Trapped

FREE

E. L. Cochran, F. J. Adrian, and V. A. Bowers

We are forced to forewarn the reader that the juxtaposition of apparently contradictory terms in our title is a result of evolution. When organic chemists first began to understand molecular structure, the term *radical* came generally to be used to refer to the parts of molecules. Thus, in this context, a radical had only formal significance and referred to the molecular groupings which would result if a particular bond in a molecule were imagined to break. Somewhat later, physical chemists found that when chemical bonds actually do break, these molecular groups or radicals can have a transitory existence of their own. These radicals, which were thought of only as intermediates in chemical reactions, were called *free radicals*. The study of free-radical kinetics soon became a major field of chemistry, resulting in the generation of much interest in the free radicals themselves, their spectra, and their structures. Techniques for obtaining free radicals in sufficiently high concentration for spectroscopic study in the gas phase gradually evolved. These included electric discharge and flash photolysis techniques. More recently it was recognized that stable radical concentrations of a few tenths of a percent could be obtained by isolating the radicals from one another

in inert matrices—thus the term *trapped free radicals*.

Molecules, with very few exceptions, have an even number of electrons that are paired off in the process of chemical-bond formation so that the spin magnetic moments of the individual electrons are cancelled. They are thus diamagnetic, generally speaking. When a bond in a molecule is broken, two free radicals are formed, each of which has an odd number of electrons. Free radicals, therefore, are characteristically paramagnetic.

The development of magnetic resonance spectroscopy has provided a convenient and powerful tool for the study of magnetic materials. The branch of magnetic resonance that applies particularly to free radicals is called *electron spin resonance* (ESR) *spectroscopy*. The exploitation of this technique for the study of trapped free radicals has resulted in much progress in our understanding of the structure of trapped radicals and of their interaction with their environment.

The ESR Method

With ESR, as in all forms of absorption spectroscopy, we detect the species of interest by stimulating transitions from a lower to a higher energy level and measuring the energy absorbed. The energy levels utilized in ESR spectroscopy are the Zeeman energy levels of the unpaired electron in

Recent development of electron spin spectroscopy has brought about greatly increased interest in trapped free radicals, and, in many cases, has permitted a more or less complete determination of their structure. This work has also provided reliable guidelines for predicting the structure of more complex radicals. The radicals in the experiments discussed were formed by means of elementary photochemical processes or by simple addition reactions, providing knowledge of basic chemical processes.

RADICALS

an applied magnetic field. These Zeeman levels result from the fact that the unpaired electron possesses spin and a resultant magnetic moment. The electron may be regarded as a small bar magnet, restricted by quantum mechanical principles to be either parallel or antiparallel to an external magnetic field. These two directions have different energies, the difference (in frequency units) being given by

$$\nu = \frac{g\beta}{h} H_o, \qquad (1)$$

where g (the ratio of the magnetic moment in units of the Bohr magneton to the angular momentum in units of $h/2\pi$), β (the Bohr magneton) and h (Planck's constant) are constants, and H_o is the magnitude of the applied DC magnetic field. If electromagnetic energy of frequency ν is applied to a suitable sample, the unpaired electrons will be found to absorb energy at the value of the applied magnetic field which satisfies Eq. (1). For these studies the frequency used was $\approx$9000 mc, corresponding to an applied magnetic field of $\approx$3000 oersteds (oe).

Unpaired electrons in free radicals differ from free electrons in that in the former the electron is constrained to an electronic orbital, i.e., occupies a well-defined region of space relative to the nuclear framework of the radical. This means that the

electron is intimately associated, and in a definite manner, with one or more of the atomic nuclei in the free radical. Since many of these atomic nuclei have their own small magnetic moments (about one thousandth as large as the magnetic moment of the electron), their proximity to the electron will alter slightly the magnetic field it experiences. This magnetic interaction between the electron and the nuclei of the radical is known as the *hyperfine interaction*; its magnitude depends on the relative orientation of the electronic and nuclear magnetic moments. Because the nuclear moment, like the electronic moment, is constrained by quantum principles to certain preferred orientations, the magnetic hyperfine interaction will split the ESR line into a discrete set of lines, one for each permissible orientation of the nuclear moment.

