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The absorption band profiles of the solvated electron in aqueous and alcohol glasses at 6, 77, and 115 K were calculated in terms of the theory presented in our previous paper. We have concentrated our attention on the problem of the IR-absorbing electrons (eIR⁻), trying to explain their appearance in alcohols, deuterated water, and deuterated glasses and their lack of H₂O glasses at low temperatures. The comparison between the experiment and the theoretical models provides new arguments to the discussion on the initial spectra of trapped electrons.

Introduction

One of the most interesting results of the stationary and time-resolved measurements in radiation chemistry is the detection of an absorption band of the solvated electron in the near-infrared spectral range for many liquids and glasses. This problem has received much attention in the literature. The absorption bands of the solvated electrons in the near-infrared eIR⁻ have been observed in crystalline ice D₂O at 4°K and 76 K, aqueous glasses at 4°K and 77 K, and alcohols at 4°K, 77, 115°K, and 295 K. It is worth emphasizing that unlike D₂O the eIR⁻ absorption in aqueous glasses and in crystalline ice D₂O at 4°K has not been observed at low temperatures. Pulse radiolysis of glasses and liquids shows that the eIR⁻ absorption disappears with time and is accompanied concurrently by the appearance of the band in the visible region. In ethanol, for example, at 4°K eIR⁻ reported at 0.8329 eV and 0.62 eV has a lifetime of 10²s. At 77 K in ethanol, the maximum is observed at 0.954 eV with the decay taking place over 10⁶s. At 115°K the absorption of the eIR⁻ in ethanol observed at 0.95 eV is short-lived with a lifetime of 10⁸s. The decay rate of the IR band and the growth rate of the visible one is of the first order for liquids but not for glasses. The efficiency of the conversion eIR⁻ → evis is only 10% for water. No conversion is found for aqueous glasses.

The current descriptions of the near-IR and visible bands of the excess electron can be divided into the following groups: (a) presolvated (IR) and fully solvated electron (visible), (b) two distinctly different in nature electronic species in structurally different traps, and (c) the solvated electron in an excited state (IR) and the solvated electron in the ground state (visible). Some arguments in favor of eIR⁻ being the precursor of evis seem to arise from the time shift of the IR absorption to the visible range. Higashimura et al. studied γ-irradiated ethanol at 4°K and found a strong absorption band in the near-IR. On annealing to 77 K one observes an irreversible stepwise change in the IR band which finally disappears whereas a new band grows in the visible. However, if the initial trapping site is a statistically controlled inhomogeneity in the glass or liquid, the relaxation of this site resulting in a deeply solvated electron should surely be a continuous process rather than a stepwise one, at least in the framework of the theories belonging to group a. The results of most papers however give support for the stepwise change.

The other arguments against treating eIR⁻ as the precursors of the fully solvated electrons were further indicated by their different reactivities toward electron scavengers. The spectra calculated by molecular dynamic simulations of the excess electron in liquid water show a continuous blue shift in the optical absorption maximum from initially formed IR band to fully equilibrated state in the visible. Rossky et al. have postulated that in the first step (0–110 fs) the electron is solvated in an effective competition with nonradiative energy loss so that the electron is not in its ground state. The shifted IR spectrum observed experimentally at this early stage is thus a characteristic of the solvated excited state. The second step process would then be characterized by the time scale for nonadiabatic transition between the ground state with the absorption band shifting to visible. The equilibrium absorption spectrum of the fully solvated electron is achieved when the solvent relaxes around this new ground state.

Therefore, to our best knowledge, it is not possible at this stage to clearly define the origin of the IR-absorbing state in water and alcohols. The purpose of our paper is to provide some new arguments which should provoke further thought and discussion on the interpretation of eIR⁻ and evis spectra.

