MASTER

RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES. # 315

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Larry Kevan

Department of Chemistry

Wayne State University

Detroit, Michigan 48202

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ABSTRACT

During the past year, we have improved our analysis methods for electron spin echo modulation patterns and have used them to determine the silver atom solvation structure in water and methanol and the geometry of solvated electrons in organic matrices. New evidence for presolvated electrons in polar matrices has been obtained and the mechanism of electron solvation in pure and in mixed matrices has been clarified.

A ratio analysis method for electron spin echo modulation data has been developed which compensates for decay of the echo envelope. High power electron spin echo results reveal both nearest and next nearest neighbor deuterons in the first solvation shell of silver atoms in ice matrices. The silver cation is solvated tetrahedrally by four waters. Upon conversion of the cation to an atom and thermal excitation, one of the four water molecules reorients to solvate the silver atom by a hydrogen bonding type of interaction. In methanol, this specific solvation interaction does not seem to occur. The geometry of the silver cation and atom in methanol consists of four first solvation shell methanols with their molecular dipoles oriented toward the silver.

The detailed geometry of solvated electrons in organic matrices is becoming clear. A 70 GHz electron spin resonance study has revealed forbidden proton spin flip satellites of solvated electrons in methanol. Analysis gives an electron-proton distance of $2.3 \text{ \AA}$ and suggests a tetrahedral first solvation shell. An electron spin echo study has given a detailed geometrical picture of the solvated electron in ethanol. The electron is tetrahedrally coordinated with the molecular dipole, which approximately bisect the HOC bond angles, oriented toward the electron. The electron to nearest proton distance is $2.2 \text{ \AA}$. Electron spin echo results have also given an improved picture of the electron solvation geometry in methyltetrahydrofuran. Three molecules form the first solvation shell with their ring carbon planes perpendicular to a line toward the electron, and oriented statistically. The closest protons are $3.4 \text{ \AA}$ from the electron.

Optical absorption evidence for presolvated electrons in methanol and various aqueous matrices has been obtained from radiolysis at 1.6 K. Long infrared tails assignable to presolvated electrons are seen. A comparison of the optical bands associated with localized electrons in 10 M LiCl glass at 77, 4.2 and 1.6 K and scavenging experiments at these same temperatures suggest that both presolvated and solvated electrons are also stabilized in this matrix.

It does not seem that "special" types of electrons need to be postulated in polar matrices as have been sometimes suggested. The hindered molecular reorientation model of electron solvation has been shown to provide an explanation of the apparent ignorance of hydrogen bonding by electron solvation in polar liquids. Electron solvation studies in methanol-methyltetrahydrofuran mixed matrices irradiated at 4 K indicate that electron solvation proceeds by a stepwise instead of a tunneling mechanism.

The theory of solvated electrons has been reviewed and current needs for better theoretical understanding summarized. Reactions of isolated ion pairs in solution have been theoretically modeled. Laser excitation has been used to obtain limits for photoexcited electron lifetimes. A new tunneling model of electron spin lattice relaxation has been applied to silver atoms and methyl radicals in several matrices of different polarity.

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RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

Report Period: November 1, 1978 - November 1, 1979

The efficient utilization and storage of energy requires an incisive understanding of energetic chemical reactions. In order to optimize and control chemical reactions, it is necessary to develop a thorough knowledge of the physical and chemical characteristics of energetic reaction intermediates.

During the present report period, our research has focussed on the determination of the immediate matrix structure of trapped radicals, atoms and electrons and on the localization and solvation of radiation-produced electrons in disordered systems such as glasses. Our advances in understanding the localization, trapping and solvation of reactive chemical species have led to methods of stabilizing energetic intermediates in nonequilibrium states. New analysis methods and applications of electron spin echo spectrometry have been used to deduce structural information on the molecular surroundings of trapped reactive species.

Fourteen papers have been published or submitted for publication during this report period. In addition, ten invited lectures on topics related to the DOE supported research have been presented. The following sections present (1) research highlights, (2) research publication list, and (3) scientific talks presented.

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.

1. Research Highlights

Reference numbers indicated below refer to the numbered research publications listed in section 2.