The allowed orientations of the nuclear moment are described by the projection M_I of the nuclear spin angular momentum vector $\mathbf{I}$ along the magnetic field direction; M_I may assume the values $I, I-1, \cdots, -I$. Each atomic nucleus has its characteristic value of I (although many possess the same value). Values are integral or half-integral in units of $h/2\pi$, and nuclei have been found for which I is as great as 6. Thus for C^{12}, $I = 0$; for H^1, $I = \frac{1}{2}$; for N^{14}, $I = 1$, etc. The details of the hyperfine interaction are often very

complicated but, for a single nucleus, may be described for one rather general case by adding an appropriate term to Eq. (1):

$$\nu = \frac{g\beta}{h} H_o + \frac{A}{h} M_I + \frac{BM_I}{h} (3\cos^2\theta - 1). \quad (2)$$

This is a good approximation only when A is substantially larger than B and when the electron charge distribution is axially symmetric with regard to the nucleus in question—conditions which are met in a surprisingly large number of cases.

As Eq. (2) indicates, the hyperfine interaction with the nucleus may be divided into two components. The term AM_I/h is isotropic with respect to the external field and arises because the electron has a finite density at the position of the nucleus. The magnitude of the parameter A depends on this density as well as on the magnitude of the nuclear moment. The component $BM_I/h\ (3\cos^2\theta - 1)$, depends on θ, the angle between the external magnetic field and the symmetry axis of the charge distribution of the unpaired electron. This is the classical expression for the interaction of two magnetic dipoles; the magnitude of B depends on the magnitude of the nuclear moment and decreases with the cube of the distance between the electron and nucleus.

An additional assumption implicit in Eq. (2) is that the g-factor is isotropic. It sometimes happens that there is a small orbital contributi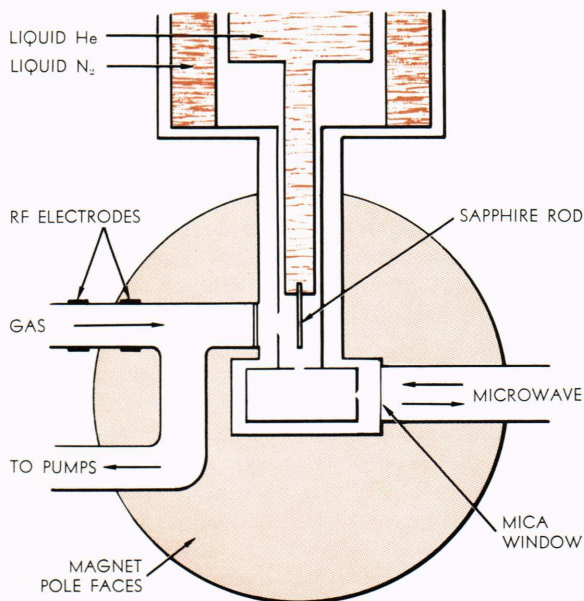on to the total magnetic moment of the electron. This contribution depends on the orientation of the radical relative to the external magnetic field, and thus makes the g-factor anisotropic. Additional terms must be included in Eq. (2) to describe such cases as this. Where the electron charge distribution is axially symmetric with respect to the symmetry axis of the free radical, and where for simplicity we again consider hyperfine interaction with only one nucleus, Eq. (2) becomes

$$\nu = (\tfrac{1}{3}g_\parallel + \tfrac{2}{3}g_\perp)\beta H_o/h + \frac{A}{h} M_I +$$
$$[\tfrac{1}{3}(g_\parallel - g_\perp)\beta H_o + BM_I](3\cos^2\theta_H - 1)/h. \quad (3)$$

Here, $g_\parallel$ and $g_\perp$ are the electronic g-factors for the magnetic field, respectively parallel and perpendicular to the symmetry axis, and θ_H is the angle between the magnetic field and the symmetry axis of the radical. Equation (3) is strictly valid only when $(g_\parallel - g_\perp)$ is much smaller than $g_\parallel$ or $g_\perp$, which is the usual case for free radicals.

On the basis of Eq. (3) we can distinguish three types of ESR spectra:

1. *Fluid-media spectra*, where $(3\cos^2\theta_H - 1)$ is averaged to zero by the rapid tumbling of the free radical. Here we observe sharp-line spectra whose hyperfine structure is a result of A only;

2. *Single-crystal spectra*, where the free radicals are all oriented in the same way by the crystal field, and the spectrum is different for each orientation of the crystal in the magnetic field; and

3. *Spectra in polycrystalline solids and glasses*, where the free radicals are randomly oriented relative to the magnetic field. Here, hyperfine structure is due to A in Eq. (3), with the term in brackets contributing only to line broadening.

In studying trapped radicals, one deals with the latter two categories; at APL we have been almost exclusively concerned with polycrystalline-type spectra.

