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MAGNETOPHOTOSELECTIVE PHOTOCHEMISTRY IN SOLIDS

Photochemical reactions initiated in solids by polarized light can result in the reactants and products being partially oriented with respect to the optical electric vector. For paramagnetic species, the orientation can also be with respect to an external magnetic field, whence the term magnetophotoselection. Using electron spin resonance spectroscopy, magnetophotoselection has been observed for the first time in a class of reaction intermediates known as free radicals. The specific radicals observed were formyl and nitrogen dioxide. The orientation effects provide important basic information about the electronic structure and photochemistry of the reactants and may also have useful applications in such areas as optical data storage, information processing, and improved spatial localization in the photochemical processing of microcircuits.

INTRODUCTION

Chemical and physical changes produced in matter by visible and ultraviolet light are of great fundamental interest as well as widespread practical importance. Some of the existing and potential applications important in defense technology are lasers, optical sensing and information processing,[1] and materials synthesis and processing. In the last category, a recent development of special interest is the possibility of fabricating microcircuits using thermal and photochemical processes initiated by high-energy lasers.[2] The versatility of such lasers, which now can generate high peak-power radiation over a wide range of photon energies from the visible to the ultraviolet, combined with the high spatial resolution of the optical beam, may enable custom fabrication, changing, and repair of microcircuits on semiconductor substrates by such processes as thermal evaporation, the deposition of photochemically produced metals and insulators, and doping by thermal diffusion of deposited materials into the substrate.

Current photochemical research at APL is directed toward the fundamental understanding of photochemical and photophysical processes in microcircuit fabrication and of radiation damage in semiconductors and optical materials. It is also directed toward the possible application of photoinduced color centers to optical information processing.

A recent development in that work and the subject of this article is photolysis in solids and glasses by polarized light combined with electron spin resonance (ESR) determination of the resulting orientational nonuniformity of certain paramagnetic reactants and products known as free radicals.[3,4] In that experiment, the reference axis for the photoinduced orientational anisotropy is the external magnetic field required by ESR; consequently, the process is commonly called magnetophotoselection even though that is something of a misnomer because it implies that the field alters the reaction mechanism, which is not the case.

Although the technique is not new, it is the first application of ESR spectroscopy in detecting oriented free radicals (even though paramagnetic triplet state molecules have been studied this way and a few relatively stable free radicals have been investigated using visible and infrared spectroscopy). However, ESR usually has great advantages in sensitivity and resolution over visible and infrared spectroscopic methods. Another advantage is the aforementioned relation of the orientational anisotropy to an external magnetic field so that changing the relation by simply rotating the sample or the field allows some important experiments. As will be described in more detail, such experiments can provide fundamental knowledge of optical transition dipole moments; photochemical reaction mechanisms; slow, thermally activated reorientation of molecules in solids; and so forth. With regard to applications, the orientational manipulation of color centers in solids holds promise for optical information storage and processing, and polarized laser photolysis may improve spatial resolution in microcircuit applications.

BACKGROUND

Free radicals are reactive molecular fragments formed by breaking chemical bonds in normal, fully bonded molecules. They are common intermediates during chemical reactions, including those initiated by an optical photon whose energy puts the receptor molecule into an electronically excited state in which one or more of the bonds are considerably weaker than in the ground state. Thus, the molecular structure and chemical reactions of free radicals are subjects of great importance in photochemistry.

A structural feature of many free radicals (one that greatly facilitates their detailed structural investigation) is that they are paramagnetic because of the magnetic moment of an unpaired electron that was originally part of the photolytically broken electron-pair chemical bond of the parent molecule. In an external magnetic field, the radical will have two magnetic energy levels corresponding to the electron magnetic moment oriented either parallel or antiparallel to the field. The spectroscopic observation of transitions between the levels, transitions that occur in the X-band microwave region for typical field strengths (approximately 9000 megahertz for a magnetic field of 3000 gauss), constitutes the spectroscopic technique known as ESR. The method's importance lies in its high sensitivity and high energy resolution. Small shifts (one part in 10^4 or fewer) of the ESR line from the free electron spin position can be observed and related to small contributions to the electron magnetic moment resulting from the orbital motion of the electron over the molecular framework. (These shifts are called g shifts following the custom of writing the electron magnetic moment as $g\mu_B\mathbf{S}$, where $\mathbf{S}$ is the spin and μ_B is the Bohr magneton.) Similarly, small splittings of the ESR line resulting from magnetic interactions between the electron and various magnetic nuclei in the radical (hyperfine structure) give information about the distribution of the unpaired electron density near the nuclei. Both effects are important in identifying the radical and in determining details of its electronic and molecular structure.

