RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Technical Progress Report

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MASTER

November 1, 1973 - November 1, 1974

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ABSTRACT

During the past year knowledge of the characteristics of ions and radicals produced by high energy radiation has advanced significantly. A model for electron transport in organic glasses and its extrapolation to liquids has been developed and partially substantiated experimentally. The conduction energy level for excess electrons in liquid methane and ethane has been measured and found to require modification of existing transport theory. The energy level structure and mobility of excess electrons in aqueous glasses is now understood in terms of solute ion effects. The semi-continuum model for solvated electrons has been further developed to account for solvation rates in alcohols, the effect of Gaussian wavefunctions and electron stabilization in nonpolar media. Spin trapping has demonstrated that both CH_3O and CH_2OH are primary radicals in liquid methanol radiolysis and that H atoms can be trapped in γ -irradiated liquid alkanes. The thermal decay kinetics of radical pairs in irradiated solids has been delineated. Electron spin echo methods have been applied to probe the molecular dipole arrangement around trapped electrons in solids. Matrix polarity effects on recombination luminescence from electrons and cations in glasses suggests that tunneling recombination occurs in polar matrices.

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RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Report Period: November 1, 1973 - November 1, 1974

During this period the general areas of investigation have included electron-electron double resonance studies of trapped radicals, pulsed electron spin resonance studies of magnetic energy coupling between radicals and their matrices, thermal decay studies of radical pairs in irradiated solids, application of the semicontinuum model to trapped electrons, spin trapping of radiolytic intermediates, interpretation of modulation effects in electron spin echo signals associated with trapped radicals, measurement of conduction electron levels in liquid alkanes, polarized recombination luminescence associated with trapped electrons, and excess electron transport in glassy matrices.

Fifteen papers have been published or accepted for publication and have been issued as technical reports; their abstracts are given below. In addition, the reference citations of papers abstracted in the previous progress report, which have since been published, are listed.

The following sections describe (1) research publications, (2) scientific talks presented and (3) current research summary. No Ph. D. Theses were completed during the current period.

The principal investigator has spent an average of 35% of his time during the academic year and 100% of two summer months on this project. He anticipates that this average percentage will remain the same for the rest of this academic year.

1. Research Publications

The following publications were abstracted in the previous report (COO-2086-52) and have since been published.

- COO-2086-47 Trapped Electrons in Organic Glasses, L. Kevan, Adv. Radiation Chem., 4, 181 (1974).
- COO-2086-49 Effect of Photoionization Energy on the Distance Distribution Between Trapped Electrons and N,N,N',N' -Tetramethyl-p-phenylenediamine Cations in Organic Glasses, H. Mockel, J. Yuen and L. Kevan, J. Phys. Chem., 77, 3035 (1973).
- COO-2086-50 Electron Drift and Hall Mobility in γ -Irradiated 10 M NaOH Glassy Alkaline Ice, T. Huang, I. Eisele and L. Kevan, J. Chem., Phys., 59, 6334 (1973).
- COO-2086-51 Bound-Free Transition of Trapped Electrons in Polar Matrices, K. Fueki, D.F. Feng and L. Kevan, J. Chem. Phys., 59, 6201 (1973).

The following publications have been published or accepted for publication during the current report period.

- COO-2086-53 Spin Trapping of Hydrogen Atoms in γ -Irradiated Liquid Alkanes, S.W. Mao and L. Kevan, J. Phys. Chem., 78 91 (1974).

Abstract: Thermal hydrogen atoms have been observed in the γ -radiolysis of several organic liquids, including alkanes, by spin trapping with phenyl-t-butyl nitron.

- COO-2086-54 On the Solvation of the Trapped Electron in γ -Irradiated Deuterated Ethanol Glass at 4 K, B. L. Bales and L. Kevan, J. Chem. Phys. 60, 710 (1974).

Abstract: EPR data for trapped electrons in γ -irradiated deuterated ethanol glass at 4 K were analyzed under the assumption that trapped electrons are not fully solvated when formed at 4 K either in partially or fully deuterated ethanol glasses. Second moment analysis supports this assumption and also allows estimation of the average hyperfine coupling to the ethyl protons as well as to the hydroxyl protons of the alcohol molecules.