Instrumentation

In most of our work, trapped free radicals are produced by the ultraviolet photolysis of a compound present in low concentration in an inert matrix maintained at $4.2°K$ (the boiling point of liquid helium at normal pressure). Figure 1 is a diagram of the liquid-helium cryostat, which is a modified version of a cryostat originally developed at APL by W. H. Duerig and I. L. Mador for optical spectroscopy.[1] The sample is collected on a

LIQUID He
LIQUID N₂
RF ELECTRODES
GAS
TO PUMPS
MAGNET POLE FACES
SAPPHIRE ROD
MICROWAVE
MICA WINDOW

Fig. 1—Liquid-helium cryostat shown in vertical cross section.

[1] W. H. Duerig and I. L. Mador, "An Optical Cell for Use with Liquid Helium," *Rev. Sci. Instr.*, **23**, Aug. 1952, 421–424.
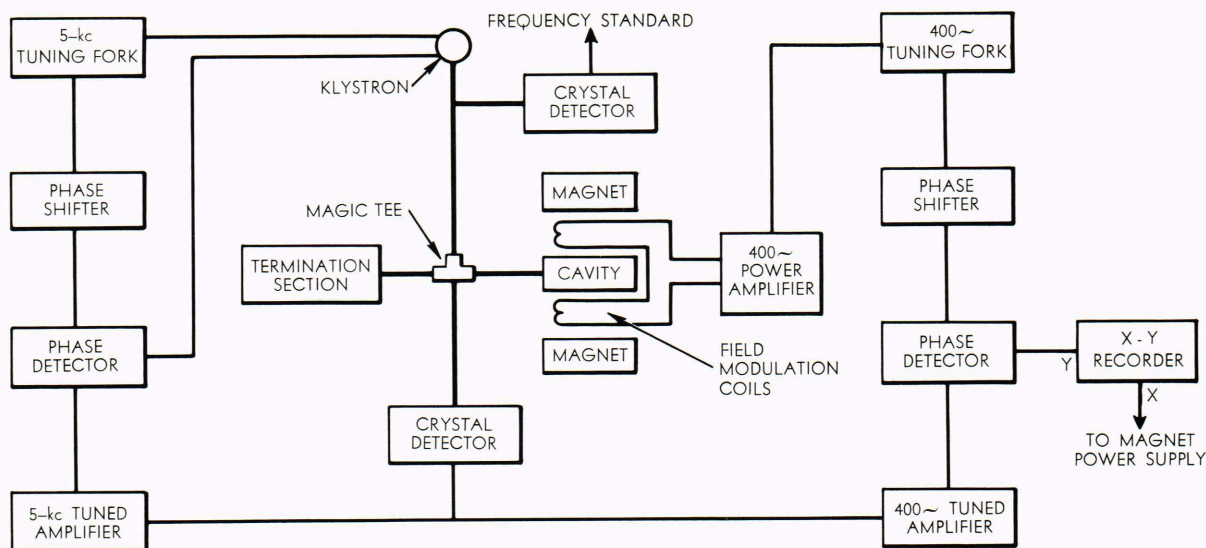
Fig. 2—Block diagram of an ESR spectrometer.

sapphire rod in direct thermal contact with liquid helium. The rod, 2 mm in diameter and 50 mm long, projects into the liquid–helium reservoir through a vacuum-tight solder joint. The temperature of the sample is measured by means of a thermocouple soldered to the rod.

The liquid–helium assembly can be raised or lowered mechanically by means of a bellows arrangement. In the lowered position the sapphire rod extends 16 mm into the rectangular cavity which is resonant at a frequency of ≈ 9000 mc. The cavity is maintained at liquid-nitrogen temperature by thermal contact with the copper radiation shield. The sample is deposited on the sapphire rod through two entrance pipes terminating in slits in planes 45° removed from the plane of the drawing. During and/or after deposition, the samples are exposed to ultraviolet light from an RF discharge in the tube shown. The lower wavelength limit of the light is selected by means of appropriate window materials; lithium fluoride (threshold = 1000 Å), sapphire (1450 Å), fused quartz (1800 Å), and Vycor 7910 (2400 Å) are used. In other experiments the window is replaced by a slit through which radicals may be deposited from the gas phase in which they are produced by electrical discharge or thermal dissociation in an oven. The effect of temperature on the ESR of the sample is observed by removing the liquid helium and allowing the sample to warm up at a rate controlled by an adjustable heat leak.

