RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Technical Progress Report

Larry Kevan

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

April 1, 1972 - November 1, 1973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PREPARED FOR THE U.S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-2086

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

During the past year considerable new knowledge has been found about the characteristics of radiation produced ions and radicals in solids. Electron transport in glassy alkaline ices can be understood in terms of a band model and is governed by lattice phonon scattering above about 50 K and by ionic scattering from O^- centers below 50 K. The radii of spatial extent of trapped electron wavefunctions in 10M NaOH, methanol and methyltetrahydrofuran (MTHF) glasses have been measured to be 2.3 Å, 2.5 Å and 2.8 Å respectively. The semicontinuum model for trapped electrons in polar systems has been improved and extended to MTHF and amine glasses, applied to explain pressure shifts of solvated electron spectra in alcohols, and applied to dielectron species. The energy level structure of trapped electrons in 3-methylhexane glass has been elucidated and two photon transitions to the conduction state have been found. Electron-electron double resonance has been used to demonstrate cross relaxation between radicals and electrons in MTHF, to demonstrate the limitations of the spin packet model for the relaxation of inhomogeneously broadened lines and to demonstrate spin diffusion in trapped electron electron paramagnetic resonance lines in alkaline ice glass. About 20% of the second shell molecular dipoles around trapped electrons in alkaline ice appear to be oriented toward the electron, and forbidden matrix proton spin flip satellites associated with the trapped electron in this matrix can be observed. The average distance distribution between trapped electrons and N, N, N', N'-tetramethyl-p-phenylenediamine cations in organic glasses increases with increasing photoionization energy. A theoretical model of the bound-free transition for trapped electrons in polar matrices has been formulated and indicates that optical transitions may occur directly to the conduction state.

RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Report Period: April 1, 1972 - November 1, 1973

During this period the general areas of investigation have included electron-electron double resonance studies of trapped radicals, thermal decay studies of radicals and radical pairs in irradiated solids, application of the semicontinuum model to trapped electrons, mechanisms of electron trapping in glassy matrices, measurement of conduction electron levels in glasses, polarized recombination luminescence associated with trapped electrons, and drift and Hall mobility measurement of photo excited electrons in glassy matrices.

Twenty-one 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 report which have since been published are listed.

The following sections describe (1) research publications, (2) scientific talks presented (3) Ph. D. Theses completed and (4) current research summary.

The principal investigator has spent an average of 25% of his time during the 1972-73 academic year, 35% of his time during the 1973-74 academic year and 100% of one summer month on this project.

Four students have completed Ph. D. theses during this report period; their thesis titles and present positions are given below.

1. Research Publications

The following publications were abstracted in the previous report (COO-2086-30) and have since been published.

- COO-2086-25 Energy Level Structure of Trapped Electrons in Methyl-tetrahydrofuran Glass from Photoconductivity and Optical Bleaching Studies, T. Huang, I. Eisele, D. P. Lin and L. Kevan, J. Chem. Phys., 56, 4702 (1972).
- COO-2086-26 A Semiempirical Estimate of the Scattering Cross Section and Mobility of Excess Electrons in Liquid Hydrocarbons, K. Fueki, D. F. Feng and L. Kevan, Chem. Phys. Lett., 13, 616 (1972).
- COO-2086-27 High Temperature Dependence of the Electron Hall Mobility in γ -Irradiated KCl, I. Eisele and L. Kevan, J. Chem. Phys., 56, 5738 (1972).
- COO-2086-28 Application of the Semicontinuum Model to the Effect of Dipole Reorientation on Trapped Electron Spectra in Glassy Ethanol, K. Fueki, D. F. Feng and L. Kevan, J. Chem. Phys., 56, 5351 (1972).
- COO-2086-29 Paramagnetic Relaxation Study of Spatial Distribution of Trapped Radicals in γ -Irradiated Alkaline Ice and Organic Glasses at 4.2 K, D. P. Lin, P. Hamlet and L. Kevan, J. Phys. Chem., 76, 1226 (1972).

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

- COO-2086-31 Temperature Dependence of the Drift Mobility of
Electrons in Glassy 10M NaOH Ice, T. Huang, L.
Eisele and L. Kevan, J. Phys. Chem., 76, 1509 (1972)

Abstract: The drift mobility of photoexcited electrons in glassy 10 M sodium hydroxide ice was measured between 4 and 100 K with a time-of-flight method. From 100 to 50 K the drift mobility increases as the temperature decreases which indicates electron scattering by lattice phonons and suggests that the electron motion can be treated in terms of a band model. Below 50 K the temperature dependence of the electron mobility is consistent with ionic species scattering from O^- centers.