- COO-2086-55 Application of the Semicontinuum Model to Temperature Effects on Solvated Electron Spectra and Relaxation Rates of Dipole Orientation Around an Excess Electron in Liquid Alcohols, K. Fueki, D. F. Feng and L. Kevan, J. Phys. Chem. 78, 393 (1974).

Abstract: A method is developed for calculation of relaxation times for dipole orientation in liquid alcohols induced by localized excess electrons. A microscopic model is used which utilizes quantities calculated from the Fueki, Feng, Kevan semicontinuum model of solvated and trapped electron energy levels. Calculated results for methanol, ethanol, and 1-propanol vs. temperature agree well with the limited experimental data available. The semicontinuum model has also been applied to the calculation of temperature effects on solvated electron spectra in liquid methanol, ethanol, and 1-propanol. The temperature dependence of the quasifree electron state, V_0 , and of the effective dipole moment of molecules in the first solvation shell around the electron are considered for the first time. The calculated results account for about 70% of the observed temperature dependence.

- COO-2086-56 Electron Paramagnetic Resonance Studies of Spin Trapping of the Primary Neutral Radicals Formed in γ -Irradiated Methanol, S. W. Mao and L. Kevan, Chem. Phys. Letters, 24, 505 (1974).

Abstract: The primary neutral radicals in γ -irradiated liquid methanol at 194 K have been spin trapped with phenyl-t-butyl nitron. The principal primary radicals are CH_2OH and CH_3O . In contrast to earlier work, these radicals are formed with an initial ratio of $\text{CH}_2\text{OH}/\text{CH}_3\text{O} = 1.5$ which agrees with gas phase mass spectrometric results. H atoms are also spin trapped although their apparent yield is several times lower than that of the other radicals. In methanol glass at 77 K only CH_2OH becomes spin trapped upon warming.

COO-2086-57 Gaussian Wavefunctions in a Semicontinuum Model for Solvated Electrons, D.F. Feng, D. Ebbing and L. Kevan, J. Chem. Phys., 61, 249 (1974).

Abstract: Gaussian wavefunctions have been compared with previously used hydrogenic wavefunctions in a semicontinuum model for solvated electrons. Although the Gaussian function eliminates the physically unreal cusp associated with a hydrogenic function there is little significant difference in the total energies and optical transition energies calculated with the two functions. The most significant difference is that the fraction of charge density enclosed within a given radius is greater for Gaussian than for hydrogenic functions.

COO-2086-58 Conduction State Energy of Electrons in Liquid Methane and Ethane, S. Noda and L. Kevan, J. Chem. Phys., 61, 2467 (1974).

Abstract: The conduction state energies of electrons in liquid methane and liquid ethane have been measured by a photoelectric method to be 0.0 eV at 109 K and 0.02 eV at 182 K respectively. These results suggest that there is no overall correlation of electron mobility with the conduction state energy of liquid alkanes.

COO-2086-59 Theoretical Relaxation Rates of Dipole Orientation Around an Excess Electron in Liquid Alcohols, K. Fueki, D.F. Feng and L. Kevan, Curr. Top. Radiat. Research

Abstract: A method is developed for calculation of relaxation times for dipole orientation in liquid alcohols induced by localized excess electrons. A microscopic model is used which utilizes quantities calculated from the Fueki, Feng, Kevan semicontinuum model of solvated electron energy levels. Given the semicontinuum model results, the relaxation times are calculated vs temperature with no adjustable parameters. Calculated results for methanol, ethanol and 1-propanol agree well with the limited experimental data available from Hunt, Baxendale and Wardman, and Thomas and Beck. The calculated results agree best for propanol and imply that the theoretical model is most applicable to large molecule solvents. The impressive agreement between experiment and theory suggests that simple dipole orientation is the mechanism of rapid electron solvation in polar liquids.