The ESR spectrometer, shown in block diagram in Fig. 2, is a standard bridge-type instrument. The klystron tube, which is the microwave source,

is stabilized at the resonant frequency of the cavity by frequency modulating the klystron at 5 kc over a very narrow frequency region. If the klystron frequency is not centered at the cavity resonance frequency, this modulation produces a 5-kc error signal that is fed back to the klystron in order to correct its frequency to the cavity resonance. The use of fixed tuned cavities makes it difficult to sweep the frequency through an ESR absorption line, so the normal procedure is to sweep the magnetic field at fixed microwave frequency. As may be seen from Eq. (2), these are equivalent procedures. When the DC magnetic field satisfies the resonance condition of Eq. (2), the sample will absorb power from the microwave field.

This absorption is most easily detected by modulating the magnetic field strength very slightly at 400 cps, which causes a corresponding fluctuation in the microwave power absorption. Since AC signals are much more easily amplified and discriminated from noise than are DC signals, the use of field modulation results in a large increase in sensitivity over DC operation. Since the amplitude of the magnetic field modulation corresponds to only a fraction of the ESR absorption line width, the resulting signal is proportional to the slope of the absorption line (Fig. 3). The use of 400 cps for field modulation in our experiment is a compromise between the higher signal-to-noise ratio obtainable at higher frequencies (due to the noise characteristics of the crystal detector) and the decreased eddy-current losses in the cavity walls at lower frequencies. Somewhat better sensitivity may be obtained at the expense of simplicity by using low-
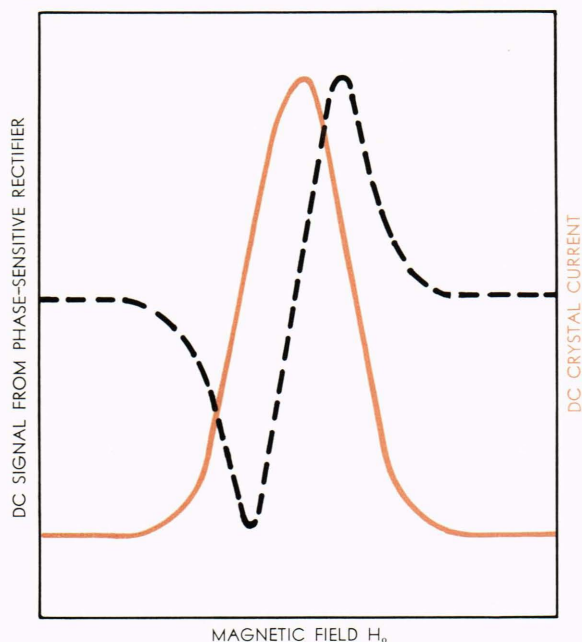
Fig. 3—ESR signal in the absence of field modulation (solid line) and with field modulation and phase-sensitive detection (dotted line).

frequency modulation together with superheterodyne detection.

Some Selected Results

Observation of ESR spectra of trapped free radicals provides information of several types. First, the unambiguous assignment of a previously unknown spectrum to a particular radical is in itself useful for analytical purposes. Second, the spectrum often provides knowledge about the physical environment of the radical. Thus, we have seen that a freely-rotating polyatomic radical will have a spectrum consisting of sharp lines, while a rigidly oriented radical will be subject to line broadening by g-factor or hyperfine anisotropies. In some cases, it is possible to vary the temperature through the transition region between these two extremes, giving, at least potentially, the activation energy for rotation in various matrices. For spherically symmetric atomic species, A and g are usually accurately known from atomic-beam studies. The determination of these quantities for the trapped atom therefore provides knowledge about the perturbing effects of the matrix.