1.1 Electron Spin Echo Studies of Molecular Surroundings

The geometrical details of the molecular surroundings of trapped energetic chemical intermediates are generally unknown. However, if the trapped species is paramagnetic, one can hope to probe this geometrical question by using electron spin resonance methods. Both ordinary electron spin resonance and double resonance methods such as electron nuclear double resonance have not proved generally successful in disordered systems for detecting the very weak hyper-

fine interactions which give such structural information. However, we have recently shown that a powerful method for successfully looking at the geometrical surroundings of trapped radicals in disordered systems is realized by electron spin echo modulation experiments. Electron spin echos can be generated by pulsed electron spin resonance sequences. Two microwave pulses separated by time, τ , are applied to a spin system located in an external magnetic field and an echo is observed at time, 2τ , after the first pulse. The amplitude of the echo decays with τ because of the various relaxation processes taking place in the system. However, in a number of cases, it is observed that the echo envelope exhibits an intensity modulation. This can be interpreted as mainly due to the dipolar coupling between the unpaired electron on the radical species and the nuclear magnetic moment of the surrounding nuclei in the neutral molecules surrounding the radical. We have shown how this modulation can be analyzed to obtain information about the number of equivalent interacting matrix nuclei, their anisotropic hyperfine interaction which gives distance information and their isotropic hyperfine interaction which gives a measure of the delocalization of the unpaired electron wave function over the surrounding matrix molecules.

The experimental modulation spectra are a product of the modulation pattern and the spin echo decay function. The form of the echo decay function depends on the various electron and nuclear relaxation pathways in the system and, in general, is complex and not known. In past analyses the echo decay function has been estimated from the experimental spectra and divided into the experimental spectra to obtain the pure modulation pattern which was compared with theoretical simulations.

During this contract period, we have described a new method of analyzing modulated electron spin echo spectra which obviates estimation of the echo decay function.⁵ This analysis is based on the ratio of maxima to minima in the modulation pattern as a function of decay time. We have described an analytical approach to this ratio analysis method and shown how it may be easily applied to both two pulse and three pulse echo sequences. A graphical form of log log plots of the ratio versus the time between the pulses has been shown to be particularly convenient for determining the number of equivalent interacting nuclei. In addition, we have also pointed out the utility of using the redundant information in two and three pulse echo modulation data to better determine the geometrical structure, particularly in complex molecular systems.

We have used this improved method of ratio analysis of electron spin echo modulation to deduce the structure of solvated electrons in organic matrices. New results have been obtained for the first solvation shell structure of electrons in a cyclic ether glass, 2-methyltetrahydrofuran⁵ and in ethanol glass.¹⁴ The details of these new geometrical findings will be described in the next section.

During the last year we have also completed construction of a high power electron spin echo spectrometer with pulse power as high as 1 kilowatt.¹⁰ We have used the high power spin echo spectrometer to study the geometry of stabilization and solvation of silver atoms in ice and methanol matrices. Silver atoms may be produced in a nonequilibrium environment in ice matrices by radiolysis of a silver salt at 4 K. The radiation produced electrons react with the silver ion to produce a silver atom in a nonequilibrium environment.⁹ This nonequilibrium environment for the silver atom is shown at the bottom of Figure 1. The geometry was determined by analysis of the electron spin echo data. It can be seen that the first solvation shell consists of four water molecules with the negative end of the water dipole oriented approximately toward the silver atom. This is in fact close to the equilibrium solvation shell environment for the atom and gentle thermal excitation induces attainment of an equilibrium or solvated environment for the atom. There is a dramatic structural change in this process as shown in the top of Figure 1. One of the water molecules reorients around one of its OH bonds to put one proton very close to the silver atom. We suggest that this probably reflects a hydrogen bonding type of interaction in the solvation process. The high power spin echo results show the nearest proton at 1.7 Å as well as 7 more distant protons at 3.1 Å for the solvated silver atoms in site II as defined in Figure 1. The observation of both nearest and next nearest magnetic nuclei in the first solvation shell of the solvated silver atom make it possible for us to conclude that only one of the four water molecules in the first solvation shell reorients in this solvation process.