COO-2086-60 Aspects of Energy Level Structure and Mobilities of Electrons
in Organic Glasses, L. Kevan, Intl. J. Radiat. Phys. Chem.,
6, (1974).

Abstract: Experimental and theoretical aspects of the energy level structure and mobilities of electrons in organic glasses are reviewed. Attention is focused upon trends with matrix polarity. The experimental picture of the energy levels associated with trapped electrons is deduced from the wavelength and temperature dependence of photoconductivity and photobleaching experiments. A reasonably successful theoretical model for the energy level structure, based on a semicontinuum potential incorporating both short range charge dipole interactions and long range polarization interactions, is described and compared with experiment. The semicontinuum model is extended to successfully describe the photoionization process in terms of a bound-free transition. Finally, the conduction electron state is considered. The temperature dependence of the electron mobility suggests that a hopping mechanism is dominant in the glass. Comparison of the mobility in glass and liquid phases indicates that the conduction mechanism may change to one dominated by trapping near room temperature.

- COO-2086-61 Phenomenology of Recombination Luminescence from Trapped Electrons and TMPD^+ in Methyltetrahydrofuran Glass at 77K, H. Mockel, J. Yuen and L. Kevan, Intl. J. Radiat. Phys. Chem., 6, (1974).

Abstract: The recombination luminescence from trapped electrons (e_t^-) and N, N, N', N'-tetramethyl-p-phenylenediamine cation (TMPD^+) in methyltetrahydrofuran glass at 77 K following polarized photoionization of TMPD has been studied. Both fluorescence (F) and phosphorescence (P) have been detected during UV excitation, after UV excitation (isothermal luminescence) and after UV excitation with additional stimulating light (stimulated luminescence) which detraps e_t^- . Polarized emission has been measured following polarized excitation and the results have been compared with theoretical polarization ratios. The TMPD triplet lifetime is 2.8 sec. The initial decay rate of the isothermal luminescence depends on the excitation energy and indicates that larger average e_t^- , TMPD^+ distance distributions are produced for higher energy excitation. The F/P ratio from stimulated luminescence depends strongly on the stimulating wavelength; only phosphorescence is observed at $\lambda > 900$ nm. This differs from previous results in less polar alkane matrices. At low stimulating light energy, it is suggested that recombination occurs by tunneling from an excited state of e_t^- which only has sufficient energy to produce triplet TMPD. At high stimulating light energy, e_t^- is excited to a conduction state from which it can recombine with TMPD^+ to produce both singlet and triplet TMPD. In alkane matrices it appears that only the second process is observed in the accessible stimulating wavelength range.

- COO-2086-62 Energy Level Structure and Mobility of Excess Electrons in γ -Irradiated 5 M K_2CO_3 Aqueous Glasses; Effect of Ions on Trapped and Mobile Electrons in Aqueous Glasses, S. Noda and L. Kevan, J. Phys. Chem., 78, (1974).

Abstract: The energy level structure of trapped electrons (e_t^-) in γ -irradiated 5 M K_2CO_3 glassy ice at 77 K has been investigated via the wavelength dependence of the photocurrent. Scavenger effects demonstrate that the photogenerated charge carrier is an electron. The photocurrent wavelength response per unit incident photon

does not coincide with the optical absorption band of the e_t^- and can be phenomenologically resolved into two bands. The optical absorption band is symmetrically bleached with monochromatic light and can also be resolved into at least two subbands. The photocurrent band at longer wavelength coincides with the longer wavelength absorption band. Thus the e_t^- in the shallower potential wells appear to have no bound excited state as is the case for e_t^- in 10 M NaOH glassy ice. For e_t^- in the deeper potential wells, the shorter wavelength absorption and photocurrent bands do not coincide and indicate a bound excited state as is found for e_t^- in crystalline ice. The difference between the energy level structure for e_t^- in different aqueous matrices can be understood in terms of a semicontinuum model of electron trapping and the modification of the polarization interactions by the ions present in the matrix. The analysis is supported by the photocurrent wavelength dependence in 4.5 M d-glucose glassy ice.

