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Structure of Solvated Electrons in Liquid Ammonia

SOLVATED electrons have been proposed to account for the properties of metal–ammonia solutions[1,2] and of water[3] and other fluid media[4] subjected to ionizing radiations. Although Kraus[5] described them as "electrons surrounded with an envelope of ammonia" as early as 1908, and various people[6–14] have since introduced the concept of polarized shells of dipolar solvent molecules around the electrons, the structure of the unit and the modification of liquid structure in the vicinity of localized electrons have received very little attention.

The purpose of this communication is first to show how magnetic resonance shift and relaxation data can be used to obtain information about the structure of the solvent shell surrounding solvated electrons in liquid ammonia, and to compare this structure with that of pure ammonia. Second, the shape of the absorption bands arising from electronic transitions in solvated electrons is shown to arise from a symmetrical distribution of a radius parameter describing the trapping site.

During a magnetic resonance experiment, electrons or protons are excited to higher spin energy levels, and the temperature of the spin system tends to exceed the temperature of the lattice. The rate at which thermal equilibrium is restored is described as the spin–lattice relaxation rate ($T_1{}^{-1}$). Spin–lattice relaxation in solution proceeds predominantly by rapid fluctuations of magnetic interactions between the spin system and the lattice, and studies of relaxation rates yield information about these interactions which are determined by spin–density distribution and geometry.

Magnetic relaxation of electron[15–18] and proton[19–21] spins in dilute (R = mol ammonia/mol metal > 300) metal–ammonia solutions proceeds[22] by rapid modulation of scalar electron–nitrogen hyperfine coupling (for T_{1e}^{-1}) and both scalar and dipolar hyperfine electron–proton coupling for $\Delta(T_{1H}^{-1}) = T_{1H}^{-1}$ (solution) − T_{1H}^{-1} (ammonia). We take these interactions to be restricted primarily to a first shell of n equivalent solvent molecules surrounding each electron. Relaxation rates are given by[22]:

$$T_{1e}^{-1} = A_{N} n a_{N}^{2} \tau \tag{1}$$

where $A_{N} = 2x_{N} I_{N}(I_{N} + 1)/3\hbar^{2}$

$$\begin{aligned} \Delta(T_{1H}^{-1}) &= T_{1H}^{-1}\ (\text{scalar}) + T_{1H}^{-1}\ (\text{dipolar}) \\ &= (C\alpha\tau/nR)[(na_{H})^{2} + B_{H}^{2}(nb_{eH}^{-3})^{2}] \end{aligned} \tag{2}$$

where $B_{H} = g_{e} g_{H} \beta_{e} \beta_{n}$

$C = 2S(S + 1)/3\hbar^{2}$

and a_N and a_H are isotropic hyperfine coupling constants, S and I_N are electron and nitrogen spin angular momentum vectors in units of Planck's constant $\hbar$, x_N is the number of nitrogen nuclei per solvent molecule, b_{eH} is the effective electron–proton separation in the solvated electron, α is the fraction of electrons with unpaired spins, τ is the correlation time for the modulation of hyperfine interactions, and g and β are g factors and magnetons for electrons and protons.

The quantity na_N can be obtained from shifts[23–25] of nitrogen nuclear magnetic resonances (Knight shifts, K_N) arising from thermal polarization of electron spins coupled to nitrogen nuclei by scalar hyperfine interactions:

$$K_N = DE_N na_N \alpha / RT \tag{3}$$

where

$$D = -S(S+1)/3k$$

$$E_N = g_e\beta_e / g_N\beta_n$$

and k is Boltzmann's constant. A plot of K_N against α/R is linear[22], indicating little change in coupling to nitrogen when solvated electrons form electrostatic aggregates with solvated cations.