- COO-2086-32 Matrix ENDOR Linewidths of Trapped Electrons in Glassy
Matrices at 77 K, J. Helbert, L. Kevan and B. Bales, J.
Chem. Phys., 57, 723 (1972).

Abstract: Matrix ENDOR lines of protons associated with trapped electrons in γ -irradiated glassy matrices of 10M NaOH, methanol and 2-methyltetrahydrofuran at 77 K have been observed. By analysis of the matrix ENDOR line shapes under comparable experimental conditions the linewidth has been related to the spatial extent of the ground state wavefunction of the trapped electron. These experimental results are compared with predictions of the semicontinuum model for trapped electrons and found to be in good agreement.

- COO-2086-33 Role of Fluoride Ion in Irradiated Aqueous Systems, B. L.
Bales and L. Kevan, J. Chem. Phys., 57, 1813 (1972).

Abstract: It is suggested that F^- can act as a hole trap in γ -irradiated single crystal ice doped with fluoride ion as well as in frozen aqueous systems. Recent data is interpreted in light of this hypothesis.

- COO-2086-34 Application of the Semicontinuum Model to Pressure Effects on Solvated Electron Spectra in Methanol and Ethanol, D. -F. Feng, K. Fueki and L. Kevan, J. Chem. Phys., 57, 1253 (1972).

Abstract: The semicontinuum model for solvated electrons has been applied to the calculation of pressure effects on solvated electron spectra in methanol and ethanol at 298 K. The pressure dependence of the density, static and optical dielectric constants and the quasifree electron energy state have all been included. The calculated results satisfactorily explain the experimentally observed blue shifts with pressure. Analysis shows that pressure affects short range interactions much more than long range interactions and results in a decrease in the electron cavity radius and an increase in the energy of the quasifree electron state.

- COO-2086-35 Thermally Stimulated Conductivity of γ -Irradiated Triethylamine and 3-Methylpentane Glasses, A. Munjal and L. Kevan, J. Phys. Chem., 76, 2781 (1972).

Abstract: Thermally stimulated conductivity of ^{60}Co γ -irradiated and unirradiated triethylamine was studied as the glassy matrix was warmed from 77 K. The unirradiated matrix gives a peak near 117 K which can be removed by field orientation upon freezing the matrix. The irradiated matrix gives evidence for three different types of radiation-produced species as indicated by conductivity peaks in different temperature ranges. At 77 K a peak is observed which decays in about 20 min and can be assigned to a small population of shallow trapped electrons. The main population of trapped electrons is released in the 107-117 K temperature range which corresponds well with epr data. This conductivity peak is reduced by the electron scavengers, carbon tetrachloride, and biphenyl. The third conductivity peak appears between 147 and 157 K and is attributed to molecular ions. At higher temperatures the background intrinsic conductivity

increases monotonically and is characterized by an Arrhenius activation energy of 0.20 eV. A few experiments were also carried out on glassy 3-methylpentane to compare with two published studies of thermally stimulated conductivity in this matrix which are divergent. Our results confirm those of Wiseall and Willard.

- COO-2086-36 Electron-Electron Double Resonance Demonstration of Cross Saturation Between Trapped Electrons and Radicals in γ -Irradiated 2-Methyltetrahydrofuran Glass, H. Yoshida, D. F. Feng and L. Kevan, J. Amer. Chem. Soc., 94, 8922 (1972).

Abstract: Electrons and radicals are trapped in γ -irradiated MTHF glass at 77 K. Cross saturation between these electron and radicals has been demonstrated by electron-electron double resonance. When a radical hyperfine line is pumped, magnetic energy is transferred to the electron spin system to partially saturate it. The most probable mechanism for this effect appears to be cross relaxation involving direct spin-spin interaction.

- COO-2086-37 A Semicontinuum Model for Trapped Electrons in Polar Liquids and Solids: Trends with Matrix Polarity, K. Fueki, D. F. Feng and L. Kevan, J. Amer. Chem. Soc., 95, 1398 (1973).

Abstract: A semicontinuum model is extended to trapped electrons in 2-methyltetrahydrofuran glass and in three amine glasses at 77 K. It is shown to account for recent experimental results quite well. The semicontinuum model has also been modified for trapped electrons in aqueous glasses like 10 M NaOH by neglecting long-range polarization interactions. This modification successfully predicts no bound excited state in agreement with experiment. Revised calculations are given for electrons in water and ice and configuration coordinate diagrams are presented for the above

matrices and for electrons in liquid and glassy methanol and ethanol. The effects of the various physical constants of the matrices on the trapped electron energy level structure is discussed from the viewpoint of matrix polarity.