Numerical Calculations

We have calculated the absorption profile of the solvated electron from the linear response theory

$$\epsilon(\omega) = \frac{2\Pi\Omega}{3h\epsilon n\hbar}(1 - \exp(-\beta\hbar\omega)) \int_0^\infty \langle M^+(t)M(0)\rangle e^{i\omega t} \, dt$$

(1)

where $\epsilon$ is the extinction coefficient. The expression for the dipole moment correlation function $\langle M^+(t)M(0)\rangle$ was developed in our previous paper.1 The theoretical development considers the contribution to the absorption band profile from the vibrational coupling, tunneling, and inhomogeneous broadening due to the statistical nature of trapping sites. The vibrational coupling includes interaction between the solvated electron and the solvent molecules forming the trap (in terms of the "cavity" or "solvated anion" model). The vibrational coupling is treated in the framework of the strong coupling limit theory. The displacement operator $A$ diagonalizes the Hamiltonian for the $q$ mode coupled with the electron when the electron is in its first excited state. The $A$ operator creates the dynamic effects of the vibrational motion on the electron between its Born-Oppenheimer eigenstates. The time evolution of the operator $A$ is governed by the Liouville equation for the vibrational density operator of the $q$ mode coupled to the bath. The interaction between the $q$ mode and the bath is described in terms of the resonance energy exchange and is characterized by the damping parameter $\Gamma$. Despite this indirect coupling of the solvated electron to the bath (through the $q$ mode), we can expect the direct coupling (inhomogeneous broadening). The direct coupling to the bath is responsible for the fluctuations of the potential well during the electronic transition (single- or double-potential well) and the electronic energy levels (dephasing).

For equilibrium averaging over these fluctuations, we have used the cumulant expansion procedure. The fluctuations of the energy levels (characterized by $a$ and $\tau_0$ in eq 5 and the fluctuations of the energy potential well ($b$ and $\tau_0$ in eq 5) are regarded as a random variable in the two-level system governed by the stochastic Liouville equation. The origin of the fluctuations of the potential well is due to the assumptions which were introduced in the strong coupling treatment of the electron-vibrational mode coupling: (i) the vibrational frequencies in the ground and excited states of the cavity (or anion) are the same, (ii) only one vibrational mode is modified in the absorption process, and (iii) equilibrium geometry of the potential well in the excited electronic state is displaced linearly with respect to the normal vibrational coordinate. Generally, these assumptions may be unjustified. The effects i-iii were formally included in our model by regarding the electronic transition as a transition in the same potential well fluctuating with time. Using this model, we have shown1 that the dipole correlation function $\langle M^+(t)M(0)\rangle$ is given by

$$\langle M^+(t)M(0)\rangle = \sum_{\gamma=0}^{2\gamma} \sum_{\gamma=0}^{\gamma} \frac{\gamma!a!}{2^{\gamma+\gamma/2!}} \sum_{m=1}^{\gamma} \sum_{a=0}^{\gamma} \sum_{a=0}^{\gamma} \sum_{a=0}^{\gamma} \frac{A_{\gamma m}}{C_{\gamma m}} \langle B_{\gamma m}\rangle + \frac{1}{2} \sum_{a=\gamma+1}^{\gamma+1} \sum_{a=0}^{\gamma+1} \sum_{a=0}^{\gamma+1} \sum_{a=0}^{\gamma+1} \frac{A_{\gamma a}}{C_{\gamma a}} \langle B_{\gamma m}\rangle$$

(2)

where

$$A_{\gamma m} = \frac{\gamma!a!(1)^{\gamma+a}}{2^{\gamma+\gamma/2!}}$$

(3)

$$C_{\gamma m} = a(2^{\gamma+\gamma/2!})$$

(4)

$$\langle B_{\gamma m}\rangle = f_m \exp[-i((\omega_m) + (\omega_m^\ast) - 2a_m\omega_m + \gamma - \alpha)] \exp[-(\gamma - \alpha)\omega_m] \exp[-(\gamma - \alpha + 2p + 2j)T] 2$$

$$\exp[-2a^2(\tau_0^2 + (\tau_0^2 - \frac{i}{\tau_0})^{-1} + \tau_0^2)] \times$$

$$\exp[-b^2(\tau_0^2 + (\tau_0^2 - \frac{i}{\tau_0})^{-1} + \tau_0^2)]$$

(5)