Although the reactivity and consequent short lifetime of most free radicals under normal conditions of temperature and pressure are obstacles to their investigation, the problem can be overcome in numerous ways. One especially useful way, which was pioneered at APL, is matrix isolation spectroscopy. The reactive intermediate is either formed within a cold unreactive matrix such as solid methane or a noble gas or is trapped and stabilized by co-condensation at low temperature with such a matrix immediately after it is formed.[5]

One variant of the matrix isolation technique that has been used extensively and was described previously[5] is slow deposition of a gaseous sample at low pressures onto a sapphire rod that is cooled by contact with a liquid helium reservoir. More recently, a rapid deposition technique using the apparatus shown in Fig. 1 has been used.[4] While attached to a vacuum line, the sample bulb is filled with an appropriate gas mixture and then is transferred to the ESR apparatus; there the ESR tube attached to the bulb is placed in the helium flow-through cryostat that passes through the center of the ESR microwave cavity. After the sample tube has been cooled to the desired temperature by cold helium gas from a liquid helium reservoir flowing through the cryostat (the temperature can be controlled accurately between 8 and 295 kelvin), the stopcock connecting the sample bulb to the ESR tube is opened; the gas mixture then expands through a narrow tube inside the ESR tube and con-
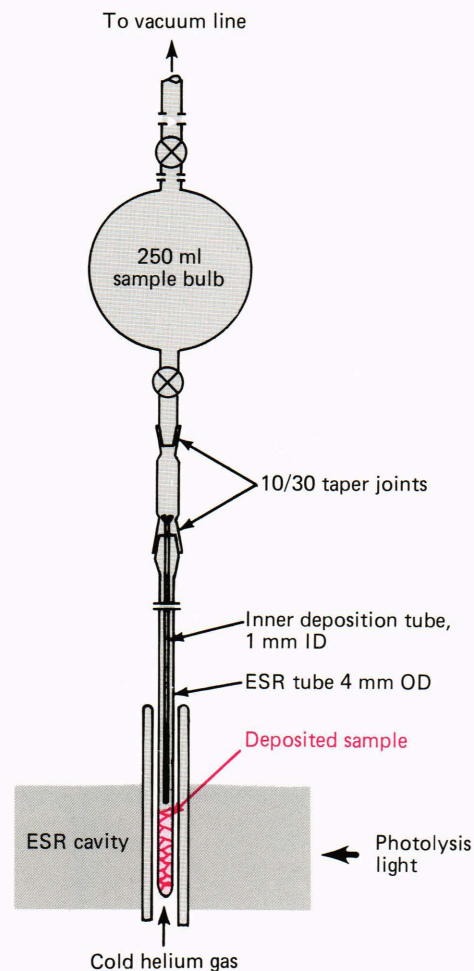
Figure 1—Simple apparatus for the preparation of matrix-isolated free radicals for ESR observation. The apparatus is shown in place in the microwave cavity of the ESR spectrometer, where the ESR sample tube can be cooled to between 8 and 295 kelvin by a flow of cold helium gas from a liquid helium reservoir through the quartz ESR Dewar. Upon opening of the stopcock connecting the ESR tube to the sample bulb, which previously had been filled with the desired matrix gas and free radical precursors, the gas sample is condensed in the bottom of the ESR tube. Photolysis of the sample in situ by light passing through the slotted back of the cavity generates free radicals that can be observed by ESR during and after the formation.

denses on the bottom of the tube. After deposition, the sample may be photolyzed in situ through the slotted port in the back of the microwave cavity. The latter method of matrix formation has the advantage of simplicity and of yielding matrices whose optical quality is usually better than that of the snow-like deposits produced by the former method. It also has disadvantages, particularly the tendency of the less volatile components of a gas mixture to condense first, yielding nonuniform matrices.

Although it might appear that the properties of such a trapped radical would be so different from those of the free species as to make data obtained on the former largely irrelevant to the latter, extensive investigations have shown that this is usually not so. As a

case in point, the ESR identification and structural characterization of the matrix-isolated cyanogen (CN) and ethynyl (C_2H) radicals[6] agreed well with data obtained from microwave emissions of those species in interstellar space and thereby helped confirm the assignments of the radioastronomical signals.

FORMYL RADICAL (HCO) SPECTROSCOPY

To illustrate ESR spectroscopy of matrix-isolated radicals, we consider the formyl radical (HCO), a species of great general interest that is the primary subject of the magnetophotoselective photolysis work described in this article. The ESR spectra of HCO shown for this radical in a solid methane (CH_4) matrix at 20 kelvin (Fig. 2a)[7] and in solid carbon monoxide (CO) at 13 kelvin (Fig. 2b)[4] illustrate the interesting and important point that the ESR spectrum
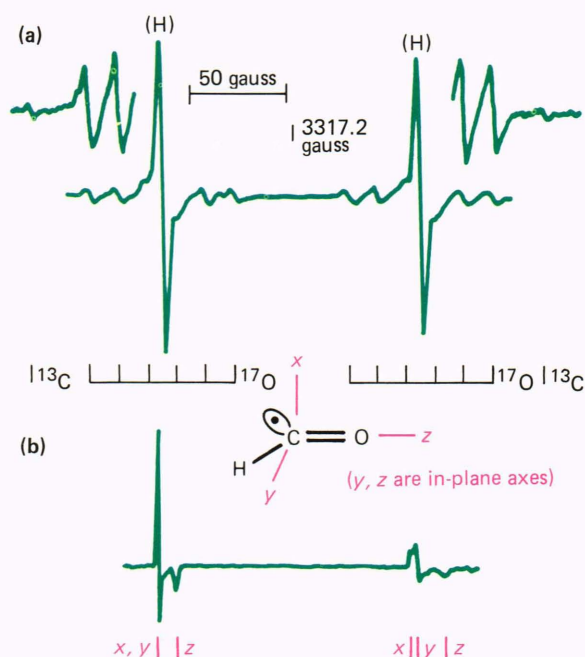
Figure 2—ESR spectra of the formyl radical in (a) a methane matrix at 20 kelvin and (b) a carbon monoxide matrix at 20 kelvin. The spectrum in methane is a sharp-line isotropic spectrum characteristic of a radical that is rotating rapidly enough to average out the orientation-dependent parts of its magnetic interactions. The two strongest lines, denoted (H), are the proton hyperfine structure doublet. The six weaker lines surrounding each of the H lines, denoted ^{17}O, are hyperfine structure splittings resulting from the rare ^{17}O isotope, in which this sample was specially enriched. The very weak lines denoted ^{13}C, shown in the amplified and expanded inserts at the high and low field ends of the spectrum, are hyperfine structure splittings resulting from the rare ^{13}C isotope in its 1 percent natural abundance. In carbon monoxide, each member of the proton hyperfine structure doublet is a broad powder pattern (as described in the text), indicating that the radical does not rotate under these conditions. The sharp-line features of the powder spectra, denoted x, y, and z, correspond to radicals oriented so that the external magnetic field is parallel to the x, y, and z molecular axes as depicted in the figure. (Note that the x and y lines are accidentally coincident in the low field hyperfine line.)