A third type of information provided by the ESR spectrum of a free radical relates to the wave function of the unpaired electron and therefore to the structure of the radical. Since A in Eq. (3) (or in Eq. (2)) is proportional to $|\psi(0)|^2$—the probability density of the unpaired electron at the nucleus in question—this much information at least is always obtained for all the nuclei which interact significantly with the electron. By a careful analysis of the line shapes for rigidly oriented radicals in polycrystalline matrices, considerably more data can be obtained. In this case the observed spectrum is the result of superposition of spectra arising from all possible orientations of the radical relative to the magnetic field. The resulting line shape is illustrated for the axially symmetric case (Eq. (3)) in Fig. 4. The two sharp peaks or "lines" in the derivative of the broadened absorption line correspond to definite orientations of the radical, namely $\theta_H = 0$ and $\theta_H = \pi/2$. Therefore, in certain cases where the various hyperfine lines do not overlap appreciably, the broadened line shapes may be analyzed to obtain the constants in Eq. (3). When the magnetic interactions are not axially symmetric, the analysis is considerably more complicated, though still tractable in favorable cases.[2]
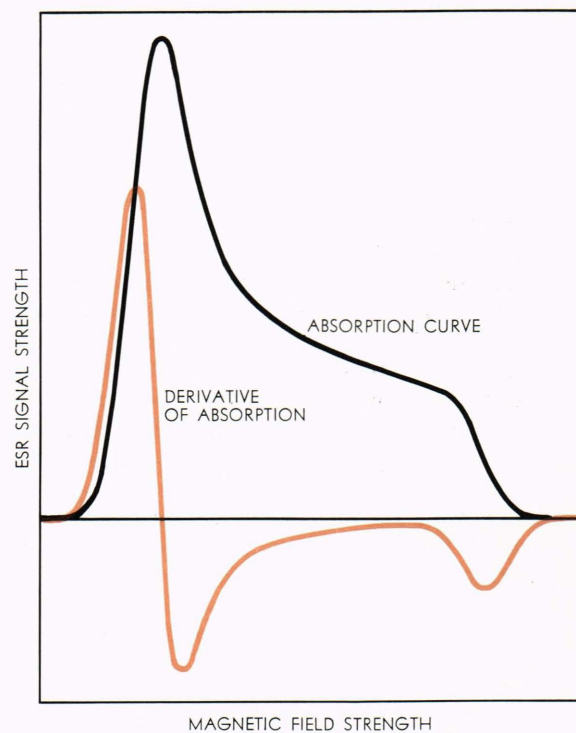

Fig. 4 — Typical ESR line shape for a randomly oriented, non-rotating free radical having an anisotropic g-factor and an anisotropic hyperfine interaction as described by Eq. (3). The strong positive peak in the derivative curve corresponds to the magnetic field oriented perpendicular to the symmetry axis; the weaker negative peak corresponds to the magnetic field oriented parallel to the symmetry axis.

[2] F. J. Adrian, E. L. Cochran, and V. A. Bowers, "ESR Spectrum and Structure of the Formyl Radical," *J. Chem. Phys.*, **36**, March 1962, 1661–1672.

Another class of information derives from the fact that trapped radicals may be prepared by photochemical processes which are themselves of considerable interest. For instance, the products of primary dissociations are observed directly, avoiding the difficulties of the usual inductive chemical kinetic analyses, and simple radical reactions can often be observed to occur in solid matrices at 4.2°K. From such observation we learn something about the processes of solid-state chemistry. In the following, we will describe some typical results that have been obtained in these areas.

Hydrogen Atoms

Trapped hydrogen atoms are produced in the photolysis at 4.2°K of many simple molecules such as HI, NH_3, PH_3, SiH_4, CH_4, HCN, etc. Since $I = \frac{1}{2}$ for the hydrogen atom, we expect two spectral lines. Because the electron charge distribution in this atom is spherically symmetric with
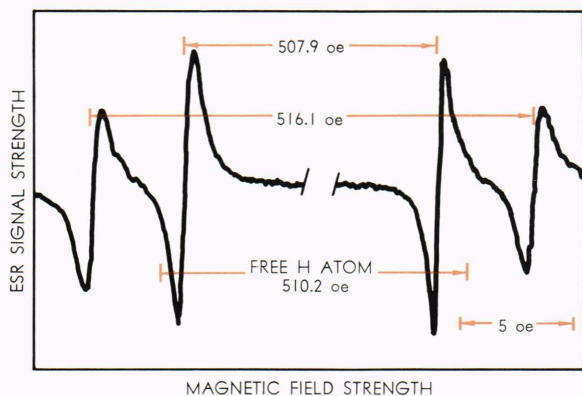

Fig. 5—ESR spectrum of hydrogen atoms produced by photolysis of water in solid argon at 4.2°K.

respect to the nucleus ($B = 0$ in Eq. (2)), the hyperfine interaction is described by the single parameter A. The ESR spectrum for photolytically produced H atoms in a solid argon matrix is shown in Fig. 5. We see that there are two different kinds of H atom in this sample; one has a value of A, 1.15% greater than, and the other 0.46% less than, that for the free atom.[3] Significantly, only the latter type of hydrogen atom is formed when a gaseous mixture of atoms and molecules is condensed—a procedure that allows the sample more time in which to equilibrate. A theoretical treatment[4] of the interaction of the atom with the matrix

Fig. 6—ESR spectrum of CH_3 produced by photolysis of CH_3I in solid argon at 4.2°K.

indicates that the H atoms with the smaller value of A are in substitutional sites in the face-centered cubic rare-gas crystallites, while those with the larger value of A are in a considerably more cramped interstitial site.