COO-2086-38 L. Kevan, "Properties of Trapped and Mobile Electrons in Pure Ice and in Alkaline Ice," in Physics and Chemistry of Ice, E. Whalley, S. J. Jones and L. W. Gold, eds., (Royal Soc. Canada, Ottawa, Canada, 1973).

Abstract: Electrons generated by γ -irradiation are trapped with high efficiency in glassy alkaline ice (10 M NaOH) and with low efficiency in single-crystal ice at 77 K. The trapped electrons (e_t^-) are characterized by an optical absorption band in the visible, and photoexcitation produces photoconductivity and optical bleaching. The wavelength and temperature dependence of photoconductivity and bleaching establishes that no bound excited state for e_t^- exists in glassy alkaline ice, but that a weakly bound state does exist in crystalline ice, γ -irradiation generates trapped electrons with a nonuniform spatial distribution. The details of this nonuniformity have been investigated by measurement of spin-spin interactions by paramagnetic relaxation methods. The electrons are trapped in regions of high local concentration called spurs, with an average radius of $41 \text{ \AA}$. Matrix ENDOR measurements have given a value for the spatial extent of the ground-state wavefunction of e_t^- in alkaline ice. This value and the energy-level structure are satisfactorily explained by a semicontinuum model incorporating both short- and long-range interactions. The transport mechanism of the photoexcited electrons in the alkaline-ice matrix has been investigated by measurement of both Hall and drift mobilities as a function of temperature and voltage. Between 4 and 50 K the drift mobility is dominated by scattering from ionized species. These ionized species are shown to be radiation produced and are not due to the Na^+ and OH^- ions which are apparently

incorporated into the conduction-band structure. Above 50 K, lattice scattering dominates the drift mobility and at 80 K the Hall and drift mobilities show good agreement.

COO-2086-39 ENDOR of Trapped Hydrogen Atoms in γ -Irradiated Glassy Acid Matrices and in Polycrystalline Oxyanion Matrices, J. Helbert and L. Kevan, J. Chem. Phys., 58, 1205, (1973).

Abstract: Trapped H atoms are produced in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ glasses and in $\text{KHSO}_4/\text{H}_2\text{O}$ and $\text{KH}_2\text{PO}_4/\text{H}_2\text{O}$ polycrystalline matrices by γ -irradiation at 77 K. High power proton ENDOR spectra of the H atoms have been obtained and analyzed. Prominent matrix ENDOR lines at the free proton frequency together with weak sidebands are observed. Two methods have been developed for increasing the resolution of weak sidebands due to isotropic hyperfine interaction. The two methods involve high irradiation dose and the addition of paramagnetic transition metal ions. The ENDOR line shapes are analyzed in terms of modulation of the electron-nuclear dipolar interaction by the relaxing electron. The isotropic hyperfine constant is about 0.75 G in all matrices and is assigned to the nearest neighbor matrix protons 1.8 Å distant. The center matrix ENDOR lines have been analyzed by computer simulation of the line shape to arrive at the spatial extent of the H atom wavefunction. In glassy matrices the wavefunction is nearly unperturbed from that of the free atom, while in polycrystalline matrices the extreme tail of the wavefunction shows significant distortion.

COO-2086-40 Energy Level Structure and Mobilities of Excess Electrons in Aqueous and Organic Glasses, L. Kevan, J. Phys. Chem., 76, 3830 (1972).

Abstract: Recent photoconductivity and optical bleaching studies of trapped electrons (e_t^-) as a function of wavelength and temperature have delineated the energy level structure of electrons in matrices of varying polarity. Results are described for alkaline ice (10 M NaOH), 5 M K_2CO_3 ice, crystalline ice, methyltetrahydrofuran (MTHF), and 3-methylhexane (3MH) solid matrices. In alkaline ice no stable bound excited state exists for trapped electrons. This conclusion is based on a wavelength-independent quantum efficiency for bleaching in the e_t^- absorption band and on temperature independent photoconductivity and optical bleaching responses between 77 and 4.2 K. In single crystal ice an excited state for e_t^- is found ~ 0.4 eV below the lowest conduction level from photobleaching quantum efficiency measurements. In MTHF two excited states of e_t^- have been found. One is optically allowed and is ~ 0.6 eV below the bottom of the conduction state in a vertical transition from the ground state. The other is optically forbidden and is 1.1 eV below the bottom of the conduction state in a vertical transition from this optically forbidden state. If the ground state is described by a $1s$ type wavefunction, the optically allowed state can be described by a $2p$ function and the optically forbidden state by a $2s$ function. Photoconductivity can be generated by both one- and two-photon processes. The two-photon process can be interpreted to occur via a $2s$ state. The energy level structure of e_t^- in 3MH is similar to that in MTHF. The energy level structure of e_t^- in 3MH is similar to that in MTHF. The energy level structure in the different matrices can be semiquantitatively accounted for by the semiconductor model for trapped electrons. Both Hall and drift mobilities have been measured for photoexcited electrons in alkaline ice. The results are well described by a band model and the main scattering mechanisms are identified as optical lattice phonon scattering and O^- Coulombic scattering. Drift mobilities of mobile electrons in MTHF indicate that the electron motion is best described by a hopping model from 40 to 77 K.

