Concluding Remarks

The properties of the R_4N_2–$R_4N_2^{+\cdot}$ electron transfer include thermodynamics which are not dominated by HOMO energy level, exceedingly slow homogeneous electron transfer rate, and conformation-dependent heterogeneous electron-transfer rate. All of these properties have been argued to be a result of the large geometry change which occurs upon electron removal, a feature which is of course shared by many other types of compounds. The advantage of R_4N_2 for study of these phenomena, which in certain aspects resemble "inner sphere" electron transfers in transition-metal systems, is the great degree of control over both the HOMO energy level and the degree of geometry change exerted by altering the geometry of the four alkyl substituents, which only interact weakly with the two nitrogen lone pair system.

It is a pleasure to thank the many students who carried out the work discussed here: P. J. Hintz, R. T. Landis, II, J. M. Buschek, G. R. Weisman, Dr. L. Echegoyen, E. L. Clennan, V. E. Peacock, W. C. Hollinsed, C. R. Kessel, and W. P. Parmelee, as well as Dr. J. C. Calabrese, without whom the X-ray work could not have been done, and Professor D. H. Evans, whose efforts have allowed us to use electrochemical techniques profitably, and his students, D. A. Corrigan and P. J. Kinlen. The work reported has been supported by the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation.

(50) A kinetic equivalent of Scheme I would place a twisted radical cation, $(\mathbf{19ae})^{+\cdot}$, between **19ae** and $\mathbf{19}^{+\cdot}$. If this intermediate only relaxed to $\mathbf{19}^{+\cdot}$ and never could be reduced to **19**, the CV curves would look the same. Our principal reason for preferring Scheme I is not only its greater simplicity but also the fact that when we make a twisted intermediate $(\mathbf{16}^{+\cdot})$, very rapid deprotonation occurs because of the high energy of the twisted radical cation. Our results require that if $(\mathbf{19ae})^{+\cdot}$ is formed, it gets to $(\mathbf{19})^{+\cdot}$ in high yield. This is not inconceivable, but at present we feel there is insufficient evidence for a twisted radical cation to justify postulating one.

Solvated Electron Structure in Glassy Matrices

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Solvated electrons were probably first produced by chemists when Weyl in 1864 dissolved sodium in liquid ammonia to generate a beautiful blue color.[1] However, this color and its spectrum were not assigned to solvated electrons as such until 1908.[2] Since that time extensive studies of these stable solvated electrons in liquid ammonia by optical and electron magnetic resonance spectroscopy, by a variety of other physical measurements, and by extensive theoretical calculations have revealed many facets of their physical characterization and reactivity.[3] However, the detailed *geometrical* structure of these solvated electrons has not yet been deduced.

In 1962 a solvated electron in water was discovered as a transient optical spectrum in the visible produced by pulse radiolysis.[4] In the same year a very similar, stable spectrum was found by radiolysis of an alkaline aqueous glass at 77 K and was assigned to a trapped electron.[5] Subsequent work has shown that transient solvated electrons may be produced in various liquids, including alcohols, ethers, amines and alkanes, and that trapped, solvated electrons are also formed by inducing molecular reorientation in *glassy* matrices of these liquids at 77 K.[6]

Many aspects of solvated electrons have received[7] and continue to receive[8] much study. Their reactivity was first extensively investigated mainly in aqueous systems.[9] We early pointed out that entropic effects seem to control solvated electron reactivity in both liquid and glass media, implying the importance of an electron-tunneling mechanism.[10] Recent comprehensive kinetic studies in glassy matrices appear to firmly establish the importance of electron tunneling for solvated electrons.[11] Investigations of optical absorption and photoconductivity spectra in glassy matrices in our laboratory have established the broad outlines of the electronic energy level structures of solvated electrons in both aqueous and organic systems.[6] Concurrent development of theoretical models of solvated electrons have led to a semicontinuum potential model which has proven modestly successful in explaining the electronic energy level structure.[12] This theoretical model has also made certain limited predictions regarding geometrical structure. However, detailed experimental data on the *geometrical* structure of solvated electrons have been lacking until very recently. In this Account

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we summarize our current knowledge of the detailed geometrical structure of solvated electrons in aqueous and organic media.

To understand solvated electron structure, one can usefully consider that solvated electrons are formed kinetically by a process that consists of two stages.[13] The first stage is localization which depends upon the relative energies of the conduction electron level of the medium and the energy of the localized electron state in the medium. The second stage, after localization occurs, is solvation in which the electron induces rearrangements in the surrounding solvent-shell molecules to create a geometry characterized by the intermolecular forces between the electron and the solvent molecules. Thus, the solvated electron geometry is not determined solely by the characteristics of the medium molecules.