Other photolytically produced atoms whose ESR spectra have been studied in inert matrices include deuterium, nitrogen, and phosphorus. In addition, the alkali metal atoms have been studied by means of a vapor-deposition technique.[5]

Small Freely Rotating Radicals

Analyses of ESR spectra for a number of polyatomic radicals have been completed. Take for example the spectrum shown in Fig. 6 for the trapped methyl radical CH_3 which can be prepared by photolysis of methyl iodide[6] or other suitable molecules in a solid argon matrix. We can compute B as comparable to A for this radical, and predict, therefore, that for a rigid and ran-

[3] E. L. Cochran, V. A. Bowers, S. N. Foner, and C. K. Jen, "Multiple Trapping Sites for Hydrogen Atoms in Solid Argon," *Phys. Rev. Letters*, **2**, Jan. 1959, 43; and S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, "Multiple Trapping Sites for Hydrogen Atoms in Rare Gas Matrices," *J. Chem. Phys.*, **32**, April 1960, 963-971.

[4] F. J. Adrian, "Matrix Effect on the Electron Spin Resonance Spectra of Trapped Hydrogen Atoms," *J. Chem. Phys.*, **32**, April 1960, 972-981.
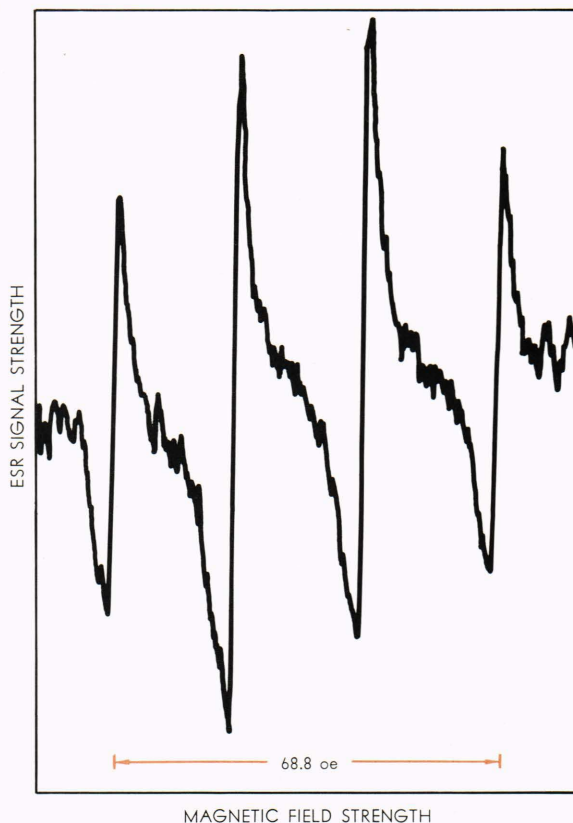
[5] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, "Electron Spin Resonance of Alkali Atoms in Inert-Gas Matrices," *Phys. Rev.*, **126**, June 1962, 1749-1757.

[6] E. L. Cochran, F. J. Adrian, and V. A. Bowers, "Anisotropic Hyperfine Interactions in the ESR Spectra of Alkyl Radicals," *J. Chem. Phys.*, **34**, April 1961, 1161-1175.

domly oriented radical, the ESR lines will be very broad. The simple sharp-line spectra can therefore be explained only if the radical is freely rotating at 4.2°K. Similar results are obtained for NH_2 and SiH_3. In the case of CN we can actually observe the transition from a rigidly oriented radical to a more-or-less freely rotating radical as the temperature is raised from 4.2°K to 37°K (Fig. 7).[7] The center line of this spectrum is narrow and sharp at all temperatures because this line corresponds to $M_I = 0$ (Eq. (3)) and there is no g-factor anisotropy. The weak line at the position of the vertical arrow is of unknown origin but is presumably due to an impurity.
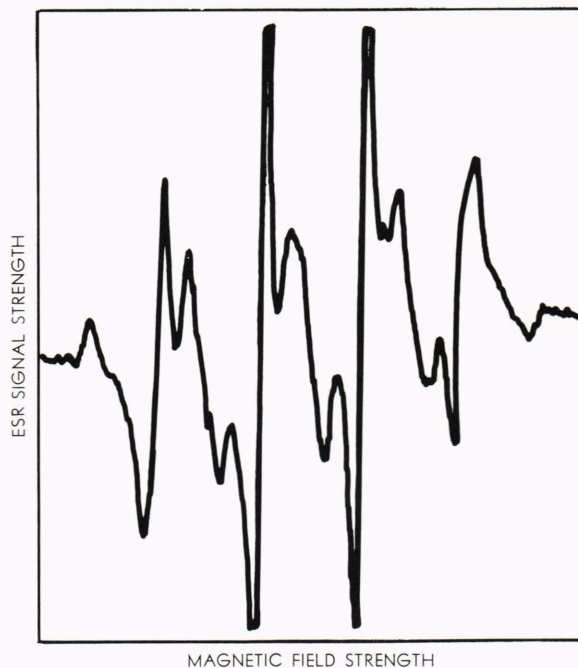
Ethyl Radical

