicals with environments, chemical kinetics (mechanism, rates of reaction, and activation energies), and energy transfer mechanisms. Instead of attempting to review the entire field, I shall give a few examples which show the type of information that can be derived from the experiments, and indicate some of the problems which have been encountered.

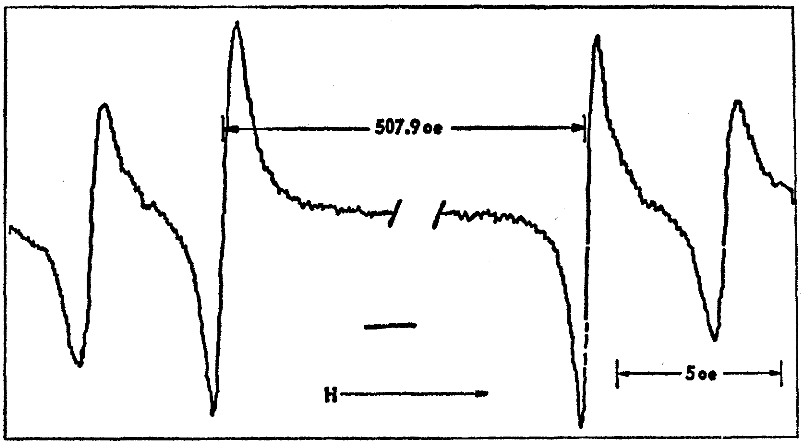


Fig. 9. Electron-spin-resonance spectrum of H atoms produced by photolysis of water in argon at 4.2°K.

Apparatus for Low-Temperature Experiments

A versatile apparatus (*20*) which has been used extensively at the Applied Physics Laboratory, Johns Hopkins University, for studying trapped free radicals is shown in Fig. 8. The sample is prepared by deposition of molecular beams onto a sapphire rod cooled by liquid helium. For trapping radicals from electrical discharges or other gas sources in selected matrices, two additional slits (matrix slits), positioned 45 degrees from the plane of Fig. 8, are used; this arrangement permits simultaneous deposition of sample and matrix material in any desired ratio. Photolytic experiments are carried out by using a radio-frequency discharge in hydrogen as a source of ultraviolet and by replacing the slit at the end of the discharge tube with a window of material having a suitable ultraviolet-transmission limit [such materials are lithium fluoride (1000 Å); sapphire (1450 Å); quartz (1800 Å); Vycor (2400 Å)]. The sample for photolysis, consisting of a mixture of photosensitive material and matrix gas, is deposited by means of the matrix slits and is irradiated with ultraviolet during or after deposition, or at both times. After the sample has been prepared, the entire liquid-helium assembly is lowered by a bellows arrangement to position the sapphire rod in the center of the microwave cavity, which is cooled by liquid nitrogen. The effect of temperature on the resonance spectra is observed by removing the liquid helium and allowing the sample to warm up at a rate controlled by an adjustable heat leak.

Atomic Species: Hydrogen Atoms and Alkali Atoms

The hydrogen atom is the logical starting point for a discussion of the study of free radicals by electron spin resonance. The H atom is the simplest free radical, and its hyperfine structure has been both theoretically calculated and experimentally measured with extremely high accuracy. When H atoms from an electrical discharge are trapped in various matrices, such as solid H_2, Ar, Kr, and CH_4, at liquid-helium temperature, a doublet spectrum is observed, as expected for a nucleus with spin $I = \frac{1}{2}$, with the spectral lines rather close to the positions calculated for free H atoms. The deviation of the hyperfine coupling constant A from the value for the atom in the free state varies from −0.2 percent for H_2 to −0.7 percent for CH_4 in the foregoing examples (*20*). The value of the hyperfine coupling constant is a direct measure of $|\psi_0|^2$, the electron density at the nucleus, and, therefore, these small deviations provide significant information on the interactions of the trapped atom with its environment.