Note also that a desolvation process is shown in Figure 1 which is light driven even at 4 K. Our results indicate that the Ag-O distance is 2.5 Å in both site I and site II. The absence of much change in the heavy atom positions is consistent with the facile optical desolvation process observed at 4 K.

Electron spin echo modulation studies have also been carried out for silver atoms generated from silver cations by radiation produced electrons in methanol glass at 4 K.¹⁰ By using the specifically deuterated molecules CD₃OH and CH₃OD

Fig. 1. Solvation shell geometries of presolvated Ag^+ (site I), which is equivalent to the geometry of aquated Ag^+ , and of solvated Ag^+ (site II) in aqueous matrices. Note that the four oxygens are arranged tetrahedrally around Ag^+ and that the $\text{Ag}-\text{O}$ distance does not change during the solvation process.

it is possible to deduce details about the orientation of the molecules with respect to the silver atom. The results indicate that the silver atom is surrounded by four methanol molecules with their oxygen ends pointing toward silver. The average distance between the silver atom and both the hydroxyl and methyl protons is about 3.3 Å. The molecular dipole in methanol approximately bisects the HOC bond angle, so the silver atom in methanol seems to be solvated by a tetrahedral orientation of molecular dipoles. In strong contrast to the water matrix, thermal excitation to 77 K does not cause any observable geometric change in the solvation shell around the silver atom. This is consistent with weaker hydrogen bonding interactions in methanol than in water. This is perhaps a reflection of the less acidic character of the hydroxyl proton in methanol as compared to water.

1.2 Geometrical Structure of Solvated Electrons

Various aspects of solvated electrons have been intensively studied over the past few years but it is only very recently that striking advances have been made in deducing the geometrical structure of solvated electrons in both aqueous and organic matrices. This is of considerable importance since solvated electrons are the primary radiolytic intermediate in aqueous systems and in many other liquid and solid chemical systems. We have previously shown (J. Chem. Phys., 64, 3153 (1976)) that solvated electrons in aqueous systems have a solvation shell of six waters octahedrally arranged with one HO bond of each water oriented toward the electron and an electron-proton distance of 2.1 Å.

During the current contract period we have been able to gain the first definitive information about solvated electron geometry in alcohols. We have carried out an electron spin resonance experiment at 70 GHz in order to detect resolvable but extremely weak proton spin flip forbidden transitions associated with the solvated electron in this glassy matrix.⁸ By measuring both the intensity and the energy separation of this forbidden transition from the allowed transition of the solvated electron, we have been able to use our previously developed analysis methods (Chem. Phys. Lett., 30, 208 (1975)) to deduce the following structural information. The solvated electron in methanol is characterized by an electron to OH proton distance of 2.8 ± 0.15 Å and 4 ± 2 equivalent first solvation shell methanol molecules. Although there is more uncertainty than we would like in the number of first solvation molecules this represents the first detailed structural information available. Unfortunately, we do not

know the exact orientation of the methanol molecules toward the electron, but we hope that future experiments will reveal this.

However, for solvated electrons in ethanol glass, the molecular orientation of the first solvation shell has been deduced for the first time by effective utilization of our ratio analysis method of electron spin echo modulation patterns.¹⁴ Here we find that there are four methanols in the first solvation shell of the electron with the molecular dipole of each ethanol, which approximately bisects the COH bond angle, oriented toward the electron. The electron to OH proton distance is 2.3 Å. The molecular dipole orientation of ethanol with respect to the electron contrasts with the OH bond dipole orientation of water toward the electron. This suggests that electron solvation in hydroxylic media has two different basic geometries depending on the size of the solvating molecule. For small solvating molecules such as water, OH bond orientation constitutes the preferred geometry reflecting a strong chemical or exchange bonding interaction, whereas for larger solvating molecules such as ethanol the molecular dipole orientation geometry is preferred. The latter geometry is what one would expect from a simple electrostatic model. An obvious intermediate case is methanol for which we do not yet have detailed data but which we hope to obtain in the future.

