MASTER

RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

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ABSTRACT

During the past year we have developed a more quantitative characterization of the localization and solvation processes of excess electrons and in particular the presolvated state of excess electrons produced by high energy chemistry. In addition, we have demonstrated how radical environments may be studied by the tunnelling mode mechanism of electron spin-lattice relaxation and have studied atom solvation and radical orientation on surfaces by electron spin-echo modulation techniques.

We have defined the localization criterion for solvated electrons in non-polar systems and have tested the structured semi-continuum model for excess electron energy levels in non-polar systems. The temperature dependence of the optical band of electrons in liquid propane has been measured experimentally and has been shown to agree quite well with the theoretical calculations based on the structured semi-continuum model. The ground state energies of excess electrons in various alkanes have been calculated and shown to correlate well with the experimental predictions of localization or non-localization in these liquid alkanes. A limit on the localized conduction electron state lifetime has been determined by laser photoionization studies. A laser photoionization study in mixed matrices has shown that preferential solvation of the photoionizable solute normally obtains.

The energy level structure of presolvated electrons in a variety of aqueous alcoholic matrices has been studied by a comparison of optical absorption and photoconductivity studies of the presolvated electron state. In general, both bound-bound and bound-continuum transitions contribute to the presolvated electron optical absorption band and general correlations have been deduced for the potential that localizes the presolvated electron,

A new tunnelling mode electron spin-lattice relaxation mechanism has been shown to be dominant for atomic and molecular radicals in disordered systems at low temperatures. Interpretation of this spin-lattice relaxation mechanism allows studies of radical environments to be made. It has been shown that tunnelling relaxation can distinguish models with different geometric configurations and can determine the relative rigidity of such configurations in disordered solids. There also appears to be a correlation between the spin-lattice relaxation rate and the decay of radicals in disordered matrices.

Atom solvation and methanol radical orientation on interior zeolite surfaces have been studied by electron spin-echo modulation methods. Continued instrumental development of electron spin-echo spectrometry and the analytical methods for treating the data has been achieved.

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RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES

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The efficient utilization and storage of energy requires an incisive knowledge of a variety of chemical reactions. In order to optimize and control chemical reactions, mechanisms of reaction must be understood in addition to gaining a thorough knowledge of the physical and chemical characteristics of energetic reaction intermediates. During the present report period our research has focused on quantitative characterization of the electronic structure and reactivity of excess electrons in glassy matrices with particular attention paid to the presolvated electron state and on the application of electron spin-lattice relaxation and electron spin-echo modulation methods for studying the geometry of radical environments and geometrical changes during atom solvation. Solvated electrons are probably the most ubiquitous and important of the reaction intermediates produced by high energy radiation and the improved knowledge of their formation and reaction is essential to fully appreciating and utilizing their high reactivity. We have continued development and application of advanced electron magnetic resonance methods for obtaining structural data about reactive radical and ionic intermediates in disordered systems such as glasses and polycrystals. New understanding of the solvation process and the resulting geometrical configurations of solvated atoms and ions has been achieved.

Sixteen papers have been published or submitted for publication during this report period. In addition, fifteen 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 Localization and Solvation of Electrons

When an electron is suddenly injected into a liquid or solid that is relatively inert to chemical reaction with electrons, one is immediately confronted with two questions. The first question is whether the electron is localized or delocalized. If the electron is localized, one then asks whether or not it becomes solvated and, if so, what the geometrical structure of the solvation shell is.

We have developed a general localization criterion in terms of the energy level of the ground state of the localized electron and the energy level of the conduction electron state.⁴ In polar media the electron generally becomes localized; however, in non-polar media such as alkanes it depends on the balance between the ground state energy of the localized state and the conduction electron state energy. Thus it is necessary to develop a model to calculate the total ground state energy of electrons in non-polar media. We have recently formulated a structured semi-continuum model which takes into account the molecular structure of the first solvation shell molecules in a rather simple way. This allows us to calculate the ground state energy of excess electrons in non-polar media such as alkanes (Can. J. Chem., 55, 1940 (1977)).

During this contract period we have compared predictions of the structured semi-continuum model with recent experimental results. First, we have carried out calculations of the ground state energy of excess electrons in n-hexane; 2,2,4-trimethylpentane, and tetramethylsilane.⁶ The calculated ground state energy of the localized excess electron in n-hexane is lower than the lowest energy of the conduction state for all configurations of n-hexane molecules around the electron investigated. Thus the model predicts that the excess electron is localized in n-hexane and this is in agreement with experimental results on electron mobility and optical absorption. In 2,2,4-trimethylpentane the calculations indicate that the excess electron is localized although the energy balance is much more delicate than in the case of n-hexane. In fact, for some configurations of the trimethylpentane molecules around the electron incipient delocalization is predicted. For electrons in tetramethylsilane the calculated energy of the (hypothetical) localized excess electron state is

higher than the conduction electron level, thus predicting that the excess electron exists as a quasi-free electron or delocalized electron in this liquid. Again this conclusion is consistent with experimental results on electron mobility. Information was also obtained about the charge distribution of excess electrons in these three liquids and it is shown that in tetramethylsilane the hypothetical localized electron extends mainly outside the first solvation shell, whereas in n-hexane the charge distribution is mainly localized in the first solvation shell. This again is completely compatible with the conclusions about localization and delocalization mentioned above.