of a matrix-isolated radical can be very different in different matrices, depending primarily on its freedom to rotate. In each case, the apparatus shown in Fig. 1 was used, and the radical was formed by reaction of a hydrogen atom produced by the in situ ultraviolet photolysis of hydrogen iodide with carbon monoxide, the latter having been introduced into the methane matrix as a 1 percent impurity. The reaction sequence is

$$HI + h\nu \rightarrow H + I$$
$$H + CO \rightarrow HCO.$$
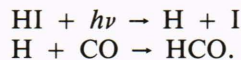
The small hydrogen atom is mobile enough in solid methane at 20 kelvin to diffuse and to react with the carbon monoxide molecules.

The ESR spectrum of HCO in solid methane (Fig. 2a), a sharp-line isotropic spectrum, results because in this matrix, even at 20 kelvin, the HCO radical is rotating fast enough to average out the dependencies of the magnetic parameters (i.e., the g factor and the hyperfine structure splittings) on the orientation of the radical with respect to an external field. The principal feature of the spectrum is a large doublet splitting (135 gauss) because of the proton. In addition, there is a sextet hyperfine structure splitting (15.5 gauss) of each proton doublet line resulting from hyperfine structure splitting by the rare ^{17}O isotope; this splitting is of considerable importance in molecular structure theory and was measured for the first time in this experiment using CO specially enriched in ^{17}O (the abundant ^{16}O isotope has no nuclear moment). Finally, in the expanded, amplified trace of the wings of the spectrum there is part of a doublet hyperfine structure splitting (134 gauss) resulting from ^{13}C in its natural 1 percent abundance. (The number of hyperfine structure lines is determined by the nuclear spin, I, the relation being $N_{hfs} = 2I + 1$, where $I = \frac{1}{2}$ for H and ^{13}C and $5/2$ for ^{17}O.)

On the other hand, in the solid carbon monoxide matrix, the HCO radical is not rotating, and the ESR lines of the proton hyperfine structure doublet—the only observable hyperfine structure lines in the spectrum—are broad and complex. Their shapes are the result of the superposition of orientation-dependent spectra from an ensemble of randomly oriented radicals. However, the complex lines, known as powder spectra, are readily interpreted because their sharp line features, denoted x, y, and z in Fig. 2b, correspond to radicals that are oriented so that the magnetic field is approximately along a principal magnetic axis of the radical. One can determine from the positions of the principal-axis lines both the isotropic and the anisotropic (i.e, the orientation-dependent) parts of the electron g factor and hyperfine splittings. These data are exactly what was desired.

Because the relative intensities of the principal-axis lines in a powder ESR spectrum are related to the orientational distribution of the radicals, the spectra can be used to measure orientational anisotropies of radicals produced or decomposed by polarized light photolysis. This is illustrated in Fig. 3, where Fig. 3a is

ORIGINS OF STRUCTURE IN POWDER ESR SPECTRA

For the reader interested in more detail, the situation in the solid carbon monoxide matrix exists because all magnetic interactions are fundamentally magnetic dipole-dipole interactions whose geometric properties are those of a second-order tensor. These properties and the resulting dependence of the ESR spectrum on radical orientations can always be described by an ellipsoid whose principal axes are the directions in which the ESR spectrum is invariant with respect to small changes in orientation. Formally, the resonant field strength (H_r) for a given hyperfine structure component of the ESR spectrum is given by a relation of the form

$$h\nu_M = \beta_0 (g_x^2 \sin^2 \ \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi$$