We have also been able to deduce the detailed solvation geometry for electrons solvated by a much larger solvating molecule, namely the cyclic ether, 2-methyltetrahydrofuran.⁵ The new ratio analysis method for electron spin echo modulation data has been applied to both 3 pulse and 2 pulse electron spin echo data. This analysis together with previous second moment data of the electron spin resonance lineshape gives a revised model for electron solvation in this matrix. The electron to nearest proton distance is significantly larger than in the alcohol matrices, namely 3.4 Å. There are 3 methyltetrahydrofuran molecules in the first solvation shell arranged trigonally with the ring carbon plane of the methyltetrahydrofuran perpendicular to a line toward the electron. Because of the methyl group in methyltetrahydrofuran there are two orientations of the methyltetrahydrofuran ring carbon plane with respect to the electron; the data shows that the solvated electron has a statistical distribution of these two orientations.

A general outline of electron solvation geometry is beginning to emerge and provides a real challenge to current theory to account for the experimental geometries and the trends deduced thus far.

1.3 Molecular Mechanisms of Electron Localization and Solvation

We may define electron localization in condensed media as the creation of an electron state characterized by an exponentially decreasing wave function from the electron coordinate origin. This includes molecular anion formation but the more interesting physically problem is the localization of the electron wavefunction over several molecules. This type of localized electron is formed in a vast variety of media including liquid helium and neon, glassy alkanes, alcohols, ice and water. In both liquid and glassy systems in which electron localization occurs the kinetics and mechanisms of the localization process are still an open question. It is convenient to describe the initially localized electron as "presolvated"; a presolvated electron is simply defined as an electron that has not yet reached an equilibrium configuration with its surrounding solvent molecules. The process of electron solvation then refers to the process of the presolvated electron attaining an equilibrium configuration of surrounding solvent molecules and typically lowering its ground state energy.

During the process of electron solvation, the spectrum of presolvated electrons typically shifts towards the blue indicating a deepening of their potential well. No complete spectra of presolvated electrons have, in fact, been observed in liquids although their presence has been inferred by decay at a single wavelength in the infrared. The best evidence for presolvated electron spectra comes from pulse radiolysis results on glassy matrices at 77 K and from the radiolysis of glasses at 4 K. The evidence is particularly clearcut for ethanol glass and to some extent for less polar organic matrices such as ethers and alkanes. However, presolvated electrons had not been clearly detected in methanol or in aqueous glasses whereas solvated electrons are readily detected in these matrices. It had been implicitly assumed that the solvation process is too fast in these matrices so that the observation of the presolvated spectra was precluded.

In order to gain more definitive evidence for presolvated electron spectra in polar matrices, we have investigated several systems after radiolysis at 1.6 K.² Glassy samples of ethanol, methanol, 10 M and 18 M sodium hydroxide in H₂O, 5 M potassium carbonate in D₂O, and 7 M sodium perchlorate in D₂O were x-irradiated at 1.6 K. After irradiation the optical absorption spectra of the localized electrons generated were recorded also at 1.6 K. Red shifts relative to spectra after irradiation at 4.2 K were observed in all matrices indicating stabilization of some presolvated electrons with

nonequilibrium first solvation shells. Particularly in the deuterated matrices, where observation further into the infrared is possible, an infrared tail assignable to presolvated electrons is detected at 1.6 K; these infrared tails are not stabilized at 4.2 K. Analysis of the spectral shifts after irradiation at 77, 4.2, and 1.6 K indicates that an increasingly larger population of presolvated electrons is stabilized as the temperature is lowered. We conclude that a parallelism for electron solvation exists in all the matrices studied including ethanol. In ethanol glass the spectra associated with presolvated electrons are distinctly separate although their tails do overlap considerably. In the methanol and aqueous matrices electron solvation is much more efficient than in ethanol and the predominant population of localized electrons is largely solvated even at 1.6 K. We find that presolvated electrons are generally detectable via the infrared tails of the overall absorption spectra. The distinct trend in the intensity of the infrared tails with irradiation at decreasing temperature confirms that a consistent, overall picture of electron localization and solvation can be formulated for both polar and nonpolar matrices. In addition, the spectral shifts in 10 M and 18 M sodium hydroxide glasses are also consistently interpreted in terms of presolvated electron stabilization. These matrices are not "special" and do not require postulation of other species such as (Na^+e^-) pairs as has been suggested in earlier, less complete work at 77 K.