The electron charge is given by $e$, $\rho_0$ is the electron density operator, and $\rho_0$ is the energy of the lower ground state (if there is splitting of the energy levels due to tunneling) and the energy of the ground state if electron motion occurs in a single-potential well. The theoretical details can be found elsewhere. Here we explain the meaning of the parameters which have been used in eqs 1–5 for calculations of the theoretical spectra. The correlation function $\langle M^+(t)M(0)\rangle$ depends on the following molecular properties: $\langle \omega_0^2, \omega_0^\ast, \omega_0, \omega_0^\ast, \gamma, \tau_0, \alpha, b, f_m, \omega_m^\ast \rangle$. We have shown1-26 that only $\alpha_0$ and $b$ are adjustable properties in our model. All of the others can be obtained from ab initio calculations ($\langle \omega_0^2, \omega_0^\ast, \omega_0, \omega_0^\ast, \gamma, \tau_0, \alpha, b, f_m, \omega_m^\ast \rangle$) or IR and Raman measurements ($\omega_0, \tau_0$), or can be reasonably estimated ($\alpha, \gamma, \tau_0$). The phase angular speed $\omega_m^\ast$ characterizes the electronic transition of the solvated electron when there is no coupling to the intramolecular vibrational modes of the solvent. This parameter can be treated approximately as the depth of the trap. It was taken as equal to 2.79 and 1.92 eV for ethanol in hydroxyl and alkyl traps, respectively and 2.29 eV for protiated and deuterated water. The vibrational frequencies of the intramolecular modes of the solvent, which are characterized by the phase angular speeds $\omega_0$ were taken from IR and Raman measurements.27-29 The coupling constant $\alpha_0$, which characterizes the strength of the coupling of the excess electron with the vibrational mode characterized by $\omega_0$, is treated as a fitting parameter and is chosen to reproduce the extinction coefficients at maximum of the visible bands ($1.1 \times 10^4$ mol$^{-1}$ L cm$^{-1}$ at 77 K and 1.9 $\times 10^4$ mol$^{-1}$ L cm$^{-1}$ at 300 K as was reported for ethanol30 and water,31 respectively). The damping parameter $\Gamma$ reflects the strength of the coupling between the vibrational mode $\omega_0$ and the thermal bath (translational, reorientation degrees of freedom, low-frequency intramolecular vibrational modes of the solvent). We have put $\Gamma$ as 222 cm$^{-1}$ for ethanol and 212 cm$^{-1}$ for water, which corresponds to the frequencies of the hydrogen bridge stretching modes. The terms $a = 2^{-\gamma/2} (\Delta \omega^2)_{\gamma/2} = b = (\Delta \omega^2)_{\gamma/2}$ characterize the root mean square fluctuations of the electronic transition energy due to the dephasing process and the fluctuations of the energy potential well during the transition. The correlation times $\tau_0$ and $\tau_0^2$ characterize the time scale of these fluctuations. In terms of the stochastic Liouville equation used in our model, $b$ is the change of the electronic angular speed when the electron jumps from the ground to the first excited state with the probability per unit time $f_0 = 1/\tau_0$. The tunneling-phase angular speeds $\omega_m^\ast$ are defined by eqs 52 and 53 in ref 1 and depend on the splitting of the energy levels due to the tunneling in the double-potential well. In the calculations we have assumed that the electron motion occurs in a single minimum potential well and that the Born-Oppenheimer potential well is static with time. So, it means that we put $\omega_0^\ast = \omega_0^\ast = \omega_0^\ast = \omega_0^\ast$ and $b$ as equal to zero. The transition matrix element $f_m$ was taken in harmonic approximation as $f_1 = h/2(T m(\omega_m^\ast))$. In all cases summation over $\gamma$ up to 20 was sufficient in order to achieve convergence in eq 2.

Results and Discussion

Using eqs 1–5 we have calculated the theoretical spectra for the electron solvated in ethanol, 1-propanol, and water matrices. The visible bands were calculated at room and at low temperatures, while the near-IR bands were calculated only at low temperatures. The reason for that is that the IR spectra are time-dependent and only at low temperatures can be regarded as a quasi-stationary.

The coupling with the other modes having frequencies higher than the infrared band of the solvated electron is much shorter, the time evolution of the IR spectra at low temperatures can be treated as the quasi-stationary process. However, an interesting result obtained from our calculations performed so far is the fact that linear response theory applied even at higher temperatures, where the evolution of the band is much faster, is able to predict remarkably well the major portion of the nonequilibrium response. Our theory, of course, is not able to predict the time evolution of the peak position of the band but only the band shape at fixed time. To study the coupling of the excess electron in ethanol with the intramolecular vibrational modes of the solvent molecules we have divided the normal modes of ethanol into the following groups:

(a) stretching mode at 3660 cm\(^{-1}\), (b) five C–H stretching modes (3000 cm\(^{-1}\)), (c) three CH\(_2\) scissoring (1450 cm\(^{-1}\)), (d) OH bending and CH\(_2\) wagging (1398 cm\(^{-1}\)), (e) CH\(_2\) twisting (1250 cm\(^{-1}\)), (f) C–O stretching (1046 cm\(^{-1}\)), (g) CH\(_2\) rocking (875 cm\(^{-1}\)), and (h) OH torsion (649 cm\(^{-1}\)). The numbers taken for calculations are given in parentheses. We have found that the visible band of the solvated electron (\(\omega_{vis}\)) in ethanol at 1.78 eV\(^{27}\) is reproduced best if we assume the coupling between the electron and OH bending mode \(\nu\) at 1398 cm\(^{-1}\) as in methanol.\(^{25}\) In Figure 1 we have shown the calculated absorption spectra of the electron solvated in ethanol and compared with the experimental spectra in the visible and the infrared.\(^{7}\) We can see that the fitting of the experimental band for the coupling electron-bending mode \(\nu\) is a little better if we include some contribution from inhomogeneous broadening due to molecular fluctuations in the environment of the solvated electron (the average distribution of these fluctuations estimated from our model is \(a = 30 \text{ cm}^{-1}, \tau = 1.0 \times 10^{-11} \text{ s, Figure 1, curve 2}\)). It is worth emphasizing that the energy of the electronic transition without vibrational coupling taken in our model (\(\langle \omega_{vis} \rangle = 2.79 \text{ eV}\)) is in good agreement with the solvation energy calculated from the ab initio method by assuming that the electron is surrounded by four ethanol molecules.

The coupling with the other modes having frequencies higher than \(\nu\) gives the unreasonably broad bands (for the OH and CH stretching modes the bands are broader by as much as twice) or too narrow (as much as twice for the OH torsion mode). None of the couplings are able to explain the existence of the near-infrared band. The coupling with OH stretching or CH stretching modes would shift the band of the solvated electron to lower frequencies, but as we can see in Figure 1, the theoretical band profile with the peak position at 1.1 eV falls completely in comparison with the near-IR experimental band (eqn 3) having the peak position at 0.88 eV\(^{3}\) and characteristic with the long asymmetric tail on the high-frequency side. However, if we assume that the IR spectra are associated with presolvated electrons,\(^{16,16,24}\) the trap would be shallower and the coupling with the \(\nu\) (OH) stretching mode could explain the origin of the IR band. Indeed, we have shown in Figure 2 that the spectra of Ogasawa et al.\(^7\) could be quite well reproduced for the coupling with the \(\nu\) (OH) stretching mode at 3660 cm\(^{-1}\) (Figure 2, curve 3) if we assume that the trap is much shallower than for the fully solvated electron \(\nu_{vis}\) (\(\langle \omega_{vis} \rangle_{IR} = 1.85 \text{ eV, } \langle \omega_{vis} \rangle_{IR} = 2.79 \text{ eV}\)). Another possible explanation for the existence of the infrared band is to assume that there are two different kinds of trapped electrons. The visible-absorbing electrons would be associated with the hydroxyl groups (the coupling with the COH bending mode), and the infrared-absorbing electrons would be coupled with alkyl group modes in the traps which are distinctly different in their structure. This structure may be analogous to the complex formed prior to the gas-phase Sn2 reaction (reaction of nucleophilic substitution at a saturated carbon atom, which proceeds in one step via a transition state in which the attacking ion (in our case, electron) becomes partially bonded to the reacting carbon atom while the bond with the incipient ion has weakened). In this geometry the electron is localized at the alkyl group acting as a nucleophile rather than forming a hydrogen bond or a dipole-oriented cavity. We have calculated the absorption spectrum of the electron solvated in the shallow alkyl trap (\(\omega_{vis} = 1.92 \text{ eV}\)) coupled with the stretching modes of the alkyl group (\(\omega_{vis} = 3000 \text{ cm}^{-1}\)). The theoretical absorption spectrum compared with the experimental one is given in Figure 2, curve 1. As we can see, the theoretical band reproduces the most characteristic features of the experimental profile quite well, much better than the coupling with the stretching mode \(\nu\) (OH) in the deep hydroxyl trap (the same as for the visible electron) (Figure 2, curve 2). Clark and Illing\(^{32}\) have found that the alkyl trap structure is by 0.516 eV\(^{3}\) less stable than the H-bond-oriented one, which is smaller than the value calculated from our model (\(\langle \omega_{vis} \rangle_{IR} - \langle \omega_{vis} \rangle_{IR} = 0.9 \text{ eV}\)). However, many results seem to suggest that the preferred geometry in alcohols is the dipole-oriented trap rather than the hydrogen-oriented one\(^{26,34,35}\) and is even more stable than that forming a hydrogen bond. The 4 K spectra of Ogasawa et al.\(^7\) taken by us for comparison are very different from the initial spectra measured by Klassen and Teacher\(^{19}\) since \(G_{vis}\) for ethanol and 1-propanol are about one-third of the values obtained by pulse radiolysis at 6 K.\(^{15,19}\) We have tried to fit the spectra of Klassen and Teacher\(^{19}\)
for 1-propanol. Their measurements were made 100 ns after the start of a 40-ns pulse at 6 and 72 K and 600 ns after the pulse at 115 K. With our model we were able to calculate (Figure 3) the absorption spectrum of the 1-propanol at 115 K by assuming that the electrons are trapped by the modes of the alkyl groups, as in methanol in Figure 2, but we were unable to find a suitable set of parameters to calculate a reasonable fit to the IR spectrum associated with the earliest stage of the electron trapping (at 6 K after a 100-ns pulse). Our results show that the spectra at relatively late stages (115 K, after 600 ns) of the electron solvation are fitted reasonably well by assuming the coupling with the carbon skeleton modes in shallow traps (in comparison with the hydroxyl traps), but the spectra interpreted by the authors as the early stages of electron trapping cannot be fitted with the assumption that the electron–vibrational mode coupling plays the dominant role in determining the IR-band profile. We could have reproduced the value of the $G_{\text{trap}}$ if we had assumed that the electron–vibron coupling is much stronger ($\alpha_0 = 2.65$) than in the case of the results of Ogasawara ($\alpha_0 = -2.435$). However, such strong coupling would cause a much broader band than that observed experimentally.