COO-2086-63 A Microdipole Model for Trapped Electrons in Nonpolar Liquids and Glassy Solids, D.F. Feng, L. Kevan and H. Yoshida, J. Chem. Phys., 61, (1974).

Abstract: A model is developed to treat the binding energy of excess electrons in nonpolar liquids and solids such as alkanes. Interaction of the excess electron with C-H bond dipoles is considered for several geometrical arrangements. On this basis it is found that a binding energy of about 0.5 eV can be explained for trapped electrons in condensed alkanes. Although long range polarization interactions are unimportant, the electron interaction with the bond microdipoles of a net nonpolar molecule appear to be the key to understanding electron binding in alkane matrices.

COO-2086-64 Electron Drift Mobility in 2-Methyltetrahydrofuran Organic Glass, T. Huang and L. Kevan, J. Chem. Phys., 61, (1974).

Abstract: The electron drift mobility in 2-methyltetrahydrofuran glass has been measured by a time-of-flight method from 4.2 to 77 K and is $0.055 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 77 K. The mobility is field independent from 16 to 40 kV cm^{-1} . The mobility is approximately temperature independent from 4.2 to 36 K and increases exponentially with temperature above 36 K with an activation energy of $\sim 0.0035 \text{ eV}$. The Debye

temperature of this matrix appears to be ~35 K. Below 35 K incoherent hopping transport is postulated which is little affected by acoustical phonon modes. Above 35 K small polaron, hopping transport is postulated which is aided by excitation of optical phonon modes. The electron mobility in this organic glass is discussed with respect to electron mobilities in organic liquids and in aqueous glasses.

COO-2086-65 Thermal Decay Kinetics of Radical Pairs in Irradiated Solids,
R. Lembke and L. Kevan, *Int. J. Radiat. Phys. Chem.*, 7, (1975).

Abstract: The thermal decay kinetics of radical pairs in gamma-irradiated polycrystalline di-p-tolyl carbonate and in single crystal N-hydroxyurea have been studied. In both systems careful techniques are worked out to separate the isolated radical and radical pair overlapping spectra so that the kinetics of each can be individually studied. In the di-p-tolyl carbonate system the radical pairs decay exclusively by reaction together in a first order process characterized by an activation energy of 35 kJ mol^{-1} . In the N-hydroxyurea system the radical pairs decay exclusively apart to form isolated radicals. Quantitative correlation of the radical pair decay with isolated radical growth is demonstrated. The concurrent processes occur with a rate constant of $k = 9.5 \times 10^{-5} \text{ s}^{-1}$ at 235 K. Although we have a precisely known inhomogeneous spatial distribution in these two systems, it is noted that only first order decay kinetics are observed.

COO-2086-66 Ground State Structure of Trapped Electrons in Glassy Matrices,
L. Kevan, in *Proc. Fifth Int. Congress on Radiation Research*,
H. L. Adler, O. F. Nygaard and W.K. Sinclair, eds., Academic
Press, New York, 1975.

Abstract: The molecular dipole arrangement around excess trapped electrons in aqueous and organic glasses has recently been deduced from a combination of advanced electron magnetic resonance measurements. Trapped electrons in glassy matrices typically show only a single resolved EPR line. However, spin flip satellite lines due to interactions with matrix nuclei have now been observed at 35 GHz for electrons in 10 M NaOH glass. By means of a new theoretical analysis we can determine the number of interacting nuclei in the first solvation shell and the distance to

these nuclei. In this aqueous glassy matrix we find that the trapped electron interacts with eight protons at a distance of ~ 2.1 Å. This is consistent with a model of four oriented water dipoles around the electron with their oxygens at the points of a tetrahedron and their dipoles pointing toward the center of the tetrahedron at which position the electron is located. Electron spin echo signals of trapped electrons in deuterated and partially deuterated matrices show modulation phenomena from electron-nuclear dipolar interactions which are related to the spatial arrangement of surrounding deuterons. In 10 M NaOH glass these results have been analyzed to show that the second shell water dipoles are partially oriented toward the electron. In addition, features due to interactions with the first shell water dipoles seem consistent with a model of about 8 deuterons at a distance of ~ 2 Å. Three pulse electron spin echo signals indicate that the second solvation shell begins at about 3.5 Å. In deuterated and partially deuterated methyltetrahydrofuran (MTHF) glasses, electron spin echo results show that the trapped electron interacts about equally with the ring bonded protons and much more weakly with the methyl protons. Preliminary analysis indicates that two to four MTHF molecules surround the electron with the plane of the ring carbons about 3.8 Å distant from the electron. The picture of the electron trapping potential being formed by orientation of surrounding molecular dipoles in response to the field of the excess electron is supported by these structural results.