This picture of electron solvation applies to both glasses and liquids. The initially localized, but presolvated, electron is experimentally characterized by an optical absorption in the infrared and an electron spin resonance (ESR) line. This presolvated or trapped state can be stabilized in 4-K glasses for organic solvents, except methanol, and was first observed in such experiments.[14-17] The solvated state is experimentally characterized by an optical absorption shifted to higher energy, in the visible for alcohols and the near-infrared for ethers and alkanes, and by an ESR line of different width. The solvated state can be induced in glassy matrices by warming from 4 to 77 K. Thus it became obvious that the spectral shift characteristic of the solvation of presolvated electrons to become solvated electrons could be observed in glasses at 77 K by a fast detection method like pulse radiolysis and even in liquids, with sufficient time resolution. This was subsequently realized in 77-K glasses,[18-22] in cold alcohols,[23,24] and in room temperature alcohols[25-29] which definitely show that electron solvation occurs with similar optical consequences in both glasses and liquids. The most definitive work is that which actually observes the spectral shift by detection in both the infrared and visible.[22,24,27]

An ESR line for solvated electrons can also be detected in liquids[30] but it cannot be used to follow the solvation process because the anisotropic interactions are averaged out and the detection time resolution is too slow. However, the ESR line-width changes in glasses[31] as well as electron–nuclear double resonance line-width changes have been analyzed[32] to show that the major geometrical changes during electron solvation involve distances corresponding to protons in the first solvation shell. Thus it appears that a first solvation shell molecular reorientation will account for electron solvation in glasses and liquids, except perhaps in water.[33]

Since the solvation structure is dynamic in liquids, one can only hope to study it in detail in a frozen liquid, such as glass. A natural method to determine the solvation structure is by electron spin resonance since the solvated electrons are present as trapped reactive intermediates in only low concentration but are tagged by their unpaired electron spin. However, by electron spin resonance, only a single Gaussian shaped line is seen for solvated electrons in the different polarity glasses.[6] Essential structural information is hidden within the unresolved hyperfine structure that composes the substructure of the single observed line. Thus, it was necessary for us to develop new techniques for looking at very weak hyperfine interaction in order to solve the problem of the structural geometry of solvated electrons.

A classic way to increase the resolution of electron magnetic resonance and to look at unresolved hyperfine structure is to use electron–nuclear double resonance (ENDOR) spectroscopy.[34] However, in a frozen disordered matrix the ENDOR line is also a single broad line near the free nuclear frequency in which most of the unresolved hyperfine interaction is hidden by the width of the line. Although we have developed a fairly comprehensive analysis of ENDOR line shapes in disordered solids,[35,36] the wealth of detail is not nearly as great as can be obtained by several other electron magnetic resonance methods.

The determinations of solvated electron geometry have been made possible by the development in our laboratory of new methods of analysis of electron magnetic resonance spectra to obtain very weak hyperfine interactions characteristic of the solvated molecules around a paramagnetic species in disordered solids. The most important of these methods has been the analysis of electron spin–echo modulation patterns.[37-41] Supporting information has come from the analysis of electron spin resonance second moment line shapes[39,42,43] and forbidden proton spin flip transi-

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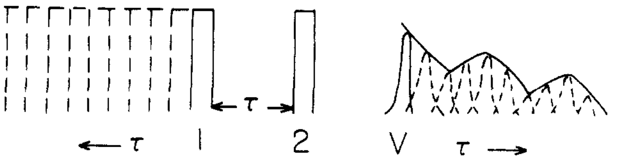

Figure 1. Illustration of modulation of a two-pulse electron spin–echo decay envelope. Microwave pulses 1 and 2 separated by time τ produce the echo signal at time τ after pulse 2. As τ is increased the echo amplitude changes and traces out an echo envelope which may be modulated.

tions,[44,45] specifically for paramagnetic species in disordered solids. The use of specifically deuterated solvent molecules has been crucial in these studies, to give not only the numbers of first solvation shell molecules and their distances from the solvated electron but also the *orientation* of the first solvation shell molecules.

The analysis of electron spin–echo modulation represents, in many senses, a new technique for looking at the detailed solvation geometry of radicals and paramagnetic ions in frozen solutions. It has a wide degree of applicability to a variety of interesting chemical problems which are not readily addressed by other experimental techniques.[37] We will first discuss the essential details of this technique before considering solvated electron geometries in media of different polarity. Unfortunately we cannot include the geometry of solvated electrons in ammonia because electrons are not stabilized in frozen polycrystalline ammonia.

Electron Spin-Echo Modulation Analysis

A comprehensive discussion of electron spin–echo methods has recently been published.[37] Here we only summarize the essential details to help understand the data that will be presented concerning the geometry of solvated electrons. Electron spin echoes are generated in pulsed electron spin resonance experiments. The most common type of pulse sequence consists of two pulses. The first pulse is 90°, which flips the spins oriented along the magnetic field in the Z direction into the XY plane. The spins are allowed to process in the XY plane where they are subject to any time-dependent magnetic interactions, including weak hyperfine interactions for a time, τ. Then a second 180° pulse is applied which flips the spins to the opposite direction in the XY plane so that the spins then precess together and refocus at time 2τ after the original pulse to produce a burst of microwave energy called an echo. This echo intensity is then measured as a function of the time between the pulses to generate an echo decay envelope. This is shown schematically in Figure 1.