Interestingly enough, when H atoms are produced photolytically in inert matrices, the spectra very often consist of two closely spaced doublets (*21*). An example is given in Fig. 9, which is the spectrum obtained by photolysis of water in solid argon at 4.2°K. One of the doublets has a line-to-line separation of 507.9 oersteds (a value which is identical with that obtained for deposited H atoms), corresponding to a coupling constant A which is 0.46 percent *less* than the value for the free atom. The other set of lines, with separation of 516.1 oersteds, has a coupling constant 1.15 percent greater than the value for the free atom. The two doublets clearly arise from the subjection of H atoms to different highly reproducible matrix fields, and they suggest trapping of the atoms in two different crystalline sites. The spectra have been interpreted experimentally (*21*) and theoretically (*22*) as evidence for H atoms in substitutional and octahedral sites in the face-centered cubic argon lattice. The deposited atoms apparently are readily trapped in substitutional sites, which are about 3.75 Å in diameter, but are unable to get into the smaller octahedral sites, which, on a hard sphere model, are only 1.55 Å in diameter. The photolytically generated atoms, however, have sufficient initial kinetic energy to squeeze into the more cramped sites, as well as to occupy the larger substitutional sites. The shifts in the hyperfine coupling constant can be explained (*22*) as the sum of two effects: the van der Waals attraction by the matrix atoms, which tends to expand the electron wave function of the H atom and thereby reduce the density at the nucleus, and the Pauli exclusion forces, which tend to push the electron wave function away from the matrix atoms. In a fairly large lattice site the long range van der Waals forces predominate and there is a negative A shift, while in a cramped lattice site the Pauli forces are larger, resulting in compression of the electron wave function and a positive A shift.

Multiple-trapping-site phenomena have also been observed for H atoms in krypton and xenon. In the case of neon, H atoms have been trapped in only one site, and this only in photolysis experiments. Efforts to deposit H atoms in neon have not been successful.

The perturbations produced by the environment on the electron-spin-resonance spectra of trapped H atoms can be measured with high precision, and this suggested the deliberate introduction of H atoms in various crystals as a means of probing the crystal fields. The H atom is sufficiently small to diffuse into many lattices. The recent experiments of Hall and Schumacher (*23*) on the electron spin resonance of an H atom trapped at a body-center position in a fluorite (CaF^2) lattice have shown that this type of analysis can, in fact, be carried out to a considerable degree. They resolved the interactions of the H atom with its eight nearest-neighbor fluorine nuclei, determined the interaction with the 24 next-nearest fluorine nuclei in the second shell, and observed indications of interactions with fluorines in the third shell.

An obvious extension of the study of trapped H atoms is the examination of the alkali atoms (Li, Na, K, Rb, and Cs). These also have spherically symmetric $^2S_{1/2}$ ground states. There are, however, some notable differences. The alkali atoms are larger than the H atom, have higher polarizabilities, and possess a variety of spins, thus affording greater scope for the study of environmental perturbations on trapped radicals. The spectra of the five alkali atoms have been examined in solid argon, krypton, and xenon (*24*). The source of alkali atoms was a heated oven containing the alkali metal (the oven replaced the electrical charge tube in Fig. 8).

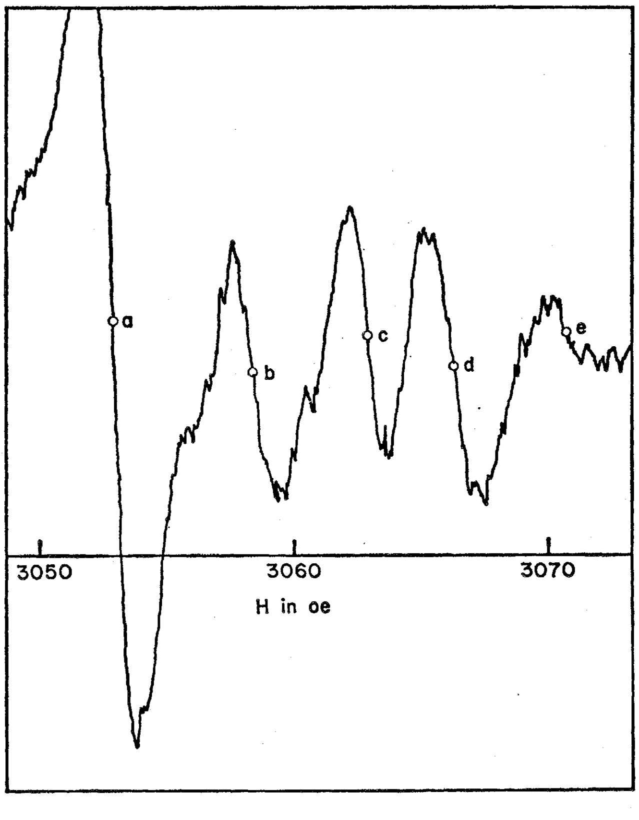
In gross respects, the alkali spectra followed the theoretically predicted patterns. The most striking feature observed was the general occurrence of multiple-line structure at each of the expected hyperfine-line positions. An example of this is shown in Fig. 10, which is a tracing of one of the four hyperfine components ($M_I = 1/2$) of the spectrum of Na^{23} ($I = 3/2$) in argon. It may be readily seen that there are five components in the spectrum. Warm-up experiments showing the sequential disappearance of the lines have demonstrated that the spectrum is produced by Na atoms in several discrete trapping sites.