In addition, the effect of the irradiation temperature on the optical absorption spectra and the scavenging efficiency of localized electrons in aqueous 10 M lithium chloride glasses was studied.³ This matrix is particularly interesting because irradiation at 77 K stabilizes only a solvated electron species with an optical absorption maximum near 575 nm while irradiation at 4.2 K or 1.6 K shows two distinct absorption bands indicating stabilization of two localized electron species. The absorption band with a maximum near 680 nm is attributed largely to solvated electrons while that with a maximum greater than 2400 nm is attributed largely to presolvated electrons. Since these two optical absorption maxima are rather separated in this matrix, although the tails of course do overlap very significantly, it has been speculated previously that this system may not fit into the general framework of predominant initial electron localization as presolvated electrons followed by a molecular reorientation process to produce solvated electrons. However, the study of irradiation between 4.2 and 1.6 K shows that the band attributed to presolvated electrons is shifted to lower energy at 1.6 K as would be expected for this assignment. In addition, electron scavenging efficiencies of bromate, nitrate and chromate for both bands were

studied and are consistent with the assignment of the infrared band to a pre-solvated electron with a nonequilibrium orientation of first solvation shell waters and of the visible band to a solvated electron with an equilibrium orientation of first solvation shell waters.

The molecular mechanism of electron solvation in pure matrices both in liquids and glasses is understood best in terms of a molecular reorientation mechanism. In liquid ethanol for example, presolvated electrons exhibit an absorption band in the near infrared while solvated electrons absorb further into the blue with an absorption maximum typically in the visible. The optical spectral changes during the solvation process can be followed kinetically by pulse radiolysis and the decay of the presolvated electron correlates with the growth of the solvated electron. First order kinetics and solvation times, defined as the reciprocal of the observed rate constant, appear to correlate with the alcohol monomer rotation times as determined from dielectric relaxation measurements. However, since the correlation is with alcohol monomer rotation times, electron solvation in liquids appear to ignore hydrogen bonding. We have recently suggested an explanation for this.¹²

The explanation is based upon our studies of the kinetics of electron solvation in ethanol glass over a sufficiently large temperature range to connect the kinetics of electron solvation observed in liquids with that in glasses (J. Phys. Chem., 82, 378 (1978)). In glasses, the kinetics are not first order and the decay of the presolvated electrons is usually faster than the growth of the solvated electrons. In addition, the activation energy of the dielectric relaxation and of the viscosity in glassy matrices is significantly larger than that for electron solvation. These observations were successfully rationalized in terms of a hindered molecular reorientation mechanism in glasses in which the electron solvation process seeks out lower energy pathways than those controlling bulk viscosity and bulk dielectric relaxation.

This hindered molecular reorientation model appears to suggest an explanation for the ignorance of hydrogen bonding in electron solvation in liquids. We suggest that single molecule rotation, which appears to be involved in electron solvation in liquids, is simply an example of the electron seeking out the lower energy processes for molecular reorientation available to it, even in the liquids. If we invoke the concept of "flickering" hydrogen bonds in polar liquids such as alcohols, we suggest that electron solvation involves selection of the lower energy molecular orientation pathways in the liquid which correspond to monomeric

molecular rotation when the hydrogen bond of that particular monomer is weakened transiently. This provides a working explanation of the fact that electron solvation appears to ignore hydrogen bonding in liquids.

In mixed matrices involving polar and nonpolar components one can explore more detailed questions about the mechanism of electron solvation. Equilibrium studies in alcohol-alkane liquids show that the electron is ultimately preferentially solvated solely by alcohol molecules. In mixtures in which the less polar component is present in great excess the initial electron localization occurs in the less polar component followed by some sort of transfer to an environment composed of the more polar component. In the current period we have explored the molecular mechanism of the transfer of the electron from the less polar to the more polar environment by carrying out experiments in mixed matrices of methyltetrahydrofuran (MTHF) and methanol with varying mole fractions.^{7,12} By radiolysis at 4 K, we initially stabilized electrons principally in the more abundant nonpolar component and then effected conversion to the less polar component by thermal annealing at 77 K for several minutes. In a matrix of 88 mole percent MTHF and 12 mole percent methanol irradiated at 4 K the initial spectrum of the localized electrons is very close to that found for electrons in a pure MTHF matrix at the same temperature. After annealing a vast change occurs and the new spectrum can be decomposed into one component due to electrons in a purely MTHF environment, a second component due to electrons in a purely methanol environment, and a third component assigned to electrons with mixed solvation shells. The spectral decomposition requires inclusion of a significant fraction of electrons with mixed solvation shells which argues against a molecular mechanism of electron tunneling from the MTHF environment to a methanol cluster and supports a mechanism involving a stepwise change in the solvation shell.