The echo decay envelope is a product of two functions, a relaxation function and a modulation function. The relaxation function decreases monotonically with time and carries information about all of the spin relaxation processes that cause the electron spins to dephase. The modulation function carries the structural information with which we are primarily concerned.

We have developed a ratio analysis method to apply directly to experimental data. It effectively cancels out the decay function contribution and gives us a function dependent only on the spin–echo modulation pattern.[38] In this method curves are drawn through the maxima and minima of the modulated decay patterns and then the ratio of the amplitudes of the echo on these two curves as a function of the time between the pulses, τ, is determined. This experimental function is compared with a theoretical one based on a certain assumed geometry of n equivalent nuclei at an average distance r with an isotropic hyperfine coupling of a_{iso}. It should be stressed that in a disordered system we determine an average structure by this method, and we are looking primarily at the nearest magnetic nuclei surrounding the solvated electron. Since we expect more than one molecule to be arranged equivalently around the solvated electron to form its first solvation shell, an average structural analysis of this type seems to be valid. If there are magnetic nuclei that are close enough to give strong magnetic interactions and that are arranged in more than one shell from the solvated electron, they can indeed be resolved in favorable circumstances. This will be shown to be the case for the solvated electrons in aqueous matrices. Our general analysis procedure will be to analyze the spin–echo modulation pattern in terms of a number of equivalent nuclei, n, located at a distance, r, from the solvated electron and with a small overlap of the solvated electron wave function on the closest magnetic nuclei to give a small isotropic hyperfine coupling, a_{iso}.

How definitive are the solvation structures deduced from spin–echo modulation analysis? This depends on the uniqueness with which the parameters n, r, and a_{iso} can be determined. In general there is some correlation between n and r^{-6}. However, by the ratio analysis method[38] the least-squares optimization of n can be separated from that of r and a_{iso}. Ordinarily, we also constrain n to be integral since the number of equivalent interacting nuceli for one solvation structure will be integral. If both two-pulse and three-pulse spin–echo data are obtained, the modulation of each can be analyzed independently to give redundant determinations of the parameters. In addition, when second moment data on the ESR line shape are available, we have used this as an additional constraint on permissible values for n and r; this has been particularly used to deduce the trapped solvated electron structures. On the basis of analyses of a variety of different paramagnetic species we conclude that n can be uniquely determined to the nearest integer up to about $n = 10$. For larger values of n the uncertainty is about 10%. The parameter r can be uniquely determined to about ±0.01 nm and a_{iso} to about ±15% for good quality data. A somewhat independent check of the accuracy of the distances deduced is to compare ion to water oxygen distances obtained from electron spin–echo modulation analysis with the sum of ionic and van der Waals radii determined from X-ray diffraction.[46] For Cu^{2+} solvation by methanol the Cu^{2+} to methanol oxygen distance deducted is 0.21 nm, which agrees well with the sum of the Cu^{2+} radius (0.072 nm) and the van der Waals radius of oxygen (0.14 nm). Similarly, for Ag^+ solvation by methanol the Ag^+ to O distance deduced is 0.26 nm, which agrees well with the sum of the Ag^+ radius (0.126 nm) and the O radius (0.14 nm).

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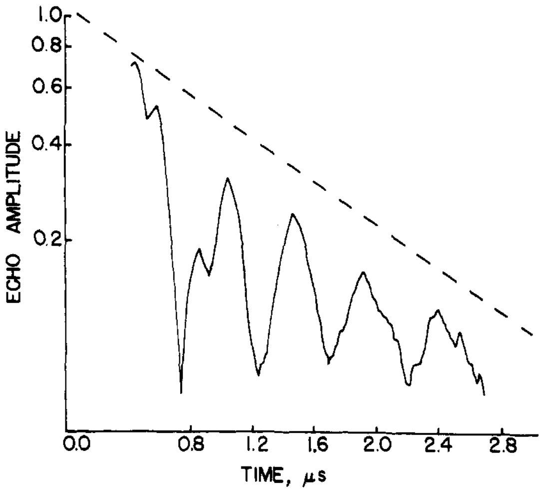

Figure 2. Two-pulse electron spin–echo signal from the solvated electron in 10 M $NaOD/D_2O$ at 77 K. The echo amplitude is proportional to microwave power. The dashed line is an extrapolation of echo decay in the absence of modulation (from ref 25).