A second test of the structured semi-continuum model was made by investigating the temperature dependence of the solvated electron optical absorption band in liquid propane.⁸ Utilizing pulse radiolysis in collaboration with Dr. H. A. Gillis at the National Research Council in Ottawa, Canada, we have made the first measurement on the temperature dependence of the solvated electron optical absorption band in alkanes, specifically for propane. The spectrum was measured in liquid deuterated propane over the temperature range of 91 to 131 K and a spectral shift of 0.10 eV was observed. The optical absorption maximum shifts from 2000 nm at 91 K to 2380 nm at 131 K. Calculations based on the structured semi-continuum model were made both for the bound-bound transition and bound-continuum transitions over this temperature range. The theoretically calculated shift for the bound-bound transition is 0.11 eV in excellent agreement with the experiments. The absolute magnitudes of the calculated optical absorption maximum lie about 0.06 to 0.08 eV below the experimental values, however. Thus the experimental values lie between the calculated bound-bound and bound-continuum transition energies, although they do lie considerably closer to the bound-bound transition energy. This suggests that the actual observed spectrum probably has contributions from both bound-bound and bound-continuum transitions but that the bound-bound contribution dominates.

Although considerable information has been obtained about the ground state of the solvated electron in various liquids and glasses, much less is known experimentally about the excited state. In particular, little is known about the excited state lifetimes because no luminescence is observed. Indirect

laser photobleaching methods suggest that the excited state lifetime is less than 10 ps in aqueous systems. We have used another approach to obtain the excited state lifetime of trapped electrons. This involves the measurement of the recombination lifetime of laser stimulated recombination luminescence.³ In this method the trapped electrons are produced by photoionization of an aromatic solute whose excited states luminesce. The closest localized electrons to the solute cations recombine with them isothermally by tunnelling to produce isothermal recombination luminescence. More distant localized electrons can be optically stimulated to recombine with the solute cation. If the optical excitation of the trapped electron is energetic enough to excite the electron to the conduction state of the matrix, the total recombination lifetime then consists of four parts: (a) lifetime of the localized continuum or quasi-continuum state of the electron, (b) the electron lifetime in the conduction state, (c) lifetime of the localized continuum state of the excited solute, and (d) the lifetime of the fluorescent state of the solute. Contribution (b) can be estimated from electron mobility data if known. We expect (c) to be short compared to (d) because lifetimes are generally shorter for more highly excited states. Thus a delay of the recombination fluorescence lifetime beyond the directly excited fluorescence lifetime of the solute (contribution d) may yield information about the excited state electron lifetime.

We have made this type of measurement by photoionizing N,N,N',N'-tetramethyl-p-phenylenediamine in the polar matrices 2-methyltetrahydrofuran (MTHF) at 77 K and in ethanol at both 4 and 77 K.³ The recombination fluorescence stimulated by 694 nm laser light was found, within an experimental limit of 1 ns, to occur with the same lifetime as the directly excited fluorescence. We concluded that the localized continuum state lifetimes of trapped electrons and of the excited solute are ≤ 1 ns at 77 K in MTHF glass and in ethanol glass between 4 and 77 K. Likewise the electron state conduction lifetime is ≤ 1 ns which suggests a lower limit to the electron mobility of $0.005 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in these matrices.

During the current contract period we have also begun to study presolvated electrons. Initially localized electrons are typically characterized by optical spectra with maxima in the infrared range of 1500 to 2500 nm. These electrons can be considered as presolvated electrons. These presolvated electrons have been observed transiently by pulsed radiolysis, often in cold liquids or glasses, or by stabilization at a sufficiently low irradiation temperature,