The relative importance of T_{1H}^{-1} (scalar) and T_{1H}^{-1} (dipolar) can be obtained from the dynamic polarization of proton spins[26,27] (Overhauser enhancement, L_H)

$$L_H = 1 + [E_H / T_{1H}^{-1}\ (\text{solution})]\ [T_{1H}^{-1}\ (\text{scalar}) - T_{1H}^{-1}\ (\text{dipolar})/2] \tag{4}$$

where $E_H = g_e\beta_e / g_H\beta_n$

Combining equations (1)–(4) we get the density of ammonia molecules (nb_{eH}^{-3}) in the electron's solvation shell

$$(nb_{eH}^{-3})^2 = [A_N 3C/(B_H D E_N)^2]\ [(R/\alpha)^3 (K_N T)^2 / T_{1e}^{-1}] \times [\Delta(T_{1H}^{-1}) - (L_H - 1) T_{1H}^{-1}\ (\text{solution}) / E_H] \tag{5}$$

For $R > 300$, $nb_{eH}^{-3} \simeq 0.18$ Å^{-3} (Table 1). The decrease for $R < 300$ arises from the neglect of electron relaxation via spin–orbit coupling which becomes important at higher metal concentrations. A relation similar to equation (5) can be obtained without employing L_H by using the proton Knight shift, K_H

$$(nb_{eH}^{-3})^2 = [(RT/\alpha)^2 / 2(B_H D)^2]\{[\Delta(T_{1H}^{-1})(R/\alpha) K_N^2 / T_{1e}^{-1})]\ (A_N / C E_N^2) - K_H^2 / E_H^2\} \tag{6}$$

but because both magnitude[28,29] and interpretation[22] of proton shifts in sodium–ammonia solutions are in dispute, we use equations (1)–(4) to determine na_H independently

$$(na_H)^2 = [A_N / 3C(DE_N)^2][(R/\alpha)^3 (K_N T)^2 / T_{1e}^{-1}] \times [\Delta(T_{1H}^{-1}) + 2(L_H - 1) T_{1H}^{-1}\ (\text{solution}) / E_H] \tag{7}$$

For $R > 300$; $x_H na_H \simeq -15.8$ gauss (see Table 1), suggesting little change in coupling to protons on ion pairing.

Correlation times per solvent molecule $[\tau/n = (6.9 \pm 1) \times 10^{-14}$ s] are again constant for $R > 300$ (Table 1). Estimates[21] of unpaired electron motion from conductivity of dilute sodium–ammonia solutions ($\tau \simeq 4.1 \times 10^{-13}$ s) and of quadrupolar relaxation of ^{14}N spins[22,30] in pure ammonia ($\tau \simeq 1.8 \times 10^{-13}$ s) suggest

$$2.6 < n < 6$$

O'Reilly[31] has suggested that spin–orbit coupling might contribute up to 20% of the electron relaxation even in dilute solutions which reduces τ/n and raises the limits on n to

$$3.3 < n < 7.4$$

Values of $n = 3$ and 7 yield effective average electron–proton distances of 2.53 and 3.35 Å.

X-ray diffraction studies[32] of liquid ammonia near room temperature suggest a nearest neighbour shell of 11 molecules at an N–N distance of 3.6–3.7 Å. If we consider an electron in a vacancy defect in this structure, and polarize the solvent shell around the vacancy so that protons are lining the hole, we can calculate a density, $nb_{\mathrm{eH}}^{-3} \simeq 0.31$ Å^{-3}, substantially greater than that obtained (0.18 Å^{-3}) from the preceding analysis of magnetic shifts and relaxation. The comparison is direct evidence for a marked decrease in density of ammonia in the region of localized electrons.

Bearing in mind the probable limits on n we propose that the solvation of electrons in ammonia occurs at single vacancy defects in the fluid structure, and that the normal shell of 11 nearest neighbours is reduced to about 7 or 8 to avoid formation of proton–proton contacts[22,23] (Bjerrum defects). The large volume expansion observed when electrons are solvated in ammonia[34], which has previously been attributed to large cavities, now resides primarily in the breakdown of the normal liquid structure (reduction in density) around the electrons trapped in small vacancy defects.