To conclude, our results for ethanol and 1-propanol seem to indicate that the electron solvated in the alkyl trap is responsible for the IR absorption. However, the presolvated electron in a shallow trap coupled with $\nu_{\text{OH}}$ cannot be ruled out. The important argument in favor of the alkyl trap in the framework of our model is the nearly complete lack of the IR band in methanol in contrast with higher alcohols. If the coupling with $\nu_{\text{OH}}$ were the factor determining the origin of the IR band, there would be no reason to expect its lack in methanol. On the contrary, the possibility of forming various distinctly different structures like hydroxyl traps or alkyl traps becomes greater for higher alcohols.

The situation in water seems to be basically different from that in alcohols. Water molecules seem to be too small to form distinctly different structures. The excess electron is solvated in the traps similar in nature but different in their depth within the limits of the inhomogeneous broadening. In Figures 4 and 5 we have shown that the theoretical absorption bands due to the coupling with all of the normal modes of H$_2$O and D$_2$O: stretching symmetric $\nu_s$, stretching asymmetric $\nu_u$, bending $\nu_b$, and torsional mode $\nu_T$. The damping constant $\Gamma$ was taken as the frequency of the stretching mode $\nu_s$ of the bridge OH−O at 212 cm$^{-1}$ for H$_2$O and 260 cm$^{-1}$ for D$_2$O. We have shown that the visible band in water at 300 K is due to the solvated electron coupled with the torsional mode at 710 cm$^{-1}$. From Figure 5 we can see that in D$_2$O the same type of coupling (with the torsional mode $\nu_T$ at 530 cm$^{-1}$) gives the band width of 0.73 eV, which is in good agreement with experiment (0.84 eV$^4$). In Figures 4 and 5 the depths of the traps as well as the coupling constants with $\nu_s$, $\nu_u$, and $\nu_T$ are assumed to be the same ($\alpha_0 = -2.42$) for H$_2$O and D$_2$O. Using this assumption, we can see that the contribution from the coupling with $\nu_T$ is negligible for both H$_2$O and D$_2$O. However, it can be expected that the stretching mode $\nu_T$, which represents the most sensitive one upon H-bond formation, is more strongly coupled with the excess electron than the others. Especially in the initial stages of solvation, where the hydrogen bond interactions play a role in the dynamics of the excess electron during reorganization in the vicinity of the electron, coupling with the high-frequency modes seems to be very important.$^{40}$ The comparison of our results with the experiment for 1-propanol (Figure 3) in the early stages of the initial spectra in the IR suggests that the electron–vibrational mode coupling is stronger in this case than for the equilibrated stage associated with the visible band. The same conclusion can be drawn from comparison of the visible bands in D$_2$O glasses at 77 K for the absorption observed 100 ns after a 40-ns pulse$^4$ and in γ-irradiated samples.$^{40}$ In all cases, $G_{\text{max}}$ is larger for earlier spectra and the bands are broader (about 1.0–1.2 eV$^4$ than for more equilibrated ones where the band widths are 0.8 eV$^{41}$ as in water.$^{44}$ In Figure 6 we have shown...
aqueous deuterated glass at
Figure 6. Absorption profiles are given in Figures for both early and later stages of solvation.