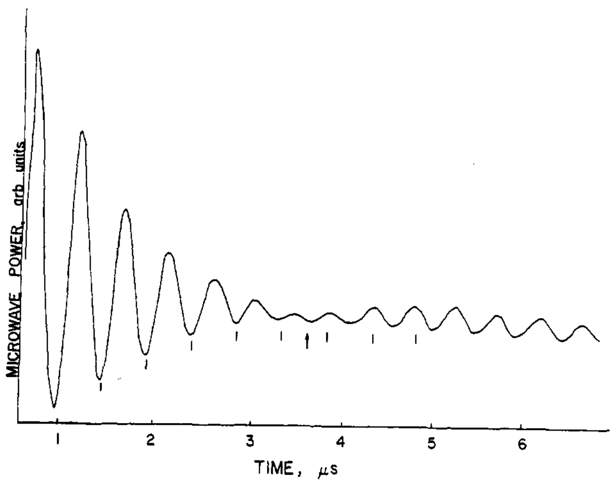

Figure 3. Three-pulse electron spin–echo signal from the solvated electron in 10 M $NaOD/D_2O$ at 77 K. The value of τ is 0.07 μs. The arrow indicates the approximate time where the phase of the modulation changes (from ref 25).

One condition for observation of the modulation is that both allowed and nuclear spin flip forbidden ESR transitions be simultaneously excited by the microwave pulses.[37] Thus the amplitude of the microwave pulse must be greater than the nuclear splitting. Since the nuclear splitting of protons is about 6 times greater than that of deuterons, it is possible to select the microwave pulse amplitude so as to excite only deuteron and not proton modulation. Therefore, the use of specifically deuterated sovlent molecules allows one to determine not only the number of solvent molecules in the first solvation shell but also their specific orientation with respect to the solvated electron. This will not work in all cases, such as for water, but for the other solvating molecules discussed it will be a very useful aspect of the analysis.

Solvated Electrons in Aqueous Systems

Electrons can be solvated and stabilized in a variety of aqueous glasses. Perhaps the best studied one is 10 M sodium hydroxide aqueous glass. Even though there is a very large concentration of sodium ions, the electron spin–echo results show that the solvated electron has only water molecules in its first solvation shell. Thus, we think what we learn about the structure in this glassy aqueous system is also characteristic of the solvated electron in liquid water. This has been supported by experiments in which the sodium concentration was reduced to less than 0.01 M by codepositing sodium atoms and water vapor on a cold finger at 77 K.[47]

In the electron spin–echo modulation experiments, deuteron interactions give deeper modulation than protons due to their larger nuclear spin.[37] Thus deuterium modulation can be analyzed more easily and quantitatively than proton modulation. Figure 2 shows the electron spin–echo modulation pattern for solvated electrons in a deuterated glassy aqueous matrix. One observes that the modulation pattern is somewhat irregular. In particular, there are several sharp features in the early parts of the modulation pattern. By experience, we now recognize that this indicates that there are some very close nuclei contributing to the modulation pattern, but the persistence of a relatively regular modulation at longer times suggests that more distant nuclei are also contributing to the modulation pattern. In this case we deduce that there are at least two shells of nuclei contributing to the electron spin–echo modulation pattern.

To make the analysis easier we have carried out another experiment involving three pulses to generate the echo instead of two.[48] In the three-pulse scheme, one applies a 90° pulse to flip the spins from the Z into the XY plane. Then after time τ, one applies a second 90° pulse which flips the spins into the negative Z-axis direction and puts them into a sort of holding pattern which can be a time much longer than τ, usually denoted by T. After time T a third 90° pulse is applied which acts to refocus the spins and generates the echo at time τ after this third pulse is applied. The advantage of the three-pulse echo sequence is that it occurs over a much longer time and consequently is more sensitive to the weaker hyperfine interactions contributing to the modulation pattern. Figure 3 shows the three-pulse electron spin–echo pattern for the electron in the deuterated aqueous glassy matrices. In addition to a very nice modulation, one sees a phase change in the modulation at the arrow. This phase change can be analyzed in detail to very simply give one a distance corresponding to the nuclei that are contributing to the three-pulse echo in this time range.[49] The time at which this phase change occurs corresponds to an interacting shell of nuclei at a distance of 0.36 nm.