The electronic absorption spectra of solvated electrons in ammonia are asymmetrically broadened on the high energy side. A polaron model[35] was used to describe the energy of the transition at the band maximum (E_{max}) using a radius parameter $R_{\mathrm{max}} \sim 3.2$ Å; the asymmetry was attributed to unresolved transitions to higher, excited, bound states. A simple picture of electron trapping in infinite square wells is unsuitable for prediction of total energies[36–39] but was used[40] to show that the high and low energy positions of half maximum absorption ($E_{1/2}^{+}$ and $E_{1/2}^{-}$) corresponded to approximately equal changes ($\delta R_{1/2}^{-}$ and $\delta R_{1/2}^{+}$) of the radius parameter from its values at the band maximum.

Instead of trapping sites all with the same radius parameter, we consider the effect of a range of trapping sites determined

Table 1 Magnetic Resonance Parameters and Calculations for Solvated Electrons in Metal–Ammonia Solutions

M (mol l.$^{-1}$)	R	α	$10^6 K_N$	$10^{-5} T_{1e}^{-1}$ (s^{-1})	$10^{14}\ \tau/n$* (s)	$\Delta(T_{1H}^{-1})$ (s^{-1})	L_H	nb_{eH}^{-3}† (Å^{-3})	$-x_H n a_H/g_e\beta_e$‡ (gauss)
0.01	3,546.0	0.862	29.1	3.02	5.38	0.170	11.0	0.209	16.2
0.02	1,772.0	0.707	42.4	3.06	6.92	0.312	20.0	0.184	15.2
0.04	884.6	0.535	61.5	3.15	7.77	0.522	36.0	0.176	14.7
0.06	588.9	0.429	76.5	3.23	7.49	0.652	48.5	0.179	15.2
0.08	441.1	0.340	89.5	3.35	6.35	0.727	59.0	0.197	16.9
0.10	352.4	0.325	100.9	3.47	7.40	0.770	67.5	0.170	16.3
0.20	174.9	0.231	147.0	4.27	8.81	0.750	98.0	0.125	12.8
0.30	115.8	0.183	183.5	6.15	11.70	0.670	124.0	0.092	9.9
0.50	68.5	0.133	243.3	31.60	51.40	0.500	215.0	0.032	4.0

Mean values for $3{,}546 > R > 352$: * 6.89, † 0.186, ‡ 15.8.

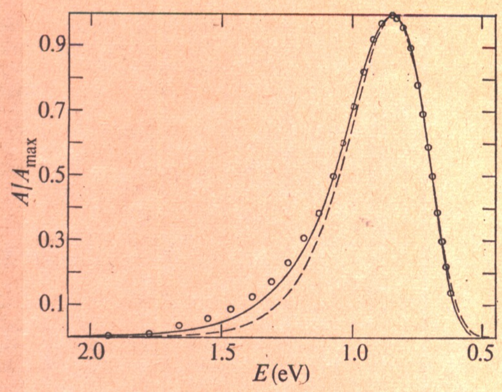

Fig. 1 Comparison of calculated electronic absorption band shapes with that from solvated electrons in sodium–ammonia solutions– (O). – –, Square well calculation, $\delta R^{\pm}_{\frac{1}{2}} = 0.708$ Å; ———, polaron calculation, $\delta R^{\pm}_{\frac{1}{2}} = 0.770$ Å.

by thermal energy. Band shapes calculated assuming a Gaussian distribution of radius parameters for both these models are compared with the observed spectrum of a dilute solution of sodium in ammonia in Fig. 1. Both approaches yield a satisfactory fit to the asymmetric broadening of the high energy side, and there is no need to invoke transitions to higher excited states. Selective thermal and photochemical bleaching in the low energy tail of the band from electrons trapped in solid alcohols[41,42] provides evidence for the physical reality of a range of trapping sites.

It has been argued[43] that a distribution of cavity sizes cannot be responsible for the band width in fluid alcohols (~1 eV) because widths are much greater than thermal energies. This criticism is only valid for a centrosymmetric breathing mode of a spherical cavity. If the variations in the parameter R correspond rather to distortions from spherical symmetry, then the admixture of p-states into the ground state removes the simple identity between δE and thermal energies. Distortions of this type are discussed for electrons trapped in large cavities in liquid helium[44].

A similar calculation of the band shape of aquated electrons is not feasible because the polaron model[45] requires $R_{max} < 0$ to yield agreement with the observed E_{max}.

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