... conditions for recording the eV. This discrepancy may be due to the cm-I, a... coupling with the torsional mode (figure ... can be reproduced by the coupling with \( u_\text{(OH)} \) is much stronger in... D_2O. The decay with time, which was interpreted by them as the geminate recom... In agreement with experiment.43."

... that in the visible region. However, there is evidence from pulse radiolysis45-48 and temperature measurements49,50 that at earlier stages the electrons are located in shallower traps. For example, the visible band is blue shifted about 0.23 eV with increasing the temperature from 4 to 77 K for 8 M NaOH aqueous glass.50

We can see from Figures 7 and 8 that the IR band due to the coupling with \( \nu_\text{(OH)} \) is much stronger in D_2O than in H_2O. This may be the reason that the IR-absorbing band has been observed in D_2O ice and deuterated aqueous glasses while it could not be seen in H_2O and aqueous glasses at low temperatures.4,6,10,12,40

Recently, pulse laser studies51-53 have shown that at a femtosecond scale the IR band can also be observed in H_2O at room temperatures. Eisenthal et al.52 have shown that the rate of appearance of the solvated electron is slower in D_2O than in H_2O. The decay with time, which was interpreted by them as the geminate recombination dynamics of the cation-electron pair, is also isotope-dependent. However, this effect is not as strong as that for the absolute value of the extinction coefficients of the IR bands presented in Figures 7 and 8. If the IR spectra could be treated as the initial but relatively well equilibrated spectra, the band width in frequency domain, not the absolute value of \( \epsilon \) would be simply related to the relaxation spectra in the time domain according to the linear response theory. As we can see from Figures 7 and 8, IR band widths for H_2O and D_2O are isotope-dependent but rather equivalent, which is in agreement with the time-dependent relaxation spectra of Eisenthal.

If the isotope effect on the IR absorption of an excess electron is due to the different vibrational frequencies of protio and deuterio matrices, the differences in the visible bands in D_2O and H_2O should be explained in the same way. Deuteration shifts the maximum of the theoretical band toward higher frequencies by 0.12 eV (experiment, 0.03 eV). The comparison of the spectra from Figures 4 and 5 shows that the band width in H_2O is broader than that in D_2O by as much as 0.04 eV, which is in excellent agreement with experiment.43,44