COO-2086-67 Classical Trajectory Study of the Unimolecular Decomposition
of $\text{H-C}\equiv\text{C-Cl}$, $\text{H-C}\equiv\text{C-H}$ and $\text{Cl-C}\equiv\text{C-Cl}$, William L. Hase
and Da-Fei Feng, J. Chem. Phys., 61, 0000 (1974).

Abstract: Monte Carlo rate constants and lifetime distributions for $\text{H-C}\equiv\text{C-H}$, $\text{H-C}\equiv\text{C-Cl}$ and $\text{Cl-C}\equiv\text{C-Cl}$ at 200 kcal/mole were determined by classical trajectories. The Monte Carlo rate constants agree to within 30% of the RRKM prediction. Energy randomization is faster in $\text{Cl-C}\equiv\text{C-Cl}$ than in $\text{H-C}\equiv\text{C-H}$ and $\text{H-C}\equiv\text{C-Cl}$. An analysis of nonrandom lifetime distributions indicates that energy randomization is complete by 10^{-12} sec. for each of the molecules. Comparisons are made between our results and other unimolecular studies.

2. Scientific Talks Presented

- AEC-138 Proton Arrangement Around Trapped Electrons in Alkaline Ice from Magnetic Resonance Studies, L. Kevan, Invited Lecture at Symposium on Radiation Chemistry of Aqueous Systems, Moscow, USSR, December 10-12, 1973.
- AEC-139 EPR Double Resonance of Radicals in Glassy Matrices, L. Kevan, Chemistry Seminar, Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR, January 30, 1974.
- AEC-140 EPR Double Resonance of Radicals in Glassy Matrices, L. Kevan, Physics Seminar, Institute of Semiconductors, Kiev, USSR, February 27, 1974.
- AEC-141 EPR Double Resonance of Radicals in Glassy Matrices, L. Kevan, Physics Seminar, Tbilisi State University, Tbilisi, USSR, March 4, 1974.
- AEC-142 Structure of Trapped Siberian Electrons, L. Kevan, Chemistry Seminar, Hahn-Meitner Institut, Berlin, Germany, March 11, 1974.
- AEC-143 Structure of Trapped Siberian Electrons, L. Kevan, Chemistry Seminar, University of Paris, Laboratory of Chemical Physics, Orsay, France, March 18, 1974.
- AEC-144 Structure of Trapped Siberian Electrons, L. Kevan, Chemistry Seminar, University of Salford, Salford, England, March 20, 1974.
- AEC-145 Proton Arrangement Around Trapped Electrons in Alkaline Ice and Trapped Hydrogen Atoms in Acid Glass Deduced from a Study of Satellite Lines in Electron Spin Resonance Spectra, M. K. Bowman, L. Kevan and R. N. Schwartz, Central Regional Amer. Chem. Soc. Meeting, Detroit, Michigan April 22-24, 1974.