The two-pulse echo modulation pattern shown in Figure 2 can then be analyzed in terms of a two-shell model in which the most distant shell is at 0.36 nm. The complete two-shell simulation gives a nearest shell of six deuterons at 0.21 nm with an isotropic coupling of 2.1 G and a next nearest shell of six deuterons at 0.36 nm. Since it is not possible chemically to partially deuterate the water solvent molecule, these results do not unambiguously tell us that these two shells of deuterons belong to the same first solvation-shell water molecule. For example, it might be possible from thse data alone that the first solvation shell consists of three

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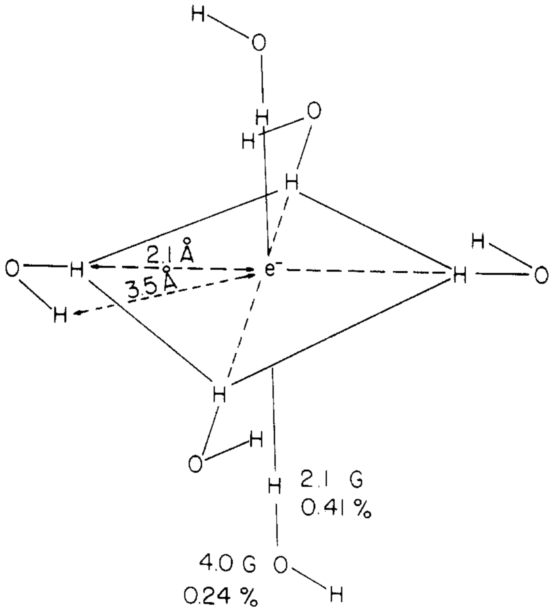

Figure 4. Geometrical structure of the solvated electron in aqueous glasses determined from electron spin–echo modulation analysis. The isotropic couplings to H and ^{17}O are given along with the corresponding percentage of solvated electron spin density on these atoms.

water molecules with their molecular dipoles oriented toward the solvated electron such that there are six closest deuterons from three water molecules in the first solvation shell. Then the next shell of deuterons would come from the second solvation shell water molecules. However, this possibility has been excluded by carrying out experiments with oxygen-17-enriched water. In these, a detailed second moment line-shape analysis has shown that there are six oxygens in the first solvation shell around the solvated electron.[50]

From all the data available, we deduce the geometrical structure for solvated electrons in aqueous systems as shown in Figure 4. The electrons are solvated by six water molecules, each with one of its OH bonds oriented toward the electron. Since these water molecules are approximately equivalent, it is reasonably assumed that they are arranged approximately octahedrally around the electron. The distance to the closest proton of the solvent water molecules is 0.21 nm and to the more distant water molecule proton is 0.36 nm. These two distances together with an OH bond orientation are consistent with the known structure of the water molecule. The total unpaired electron spin density on the first solvation shell molecules is about 4%, as judged from the isotropic couplings. Thus for a solvated electron described by a hydrogenic 1s wave function, as is done in the current semicontinuun potential model,[12] 96% of the spin density is in this 1s orbital and concentrated near the center of the solvation structure. Hence, a solvated electron looks very much like an ordinary solvated anion. If the solvated electron wave function contains significant contributions from the water oxygen p orbitals, some unmeasured spin density would reside there and decrease the amount near the center of the solvation structure.

The geometry of the solvated electron in aqueous systems shown in Figure 4 provides a critical test for any theoretical model for solvated electron structure. In essence, the structure deduced indicates that there are relatively strong chemical bonding or exchange-type interactions between the solvated electron and the first solvation shell water molecules which give rise to this OH-bond-oriented solvation structure. It is noteworthy that the same orientation is found for single crystals of potassium fluoride dihydrates by X-ray crystallography.[51] There the fluoride ion is solvated by water molecules with an OH bond orientation. In contrast, the present theoretical models predict a molecular-dipole-oriented structure.[12]

Finally, we point out that a completely independent study of the solvated electron geometry carried out by analysis of forbidden proton spin-flip satellite lines[43] confirms the structure shown for aqueous systems in Figure 4. More will be said about this spin-flip satellite analysis in the next section.

Solvated Electrons in Methanol

Solvated electrons are generated in glassy methanol by radiolysis, but the electron spin resonance (ESR) spectrum of the solvated electron is superimposed on top of a spectrum associated with CH_2OH radicals. Furthermore, the electron spin–echo decay envelope decays quite rapidly in this ststem. Thus, there are only one to two modulation cycles to attempt to analyze, and analysis by this approach becomes difficult. The electrons can be removed by optical bleaching, leaving only the radicals, and the background electron spin–echo signal from these radicals can be measured independently of the electron. In this system it turns out that the radical background electron spin–echo contribution is so large that it interferes with a quantitative analysis of the solvated electron structure by this method. So it is necessary to try other approaches.