- COO-2086-41 On the EPR Spectrum of the Matrix Stabilized Hydronium Radical, S. Noda, H. Yoshida and L. Kevan, Chem. Phys. Lett., 19, 240 (1973).

Abstract: A previous report of the discovery of the EPR spectrum of H_3O in UV-irradiated perchloric acid glass has been reinvestigated. The EPR spectrum previously assigned to H_3O has been compared with an authentic spectrum of CH_3 and has been found to be identical within experimental error in hyperfine splitting, g-factor, lineshape and linewidth. It is concluded that the existence of H_3O has not yet been experimentally demonstrated.

- COO-2086-42 Energy Level Structure of Trapped Electrons in 3-Methylhexane Glass from Photoconductivity and Optical Bleaching Studies, T. Huang and L. Kevan, J. Amer. Chem. Soc., 95, 3122 (1973).

Abstract: Electrons are trapped in γ -irradiated 3-methylhexane (3MH) glass at 77 K. Monochromatic photoexcitation produces photoconductivity and optical bleaching with a threshold near 1240 nm (1.0 eV) and a peak near 1000 nm (1.24 eV). This transition is linear in light intensity and independent of temperature between 77 and 4.2 K, so it is interpreted as a one photon transition directly to the conduction band or to an autoionizing state. Photoexcitation near 1650-1700 nm discloses a two photon transition which depends on the light intensity squared. The first photon corresponds to the well-known optical absorption of trapped electrons in 3MH at 1650 nm. This transition is interpreted as a $1s \rightarrow 2p$ type. The $2p$ state then presumably crosses to an intermediate $2s$ -type state from which the second photon is absorbed. The threshold of the second photon transition was not determined but the transition appears to have a peak near 1700 nm. The temperature dependence of both optical bleaching and photoconductivity under photoexcitation with $\lambda > 1400$ nm shows that population of the intermediate $2s$ -type state involves an activation energy ~ 0.001 eV. The deduced energy level

structure of trapped electrons in 3 MH is remarkably similar to the structure in the more polar matrix, methyltetrahydrofuran.

COO-2086-43 Semicontinuum Model for Trapped Dielectron in Polar Liquids and Solids, D. F. Feng, K. Fueki and L. Kevan, J. Chem. Phys., 58, 3281 (1973).

Abstract: A semicontinuum model for trapped dielectrons, two electrons in the same cavity, has been developed and applied to liquid ammonia, water, ice at 77 K, and methyltetrahydrofuran and amine glasses at 77 K. In all matrices the configurational stability of the ground state of the dielectron has been established, and the dielectron is found to be stable with respect to two single trapped electrons. In general the cavity radius for the dielectron is slightly smaller than that for the single electron. The excited state of the dielectron is bound, and only slight shifts of the optical absorption band of the dielectron compared to the single electron are predicted.

COO-2086-44 Electron-Electron Double Resonance Study of Trapped Electrons in 10 M NaOH Alkaline Ice Glass, H. Yoshida, D. F. Feng and L. Kevan, J. Chem. Phys., 58, 3411 (1973).

Abstract: Electron-electron double resonance (ELDOR) has been used to test the validity of the noninteracting spin-packet model for inhomogeneously broadened electron paramagnetic resonance (EPR) lines as applied to trapped electrons in 10M NaOH ice. Spectral simulation of field-swept ELDOR spectra based on the spin-packet model qualitatively, but not quantitatively, accounts for the observed spectra. The quantitative failure of the spin-packet model is interpreted in terms of spin diffusion within the EPR line. Structure in frequency-swept ELDOR spectra, which is not predicted by the spin-packet model, has been observed and interpreted as ~ 5.7 G hyperfine coupling with eight matrix protons. This supports a tetrahedral model of oriented water dipoles for the immediate environment of the trapped electron in alkaline ice.