The ethyl radical is representative of a large class of radicals which have only partial rotational
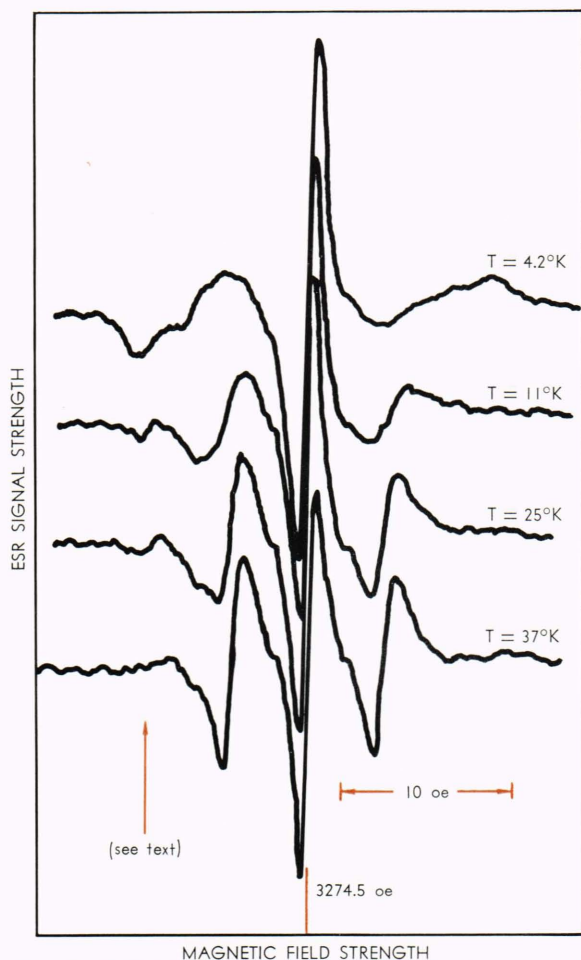
Fig. 7—ESR spectrum of the CN radical produced by photolysis of HCN in solid argon at 4.2°K.

[7] E. L. Cochran, F. J. Adrian, and V. A. Bowers, "ESR Detection of the Cyanogen and Methylene Imino Free Radicals," *J. Chem. Phys.*, **36**, April 1962, 1938–1942.

Fig. 8—ESR spectrum of the ethyl radical produced by photolysis at 4.2°K of HI in solid argon containing 9% ethylene.

freedom. As may be seen from its structural formula,

$$H\text{---}\underset{\beta}{C}\text{---}\underset{\alpha}{C}\text{---}H,$$
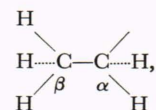
there are two classes of H atoms in this radical: those attached to the α carbon (α protons) and those attached to the β carbon (β protons). The spectrum for this radical (Fig. 8) shows a quartet of relatively sharp lines due to the splitting by the β protons.[6] This indicates that the unpaired electron "sees" the β protons equally, i.e., that the radical is free to execute internal rotation about the carbon-carbon bond. Each of the lines of the quartet is further split into a triplet by the α protons. The outer lines of these subtriplets are broad because of hyperfine anisotropy which cannot be averaged out by the internal rotation alone. The center lines of the triplets are somewhat sharper than the side lines because these lines correspond to states in which the two α-proton spins are opposed to each other (antiparallel). This, combined with the internal rotation that makes the two α protons spatially as well as chemically equivalent, permits cancellation of the anisotropy due to the individual protons. This spectrum shows, therefore, that the ethyl radical is executing internal rotation and may be undergoing overall rotation about the C—C axis; it is not, however, free to execute end-over-

end rotation. Similar results have been obtained for other alkyl radicals.[5]