$$+ g_z^2 \cos^2 \theta)^{\frac{1}{2}} H_r + (A_x^2 \sin^2 \theta \cos^2 \phi$$

$$+ A_y^2 \sin^2 \theta \sin^2 \phi + A_z^2 \cos^2 \theta)^{\frac{1}{2}} M_I,$$

where θ and ϕ are the polar and azimuthal angles specifying the orientation of the external magnetic field with respect to the principal magnetic axes of the radical; g_x, g_y, and g_z are the magnitudes of the electronic g factor along the principal axes; A_x, A_y, and A_z are the magnitudes of the hyperfine structure splitting along those axes; $M_I (-I \leq M_I \leq I)$ specifies the hyperfine structure component; and ν_M is the microwave frequency. The orientational invariance condition is $\partial H_r / \partial \theta = \partial H_r / \partial \phi = 0$ for $\theta = 0$ or 90 degrees and $\phi = 0$ or 90 degrees, i.e., $\mathbf{H}_r$ along one of the principal axes. This results in a piling up of ESR intensity and hence sharp lines at those orientations, as shown in Fig. 2b. Thus, one can determine from the positions of the principal-axis lines the principal values of the underlying g factor and the hyperfine structure splitting tensors. The directions of the principal magnetic axes with respect to the molecular axes cannot be determined from experiment except insofar as they are determined by molecular symmetry. (In a planar molecule such as HCO, one principal axis must be perpendicular to the molecular plane.) Nor can experiment assign the observed principal-axis lines and corresponding magnetic constants to specific principal axes. Fortunately, these tasks usually can be carried out with the aid of simple molecular structure theories. The resulting axis assignments for HCO are shown in Fig. 2.[8]

the calculated ESR powder spectrum of the high field member of the proton hyperfine structure multiplet of the HCO radical for a microwave frequency of 9200 megahertz and the magnetic constants $A_x/h = 372.1$, $A_y/h = 381.7$, $A_z/h = 397.9$ megahertz, $g_x = 2.0041$, $g_y = 2.0027$, and $g_z = 1.9960$. The values of the constants were determined from the observed spec-
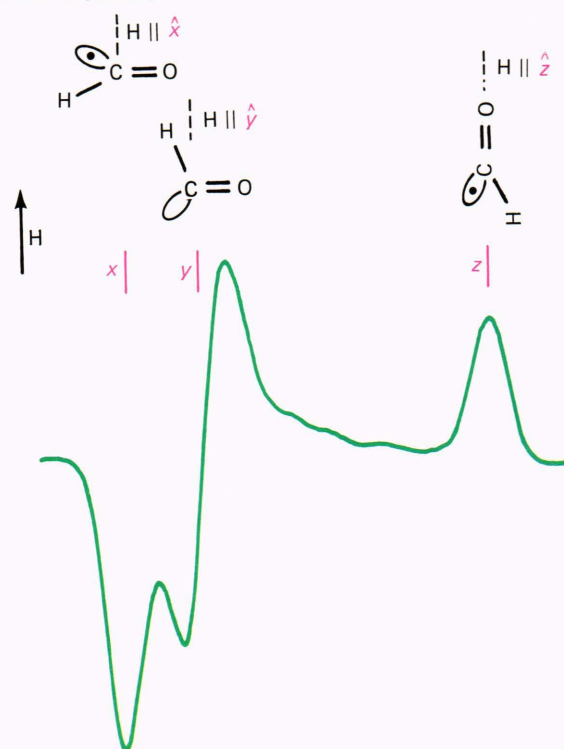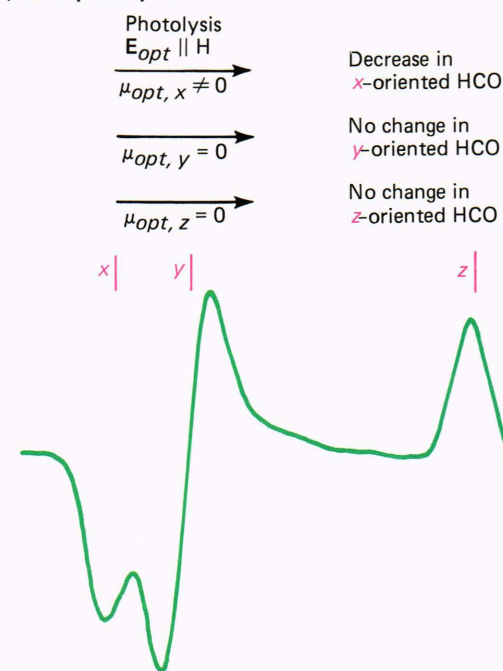
Figure 3—The effect of magnetophotoselective photolysis on an ESR powder line. (a) The calculated powder spectrum for the high field member of the proton hyperfine structure doublet of the formyl radical for magnetic parameter values given in the text. The *x, y,* and *z* sharp-line features correspond to the indicated orientations of the radical with respect to the magnetic field (**H**). (b) The calculated powder spectrum following polarized light photolysis with the optical electric vector (**E**$_{opt}$) parallel to the external magnetic field (**H**) for the case where the dipole moment (μ_{opt}) for the optical transition that decomposes the molecule is parallel to the *x* molecular axis.

tra, and the locations of the principal axes in the molecule were determined by comparing the observed magnetic constants with theoretical predictions for different assignments of the axes.[8]