- COO-2086-45 Electron-Electron Double Resonance Study of Trapped Electrons in γ -Irradiated 2-Methyltetrahydrofuran Glass: Magnetic Energy Transfer Between two Different Spin Systems, H. Yoshida, D. F. Feng and L. Kevan, J. Chem. Phys., 58, 4924 (1973).

Abstract: Electron-electron double resonance (ELDOR) of trapped electrons and radicals in γ -irradiated 2-methyltetrahydrofuran (MTHF) glass at 77 K was investigated. Magnetic energy pumped into the radical spin system is transferred to the trapped electron spin system to partially saturate it. The cross saturation mechanism is consistent with dipolar cross relaxation in which a radical spin flips down and an electron spin flips up. Analysis of the rate of spin relaxation shows that the reciprocal ELDOR reduction is linear with pumping microwave power with an intercept which gives the ratio of the cross-relaxation time to the electron spin-lattice relaxation time. The experimental data are found to fit this relationship. This ratio of relaxation times is of the order of 0.5 while the relaxation times themselves are in the 10^{-4} sec range. The observation of cross relaxation in this system supports the concept that the trapped electron and radical are spatially correlated in γ -irradiated MTHF.

- COO-2086-46 Electron Spin Echo Envelope Modulation from Trapped Electrons in a Glassy Medium, Chem. Phys. Lett., 22, 16 (1973).

Abstract: An amplitude modulation of the electron spin echo envelope has been observed for radiation-produced trapped electrons in 10M NaOD/D₂O at 77 K but not in 10M NaOH/H₂O. The modulation has been simulated theoretically by generalizing the single crystal model of Rowan, Hahn and Mims to disordered systems. The modulation has been interpreted as due to dipolar interactions with deuterons in molecules of the second solvation shell around the trapped electrons.

COO-2086-47 Trapped Electrons in Organic Glasses, L. Kevan, Adv. Radiation Chem., 4, 000 (1974).

Abstract: A review of the following topics: 1) Physical Characteristics of Trapping Matrices, 2) Production and Trapping of Electrons, 3) Ground State Characteristics of Trapped Electrons, 4) Energy Level Structure of Trapped Electrons, 5) The Delocalized Conduction State and 6) Theoretical Models for Trapped Electrons.

COO-2086-48 Forbidden Matrix Proton Spin Flip Satellites in Trapped Electron EPR Spectra, M. Bowman, L. Kevan, R. N. Schwartz and B. Bales, Chem. Phys. Lett., 22, 19 (1973).

Abstract: Observation of the 35 GHz EPR spectrum of γ -irradiated 10M NaOH/H₂O and 10 M NaOD/D₂O glassy ices at 77 K has revealed proton spin flip satellites associated with the trapped electron EPR line. This suggests that forbidden satellite transitions contribute to the lineshape of the trapped electron line in the 9 GHz spectrum which has commonly been studied.

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, J. Phys. Chem., 77, 0000 (1973).

Abstract: The recombination luminescence from trapped electrons (e_t^-) and N,N,N',N',-tetramethyl-p-phenylenediamine cation (TMPD⁺) in methyltetrahydrofuran and 3-methylpentane glasses at 77 K following photoionization of TMPD has been studied. The initial decay rate of the isothermal fluorescence depends on the excitation energy used for photoionization and indicates that larger average e_t^- , TMPD⁺ distance distributions are produced for higher energy excitation.

COO-2086-50 Electron Drift and Hall Mobility in γ -Irradiated 10M NaOH
Glassy Alkaline Ice, T. Huang, I. Eisele and L. Kevan,
J. Chem. Phys., 60, 0000 (1974).

Abstract: The drift and Hall mobility of electrons in 10M NaOH glassy alkaline ice has been studied to determine the relevant charge transport mechanisms in this disordered system. The electrons are photoexcited to a conduction state after being trapped in the matrix at 77 K by γ -irradiation. The dominant electron scattering mechanisms have been deduced from variation of voltage and temperature, and it appears that electron transport in this matrix is well characterized by a band model. Field dependent mobilities are observed and indicate that hot electron effects exist. In the field independent mobility region, the limit of which depends on temperature, the dominant mechanism is scattering by acoustical and optical phonons. This holds above 77 K and probably to much lower temperatures. In the field dependent mobility region the dominant mechanism is ionic species scattering, notably by O^- , at lower temperatures, and acoustical and optical phonon scattering at higher temperatures; the dividing temperature decreases with increasing field and is ~ 50 K at 4 kV cm^{-1} . At constant temperature versus field, the mobility is dominated by phonon scattering in the field independent mobility region, by ionic species scattering in the initial part of the field dependent mobility region, and by phonon scattering again at high fields. Drift mobility, Hall mobility and photoconductivity results are interrelated and give a consistent picture of electron transport in 10M NaOH. The superOhmic photocurrents, previously observed, are seen to be due to dominance of ionic species scattering. The temperature and field dependence of the mobility is satisfactorily predicted by a simple band model and the mobility magnitude is at least semiquantitatively predicted. However, the critical field, at which hot electron effects occur, is predicted to be too high by the band model.