- AEC-146 Electron Conduction Band Levels in Liquid Alkanes, S. Noda and L. Kevan, Central Regional Amer. Chem. Soc. Meeting, Detroit, Michigan April 22-24, 1974.
- AEC-147 Effect of Photoionization Energy on the Distance Distribution Between Trapped Electrons and Phenolate Radicals in 10 M Sodium Hydroxide Glass and Alcohol Glasses at 77 K, K. K. Ho and L. Kevan Central Regional Amer. Chem. Soc. Meeting, Detroit, Michigan, April 22-24, 1974.
- AEC-148 Electron Spin Echoes from Trapped Electrons in Glassy Matrices, L. Kevan, Chemistry Seminar, University of Illinois at Chicago Circle, Chicago, Ill., May 7, 1974.
- AEC-149 Electron Spin Echoes from Trapped Electrons in Glassy Matrices, L. Kevan, Chemistry Seminar, Argonne National Lab, Argonne, Illinois, June 14, 1974.
- AEC-150 Trapping Site Structure of Trapped Electrons in Gamma-Irradiated Glassy Methyltetrahydrofuran Deduced from Electron Spin Resonance, Electron Nuclear Double Resonance and Electron Spin Echo Studies at 77 K, M. K. Bowman, L. Kevan and I. Brown, Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974.
- AEC-151 Ground State Structure of Trapped Electrons in Glassy Matrices, L. Kevan, Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974. Invited Lecture
- AEC-152 Electron-electron Double Resonance Study of Trapped Electrons in Gamma-Irradiated 2-Methyltetrahydrofuran Glass, D. F. Feng and L. Kevan, Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974.

- AEC-153 Spectral Shifts of the Solvated Electron in Ethanol and Deuterated Ethanol Glasses at 76 K, N. V. Klassen H. A. Gillis, G. G. Teather and L. Kevan, Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974.
- AEC-154 Trapped Electrons in Ice Matrices Highly Doped with Sodium Hydroxide, Larry Kevan, International Conference on Color Centers, Sendai, Japan, August 19-23, 1974. Invited Lecture
- AEC-155 Ground State Structure of Trapped Electrons in Disordered Matrices, Larry Kevan, Chemistry Seminar, Hokkaido University, Sapporo, Japan, August 26, 1974.
- AEC-156 Double Resonance Studies in Disordered Matrices, Larry Kevan, Government Industrial Research Institute, Nagoya, Japan, August 28, 1974.

3. Current Research Summary

Several current areas of research in radiation chemistry supported by the AEC at Wayne State University, on which substantial progress has been made but which are not yet complete, are briefly described below.

1. Electron-Electron Double Resonance Studies of Cross Relaxation

Electron-electron double resonance (ELDOR) has been used to examine cross relaxation between trapped electrons and radicals in γ -irradiated methyl-tetrahydrofuran (MTHF) glass. ELDOR has been used to measure the ratio of the cross relaxation time T_{pd} to the electron spin-lattice relaxation time T_{le} . Independent direct measurements of T_{le} have been made with a newly constructed pulsed EPR spectrometer in our laboratories. Thus, from the ELDOR measurements we can obtain T_{pd} . We find that T_{pd} is temperature independent from 44-77 K which implies that electron-nuclear-dipolar interactions do not dominate the

cross relaxation mechanism. A direct electron spin-electron spin interaction between the radical and trapped electron is thus indicated for the cross relaxation mechanism. It was also possible to measure T_{pd} as a function of the frequency difference between the pumped radical spin and the detected electron spin. T_{pd} increases slowly and roughly linearly with increasing frequency difference; this indicates direct cross relaxation involving very weak overlap of the tails of the spectral lines of the electron and radical spins. Based on direct electron spin-electron spin interaction a simple model predicts that the electron: radical correlation distance $\geq 10 \text{ \AA}$. Further work is in progress to better define this correlation distance and the radiation dose dependence of the cross relaxation process.

2. Analysis of Matrix Nuclei Spin Flip Satellite Lines In EPR Spectra

In the past year a new 35 GHz EPR bridge has been set-up to enable more detailed study of the information available in so-called spin flip satellite lines in EPR spectra in disordered systems. The relative intensities of allowed EPR lines of a paramagnetic species and partially forbidden spin flip satellite lines due to dipole-dipole coupling between the paramagnetic species and the matrix nuclei have been analyzed previously. This analysis allows one to determine a distance r to the matrix nuclei if a particular number of matrix nuclei is assumed. We have been able to extend this analysis to make it much more useful by considering the energy separation of the allowed and forbidden EPR lines. We have shown that the energy separation can be used to obtain another average over the distance to the nearest protons contributing to the satellite lines. If we combine this with the intensity analysis we can show that the interaction distance to a unique number of closest matrix protons can be determined. We have used 35 GHz EPR data to obtain well resolved satellite lines associated with trapped hydrogen atoms in γ -irradiated oxyacid glasses. For hydrogen atoms trapped in γ -irradiated sulfuric acid glass at 77K the analysis indicates that interaction occurs with four matrix protons at a distance of $2.15 \text{ \AA}$. For trapped hydrogen atoms in phosphoric acid glass the analysis indicates interaction with four matrix protons at $2.37 \text{ \AA}$. It is interesting that the number four comes out in both cases. Although