If we assume that the transition dipole moment for a photoinduced electronic transition that decomposes the HCO molecule is perpendicular to the molecular plane (i.e., parallel to the molecular x axis, which will turn out to correspond closely to the actual situation in HCO), the probability of photoexcitation and consequent decomposition of a given HCO molecule in the ensemble of randomly oriented molecules will be determined by the magnitude of the component of the optical electric vector ($\mathbf{E}_{opt}$) along the molecular x axis or, quantitatively speaking, proportional to $|\mathbf{E}_{opt} \cdot \hat{x}|^2$, where $\hat{x}$ is a unit vector along the x axis. If the light is polarized with the optical electric vector parallel to the external magnetic field ($\mathbf{E}_{opt} \| \mathbf{H}$), the photolysis will remove primarily those molecules oriented so that their molecular x axes are parallel to the external magnetic field. Consequently, the intensity of the x principal-axis line in the ESR powder spectrum will be reduced relative to the intensity of the y and z principal-axis lines. This prediction is confirmed by a calculation of the resulting ESR spectrum for a polarized light photolysis of sufficient duration and intensity to decompose 50 percent of the molecules whose optical transition (x) axis is exactly parallel to the optical electric vector. The resulting spectrum (Fig. 3b) has the intensity of the x line reduced to approximately half the intensity of the corresponding line in the spectrum of the unphotolyzed radical, while the intensities of the y and z lines are the same for the unphotolyzed and the photolyzed spectra.

RESULTS AND DISCUSSION

Formyl (HCO) Radical

The formyl (HCO) radical is of widespread interest from many standpoints, including its appearance in hydrocarbon flames (where it is responsible for emissions known as flame bands), its existence in interstellar space, and as a molecule whose simple structure conceals complexities that make it a challenging testing ground for current theories of molecular structure, spectroscopy, and chemical kinetics. In its ground state, the radical is bent (the bond angle is 120 degrees) and has an optical absorption band in the visible range corresponding to excitation to a low-lying linear excited electronic state. In that state, it can dissociate into hydrogen and solid carbon monoxide because its carbon-hydrogen bond is exceptionally weak.

A recent discovery of significance both for investigation of the HCO radical and for radiation-induced defects in glasses was made by investigators at the Naval Research Laboratory who found that HCO can be formed in certain high-purity synthetic fused silicas by x-irradiation.[9] The process, shown in Fig. 4, depends on the facts that (a) all silicas contain a number of hydroxyl groups, i.e., $\equiv$Si–O–H structures in which the silicon-oxygen network is terminated by the bonding of a hydrogen atom to an oxygen atom, and (b) certain synthetic silicas produced by flame fusion of silicon dioxide incorporate traces of carbon monoxide from the flame gases. The x-irradiation of such a silica, whose original structure is shown in Fig. 4a, breaks many of the hydrogen-oxygen bonds, forming (Fig. 4b) a hydrogen atom and an oxygen-hole center ($\equiv$Si–O), both of which are paramagnetic. The hydro-
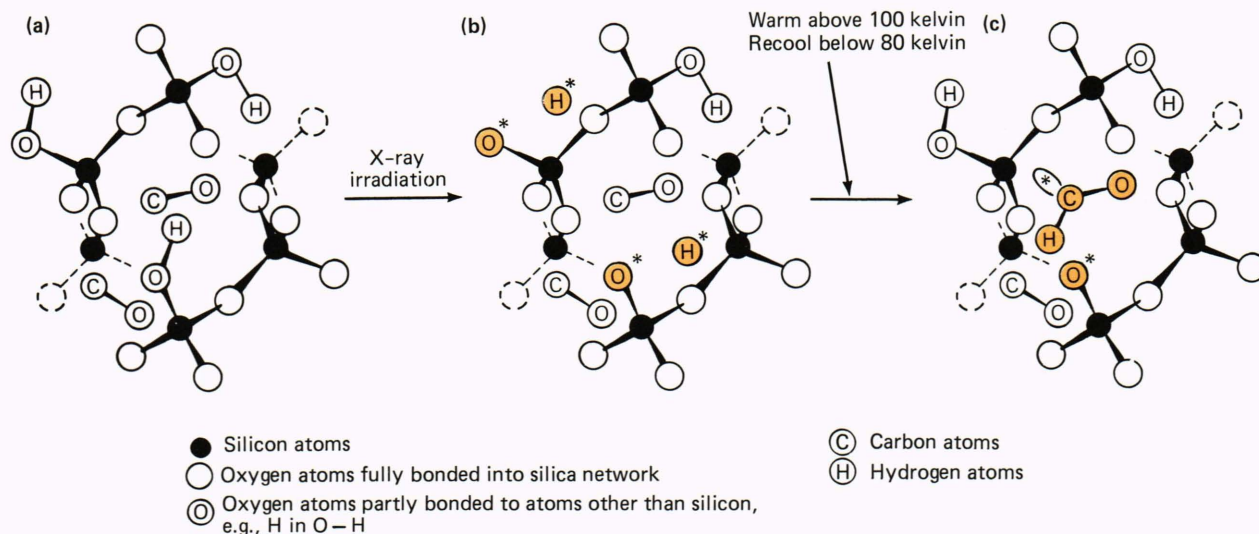