The number of trapping sites observed depended on the alkali-matrix combination and varied from as few as two, for the case of lithium in argon, to as many as seven, for the case of rubidium in argon. The atoms responsible for the lines are in essentially isotropic, highly reproducible environments—a finding which would appear to exclude the possibility of trapping at crystalline defects, at surface sites, or in amorphous regions. The matrix perturbations on the electron-spin-resonance spectra were similar to, but considerably larger than, the corresponding effects for trapped H atoms. This result was expected, in view of the more extended wave functions of the alkali atoms and the consequently larger dispersion and exchange energies involved. However, the occurrence of high-order multiple trapping sites is rather mysterious, and no adequate explanation of this phenomenon has been proposed.

Polyatomic Free Radicals

Although the electron-spin-resonance spectra of polyatomic free radicals in solids are frequently complicated by anisotropic effects, as mentioned earlier, in the case of small radicals the hyperfine anisotropy may be averaged to zero by rotation of the radical in the matrix. For example, the CH_3 radical at 4.2°K in matrices of H_2, Ar, and CH_4 gives a spectrum of four equally spaced lines (as is expected for three equivalent protons having spins $I = 1/2$) with line-to-line separation of 22.9 oersteds (*20*). From the sharpness of the lines (the width is only 1.4 oersteds in H_2) it is concluded that the radicals are freely rotating in these matrices.

The spectrum of another small radical, NH_2, is shown in Fig. 11. The NH_2 radical can be obtained by means



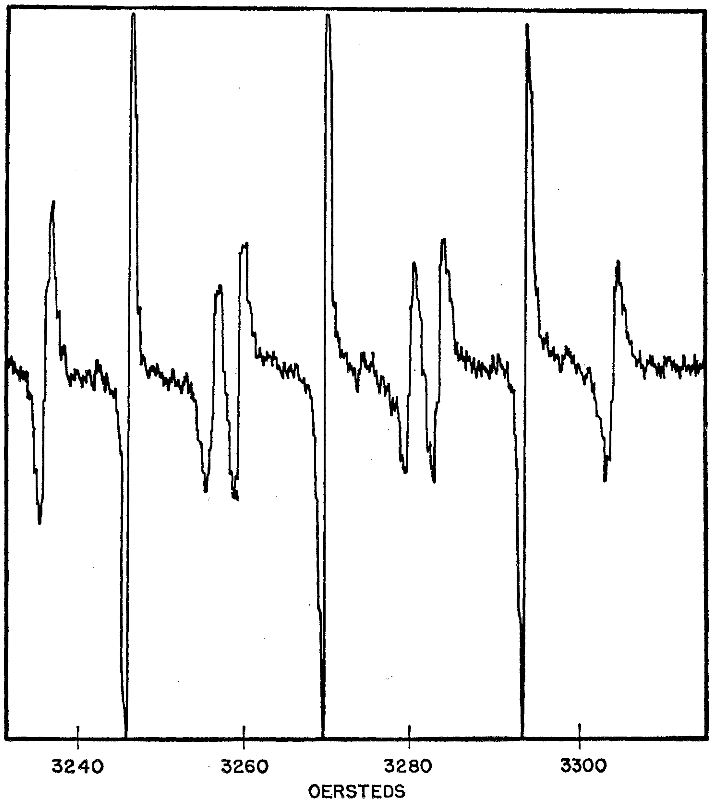
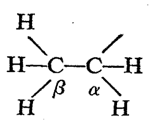