we can still not suggest a specific geometrical model for the H atom trapping site, we do note that the trapping site seems larger in phosphoric acid glass than in sulfuric acid glass. However, the same geometrical structure is indicated since in both cases four closest protons appear to be interacting with the trapped hydrogen atom. This suggests that the H atoms are not trapped in the bulk ice but are trapped somewhere close to the oxyanions themselves. It would appear that the H atoms may be trapped by water molecules that are hydrogen bonded to the oxyanion. Since P-O bonds are somewhat longer than S-O bonds, a somewhat larger trapping site is then expected in the phosphoric acid matrix as observed. We think that this new analysis of the information available from satellite lines will be particularly useful in deducing the molecular geometrical structure around trapped radicals in disordered systems.

3. Analysis of Slow Passage EPR Saturation Curves

Slow passage EPR power saturation measurements of trapped electrons produced in γ -irradiated organic glasses have proved to be a powerful method to obtain information about the spatial distribution of radiation produced trapped species. However, we have found that the experimental microwave power saturation curves for trapped electrons in organic glasses do not fit the simple paramagnetic relaxation theories developed for inhomogeneously broadened lines in the absence of magnetic field modulation. These theories have been previously applied to these systems to obtain approximate relaxation time information. The part of the power saturation curve at low microwave power can usually be fit quite well by these theories. However, the part of the power saturation curve at high microwave power does not at all fit the previous theoretical models used. We have shown that a generalized treatment in which both the spin packet width and the spin packet lineshape is changed relative to the overall observed line width and lineshape still does not account for the observed experimental power saturation curves. However, for reasons of sensitivity, almost all experimental saturation data are obtained in the presence of magnetic field modulation. Our analysis indicates that a satisfactory theoretical model must include the effects of magnetic field modulation. This is somewhat difficult to do, but we believe that we now see how to do it. A better description of the saturation curve shapes for trapped

electron and radical systems is indeed desirable in order to exploit the maximum amount of information available in slow passage EPR saturation studies.

4. Temperature Dependence of the Recombination Fluorescence of Photoionized Tryptophan in Alkaline Ice Glasses

Recombination luminescence of photoionized solutes in glassy matrices reveals aspects of the electron recombination process with the parent cation. In polar media it seems that a significant fraction of the ejected electrons are initially stabilized by minimum energy regions in the "rough" potential of the disordered matrix which are often described as shallow, pre-existing traps. Such electrons may either become more deeply and stably trapped by inducing rotational relaxation of the surrounding molecules, or may recombine with their parent ions on a short time scale. When the temperature increases the ease of rotation of molecular dipoles increases and facilitates the trapping process. This probably explains the increase in the yield of trapped electrons with irradiation temperature observed in ethylene glycol/water glass and in 9 M LiCl/H₂O glass. In correspondence with an increased trapped electron yield one expects that the fraction of shallowly trapped electrons that recombine with their parent ion should decrease with increasing temperature. We have used the recombination fluorescence from photoionized tryptophan in the above aqueous glasses to test this thesis. It is found that the intensity as well as the initial decay rate of the recombination fluorescence does decrease as the UV-irradiation temperature increases above 77K. This is interpreted in terms of a tunneling process in which the electron trap depth increases slightly with increasing irradiation temperature. This causes the tunneling rate constant to decrease, and as the trap depth drops below the lowest singlet level of tryptophan, an increasing fraction of the recombination events lack the energy necessary to generate recombination fluorescence.