typically 4K. With sufficient thermal excitation or sufficient time these presolvated electrons become solvated by establishing an equilibrium configuration of solvent molecules around themselves with a concomitant shift of their optical absorption maximum to higher energy. Most previous studies of the energy level structure of localized electrons have dealt with solvated electrons with an equilibrium first solvation shell orientation. We have previously pioneered the approach of obtaining information about the electronic structure of solvated electrons by a comparison of their photoconductivity and optical absorption spectra. This comparison leads to information on the nature of the optical transitions involved in the absorption band. During the present contract period we have carried out the first such measurements on presolvated electrons with a non-equilibrium configuration of first solvation shell molecules.^{5,7,12} Experiments have been performed on presolvated electrons localized in aqueous and alcoholic glasses at 4 K. We have developed methods to carry out photoconductivity studies at this temperature. Studies have been carried out on electrons in ethanol, ethylene glycol-water, 10M NaOD/D₂O, 7M NaClO₄/D₂O and 5M K₂CO₃/D₂O glassy matrices.¹² Our results on presolvated electrons in these various polar matrices imply that bound-continuum transitions predominate. This suggests a trapping potential that does not sustain a bound excited state. We have widely applied a semi-continuum potential model to explain the energy levels of solvated electrons in matrices of varying polarity in the past (J. Am. Chem. Soc., 95, 1398 (1973)). This potential is like a particle in a box near the electron origin and has a coulombic tail from the charge-matrix polarization interaction. The coulombic tail gives rise to bound excited states. Thus the solvated electron in ethanol has both bound-bound and bound-continuum transitions. The coulomb tail of this potential may be cut off by the addition of a large solute ion concentration or by totally disoriented dipoles. Then, the bound excited state may be eliminated. The aqueous matrices we have studied contain large ion concentrations, so bound-continuum transitions dominate for both solvated and presolvated electrons. Totally disoriented dipoles are hypothesized as the environment for presolvated electrons in ethanol. This model is consistent with a shallower potential than for solvated electrons in ethanol and with predominantly bound-continuum transitions. In ethylene glycol/water matrices it appears that totally disoriented dipoles cannot be achieved around a localized electron because of

the constraints of molecular structure on the two OH dipoles in one molecule. This can qualitatively explain why both bound-bound and bound-continuum transitions appear to be associated with presolvated electrons in the ethylene glycol-water matrix. A larger dipole-dipole repulsion term should also be a consequence of these molecular structure constraints for ethylene glycol. This will lower the energy of the presolvated electron more than in ethanol, as observed. Thus solvated and presolvated electron energy levels in the various polar matrices we have studied can be qualitatively understood within the same basic framework.

From our photoconductivity spectra of solvated electrons generated at 77 K and of presolvated electrons generated at 4 K we have been able to determine the ratio of solvated to presolvated electron trap depths.¹² The measurements are somewhat difficult and consequently the thresholds are not always well defined. Therefore it is desirable to use an independent method to obtain similar data on the trap depth ratio of solvated to presolvated electrons.

Many solutes can be added to polar glassy matrices which act as electron scavengers. The electrons react with these scavengers by a tunnelling process so the rate or relative efficiency depends on the electron trap depth. This suggests that added scavengers can be used to obtain solvated to presolvated electron trap depth ratios. The trap depth ratio may be estimated from the scavenging concentration necessary to reduce the yield of solvated and presolvated electrons by some constant fraction via a tunnelling process. It is necessary to use the most efficient electron scavengers so that the trap depth is more important than other factors such as Franck-Condon overlap and state density effects on the tunnelling efficiency. The trap depth ratios determined by this solute scavenging method are 10 to 30% lower than the same ratios deduced from the photoconductivity thresholds but the trends are the same and reinforce our above conclusions.

We have also carried out a detailed optical absorption and photoconductivity study of localized electrons in 10M lithium chloride glasses at 4 K.⁷ These glasses are particularly interesting because they have a strong infrared absorption band associated with the localized electron which is distinctly separate from the absorption band associated with solvated electrons

in the same matrix. Normally in these polar matrices the solvated and presolvated electron bands strongly overlap. There has been considerable speculation as to the exact nature of this infrared absorbing electron (G. V. Buxton, et al., Can. J. Chem. 55, 2835 (1977)); however, we now believe that this species can be interpreted as a presolvated electron within the framework and definition discussed above. In our studies on the 10M lithium chloride glasses we were able to show that this infrared absorbing electron has the same characteristics as those observed previously by Buxton et al. by pulse radiolysis at 76 K. In addition, since this electron can be stabilized for hours at 4 K, we have been able to carry out photoconductivity measurements as a function of exciting wavelength to probe the energy level structure of this species in terms of the possible bound-bound and bound-continuum transitions. We find that both bound-bound and bound-continuum transitions are involved in the optical absorption band and that the trap depth of the solvated electron in this lithium chloride matrix appears to be two or more times deeper than that of the infrared absorbing presolvated electron. Furthermore, we were able to determine that the photoconductivity quantum efficiency of both solvated and presolvated electrons is 0.1 to 1 at 4 K at their respective photoconductivity maxima of 400 and 1400 nm.

In most polar matrices we still are not able to cleanly study presolvated electron spectra when the electrons are generated at 4 K because solvated electrons are still formed at 4 K which have spectra which strongly overlap with presolvated electron spectra. In an attempt to better characterize the spectra of presolvated electrons we have developed a Dewar for irradiation and optical absorption measurements at 1.5 K. Preliminary results suggest that indeed further red shifts are observed for radiolysis at 1.5 K versus 4 K indicating better resolved presolvated electron spectra. This is particularly significant in polar aqueous matrices where the presolvated electron state has been poorly characterized. These measurements are being continued.