We have therefore analyzed forbidden proton spin-flip satellite lines due to an electron dipole–nuclear dipole interaction between the solvated electron and the nearest matrix protons. This technique is not generally applicable to the detection of weak hyperfine structure with matrix nuclei because the weak spin-flip satellite lines are often not resolved. In fact, the electron spin–echo modulation analysis that we have discussed depends on the excitation of both allowed and forbidden transitions, the same forbidden transitions that give rise to the spin-flip satellite lines. However, in the spin–echo analysis it is not necessary to explicitly resolve the spin-flip satellite lines in the electron spin resonance spectrum. It was originally pointed out[52] that spin-flip satellite lines can give structural information in that the ratio of the satellite line intensity to the allowed main line intensity is a function of nr^{-6}, where n is the number of equivalent interacting matrix nuclei at a distance of r. It was later shown in our laboratory that analysis of both the relative intensities and the energy separation of the allowed ESR lines and the spin-flip satellite lines allows one to determine *both* the distance to and the number of matrix nuclei that contribute to a given satellite transition.[44] Subsequently this was generalized to an arbitrary number of equivalent matrix nuclei.[45] Single-crystal studies with known geometry have veri-

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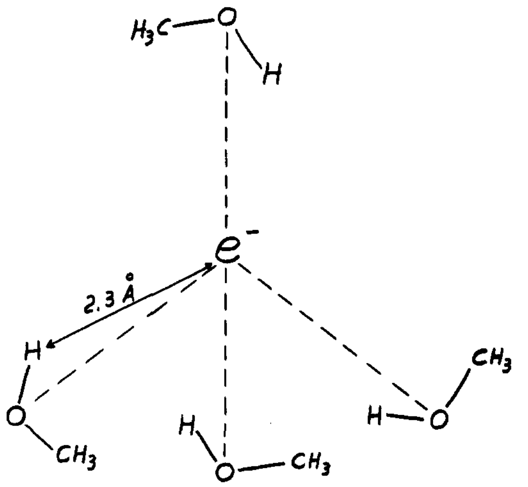

Figure 5. Suggested geometrical structure for the solvated electron in methanol glass deduced from electron magnetic resonance data.

fied this method for the derivation of electron–proton distances.[53]

In the case of solvated electrons in methanol, a CH_2OH radical is produced simultaneously with the electron and its ESR spectrum precludes observation of any proton spin-flip satellite line associated with the solvated electron at 9- or 35-GHz ESR. However, with 70-GHz ESR we were able to successfully detect the proton spin-flip satellites since they are separated approximately 40 G from the allowed ESR transition at this microwave frequency and are just outside the spread of the CH_2OH radical spectrum.[54] Analysis indicates an electron to OH proton distance of 0.23 ± 015 nm and 4 ± 2 equivalent first solvation shell methanol molecules. The relatively large errors are a consequence of the high magnetic field used at 70 GHz.

Figure 5 shows a suggested structure for the solvated electron in methanol based on this information. We assume the molecular-dipole-oriented solvation shell structure shown based on the structure of solvated electrons in ethanol[55] and on methanol solvation of tetracyanoethylene anion.[56] Recall that microwave spectroscopic studies have shown that the molecular dipole of methanol approximately bisects the C–O–H bond angle rather than being oriented along the OH bond.[57]

Solvated Electrons in Ethanol

For solvated electrons in ethanol, good electron spin–echo modulation patterns have been obtained for three different specifically deuterated ethanols, C_2H_5-OD, CD_3CH_2OH and CH_3CD_2OH; they allow a detailed solvation structure to be deduced. In this matrix the electron spin–echo phase memory time is somewhat longer than in the methanol matrix and, more importantly, the contribution to the electron spin–echo modulation pattern from the background C_2H_4OH radical is sufficiently small that it may be subtracted out.[55] Each specifically deuterated ethanol indicates four first solvation shell molecules. Furthermore, the distances determined to the CD_3, CD_2, and OD groups unambiguously determine the *orientation* of an individual ethanol molecule with respect to the solvated electron.

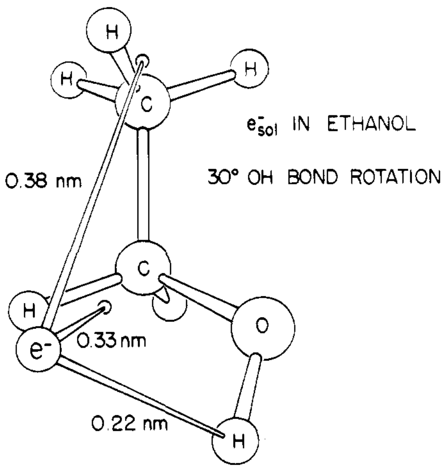

Figure 6. Orientation of an individual first solvation shell molecule with respect to the solvated electron in ethanol. The OH bond is rotated 30° around the OC bond from the CCO plane in ethanol. The distances are averages to the OH, CH_2, and CH_3 proton groups. The entire solvation shell includes four ethanol molecules so oriented and arranged tetrahedrally about the electron. The molecular dipole of ethanol approximately bisects the COH angle and can be seen to be oriented approximately toward the electron.

Within the constraints of the deduced distances, it is not possible to orient the electron such that it is in line with an OH bond in ethanol. The most plausible orientation is shown in Figure 6 in which the OH bond is rotated 30° around the OC bond from the CCO plane in the ethanol molecule. Any rotation between 30° and 60° seems to be about equally acceptable, but a 30° rotation minimizes steric interactions within the ethanol molecule. In all cases, however, the interesting point is that the electron is located approximately on the bisector of the C–O–H angle in ethanol, and hence the solvation shell has a *molecular dipole orientation.* This is consistent with a simple electron-charge–molecular-dipole interaction as the dominant influence determining the solvation shell geometry.