Figure 4—Production of the formyl radical in Suprasil 1 synthetic fused silica. (a) Schematic of the original silica structure showing the hydroxyl groups ($\equiv$Si–O–H) and the traces of carbon monoxide incorporated into the structure during its production by flame fusion of silicon dioxide. (b) The structure following x-irradiation below 100 kelvin, which breaks the hydrogen-oxygen bonds of the $\equiv$Si–O–H hydroxyl groups forming hydrogen atoms denoted H* and oxygen-hole centers denoted $\equiv$Si–O*, where * indicates a paramagnetic species. (c) The structure following a brief warming in the x-irradiated silica above 100 kelvin followed by recooling below 80 kelvin. Above 100 kelvin, the hydrogen atoms have diffused through the silica and have either recombined with oxygen-hole centers to reconstitute the $\equiv$Si–O–H hydroxyl group or have reacted with carbon monoxide molecules to form formyl radicals.

gen atom is fixed in the silica network below 100 kelvin but becomes mobile above that temperature and, as shown in Fig. 4c, can either recombine with the oxygen-hole centers or react with the carbon monoxide molecules to yield HCO radicals. After formation by the foregoing process, the HCO radical can be stabilized indefinitely in the silica by cooling below 80 kelvin. The formation and stabilization of this radical in a high-optical-quality medium permit a number of interesting experiments such as the production of photoinduced orientational anisotropy,[3] which we will describe next.

A 4-millimeter rod of Suprasil 1 fused silica, treated as was just described to produce the HCO radical, was placed in an Air Products variable temperature system located in an ESR microwave cavity (Fig. 1). In this slotted cavity, the sample could be exposed to polarized light using a 200-watt high-pressure mercury lamp, optical filters, and a Glan polarizing prism. At 20 kelvin, each member of the ESR proton hyperfine structure doublet of HCO in silica is a separate powder pattern with fully resolved principal-axis lines. Initially, the high field member of this doublet was as shown in Fig. 5a; that shape agrees well with the calculated one for a randomly oriented ensemble of HCO radicals (cf. Fig. 3a).

Irradiation of the sample for 8 minutes using light in the visible-region optical absorption band of HCO (wavelength, λ, greater than 500 nanometers) and polarized with the electric vector (E_0) parallel to the external magnetic field (H) produced the spectrum shown in Fig. 5b. The spectrum is similar to the one calculated for polarized light photolysis, assuming that the optical transition dipole moment is nonzero only along the x molecular axis (cf. Fig 3b). This establishes that the optical transition is strongly x-axis polarized, in agreement with theory, which predicts that the dipole moment for the transition to the first excited state of a rigid HCO radical is perpendicular to the molecular plane. The small decrease in the z component of the experimental spectrum (20 percent versus 55 percent for the x component) is due to partial depolarization of the exciting light by scattering inside the microwave cavity. The decrease of the y component, which is intermediate between those of the x and z components and which also should be zero in a nonrotating radical, indicates that the radical is not completely rigidly fixed in the silica host but executes a torsional oscillation about the z (C=O bond) axis, thereby enabling the y molecular axis to "steal" optical transition intensity from the x axis.

Finally, the change in the spectrum upon a 90-degree rotation of the sample (Fig. 5c) also demonstrates the partial orientation of the radicals in the photolyzed sample; the x line, which suffered the greatest photoreduction, is enhanced at the expense of the less photodepleted y and z lines as the rotation effectively interchanges the axes. This method of establishing the presence of a photoinduced nonuniform distribution of radical orientations has several uses, including the observation of thermally activated reorientation of the
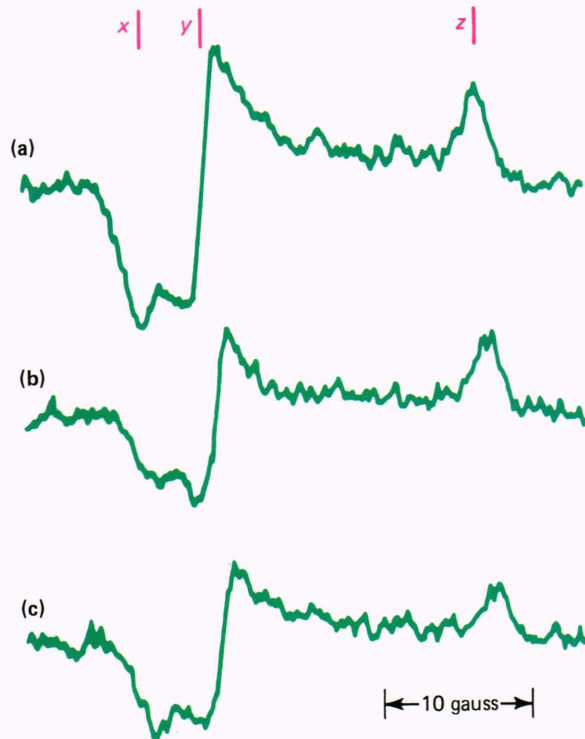
Figure 5—The effect of polarized light photolysis with the optical electric vector parallel to the external magnetic field on the ESR spectrum of the formyl radical in fused silica at 20 kelvin. (a) The high field member of the proton hyperfine structure doublet before photolysis. (b) The same line after photolysis. (c) The effect of rotating the photolyzed sample 90 degrees about the axis perpendicular to both the magnetic field and the direction of the photolyzing light.

radicals by means of the resulting decay of the orientational anisotropy.