Solid-State Photochemistry

Photochemical processes in the solid state differ in at least two important ways from those in liquid or gaseous media. First, there are large "cage" effects in the solid which tend to prevent the primary dissociation products from diffusing away from one another. This promotes recombination and drastically lowers the observed quantum yields. These effects become more pronounced as the size of the primary radicals increases. Thus, minor dissociation modes in fluid media which involve, say, the production of an H atom are sometimes found to account for the major part of the decomposition in solid-state photolysis. Another consequence of the absence of diffusion in the solid is that radical concentrations build up; and depending on their absorption spectra, they may compete effectively for the actinic light. Thus, products resulting from the successive absorption of several quanta of light are observed. An example of this is the photolysis of deuterated methanol,
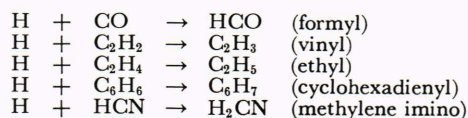
$$CH_3OD \rightarrow CH_2OD + H$$
$$\hookrightarrow CH_2O + D$$
$$\hookrightarrow CHO + H,$$
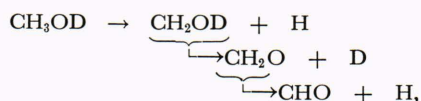
for which the major radicals observed are H, D, and CHO.[2]

Photochemically Induced Addition Reactions of H Atoms at 4.2°K

It has been found that when HI is photolyzed at 4.2°K in the presence of molecules containing multiple bonds, addition reactions very often occur. Since the activation energies for these processes are not known, it is not clear whether they are "thermal" (with the H atom at 4.2°K) or "hot" (where the H atom possesses excess energy from the dissociation process). However, the 2537 Å quantum used in these experiments possesses 113 kcal of energy while the HI bond strength is only 71 kcal. The remaining 42 kcal of energy can only appear as translational energy of the products if, as appears to be the case, the iodine atom is formed in its ground electronic state. Conservation of momentum requires that 99% of this go to the H atom. Since the average translational energy of H at 4.2°K is only about 12 calories, it would appear that the H atom would have to undergo many collisions with the lattice before being reduced to thermal energy. In a typical experiment, 10% of the matrix molecules possess multiple bonds, so conditions would appear to be favorable for the

occurrence of hot reactions. The following reactions have been observed:

|			
H + CO	→	HCO	(formyl)
H + C_2H_2	→	C_2H_3	(vinyl)
H + C_2H_4	→	C_2H_5	(ethyl)
H + C_6H_6	→	C_6H_7	(cyclohexadienyl)
H + HCN	→	H_2CN	(methylene imino)

There are clearly many other possibilities which have not yet been tried. A photochemically induced addition reaction is often the cleanest and most direct way to prepare a radical of interest. Addition reactions for methyl radical have not been observed, which is probably not surprising because the factors that favor hot reactions in the case of H atoms are distinctly less favorable for CH_3. Specifically, CH_3 has a larger number of degrees of freedom over which to distribute excess energy; its larger mass means that a larger fraction of the excess translational energy will go to the iodine atom; and finally, the CH_3 will be able to transfer translational energy more efficiently to the matrix molecules. In addition, there may be steric factors and activation energy considerations which could help to account for the differing behavior of H and CH_3 with regard to addition to multiple bonds.

These low-temperature reactions may provide an important experimental approach to the elucidation of the detailed mechanism by which elementary reactions occur. As an example, when an H atom is added to deuteroacetylene we obtain the 1,2-dideuterovinyl radical,

$$H + DC\equiv CD \rightarrow HDC=CD.$$

The structure of the vinyl radical is not known but should be planar by analogy with ethylene. Since internal rotation about C—C multiple bonds cannot occur, there are thus two possible structures for the 1,2-dideuterovinyl radical:
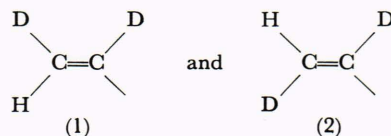
Normally, since the energies of the two structures are the same, we could expect that they would be formed in equal amounts. In solid argon at 4.2°K, however, we observe only one of these structures. A comparison of the observed hyperfine splittings in this radical, with theoretical estimates of these quantities, indicates that structure (2) is formed. This result is of interest because it is related to the detailed mechanics of the manner in which the H atom approaches the acetylene molecule and forms the activated complex, which then relaxes to the characteristic structure of the vinyl radical.