The results also suggest that alcohol clusters are indeed formed in these mixed matrices. For example, in the 45 mole percent methanol mixture with MTHF, the fraction of electrons initially localized in a pure MTHF environment appears to be about 55% which is about equal to the mole fraction of MTHF in that mixed glass, but the fraction of electrons initially localized in a pure methanol environment is only 25% which is significantly less than the methanol mole fraction. If the methanol molecules were isolated, one would expect in a 45 mole percent mixture to have about the same number of initially localized electrons in the MTHF environment as in the methanol environment. However, if the methanol molecules form clusters the effective local concentration of methanol units will be less and the results become explicable.

Although we believe we have demonstrated that electron solvation in mixed matrices of polar and nonpolar components does occur by a stepwise change in the first solvation shell of the localized electron, further studies are necessary to more clearly delineate the exact molecular mechanism that effects this change.

We have also reviewed current theoretical models for solvated electrons.¹³ These include molecular orbital models, molecular field models, the continuum model, the dipole orientation model, and the more generally successful semicontinuum model.

The semicontinuum model appears to be a reasonably successful theoretical model for treating the energy level structure of solvated electrons. It is particularly useful because it is simple enough to apply to a wide variety of solvent systems at different temperatures and pressures, and it gives consistent results. It is successful at predicting many experimental trends. Nevertheless the model has demonstrated defects in both the potential and in the wavefunctions used. The potential is too long range and the wavefunctions are too diffuse.

It is desirable to use the "ab initio" semicontinuum model to study the geometrical structure of solvated electrons. Since good experimental data now exist for solvated electrons in, at least, water and ethanol with greatly contrasting geometries, it is possible to test the success of the "ab initio" model for treating geometry. However, the "ab initio" modification of the semicontinuum model makes it expensive and time consuming to apply.

The semicontinuum model is also notably unsuccessful in treating the optical absorption band shape. A number of other models have been proposed, some of which claim successful fits. In all cases, it appears that some contribution from bound continuum transitions must be invoked. This seems consistent with experiment. However, none of the theories have yet been able to give a clear physical basis for the observed lineshape.

1.4 Other Studies

Reaction between ions produced by photolysis and radiolysis is of considerable importance in chemistry. These ions are produced nonuniformly as ion pairs and special kinetic treatments must be used to treat their rates of reaction. Reactions of isolated ion pairs in solution have been modeled by the Debye-Smolukowski equation for diffusion and conduction.¹ An activation step has been incorporated using a partially reflecting boundary condition. We have shown how the Debye-Smolukowski equation may be solved approximately with a partially reflecting

boundary condition for both random and Boltzmann initial distributions of pair distances. The method involves matched expansions and the Abelian theorem of Laplace transforms. Numerical integrations have been carried out based on the finite distance method and have confirmed the approximate analytic formulas obtained. We also find a large difference in the magnitude between the time dependent terms for a Boltzmann initial distribution and a random initial distribution which seems to be of significance for the theory of electron-cation pair recombination.

New experiments have been carried out using laser pulse excitation to study the lifetime of photoexcited electrons by photocurrent time of flight measurements.⁶ The results indicate that the lifetime of photoexcited electrons in aqueous and organic glasses is less than 20 nanoseconds which is consistent with previous laser photobleaching experiments.