We have also studied the interesting question of how electron solvation occurs in mixed matrices involving both polar and non-polar components. Equilibrium studies in alcohol-alkane solutions show that the electron is preferentially solvated by alcohol since this is the most energetically favorable situation. However, in a mixture containing an excess of the non-polar

component we ask whether or not the electron is first solvated or at least localized in the non-polar medium before it is converted to a solvated electron surrounded by the more polar molecules in the mixed matrix. We studied this question last year by pulse radiolysis of methanol-MTHF glassy mixtures (N. Ogasawara et al., Chem. Phys. Lett., 49, 459 (1977)). We observed that the electron was initially solvated in an MTHF environment before becoming completely solvated in a pure methanol environment. The kinetics suggested that conversion of the electron solvation shell occurs by a diffusive process involving more than one step with methanol clusters in the mixed organic glass. We have now studied similar electron solvation processes in mixed organic matrices by laser photoionization.¹⁵ Electrons were generated by photoionization of β -naphtholate in MTHF-methanol mixtures and dramatically different results were obtained than those previously by pulse radiolysis. The laser photoionization experiments showed that the excess electron is solvated in a pure methanol environment at least within 0.1 microsecond after the laser pulse. The similar experiment done by pulse radiolysis shows that the electron is in a MTHF environment on this time scale. This anomaly can be explained by preferential solvation of the β -naphtholate by methanol clusters in the methanol-MTHF mixtures. An interesting implication of this explanation is that the initially ejected electron is apparently solvated by the first solvation shell molecules around the photoionizable solute. Alcohol clusters in less polar matrices are typically thought to be composed of four to six molecules, so that it would appear that the electron produced by photoionization from β -naphtholate is essentially solvated almost directly from the excited state of β -naphtholate. We further concluded that laser photoionization does not seem to be a promising method for studying electron solvation in mixed matrices since almost any solute will be preferentially solvated by one component in a mixed matrix.

1.2 Studies of Radical Environments by Electron Spin-Lattice Relaxation

The electron spin-lattice relaxation of a radical in a solid can serve as a probe of the dynamics of a radical's environment as well as of the radical itself. When the magnetic relaxation rate is dominated by the environmental dynamics, it may be expected to reflect different geometrical

configurations around trapped radicals, the rigidity of such configurations and perhaps the reactivity of the radical with the environmental molecules. In spite of this potential chemical importance for the electron spin-lattice relaxation rate, few investigations of its applicability to these problems have been made. This is partly because the literature of electron spin-lattice relaxation has dealt mainly with transition metal ions and rare earth metal ions in ionic crystals where chemical reaction is minimal and partly because commercial instrumentation for direct measurement of electron spin-lattice relaxation times is lacking.

Previous electron spin-lattice relaxation studies of molecular radicals have focused on crystalline systems and have generally suggested that the relaxation occurred by spin-orbit coupling or by internal motions in the radical. These results are not promising for extracting chemical information relating to the environmental dynamics of the radical.

We have recently initiated a series of investigations of electron spin-lattice relaxation of radicals with little spin-orbit coupling in disordered solid systems. In general we have found that the relaxation rate at low temperature (~5 to 50 K) is proportional to the temperature and is several orders of magnitude faster than for similar radicals in single crystals. This has led to the theoretical development and experimental test of a new electron spin-lattice relaxation mechanism for atomic and molecular radicals in disordered systems (J. Phys. Chem., 81, 456 (1977)). The new mechanism depends on modulation of the electron nuclear dipolar (END) interaction between a trapped radical and nearby magnetic nuclei by the motion of tunneling nuclei or groups of nuclei in the disordered matrix. In disordered systems it appears that modulation by tunnelling modes is much more effective than modulation by lattice phonons for electron spin-lattice relaxation at lower temperatures. Analysis of this tunnelling mode relaxation mechanism does seem to reflect the environmental dynamics of trapped radicals. During the current contract year we have completed three studies on this problem involving several different types of radicals^{2,9,16} and have prepared a comprehensive review on electron spin-lattice relaxation in non-ionic solids.¹⁴

The electron spin-lattice relaxation of trapped silver atoms in polycrystalline ice matrices and in methanol, ethanol, propylene carbonate and 2-methyltetrahydrofuran organic glasses has been directly studied as a function of temperature by the saturation-recovery method.² Below 40 K the dominant electron spin-lattice relaxation mechanism involves modulation of the electron nuclear dipolar interaction with nuclei in a radical environment by tunnelling of those nuclei between two nearly equal energy configurations. The efficiency of this relaxation mechanism seems to decrease with decreasing polarity of the matrix. Deuteration experiments show that the nuclei are protons and in methanol it is shown that the methyl protons have more tunnelling modes available than do the hydroxyl protons. Thus the environmental dynamics around a radical are directly reflected by this analysis.