- COO-2086-51 Bound-Free Transition of Trapped Electrons in Polar Matrices, K. Fueki, D. F. Feng and L. Kevan, J. Chem. Phys., 60, 0000 (1974).

Abstract: The photon energy dependence of the bound-free transition probability for trapped electrons in polar matrices is calculated for ice, ethylene glycol-water (50/50), 2-propanol, 2-methyltetrahydrofuran, diisopropylamine and triethylamine. A hydrogenic model is used for the transition probability, and the necessary parameters are calculated from a semicontinuum potential model. Both distorted wave and plane wave approximations are made. The calculated results are in reasonable agreement with the available experimental data on the photon energy dependence of photobleaching and photoconductivity efficiencies for trapped electrons in several matrices and support the assignment of bound-free transitions to these processes. Distinct trends with matrix polarity are reproduced by the calculations.

2. Scientific Talks Presented

- AEC-115 Energy Level Structure and Mobilities of Electrons in Aqueous and Organic Glasses, L. Kevan, Plenary Lecture, International Conference on Elementary Processes in Radiation Chemistry, Notre Dame, Indiana, April 4-7, 1972.
- AEC-116 Matrix ENDOR Linewidths of Trapped Electrons in Glassy Matrices at 77 K, J. Helbert, B. L. Bales and L. Kevan, International Conference on Elementary Processes in Radiation Chemistry, Notre Dame, Indiana, April 4-7, 1972.
- AEC-117 Ion Chemistry in Solids and Gases, L. Kevan, Chemical Engineering Department Seminar, Wayne State University, Detroit, Michigan, May 30, 1972.
- AEC-118 Matrix ENDOR of Trapped Electrons, L. Kevan, Gordon Conference on Radiation Chemistry, New Hampton, New Hampshire, July 3-7, 1972.

- AEC-119 ENDOR and ELDOR of the Simplest Radical Ion - A Trapped Electron, L. Kevan, Gordon Conference on Radical Ions, Tilton, New Hampshire, July 10-14, 1972.
- AEC-120 Properties of Trapped and Mobile Electrons in Pure Ice and in Alkaline Ice, L. Kevan, International Symposium on the Physics and Chemistry of Ice, Ottawa, Canada, August 14-18, 1972.
- AEC-121 ENDOR of Trapped Hydrogen Atoms in Sulfuric and Phosphoric Acid Glasses and in Polycrystalline Oxyanion Ices, J. Helbert and L. Kevan, National Amer. Chem. Soc. Meeting New York, New York, August 28-31, 1972.
- AEC-122 Electron Spin Double Resonance - ENDOR and ELDOR, L. Kevan, Chemistry Seminar, Western Michigan University, Kalamazoo, Michigan, September 25, 1972.
- AEC-123 EPR Lineshape Studies of Trapped Electrons in Glassy Matrices, B. L. Bales, J. Helbert and L. Kevan, American Physical Society Meeting, New York, New York, 29 January - 1 February, 1973.
- AEC-124 Electron Magnetic Double Resonance Studies in Glassy Matrices, L. Kevan, Chemistry Seminar, University of Colorado, Boulder, Colorado, January 29, 1973.
- AEC-125 Electron Magnetic Double Resonance Applications to Radiation Produced Electrons and Radicals, L. Kevan, Invited Lecture, U. S. -Japan Radiation Chemistry Conference, Catalina Island, California, February 4-9, 1973
- AEC-126 How Big is a Trapped Electron and are Its Second Solvation Shell Dipoles Oriented?, L. Kevan, Chemistry Seminar, University of Notre Dame Radiation Laboratory, South Bend, Indiana, March 15, 1973.
- AEC-127 ENDOR and ELDOR Magnetic Double Resonance Studies of Trapped Electrons, L. Kevan, Chemistry Seminar, UCLA, Los Angeles, California, March 19, 1973.
- AEC-128 Magnetic Energy Transfer Between Two Different Spin Systems Studied by Electron-Electron Double Resonance, H. Yoshida, D. F. Feng and L. Kevan, American Physical Society Meeting, San Diego, California, March 20-22, 1973.