A new electron spin lattice relaxation mechanism for molecular radicals in glassy matrices has been described based on the modulation of the electron nuclear dipolar interaction between a trapped radical and nearby tunneling magnetic nuclei.⁴ This provides an efficient electron spin lattice relaxation mechanism at very low temperatures and explains relaxation times determined by saturation recovery electron spin resonance measurements. This mechanism gives a spin lattice relaxation rate linear in temperature and is much more efficient than the "direct" process which is also linear in temperature and important at low temperatures. The tunneling relaxation process is generally effective up to about 50 K and is typically several orders of magnitude more efficient than the direct spin lattice relaxation process. The electron spin lattice relaxation rate versus temperature of trapped silver atoms produced by irradiation of silver atoms in polycrystalline ice matrices and in methanol, ethanol, propylene carbonate and methyltetrahydrofuran organic glasses has been analyzed in terms of this mechanism. In addition, the electron spin relaxation rate of trapped methyl radicals in methanol, methyltetrahydrofuran, and 3-methylhexane organic glasses has also been studied successfully by this mechanism.

2. Research Publication List

Updated Reference Citations

The following publications were listed in the previous progress report, COO-2086-89, but had not yet been published. Their full reference citations are now given here.

1. L. Kevan and P. A. Narayana, ENDOR and ELDOR of Disordered Matrices, Chap. IV in Multiple Electron Resonance Spectroscopy, M. Dorio and J. Freed, eds., Plenum Press, New York, 1979, pp. 229-259.
2. S. A. Rice, G. Dolivo and L. Kevan, Comparison of Photoconductivity and Optical Spectra for Trapped Electrons in Aqueous and Alcoholic Glasses at 4.2 K, J. Chem. Phys., 70, 18 (1979).
3. L. Kevan, "Modulation of Electron Spin Echo Decay in Solids" in Time Domain Electron Spin Resonance Spectroscopy, L. Kevan and R. N. Schwartz, Editors, Wiley-Interscience, New York, 1979, pp. 279-341.
4. M. K. Bowman and L. Kevan, "Electron Spin Lattice Relaxation in Non-Ionic Solids" in Time Domain Electron Spin Resonance Spectroscopy, L. Kevan and R. N. Schwartz, Editors, Wiley-Interscience, New York, 1979, pp. 67-105.
5. G. Dolivo and L. Kevan, Apparent Faster Electron Solvation by Laser Flash Photoionization Than by Pulse Radiolysis in Methanol-Methyltetrahydrofuran Glasses, J. Chem. Phys., 70, 5321 (1979).
6. J. Michalik and L. Kevan, Temperature Dependence of Electron Spin Lattice Relaxation of Presolvated and Solvated Electrons in Methanol-Water Matrices, J. Chem. Phys., 70, 2438 (1979).

Current Period Publications

The following 14 publications have been published or submitted for publication during the current report period. The numbers correspond to those cited as references under Research Highlights.

1. S. A. Rice, P. R. Butler, M. J. Pilling and J. K. Baird, A Solution of the Debye-Smoluchowski equation for the Rate of Reaction of Ions in Dilute Solution, J. Chem. Phys., 70, 4001 (1979).