In polycrystalline ice matrices silver atoms can be stabilized with at least two different orientations of surrounding water molecules. Let us designate these two sites as A and D. In the deuterated aqueous matrix, site A relaxes about five times more efficiently by tunnelling mode interaction than does site D. This difference is qualitatively consistent with our current models for sites A and D in aqueous matrices. Silver atoms in site A are hydrogen bonded to their first solvation shell waters and should have a stronger END interaction with the nearest protons or deuterons than silver atoms in site D, in which the first solvation shell waters are hydrogen bonded more efficiently to the bulk water. If the densities of the deuteron tunnelling modes are similar in the two cases, site A should show a stronger tunnelling relaxation as is observed.

The correlation between tunnelling mode relaxation and matrix polarity as indicated by the static dielectric constant in the various matrices studied apparently reflects a change in the strength of END interaction that is modulated by the tunnelling modes. This interesting effect deserves further study. From these and previous results on tunnelling relaxation of trapped electrons in glassy matrices (Disc. Faraday Soc., 63, 7 (1977)) it appears that tunnelling relaxation may be used to distinguish models with different geometrical configurations and to determine the relative rigidity of such configurations around trapped radicals in disordered solids.

The electron spin-lattice relaxation of trapped methyl radicals in methanol, 2-methyltetrahydrofuran and 3-methylhexane glasses has also been directly studied as a function of temperature from 5 to 100 K by the saturation-recovery method.⁹ Again the tunnelling relaxation mechanism seems to dominate, in the lower temperature region. Deuteration of the methyl radical itself does not affect the tunnelling relaxation coefficient. However, the methyl radical is rotating in these glassy matrices as shown by its ESR spectrum; this motion does not affect its electron spin-lattice relaxation. This is reasonable since the rotating methyl does not change the orientation of the unpaired electron orbital due to its rotation. In contrast to deuterating the methyl radical, deuteration of the methanol matrix does affect the tunnelling relaxation coefficient at lower temperatures by about four-fold. Thus a tunnelling motion of the matrix protons does dominate the relaxation rate.

It is also interesting to analyze the tunnelling relaxation efficiency for methyl radicals in the three different matrices studied. The tunnelling relaxation appears to be primarily due to the methyl groups in the matrix molecules. The tunnelling relaxation coefficients in methanol and 3-methylhexane matrices are comparable suggesting that the distance from the methyl radical to the rotating methyl groups of these matrices is comparable. This implies some interesting constraints about the orientation of 3-methylhexane molecules around trapped methyl radicals. In MTHF the tunnelling relaxation coefficient is two-fold lower than in the other two matrices, which implies that the distance of the methyl radical to the matrix methyl group is greater in MTHF.

If spin-lattice relaxation is primarily due to environmental effects and if the radical does not distort its surrounding matrix, one expects that different radicals will have the same relaxation rate in the same matrix. The tunnelling relaxation mechanism in disordered matrices is due to environmental effects so a comparison of the tunnelling relaxation coefficient should reveal the extent of matrix distortion in the radical's environment. In the MTHF and methanol matrices the methyl radical has a distinctly faster relaxation rate compared to matrix radicals, solvated electrons and silver atoms in the same matrices. This implies that methyl radicals do not order their first solvation shell molecules and so have the fastest tunnelling relaxation rates.

Since the spin-lattice relaxation rates associated with tunnelling relaxation are sensitive to environmental dynamics, it is interesting to explore how this may correlate with radical decay rates which are also expected to be sensitive to environmental dynamics. At 77 K the methyl radical decay rate in methanol, per-deuterated methanol and in 3-methylpentane have been measured and show the same qualitative trend as the tunnelling relaxation coefficients in these same matrices. The correlation is primitive, but suggestive that a real physical relationship may exist.

Finally, electron spin-lattice relaxation has been used to study differences in the matrix environment of presolvated and solvated electrons in methanol-water matrices.¹⁶ As described in the previous section, presolvated electrons are typically generated at 4 K where they may be stabilized for times long enough to carry out ESR experiments, but at higher temperatures such as 77 K the presolvated electron can only be observed for nanosecond or microsecond times. This precludes study of the temperature dependence of electron spin-lattice relaxation of presolvated electrons over much of a temperature range in any matrix. However, an annealed methanol-water matrix has recently been found to stabilize both presolvated and solvated electrons at 77 K (J. Moan and B. Novik, *Chem. Phys. Lett.*, **36**, 120 (1975)). This has made it possible to carry out electron spin-lattice relaxation vs. temperature measurements on presolvated and solvated electrons in this rather unique methanol-water matrix.¹⁶ It is found that a large component of the relaxation can be interpreted in terms of the model for tunnelling relaxation. We find that the tunnelling relaxation coefficient for presolvated electrons is about 76% of that for solvated electrons. This difference is understood in terms of the average electron-proton distance changes that occur during solvation. In hydroxylic matrices the average localized electron-nearest proton (i.e., OH proton) distance decreases during electron solvation as deduced from changes in electron spin resonance linewidths. This strengthens any modulation of the END interaction leading to spin relaxation. Thus the spin-lattice relaxation rate for pre-solvated electrons is predicted to be smaller than that for solvated electrons in hydroxylic matrices as is found in this study. The effect on the spin-lattice relaxation rate in hydroxylic matrices is expected to be small because the alkyl protons will also contribute to tunnelling relaxation and their effect will be opposite to that of the hydroxyl protons.