- AEC-129 Energy Levels and Mobilities of Excess Electrons in Glassy Systems, L. Kevan, Chemistry Seminar, Purdue University, Lafayette, Indiana, March 28, 1973.
- AEC-130 Second Shell Dipole Orientation Around Trapped Electrons in Aqueous Glasses, L. Kevan, Miller Conference, Portmeirion, Wales, April 9-13, 1973.
- AEC-131 On the Bound-Free Transition Probability of Trapped Electrons in Polar Matrices, L. Kevan and K. Fueki, Miller Conference, Portmeirion, Wales, April 9-13, 1973.
- AEC-132 ELDOR Studies of Cross Relaxation and Spin Diffusion in Glassy Matrices, Invited Lecture, L. Kevan, Varian ESR Double Resonance Workshop, Vanderbilt University, Nashville, Tennessee, June 6-8, 1973.
- AEC-133 Electron Spin Echo Envelope Modulation from Trapped Electrons and Hydrogen Atoms in Glassy Matrices, M. Bowman, L. Kevan and I. Brown, Natl. Amer. Chem. Soc. Meeting, Chicago, Ill., August 26-31, 1973.
- AEC-134 Photoconductivity of Trapped Electrons in γ -Irradiated $5\text{MK}_2\text{CO}_3/\text{H}_2\text{O}$ Glass, S. Noda and L. Kevan, Natl. Amer. Chem. Soc. Meeting, Chicago, Ill., August 26-31, 1973.
- AEC-135 Theoretical Relaxation Rates of Dipolar Orientation Around an Excess Electron in Liquid Alcohols, K. Fueki, D. F. Feng and L. Kevan, Fifth Gray Memorial Conference, Univ. of Sussex, Brighton, England, Sept. 10-14, 1973.
- AEC-136 Double Resonance Studies of Trapped Electrons in Glasses, Invited Lecture, L. Kevan, Southeastern Magnetic Resonance Conference, Tuscaloosa, Alabama, October 11-12, 1973.
- AEC-137 The Secret Life of Trapped Electrons as Revealed by Spin Echoes and Electron Magnetic Double Resonance, L. Kevan, Chemistry Seminar, Brookhaven National Lab, Upton, New York, October 17, 1973.

3. Ph. D. Theses Completed

Timothy Huang Energy Level Structure and Mobilities of Electrons in Aqueous and Organic Glasses: Alkaline Ice, Methanol-Water Mixtures, 2-Methyltetrahydrofuran and 3-Methylhexane, Ph. D. Thesis, September, 1972.

Dr. Huang is currently a postdoctoral research associate with Professor W. H. Hamill at Notre Dame University.

John Helbert Matrix ENDOR Studies of Trapped Electrons and Hydrogen Atoms, Ph. D. Thesis, Sept., 1972 (Only the early part of Dr. Helbert's research was supported by the AEC.)

Dr. Helbert is currently employed at the electronics research laboratory at Fort Monmouth, N. J.

Roger Lembke Thermal Decay Kinetics in Gamma-Irradiated Systems: Sodium Hydroxide Aqueous Glass, Di-p-Tolyl Carbonate and N-Hydroxyurea, Ph. D. Thesis, June, 1973.

Dr. Lembke is currently a postdoctoral research associate with Professor A. Henglein at the Hahn-Meitner Institute in Berlin.

Da-Fei Feng I. A Semicontinuum Model for Solvated and Trapped Electrons in Polar Liquids and Solids. II. Electron-Electron Double Resonance of Trapped Electrons in Alkaline Ice and 2-Methyltetrahydrofuran, Ph. D. Thesis, Sept., 1973.

Dr. Feng is currently a postdoctoral research associate in this laboratory.

For reference, the current positions of the previous Ph. D. 's supported by the AEC on this research program is as follows.

Robert D. Koob (Ph. D. 1967) Professor and Chairman, Department of Chemistry North Dakota State University.

John D. Zimbrick (Ph. D. 1967) Associate Professor, Department of Radiation Biophysics, University of Kansas.

Jo A. Beran (Ph. D. 1968) Assistant Professor, Department of Chemistry, Texas A and I University.

David L. Smith (Ph. D. 1969) Research Assistant Professor, Department of Chemistry, University of Utah.

Ding-ping Lin (Ph. D. 1971) Instructor, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, China.

Timothy C. K. Su (Ph. D. 1971) Instructor, Department of Chemistry, University of California at Santa Barbara.