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Conclusions

Our results lead to the conclusion that the IR spectra in alcohols do not have analogues for water and aqueous glasses. In alcohols there are two kinds of trapped electrons, which are distinctly different in nature. The visible-absorbing electrons are associated with the hydroxyl groups in alcohol matrices (coupling with the stretching mode \( \nu_{\text{OH}} \)) while the IR-absorbing electrons are trapped in the alkyl group (coupling with the CH stretching modes). Distinction between the two kinds of trapped electrons was further indicated by many authors\(^7\)\(^-\)\(^9\)\(^,\)\(^13\)\(^,\)\(^18\) and our results support their conclusions. In contrast, the IR absorption in water has a quite different origin. Our calculations seem to suggest that there is only one kind of trap in water. The IR bands in \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) are due to the coupling of the solvated electron with \( \nu_{\text{OD}}(\text{OD}) \) and \( \nu_{\text{OH}}(\text{OH}) \) stretching modes, respectively, in the same or a little shallower trap as for the visible electron. The visible bands are due to the coupling with the torsional modes at 530 and 710 cm\(^{-1}\), respectively. The frequency of the \( \nu_{\text{OH}}(\text{OH}) \) mode is much higher than that of the \( \nu_{\text{OD}}(\text{OD}) \) one, and this is the reason for the isotope effect on the extinction coefficient for water. Strong evidence in favor of this interpretation is indicated by the failure reported by many authors in detecting IR absorption in \( \text{H}_2\text{O} \) glasses at low temperature in contrast with \( \text{D}_2\text{O} \) matrices. Furthermore, addition of protio water to \( \text{D}_2\text{O} \) reduces the IR absorption.\(^10\) Indeed, we have shown that the value of the extinction coefficient of the IR band is much larger in \( \text{D}_2\text{O} \) than in \( \text{H}_2\text{O} \). The vibrational coupling of the electron is able not only to explain the appearance of the IR-absorbing band in \( \text{D}_2\text{O} \) and its lack in \( \text{H}_2\text{O} \) glasses at low temperature but also to reproduce the isotope effect on the profile of the visible bands in \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \). Additional evidence in favor of this interpretation is the finding that the conversion \( \text{e}_{\text{IR}} \rightarrow \text{e}_{\text{vis}} \) is observed in alcohols and but not, or to a much lesser degree, in water.\(^4\)\(^,\)\(^11\)\(^,\)\(^12\)\(^,\)\(^13\)\(^,\)\(^20\) The conversion in alcohols is possible due to the different traps responsible for the IR and visible absorption. In water there exists only one kind of trap, which means that the notion of conversion loses its meaning.

Registry No. \( \text{H}_2\text{O} \), 7732-18-5; \( \text{D}_2\text{O} \), 7789-20-0; ethanol, 64-17-5; 1-propanol, 71-23-8.

Multiple-Quantum NMR Studies of Monomeric Bonded Silica Phases†

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Covalently modified, bonded silica phases have been characterized by proton multiple-quantum (MQ) nuclear magnetic resonance (NMR) spectrometry. In the case of trimethylsilyl bonded phases, the loading has been shown to be homogeneous in that MQ coherence development plateaus at a value of approximately 10 correlated protons. Thus, at room temperature the MQ-NMR spin "counting" result is consistent with the fact that trimethylsilyl groups have 9 protons. The groups are dispersed such that intermolecular dipolar interactions are minimal, and the protons of individual trimethyl groups are isolated clusters. Similar results are presented for a C\(_8\) monomeric phase (at \( -101^\circ \text{C} \)) where isolated clusters of approximately 25 protons have been detected, and 23 are seen on the individual groups of the C\(_8\) monomeric phase. The mobility of the alkyl chain has been shown to vary depending upon the structure of the immobilized ligand. At room temperature the mobility of the C\(_8\) alkyl chain groups reduces the dipolar interaction among its protons. Therefore, MQ-NMR was run at the lower temperature to limit molecular motion while enhancing proton dipolar coupling.

Introduction

Most high-performance liquid chromatography separations are currently carried out in the reversed-phase mode. Novel bonded phases have been developed for the separation of specific classes of compounds, and new substrates have been introduced which permit usage over wide pH ranges with extended column lifetimes.\(^1\) Solute retention in liquid chromatography mechanisms, however, are not fully understood. The physical and chemical characteristics of the bonded phase are directly associated with such mechanisms.

Monomeric alkyl phases are produced by reactions of monofunctional silanes (e.g., monoalkoxy- or monosilylalkoxysilanes) with silanols as shown schematically in Figure 1.\(^1\) Monomeric phases can also be produced by the reaction of silica with di- or tri-functional silanes. Water, however, must be excluded from such reactions to preclude silane polymerization. Reaction of a monofunctional silane with silica results in the formation of a single-bond linkage for each silane molecule that reacts with the silica. The extent of surface modification is dependent upon the reaction conditions as well as the physicochemical properties of the substrate and silane reagents. Steric constraints can restrict the number of surface groups which can be chemically modified. Ligands which are already attached to the silica surfaces may shield neighboring unbonded silanol groups from reaction. The homogeneity of such loading is controversial and is the subject of considerable research.\(^2\)\(^,\)\(^3\) In this paper we examine the dispersion of groups which have been covalently linked to the silanol surface. Are the groups uniformly distributed, or do such mod-

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†Registry No. \( \text{H}_2\text{O} \), 7732-18-5; \( \text{D}_2\text{O} \), 7789-20-0; ethanol, 64-17-5; 1-propanol, 71-23-8.

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