Another class of organic matrices in which an electron is surrounded by hydroxy groups, and for which a detailed geometrical structure has been proposed is a group of crystalline sugars including dulicitol and arabinose.[58-61] These trapped electrons are only stable below ~20 K and cannot be described as solvated, but it is of interest to consider the orientation of dipoles around them. By comparison of single-crystal ENDOR data on the electron–OH proton hyperfine tensors with crystallographic data, specific trapping sites were deduced by *assuming* an undistorted lattice. It is disturbing that the dipoles are not much oriented toward the electron in these sites. Calculations based on the semicontinuum potential model indicate that electrons are not stable in these sites and that some dipole re-

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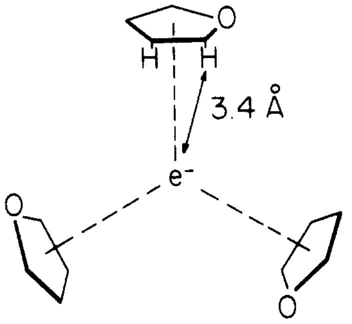

Figure 7. Geometrical structure for solvated electrons in 2-methyltetrahydrofuran glass determined from electron spin–echo modulation and other electron spin resonance data. The isotropic hyperfine coupling to the nearest protons is 0.14 G which corresponds to 0.03% of the solvated electron spin density on each of the nearest first solvation shell protons. See text for further details.

arrangement from that in the undistorted crystal is required for stability.[62] Thus the exact geometry of these trapped electrons is perhaps still uncertain.

Solvated Electrons in 2-Methyltetrahydrofuran (MTHF)

Electrons are also readily solvated in more complex and less polar molecules such as cyclic ethers. Perhaps the most studied system has been the solvation of electrons in 2-methyltetrahydrofuran (MTHF) because this solvent will solvate electrons both in liquid and in frozen glassy solution. We have been able to probe the solvation shell in this system in great detail by using a set of selectively deuterated MTHF molecules which were synthesized by R. Boeckman.[17] The basic idea in designing specifically deuterated molecules was that the oxygen end of the MTHF molecule would have a somewhat excess negative charge; molecules were therefore deuterated in the hydrogen positions near to the oxygen and in the hydrogen positions remote from the oxygen. However, the spin–echo results show that the solvated electron interacts *equivalently* with deuterons in both of the specifically deuterated molecules at the *same* interaction distance of 0.34 nm with an isotropic hyperfine coupling of 0.06 MHz. This suggests that the electron is located on a line perpendicular to the carbon atom plane of the surrounding MTHF molecules in the first solvation shell.

A more detailed analysis based on both two-pulse and three-pulse electron spin–echo results[38] shows that the first solvation shell consists of three MTHF molecules with their ring carbon planes perpendicular to a line from the center of the ring to the electron. Moreover, it is deduced that each MTHF molecule has an equal chance of being oriented with either side of its ring carbon plane toward the electron; this is called the statistical configuration model. This statistical configuration model is also quite consistent with second moment data of the ESR line shapes for the solvated electron in the different specifically deuterated matrices.[38] The overall structure of solvated electrons in MTHF is then shown in Figure 7, in which the methyl groups are intentionally not shown to imply that either side of the MTHF ring plane can be oriented perpendicular to the line toward the electron.

Solvated Electrons in 3-Methylpentane

The solvation of electrons in alkanes is of considerable interest since at first glance one would consider these molecules to be poor solvating molecules.[6] The most studied glassy alkane solvating matrix is 3-methylpentane. We have attacked the problem of electron solvation structure in alkanes by using the series of specifically deuterated 3-methylpentanes synthesized by T. Ichikawa.[63] In these matrices we have not been able to carry out good electron spin–echo modulation experiments because of interference from the radical background. However, we have been able to use another technique for deducing weak hyperfine interactions in disordered solids, namely a second moment line-shape analysis method.[39,42,43] This is not really a new method, but the application of it together with specifically deuterated molecules to deduce the geometrical details of the solvation structure is somewhat novel.

The second moments are obtained from the solvated electron ESR spectra by direct analysis of the line widths and line shapes. The observed second moment can be written as a sum of contributions from hyperfine interactions with the various proton groups plus a residual line-width contribution. From the second moments for the specifically deuterated 3-methylpentane molecules, the per proton contributions can be determined for each position in the molecule. A major limitation of the second moment analysis method is that the second moment for a particular proton group in the solvated molecule depends upon both the number of interacting solvent molecules and their distance and isotropic coupling. The isotropic coupling constant is small, so in order to obtain a detailed, structural picture we must independently obtain information on the number of interacting molecules.