Ignatz Eisele (Ph. D. 1972) Research Physicist, Siemens AG, Munich, Germany.

4. 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. Pulsed EPR Set-Up for Spin-Lattice Relaxation Studies

A versatile pulsed EPR apparatus has been designed, and partially built and tested. It is basically a 60 MHz superheterodyne spectrometer as schematically shown in Figure 1. The power of the observing arm can be varied from 30 to 130 db below the klystron output. The power of the pumping arm with diode switch on can be varied from 0 to 100 db below the klystron output and with the diode switch off is at least 50 db below the pumping power level. The phase between the pump and observing microwaves can be varied.

The detection system consists of a balanced mixer and 60 MHz IF amplifier with detection by either a video detector or a 60 MHz lock-in amplifier. The signal can be displayed on a scope, a chart recorder or can be signal averaged.

Pulsing will be controlled by a pulse programmer which controls the length of the saturating pulse, the duty cycle and number of pulses for signal averaging. The programmer will also control the trigger for oscilloscope presentation or signal averaging.

Fig. 1. Block diagram of pulsed EPR spectrometer

This system is designed to operate not only as a saturation recovery spectrometer but without pumping, can also be used as a CW superheterodyne spectrometer. It will be used to investigate new spin-lattice relaxation mechanisms of radiation-produced trapped radicals and electrons that are weakly coupled to disordered lattices.

2. Measurement of the Quasi-Free Electron State in Disordered Systems

The quasi-free electron state associated with excess electrons in liquids or glasses is the energy of the mobile electron in the matrix relative to the vacuum (V_0). It is important to measure this quantity for evaluation of electron mobilities in disordered systems and to compare with V_0 values used in the semicontinuum model of trapped electron energy levels.

We have developed apparatus to measure V_0 by photoelectric work function measurements similar to the apparatus described by Holroyd. Our apparatus is designed to work down to 77 K. Initial measurements have been made on liquid argon and methane. For liquid argon we find $V_0 = -0.12 \pm 0.05$ eV at 87 K and for liquid methane $V_0 = +0.10 \pm 0.05$ eV at 91 K. The positive value for methane is somewhat surprising, but we suspect that V_0 may be a rather strong function of temperature. More measurements are clearly indicated.

In fact, we have used the semicontinuum model to calculate the temperature dependence of V_0 and do find a large effect. We have made calculations of the V_0 temperature dependence for several alkanes and find quite good agreement with Holroyd's data for several systems near room temperature. Thus we feel that V_0 is included in a proper fashion in the semicontinuum model.

3. Thermal Decay Kinetics in Gamma-Irradiated Systems

The thermal decay kinetics of ^{60}Co , γ -irradiated 10M NaOH glass at 77 K were studied in the dose range from 0.2-2.0 Mrad. These samples decayed in the temperature range 150-180 K. The solutions of Waite's general diffusion equation for the Smoluchowski boundary condition, the radiation

boundary condition, the initial uniform distribution and the initial correlated-pair distribution were tested with the decay data. The various solutions do not give a unique fit to the thermal decay data. The decay of the e_t^- produced by photoionization of ferrocyanide ion in 10M NaOH follow the equation derived by Waite for the radiation boundary condition and an initial gaussian distribution for correlated pairs. The failure of this same solution for the γ -irradiated samples can be explained in cross of diffusion of cross-correlated pairs within the same spur.

On the basis of a proposed spur model, an empirical equation is derived which relates the isothermal decay temperature and the dose to the isotherm decay time, t_u , after which the decay is exponential. The relative concentration at the isotherm decay time, t_u , is also a function of the dose, isotherm temperature and t_u .

The thermal decay kinetics of ^{60}Co , γ -irradiated di-*p*-tolyl carbonate powder and N-hydroxyurea crystals were also studied. Radical pairs are found in these compounds on irradiation. The thermal decay kinetics of these radicals and the isolated radicals were investigated. The radical pairs decay by simple first order kinetics in each case. From this evidence, it is concluded that the radical pairs decay by one hop processes in the solid state. The radical pairs in the di-*p*-tolyl carbonate powder are found to decay together in the temperature range 130-150 K, while the radical pairs of the N-hydroxyurea single crystal are found to decay apart with a quantitatively correlated increase in isolated radicals.

4. Polarized Recombination Luminescence Studies

The recombination luminescence from trapped electrons (e_t^-) and N, N, N', N'-tetramethyl-*p*-phenylenediamine cation (TMPD^+) in methyl-tetrahydrofuran 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. 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.