A different aspect of electron spin relaxation for radicals in disordered matrices has been studied by using the technique of electron-electron double resonance (ELDOR).¹ ELDOR has been demonstrated to be useful for studying the magnetic relaxation mechanisms within inhomogeneously broadened lines and for evaluating the role of spin diffusion in these types of magnetic resonance lines. In addition, cross-relaxation has been studied between two resonance lines of two different radicals. This technique can give information about the spatial correlation between two different types of radicals in the same disordered matrix. In addition, ELDOR can reveal forbidden electron spin resonance transitions corresponding to simultaneous electron and proton spin flips. Hyperfine coupling information can also be obtained in some cases by ELDOR for disordered systems.

1.3 Atom Solvation and Radical Orientation on Surfaces

We have recently shown that a very powerful method for looking at the geometrical surroundings of trapped radicals in disordered systems is realized by electron spin echo modulation experiments.¹³ Electron spin echoes are a consequence of classically precessing dipoles. 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. In certain cases it is observed that the echo envelope exhibits an intensity modulation, predominantly due to the dipolar coupling between the unpaired electron and the nuclear magnetic moments of the surrounding nuclei. This modulation can be analyzed to obtain information about the number of equivalent interacting matrix nuclei, their anisotropic hyperfine interaction which gives the distance, and their isotropic hyperfine interaction which gives a measure of the delocalization of the unpaired electron wavefunction.

During the last year we have continued to use this technique to examine silver atom solvation. By generating silver atoms in ice matrices at 4 K by reaction of silver ions with radiation produced electrons we have been able to generate silver atoms in a non-equilibrium environment in which the solvation shell is still characteristic of the silver ion.^{10,11} This structure

corresponds to four water molecules surrounding the silver atom at a silver-oxygen distance of 0.266 nm. The silver atom can then be solvated by heating it briefly to 77 K in which case one of the water molecules reorients to produce a type of hydrogen bond with a silver atom-proton distance of 0.183 nm. In earlier studies it was not clear whether more than one water molecule reoriented during this solvation process. However, during the last year we have received a one kilowatt travelling wave tube to incorporate into our electron spin-echo spectrometer. This has improved our time resolution and we can now look at somewhat larger hyperfine interactions. With this improved spectrometer we have been able to definitely show that only one water molecule reorients in the silver atom solvation process.

We have also been able to observe silver atom desolvation in which the water molecule reorients back to the configuration characteristic of silver ion solvation. This occurs by optical excitation in the absorption band of the silver atom in the ice matrix at 400 nm. This desolvation process is best understood if we consider the optical absorption band for the silver atom to be largely of charge transfer character involving some delocalization of the excited state orbitals over the water molecules. Then when the silver atom is excited, the silver nucleus again looks like an ion and the hydrogen bonded water molecule reorients to the configuration that it would have if the silver atom were an ion.

Considerable effort has been expended during the last year in interfacing the one kilowatt travelling wave tube with our electron spin-echo spectrometer, in integrating a sophisticated, home-built pulse programmer into the spectrometer, in planning for interfacing the spectrometer output to a new departmental computer which will considerably facilitate data analysis and in developing new, more general computer programs for analysis of electron spin-echo modulation data. The experimentally observed echo modulation signal is the product of the modulation function and an echo decay function. Sometimes the echo decay function can be taken as an exponential, but in general its form is complex and unknown. The decay function can be estimated from the envelope of the maxima of the echo modulation, but inaccuracies obtain because the first few modulation periods are not observable experimentally. One method to compensate for the echo decay is to work with ratios of the maxima

and minima of the modulation pattern. Then the ratios from the experimental modulation pattern and the ratios from a calculated modulation pattern can be directly compared. It is easy to develop a method for the case in which the isotropic hyperfine coupling is zero.¹³ However, in general, the isotropic hyperfine coupling is finite and during the past year we have finally worked out an analysis for this case. We now have an efficient computer program for carrying out such an analysis and are using it in current analyses of electron spin-echo modulation patterns from radical orientation on surfaces as well as for other systems.