Although we were not able to carry out electron spin–echo modulation analyses on most of the specifically deuterated molecules, we were able to obtain data for the completely deuterated 3-methylpentane-d_{14} for which the number of interacting deuterons was found to be 18–21.[41] The electron spin–echo data and the second moment data suggest that two to four 3-methylpentane molecules constitute the first solvation shell of the electron. We therefore assume that there are an average of three equivalent 3-methylpentane molecules in the first solvation shell and then the second moment data give electron to proton group distances from 0.35 to 0.43 nm. These distances are not compatible with any single orientation of the 3-methylpentane molecules around the electron. Therefore, we have again assumed a statistical configuration model as was found for electron solvation in methyltetrahydrofuran. The interaction distances are shown in Figure 8 and seem compatible with the two configurations schematically portrayed in that figure. In both configurations the electron is in the carbon skeletal plane of 3-methylpentane, excluding the carbon of the methyl group at the 3-position, on a line approximately perpendicular to the terminal carbon–carbon bond and passing through the terminal carbon. In configuration 8a, the electron interacts with five protons and in configuration 8b with seven protons, for an average inter-

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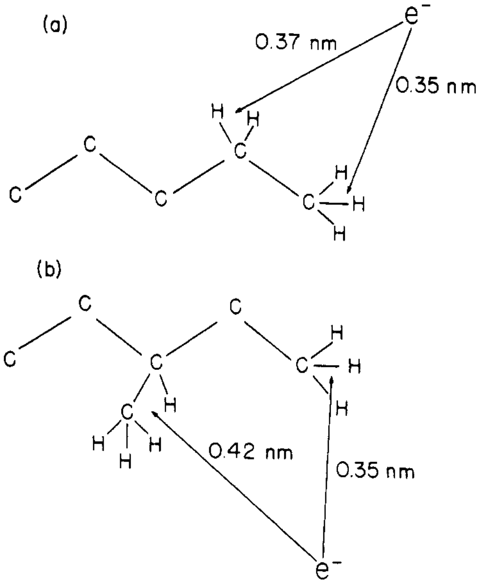

Figure 8. Two equally probable orientations of one first solvation shell 3-methylpentane molecule with respect to the solvated electron viewed perpendicular to the carbon skeletal plane of 3-methylpentane. The scale is approximate. The distances shown are average distances to the proton groups shown (see text). The solvated electron geometry in 3-methylpentane is suggested to be composed of three first solvation shell 3-methylpentane molecules each oriented statistically with configurations (a or b) and with the three molecules arranged trigonally around the electron.

action of six protons per molecule. For a total of 18 interacting protons for the first solvation shell, as deduced from the electron spin-echo data, this corresponds to three molecules in the first solvation shell. Notice that the second moment analysis does indicate that the electron interacts most strongly with a terminal methyl group of 3-methylpentane. This is likely to be the position of optimal charge-polarizability interactions for solvating the electron.[64]

Concluding Remarks

These advances in the determination of solvated electron geometry in disordered systems have been made possible by the utilization of advanced electron magnetic resonance methods and the development of new methods of analysis of electron spin echo modulation patterns, second moment line shapes, and forbidden proton spin-flip transitions for paramagnetic species in disordered systems. The use of specifically deuterated solvating molecules has also been quite crucial.

We have achieved an experimental understanding of solvated electron geometry as a function of solvent molecules of varying polarity and size. For small polar solvating molecules such as water, we find that the solvation geometry is characterized by an OH bond orientation which is presumably controlled by strong chemical or exchange interactions between the first solvation shell molecules and the electron. For larger polar molecules such as alcohols, we find that the solvation shell is characterized by a molecular dipole orientation. Here the controlling interaction appears to be a charge–dipole interaction which one can understand on simple electrostatic grounds. For large nonhydroxylic molecules such as ethers and alkanes, we find that the solvation geometry is dominated by the orientation of CH_2 or CH_3 groups toward the electron. This arrangement appears to maximize the electron–molecular polarizability interaction.

To some extent the current theory based on semicontinuum model potentials[12,65] can semiquantitatively account for the experimental geometries for solvated electrons in ethanol and in methyltetrahydrofuran solvents, that is, for the case of large, polar solvating molecules and large, nonhydroxyllic, less polar solvating molecules. For example, the electron to molecular point dipole distance for the first solvation shell in ethanol calculated on the basis of the semicontinuum model is 0.24 nm. One would presumably locate the point dipole near the oxygen in ethanol, so this theoretical distance correlates with the experimental distance range of 0.25 to 0.28 nm for the electron to oxygen distance.[55] However, for small, polar solvating molecules, as exemplified by water, the semicontinuum potential theoretical model, even in its ab initio incarnation,[66] does not satisfactorily explain the experimental geometry found.

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