An attempt at the last mentioned experiment for HCO in silica (second paragraph above) produced a puzzling result that merits further investigation. On warming from 20 to 40 kelvin, the HCO spectrum recovered nearly all of its prephotolysis intensity despite the facts that (a) the photon quantum energy should have given the leaving hydrogen atom sufficient kinetic energy to take it a considerable distance from the solid carbon monoxide molecule and (b) the X-ray-produced hydrogen atoms are immobile below 100 kelvin. Furthermore, there are indications that the recovered HCO radicals are largely in their original orientations rather than randomized with respect to the original orientation. Apparently, the hydrogen and carbon monoxide fragments of a dissociated HCO molecule have some special, as yet undetermined, relationship that, upon investigation, may provide interesting insights into the behavior of molecular defects and impurities in glasses.

Finally, polarized ultraviolet photolysis of HCO in silica (λ = 253.7 nanometers), which excites the molecule to a second higher excited state, had no effect on the radical concentration or on its orientational distribution. Although the experiment needs to be repeated

using a stronger light source, it tends to agree with other evidence, indicating that this excited state fluoresces rather than dissociates, the emission being responsible for the flame bands in hydrocarbon flames. If so, it should be possible to determine the optical transition moment(s) for the second excited state by determining the changes in the polarization of the fluorescence after altering the orientational distribution of the radicals by bleaching with visible polarized light.

Magnetophotoselection was also observed in the HCO radical trapped in a carbon monoxide matrix, at 13 kelvin.[4] The radical was produced by ultraviolet photolysis of an HI:CO matrix, as was described previously. In agreement with the results for HCO in silica, photolysis of the sample with polarized light decreased the intensity of the x principal-axis component of the high field line while increasing the y and z components. But here, unlike HCO in fused silica, the overall intensity of the spectrum was undiminished because the H atom that photodissociated from one HCO reacted with the carbon monoxide matrix to form another HCO. Since the newly formed radical is randomly oriented with respect to the orientation of the dissociated radical, the net effect of the photolysis is to transfer intensity from the most to the least readily photolyzed orientations. This result would also be obtained if the photolysis did not dissociate the radical but merely caused it to reorient to a new randomized orientation. Clearly, therefore, the method can be useful in observing photolytic reactions that produce no net chemical change but only a physical change. Such processes, if reversible, are potentially useful for optical information storage and processing.

Nitrogen Dioxide

The photochemistry of nitrogen oxides (NO_x) is of both fundamental and practical interest. The latter is primarily because of their role in atmospheric photochemistry. However, it is worthwhile also to explore whether nitrogen dioxide (NO_2) as well as its chemical cousin ozone (O_3) might be useful in the laser-induced photochemical oxidation of semiconductor substrates using the very reactive oxygen atom produced in the reaction $NO_2 + h\nu \rightarrow NO + O$. Nitrogen dioxide is a "stable" free radical that, like HCO, has very complex chemical and spectroscopic properties despite its apparently simple structure. Thus, despite extensive experimental and theoretical study, many questions and controversies remain. For example, an elegant analysis of the orientational distribution of the products of laser photodissociation of a nitrogen dioxide molecular beam indicates that the optical transition moment of the dissociating excited state is along the z axis,[10] as defined in Fig. 6, whereas rotational analysis of the spectrum indicates that the transition moment is perpendicular to the molecular plane (the y axis in Fig. 6).[10]

Our magnetophotoselective experiments on this radical, which might resolve the foregoing question, are very preliminary and are beset with the following complication. Codeposition of a trace of nitrogen dioxide
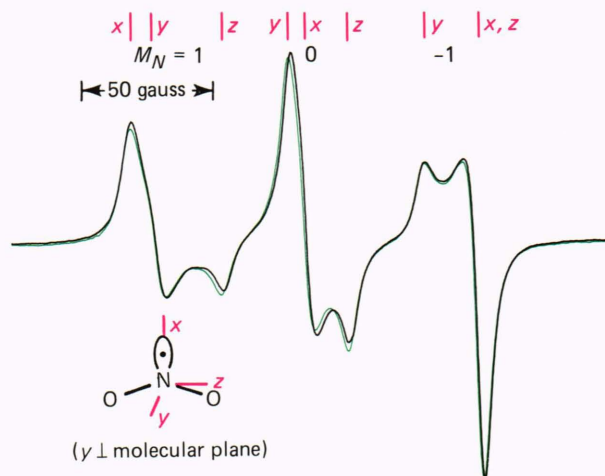
Figure 6—The ESR spectrum of nitrogen dioxide in ethane at 70 kelvin. The nitrogen dioxide was produced by ultraviolet photolysis of the ethane matrix containing (presumably) dinitrogen tetroxide. The light was polarized with the optical electric vector parallel to the magnetic field. The solid curve is the nitrogen dioxide spectrum immediately after photolysis. As indicated in the figure, x, y, and z denote the principal magnetic axes of the radical and the corresponding components of the powder patterns that comprise the nitrogen hyperfine structure triplet. The colored line is the nitrogen dioxide spectrum after rotating the sample tube 90 degrees about the axis perpendicular to the magnetic field and the direction of the light beam. A slightly nonuniform distribution of orientations is indicated by the difference between these two spectra.