Fig. 10 (left). Electron-spin-resonance spectrum of the M_I = ½ hyperfine lines for Na^{23} (I = 3/2) in argon at 4.2°K. The lines labeled *a* through *e* correspond to discrete trapping sites. Fig. 11 (right). Electron-spin-resonance spectrum of NH_2 produced by photolysis of hydrazine in argon at 4.2°K.

of an electrical discharge in ammonia or by ultraviolet photolysis of ammonia or hydrazine. The spectrum consists of a triplet of triplets as is expected for NH_2 since $I(N^{14}) = 1$ and $I(H) = 1/2$, resulting in $[2I(N^{14}) + 1]\ [2 \times 2I(H) + 1] = 9$ resonance lines. That the larger splitting should be assigned to H rather than to N was easily deduced from an experiment with the deuterated version of this radical, ND_2, and an examination of its 15-line spectrum (*25*). There is an interesting anomaly in the spectra of the isotopic radicals NH_2 and ND_2. While the ratio of the hyperfine coupling constants for H and D is exactly the ratio of their nuclear *g*-factors (6.514), as predicted by theory, the nitrogen coupling constant increases by 15 percent in going from NH_2 to ND_2. This is probably due to differences in zero-point vibrations of these molecules.

With trapping of increasingly complex radicals, it is no longer possible for all anisotropic interactions to be averaged out by free rotation in the solid. In the case of the ethyl radical, the electron-spin-resonance spectrum in argon at 4.2°K consists of a quartet of relatively sharp lines, each of which is further split into a triplet, the outer lines of which are relatively broad (*26*). There are two classes of H atoms in this radical, given by the formula



those attached to the α carbon and those attached to the β carbon. The quartet line splitting is due to the three β hydrogen atoms, and the fact that the lines are sharp indicates that the unpaired electron interacts equally with all three β hydrogen atoms and, therefore, that the CH_3 group is freely rotating about the C—C bond. The triplet subsplitting of the quartet lines is caused by the α hydrogen atoms. The outer lines of the triplet correspond to parallel orientations of the α hydrogen spins, which produce a dipole magnetic anisotropy which cannot be averaged out by internal rotation, and therefore these lines are broad. The spectrum shows that, whereas internal rotation is taking place, end-over-end rotation is not.

In contrast to the anisotropically broadened spectrum observed for the ethyl radical in the solid, the spectrum obtained (*27*) in liquid ethane at −170°C by continuous irradiation with electrons (2.5 Mev) from a Van de Graaff generator consists of 12 very sharp lines with resolved substructure in the lines associated with second-order splitting effects (*28*). In this case, anisotropic effects were canceled out by the rapid tumbling of the radicals in the solution.

A large number of organic free radicals have been studied to obtain values for isotropic and anisotropic hyperfine interactions and *g*-factors. Some spectra may have as many as several hundred hyperfine lines. The theory of the hyperfine interactions in many of these cases is fairly well understood, and this has been used to calculate electron spin densities at the various nuclei in the radical and to derive structural information not readily accessible by other means.

Triplet State Molecules

Triplet-state molecules contain two unpaired electrons and comprise a very interesting class of molecules that have only recently been studied by electron spin resonance. Phosphorescence in organic molecules is due to molecules in metastable excited triplet states. The long phosphorescence lifetimes (seconds to minutes) result from the fact that radiative transitions from the triplet state to the singlet ground state are strongly forbidden. The magnetic dipole-dipole interaction of the two spins produces a large anisotropy which makes the usual resonances strongly dependent on the orientation of the molecule with respect to the magnetic field, so that, for randomly oriented molecules in the glassy solutions normally used in phosphorescence studies, no electron spin resonances were expected. In 1958 Hutchison and Mangum (*29*) succeeded in observing the electron-spin-resonance absorption of naphthalene (excited by ultraviolet irradiation to the triplet state) in a single crystal of durene. As the single crystal was rotated, the line positions shifted over a range of about 2000 oersteds, showing that with randomly oriented molecules these lines would be excessively broadened.