We have carried out preliminary studies on the orientation of the CH_2OH radical formed from the radiolysis of methanol on zeolite surfaces. Zeolites are hydrated aluminosilicates and may be represented by the empirical formula:

where $x > y$ usually and n is the cation valence. The AlO_4 and SiO_4 tetrahedra are bonded together to form a sodalite or β -cage and several interconnected β -cages form a super cage or α -cage. The catalytic surfaces are the "interior" surfaces of the cages which constitute the great bulk of the surface area. We have generated CH_2OH radicals by absorbing methanol on type X, Y and A zeolites with sodium and potassium as cations. Gamma radiation then produces the CH_2OH radicals which we deduce are trapped in the α -cages. Electron spin-echo experiments show modulation from the aluminum atoms and the interaction distance turns out to be independent of the structure of the zeolite. In other words, the distance is the same in X, Y, and A zeolites. For sodium type zeolites this distance is 0.34 nm and the CH_2OH radical interacts with only one aluminum or silicon in the cage. Thus it is reasonable that it should be independent of the structure since it is interacting with only one of the aluminum or silicon atoms. However, we find that the interaction distance does depend upon the cation and is larger for larger cations such as potassium vs. sodium. This implies that the interaction of the radical with the interior surface is affected by the dipolar interaction with the cation. We are now in the process of refining these results and developing a specific geometrical structure for the location of the radical in the zeolite α -cage.

2. Research Publication List

Updated Reference Citations

The following publications were listed in the previous progress report, C00-2086-88, but had not yet been published. Their full reference citations are now given here.

M. K. Bowman and L. Kevan, Electron Spin-Lattice Relaxation Mechanisms of Radiation Produced Trapped Electrons and Hydrogen Atoms in Aqueous and Organic Glassy Matrices: Modulation of Electron Nuclear Dipolar Interaction by Tunnelling Modes in a Glassy Matrix, Disc. Faraday Soc., 63, 7 (1977).

R. Kummier, C. Leffert, K. Im, R. Piccirelli, L. Kevan and C. Willis, A Numerical Model of CO₂ Radiolysis, J. Phys. Chem., 81, 2451 (1977).

J. K. Baird, V. E. Anderson and S. A. Rice, Comment on "Probability of Escaping Neutralization When the Mobility is Field Dependent", J. Chem. Phys., 67, 3842 (1977).

J. K. Baird and S. A. Rice, Uniform Theory of Electron Kinetics in Nonpolar Liquids J. Chem. Phys., 69, 1989 (1978).

S. C. Pyke, M. Ogasawara, L. Kevan and J. P. Endicott, Environmental Effects in the Decay of Doublet Excited States of Thiocyanate Complexes of Cr(III), J. Phys. Chem., 82, 302 (1978).

M. Ogasawara and L. Kevan, Laser Photolysis Study of Time Dependent Spectral Shifts of Localized Electrons in Ethanol Glass: Temperature Effects, J. Phys. Chem., 82, 378 (1978).

P. A. Narayana, D. Becker and L. Kevan, Electron Spin Echo Modulation Studies of Silver Atom Solvation and Desolvation in Ice Matrices, J. Chem. Phys., 68, 652 (1978).

Current Period Publications

The following 16 publications have been published or submitted for publication during the current report period. The numbers correspond to those cited on references under Research Highlights.

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.
2. J. Michalik and L. Kevan, Temperature Dependence of Electron Spin-Lattice Relaxation of Radiation Produced Silver Atoms in Polycrystalline Aqueous and Glassy Organic Matrices: Importance of Relaxation by Tunneling Modes in Disordered Matrices, J. Magn. Resonance, 31, 259 (1978).
3. M. Ogaswara and L. Kevan, An Upper Limit to the Excited Electron-Cation Recombination Lifetimes of Trapped Electrons in Ethanol and 2-Methyltetrahydrofuran Glasses at 77 K and 4 K, Bull. Chem. Soc. Japan, 51, 2762 (1978).
4. L. Kevan, Localization and Solvation of Electrons in Condensed Media - The Simplest Radical Ion?, J. Phys. Chem., 82, 1144 (1978).
5. H. Hase, L. Kevan and T. Higashimura, Photoconductivity of Presolvated Electrons in Ethanol Glass at 4 K, Chem. Phys. Lett., 55, 171 (1978).
6. T. Kimura, K. Fueki and L. Kevan, Ground State Energy of Excess Electrons in n-Hexane, 2,2,4-Trimethylpentane and Tetramethylsilane, J. Chem. Phys., 68, 3945 (1978).
7. S. A. Rice, G. Dolivo and L. Kevan, Optical Absorption and Photoconductivity Spectra of Localized Electrons in X-Irradiated Aqueous 10 M Lithium Chloride Glasses at 4.2 K: Support for Two Types of Localized Electrons Each With Overlapping Bound-Bound and Bound-Continuum Transitions, J. Chem. Phys., 68, 4864 (1978).
8. L. Kevan, H. A. Gillis, K. Fueki and T. Kimura, Temperature Dependence of the Solvated Electron Optical Absorption Band in Liquid Propane: Comparison of Theory and Experiment, J. Chem. Phys., 68, 5203 (1978).