with various inert gases apparently results in complete dimerization of nitrogen dioxide to form the nonparamagnetic dinitrogen tetroxide (N_2O_4) because the deposited matrix shows no nitrogen dioxide or other ESR spectrum. Upon photolysis of the matrices, the nitrogen dioxide ESR spectrum appears as shown in Fig. 6 for nitrogen dioxide in ethane, probably from photolysis of the dinitrogen tetroxide dimer. (The ethane matrix was chosen in the presently unfulfilled hope that other radicals formed by reaction of the photogenerated oxygen atom with ethane would provide additional information.) On continued photolysis, the intensity of the spectrum increases and then levels off to a steady state, presumably at the point where the nitrogen dioxide forming and depleting reactions $N_2O_4 + h\nu \rightarrow 2NO_2$ and $NO_2 + h\nu \rightarrow NO + O$, respectively, have the same rate. If the first photolytic reaction is not magnetophotoselective (a condition that is likely because the two nitrogen dioxide photofragments must separate considerably to yield the isolated nitrogen dioxide radicals indicated by their ESR spectra, a process that is probably accompanied by considerable random motion), observed magnetophotoselection can be attributed to the second reaction.

The magnetophotoselection observed on photolyzing with ultraviolet light polarized with the electric vector parallel to the external magnetic field is weak for two reasons: (a) the ethane matrix is of poor optical quality and depolarizes the light considerably by scattering; and (b) at the temperature required to obtain

well-resolved nitrogen dioxide spectra (70 kelvin), the radical is slowly reorienting at a rate comparable to the photolysis rate, thereby limiting the buildup of photoinduced orientational anisotropy. Consequently, the anisotropy can be observed only by photolyzing to steady state and then shutting off the light and quickly observing the spectrum, first in the original position and then in the 90-degree-rotated position.

The nitrogen dioxide ESR spectrum is a nitrogen hyperfine structure triplet; the members of this triplet, denoted $M_N = 1, 0, -1$, respectively, in Fig. 6, are separate powder spectra whose principal-axis lines are also indicated in the figure together with the corresponding principal axes, which are completely determined by symmetry in this molecule. Although the differences between the nitrogen dioxide spectrum in the original and rotated positions are small, they are real. As can be seen in both the $M_N = 1$ and 0 hyperfine structure components, rotation from the original position causes the x principal-axis line to decrease, the z line to increase, and the y line to remain the same or perhaps decrease slightly. There is virtually no change in the high field $M_N = -1$ hyperfine structure component where the x and z principal-axis lines are accidentally coincident and the decrease in one offsets the increase in the other.

The interpretation of this result is that the transition dipole moment for the photolytic transition in nitrogen dioxide is largest along the z axis and small or zero along the x axis, but that it also has a significant component along the y axis. Consequently, photolysis to steady state, i.e., $d[NO_2]/dt = 0$, yields an orientational distribution of nitrogen dioxide that favors somewhat the unphotolyzed x orientation over the photolyzed z and, to a lesser extent, y orientations. This orientational anisotropy is reversed with the 90-degree rotation of the sample, with the resulting interchange of the axes increasing the intensity in the maximum-photolysis z orientation primarily at the expense of the unphotolyzed x orientation. Although this result is very preliminary and tentative, the indication of optical transition moments along both the z and y axes of nitrogen dioxide might explain the conflicting laser photolysis and rotational analysis experiments that suggest z and y polarization, respectively, for the low-lying nitrogen dioxide excited state. We hope this situation can be clarified by further, more refined, experiments.

SUMMARY

The foregoing experiments on magnetophotoselective photochemistry in solids by means of ESR observation of the free-radical products and reactants are a promising new method (or, perhaps more accurately, a novel application of an old method) for investigating photochemical reaction mechanisms and molecular structure. Even the rather rudimentary experiments performed to date have yielded significant and interesting new data, and there is considerable room

for improving the experiments by controlling matrix deposition more carefully to improve the optical quality of the matrices and by refining our ESR instrumentation.

Polarized photochemistry may also have some interesting applications in the areas of microcircuit fabrication and optical data processing. A gas-phase photoexcited molecule often dissociates before it can rotate appreciably, thereby yielding a selective orientational distribution of the photoproducts (e.g., a z-axis-polarized photoexcitation of nitrogen dioxide causes the oxygen atom photoproduct to be expelled along the molecular z axis). Therefore, it might be possible to use polarized laser photolysis of a gas just above a semiconductor substrate to obtain improved orientational and, consequently, spatial resolution of the reaction of the photoproducts with the surface.

Certain defects and impurities in solids have optical absorption bands in the visible (hence the term "color centers"). Some of the centers are anisotropic and change orientation upon photoexcitation. Thus, with polarized light one can create a preferential orientation of such centers that can be the basis for optical information storage, switching, etc. Such effects have already been demonstrated for color centers in alkali halides.[1] However, color centers in glasses could have a number of advantages including greater stability and incorporation into fiberoptic devices. Because the optically induced reorientation takes place very rapidly (on the order of a molecular vibration, about 10^{-12} second), such devices have potential use as ultra-rapid switches. Experiments along the foregoing lines are currently in progress or being planned.

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BORIS F. KIM's biography can be found on p. 22.

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