Subsequently, it was discovered by van der Waals and de Groot (*30*) that, if instead of trying to observe the transitions between neighboring levels of the triplet (called "$\Delta M = 1$" transitions), observations were made on transitions between the highest and the lowest levels of the triplet (called "$\Delta M = 2$" transitions), the anisotropy was much smaller and resonances could be observed for randomly oriented molecules in glassy media. This is a very useful development in that it makes it possible to study many phosphorescent molecules without the necessity, in each case, of finding a suitable host crystal in which the molecule can be incorporated as an oriented guest. It has also been found recently that even the $\Delta M = 1$ transitions can be observed in glassy media despite the large anisotropic broadening of the lines. This is due to the fact that the resonances go through maxima and minima as a function of molecular orientation, and that those molecules with orientations close to the turning points will therefore have nearly identical resonances, which add to give an observable signal.

The most definitive information on triplet-state molecules comes from studies of single crystals. It has been found, for example, in the case of naphthalene in durene that the naphthalene molecule is substitutionally incorporated with its principal axes parallel to those of the host crystal, that the crystal field effects are small but measurable, that the magnetic dipole-dipole interaction of the two electrons produces a zero field splitting of the triplets, and that the state responsible for the phosphorescence can be designated from the electron-spin-resonance data.

Molecules with triplet ground states have also been observed. These paramagnetic molecules, in contrast to the phosphorescent triplet-state molecules, can be observed for many hours after they are formed in crystals or glasses by irradiation with visible or ultraviolet light. A number of methylene and nitrene molecules have been found to possess triplet ground states, and some dozens of these molecules have been studied by electron spin resonance.

Summary

Mass spectrometry and electron spin resonance are very sensitive and versatile methods for studying transient chemical species. Aside from furnishing unambiguous identifications of free radicals and unstable molecules, a contribution quite important in itself, experiments in which these techniques have been used have contributed considerable information on the energies, reaction mechanisms, and electronic and molecular structure of these species. For radicals trapped in solids, the observed perturbations in the electron-spin-resonance spectra are quantitative measures of the interactions of the radical with its environment, and these measures can be used to assign trapping sites and to estimate crystal fields. The ability of a trapped radical to execute partial or free rotation can be determined from the degree to which anisotropic broadening effects are averaged out in the electron-spin-resonance spectra. An interesting area which has recently received considerable attention is the study of phosphorescent triplet-state molecules by electron spin resonance. In the gas phase, mass spectrometric studies have been made not only to study free radicals but also to examine metastable atoms and molecules, and to discover new chemical compounds. The study of electronically excited species by both methods appears to be a very fruitful area of research.

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NEWS AND COMMENT

The MURA Accelerator: Compromise for the Mid-West

The long-simmering midwestern revolt against research and development allocations broke out last month, and, while the noise and emotion are still too thick for any precise assessment of the consequences, it appears that the midwesterners have lost an accelerator and won a profoundly important principle.

Specifically, the $170-million, 12.5-Bev high-intensity accelerator proposed by the Midwestern Universities Research Association (MURA) has been flatly rejected. But in the eruption touched off by this decision, the midwesterners seem to have swung over the Johnson administration to a concept laden with gold—namely, that henceforth regionalism is a factor to be considered in dispensing federal research funds. It can be argued that this principle has often been tacitly at work in the allocation of research activities, but the avowed rule has always been that research expenditures are for research and not for economic development or aid to strapped universities. Just what will come of this is yet to be determined, but among some federal science administrators there is the feeling that, inadvertently or not, the administration has taken a step with enormous implications for the future of federal support of science.

In any case, the events leading up to this step present an intriguing picture of scientific decision making at the highest levels of government.

At the time of Kennedy's death, the midwestern legislators who had banded together in behalf of MURA were confident that the President was sympathetic to their cause (*Science*, 11 Oct. 1963). Some even say that one week before the assassination the President personally assured Senator Hubert Humphrey (D–Minn.) that funds for MURA would be included in the new budget. A spokesman for Humphrey denies this, and offers the view that wishful thinking on the part of some midwesterners may have converted the senator's expression of optimism into a sense of assurance. But the important thing is that, whatever the reality, the appearance was propitious for MURA, and the midwestern congressional delegations were feeling certain that they had won their long struggle. Kennedy had repeatedly demonstrated an eagerness to promote research, the midwesterners had shown their political muscle on the issue, and, with the budget scheduled to be locked up early in December, there were ample grounds for confidence.

Johnson's succession, however, again made the budget an open question, and MURA was soon to be the subject of a series of hurriedly called White House conferences. (Last week, in a letter to Humphrey, Johnson stated, "I devoted more personal time to this [the MURA] problem than to any nondefense question that came up during the budget process.")