9. J. Michalik and L. Kevan, Temperature Dependence of Electron Spin-Lattice Relaxation of Methyl Radicals in Glassy Organic Matrices: Relation to Environmental Dynamics and Radical Decay, *J. Chem. Phys.*, 68, 5325 (1978).
10. L. Kevan and P. A. Narayana, Silver Atom Solvation and Desolvation in Ice Matrices: Study of Solvation Shell Geometry by Electron Spin Resonance and Electron Spin Echo Methods, *Proc. Caribbean Chem. Conf. IX*, San Juan, Puerto Rico, *Boletín Científico del Sur*, 6, 10 (1978).
11. L. Kevan, On the Solvation Shell Geometry for Silver Atom Solvation and Desolvation in Ice Matrices, *J. Chem. Phys.*, 69, 3444 (1978).
12. 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.*, 69, 0000 (1978).
13. 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. 000-000.
14. 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. 000-000.
15. G. Dolivo and L. Kevan, Apparent Faster Electron Solvation by Laser Flash Photoionization Than by Pulse Radiolysis in Methanol-Methyltetrahydrofuran Glasses, *J. Chem. Phys.*
16. J. Michalik and L. Kevan, Temperature Dependence of Electron Spin Lattice Relaxation of Presolvated and Solvated Electrons in Methanol-Water Matrices, *J. Chem. Phys.*

3. Scientific Talks Presented

The following 15 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.

- ERDA-T214 Silver Atom Solvation and Desolvation in Ice Matrices: Study of Solvation Shell Geometry by Electron Spin Resonance and Electron Spin Echo Methods, L. Kevan and P. A. Narayana, Caribbean Chemical Conference IX, Radiation Chemistry Symposium - Invited Lecture, San Juan, Puerto Rico, December 8-11, 1977.
- ERDA-T215 Electron Spin Resonance Applications to Disordered Solids, Invited Lecture, L. Kevan, Study Institute on Data Acquisition and Processing in Magnetic Resonance, St. Vincent, West Indies, December 12-18, 1977.
- ERDA-T216 Ion and Atom Solvation Structure Studies by Electron Spin Echo Spectroscopy, Seminar, L. Kevan, Atomic Energy of Canada - Chalk River Nuclear Laboratories, January 10, 1978.
- ERDA-T217 Pulsed ESR Studies of Ion and Atom Solvation, Seminar, L. Kevan, University of Toronto, Canada, January 12, 1978.
- ERDA-T218 Applications of ESR to Chemistry, Seminar, L. Kevan, University of Illinois at Chicago Circle, Chicago, Illinois, February 9, 1978.
- ERDA-T219 Applications of ESR to Chemistry, Seminar, L. Kevan, Illinois State University, Normal, Illinois, February 10, 1978.
- ERDA-T220 Pulsed ESR Studies of Ion and Atom Solvation, Seminar, L. Kevan, Drexel University. Philadelphia, Pennsylvania, April 13, 1978.
- ERDA-T221 Optical Absorption Studies of Trapped Electrons Generated and Observed at 1.6 K, G. Dolivo and L. Kevan, Radiation Research Society Meeting, Toronto, Canada, May 15-18, 1978.

- ERDA-T222 Photoconductivity Associated with Localized Electrons in Glassy Matrices, L. Kevan, Invited Lecture, Gordon Conference on the Physics and Chemistry of Photoconductors, Holderness School, New Hampshire, June 12-16, 1978.
- ERDA-T223 Optical Absorption of Localized Electrons Generated at 1.6 K in Polar Matrices, G. Dolivo and L. Kevan, Gordon Conference on Radiation Chemistry, Holderness School, New Hampshire, July 17-21, 1978.
- ERDA-T224 Electron Spin Lattice Relaxation Via Nuclear Tunneling Modes for Trapped Radicals in Glassy Matrices, M. K. Bowman, L. Kevan and J. Michalik, XXth Colloque Ampere, Tallinn, USSR, August 21-26, 1978.
- ERDA-T225 Determination of Vibrational Frequencies Associated with Solvated Electrons, L. Kevan and D. P. Lin, Plenary Lecture, Sixth Conference of the Nordic Society for Radiation Research and Radiation Technology, Hirtshals, Denmark, August 28-31, 1978.
- ERDA-T226 Optical Studies of Trapped Electrons Generated and Observed at 1.6 K, G. Dolivo and L. Kevan, Sixth Conference of the Nordic Society for Radiation Research and Radiation Technology, Hirtshals, Denmark, August 28-31, 1978.
- ERDA-T227 Electron Spin Echo Studies of Radical Orientation on Catalytic Surfaces: CH_2OH Radicals in A, Y and X-Type Zeolites, T. Ichikawa and L. Kevan, National American Chemical Society Meeting, Miami, Florida, September 11-15, 1978.
- ERDA-T228 Electron Spin Echo Studies of Ion and Atom Solvation, L. Kevan, Chemistry Seminar, Michigan State University, East Lansing, Michigan, October 17, 1978.