2. G. Dolivo and L. Kevan, Optical Absorption Spectra of Localized Electrons Generated at 1.6 K in Polar Matrices: Evidence for Presolvated Electrons, *J. Chem. Phys.*, 70, 2599 (1979).
3. G. Dolivo and L. Kevan, Effect of Irradiation Temperature From 77 to 1.6 K On the Optical Absorption and Scavenging Efficiency of Localized Electrons in Aqueous 10 M Lithium Chloride Glasses, *J. Chem. Phys.*, 70, 5489 (1979).
4. M. K. Bowman, L. Kevan and J. Michalik, Electron Spin Lattice Relaxation Via Nuclear Tunneling Modes for Trapped Radicals in Glassy Matrices, *Proc. XXth Congress Ampere - Tallinn, U.S.S.R., Nauka Publishers, Moscow, 1979.*
5. T. Ichikawa, L. Kevan, M. K. Bowman, S. A. Dikanov and Yu D. Tsvetkov, Ratio Analysis of Electron Spin Echo Modulation Envelopes in Disordered Matrices and Application to the Structure of Solvated Electrons in 2-Methyltetrahydrofuran Glass, *J. Chem. Phys.*, 71, 1167 (1979).
6. S. A. Rice and L. Kevan, On the Lifetime and Mobility of Photoexcited Electrons in Aqueous and Organic Glasses, *Radiat. Phys. Chem.*, 13, 0000 (1979).
7. M. Ogasawara, H. Yoshida and L. Kevan, Transfer of Electrons From IR to Visible Traps in 2-Methyltetrahydrofuran-Methanol Mixed Glasses Irradiated at 4.2 K, *Chem. Phys. Lett.*, 00, 000 (1979).
8. L. Kevan, Forbidden Matrix Proton Spin Flip Satellites in 70 GHz ESR Spectra of Solvated Electrons: A Geometrical Model for the Solvated Electron in Methanol Glass, *Chem. Phys. Lett.*, 00, 0000 (1979).
9. T. Ichikawa, L. Kevan and P. A. Narayana, High Power Electron Spin Echo Modulation Studies of Silver Atom Solvation and Desolvation in Ice Matrices: Geometrical Models for Silver Cation and Silver Atom Aqueous Solvation Shells, *J. Chem. Phys.*, 71, 0000 (1979).
10. T. Ichikawa, L. Kevan and P. A. Narayana, Electron Spin Echo Modulation Studies of Silver Atom Solvation in Methanol: Geometrical Model for the Methanol Solvation Shell, *J. Phys. Chem.*, 83, 0000 (1979).
11. L. Kevan, Introduction to Electron Trapping and Transfer in Frozen Media, *Proc. Sixth Radiation Research Congress, Tokyo, 1979.*
12. L. Kevan, Current Problems in the Localization and Solvation of Excess Electron in Glasses, *J. Phys. Chem.*, 84, 0000 (1980).

13. D. F. Feng and L. Kevan, Theoretical Models for Solvated Electrons, Chem. Rev., 00, 0000 (1980).
14. M. Narayana and L. Kevan, Electron Spin Echo Modulation Study of the Geometry of Solvated Electrons in Ethanol Glass: An Example of a Molecular Dipole Oriented Solvation Shell, J. Chem. Phys., 72, 0000 (1980).

3. Scientific Talks Presented

The following 10 talks were given on DOE supported research during the current report period at several scientific conferences and by invitation at a number of universities and research institutes.

- DOE-T229 Pulsed ESR Studies of Ion and Atom Solvation, Seminar, L. Kevan, SUNY-Buffalo and Roswell Park Memorial Institute, Buffalo, New York, November 13, 1978.
- DOE-T230 Electron Spin Echo Modulation Spectrometry, Seminar, Venezuela Institute of Scientific Investigation (IVIC), Caracas, Venezuela, December 14, 1978.
- DOE-T231 Chemical Applications of Electron Spin Echoes, Frontiers in Chemistry Lecture, Wayne State University, Detroit, Michigan, January 29, 1979.
- DOE-T232 Chemical Applications of Electron Spin Echoes, Chemistry Seminar, University of Houston, Houston, Texas, March 2, 1979.
- DOE-T233 Chemical Applications of Electron Spin Echoes, Quantum Institute Lecture, University of California at Santa Barbara, May 10, 1979.
- DOE-T234 Optical Absorption Spectra of Localized Electrons Generated at 1.6 K in Polar Matrices: Evidence for Presolvated Electrons, G. Dolivo and L. Kevan, Sixth International Congress of Radiation Research, Tokyo, Japan, May 13-19, 1979.
- DOE-T235 Introduction to Electron Trapping and Transfer in Frozen Media, Invited Lecture, L. Kevan, Sixth International Congress of Radiation Research, Tokyo, Japan, May 13-19, 1979.
- DOE-T236 Electron Spin Echo Study of Nd^{3+} Solvation in Alcohol Glasses, R. Janakiraman and L. Kevan, International Symposium on Magnetic Resonance in Chemistry, Biology and Physics, Argonne, Illinois, June 24-28, 1979.
- DOE-T237 Current Problems in the Localization and Solvation of Excess Electrons in Glasses, Plenary Lecture, L. Kevan, Fifth International Conference on Excess Electrons and Metal-Ammonia Solutions, Aviemore, Scotland, June 25-29, 1979.

DOE-T238 Electron, Anion and Atom Solvation Structure in Disordered Media,
Invited Lecture, L. Kevan, Miller Conference on Radiation Chemistry,
Nafplion, Greece, September 10-14, 1979.

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