Solutions of Metals: Solvated Electrons

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1 Introduction

Kraus,[1] in 1908, suggested that when alkali metals dissolve in ammonia they give solvated cations and solvated electrons which are responsible for the intense blue colour of such solutions. This was some 44 years after their discovery by Weyl.[2] However, instead of becoming a corner-stone of chemical development, these fascinating solutions remained mere chemical oddities of use to the preparative chemist[3] but not otherwise significant. Interest was just beginning to develop when I first reviewed the properties of these solutions in 1959:[4] that was shortly before the realization that aquated electrons might be important in the radiation chemistry of water[5,6] and the subsequent use of pulse-radiolysis methods to study their optical absorption.[7,8] To those working in the almost unknown field of metal solutions, the curious factor was the instability of e_{aq}^- relative to e_{am}^-, whilst to most radiation chemists it was their stability that caused surprise.[9] Anyway, this discovery had the welcome effect of converting a chemical oddity into the important, fundamental phenomenon that Kraus[10] always insisted it to be. It seems that the delightful simplicity of taking a tube containing liquid ammonia and adding sodium was too simple: it took the great complexity and sophistication of pulse radiolysis to stimulate interest in the fundamental question—how and why are electrons solvated?

In the same way, localized electron-excess centres in solids were well-known, especially in alkali halide crystals, for which the symbols *F*, *F′*, *M*, *etc.*, were used.[11] The detailed structure of the *F*-centre had been explored by the use of e.s.r. and especially ENDOR spectroscopy, and we drew attention to the strong links that seemed to exist between the well understood *F*-centres and ill-defined solvated electrons.[4,12] The fact that simple alcohol glasses acquire an intense violet colour on exposure to ionizing radiation had just been discovered at that

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[1] C. A. Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 1323.
[2] W. Weyl, *Pogg. Ann.*, 1864, **121**, 601; **123**, 350; *Chem. News*, 1864, **10**, 85.
[3] A. J. Birch and H. Smith, *Quart. Rev.*, 1958, **12**, 17.
[4] M. C. R. Symons, *Quart. Rev.*, 1959, **13**, 99.
[5] E. Collinson, F. S. Dainton, D. R. Smith, and S. Tazuke, *Proc. Chem. Soc.*, 1962, 140.
[6] G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, 1962, **66**, 471.
[7] E. J. Hart and J. W. Boag, *J. Amer. Chem. Soc.*, 1962, **84**, 4090; *Nature*, 1963, **197**, 45.
[8] J. P. Keene, *Nature*, 1963, **197**, 47.
[9] F. S. Dainton, *Chem. Soc. Rev.*, 1975, **4**, 323.
[10] C. A. Kraus, *J. Chem. Educ.*, 1953, **30**, 86.
[11] S. Seitz, *Rev. Mod. Phys.*, 1946, **18**, 384; 1954, **26**, 7.
[12] M. C. R. Symons and W. Doyle, *Quart. Rev.*, 1960, **14**, 62.

time, but the nature and structure of the centres responsible was not appreciated. Again, the discovery of the aquated electron triggered off huge activity in the field of such colour centres, which were clearly closely related to solvated electrons formed in the liquid phase.

One great advantage of metal–ammonia solutions in addition to the simplicity of their preparation and their stability is that, at certain temperatures, the complete mole-fraction range can be studied (see Figure 1). In the very dilute region they are clearly related to the systems studied by pulse radiolysis but, as the concentration of metal is increased, the properties gradually change until they become typical of a liquid metal. For this reason, attention will be largely focused upon these solutions. A great deal of pertinent information about isolated solvated (e_s^-) and trapped (e_t^-) electrons has nevertheless been gleaned from other systems and this will be briefly discussed. I dwell largely upon information from optical and magnetic resonance studies because they seem to me to be the most directly informative techniques, and their application has been my primary concern during the past 17 years.

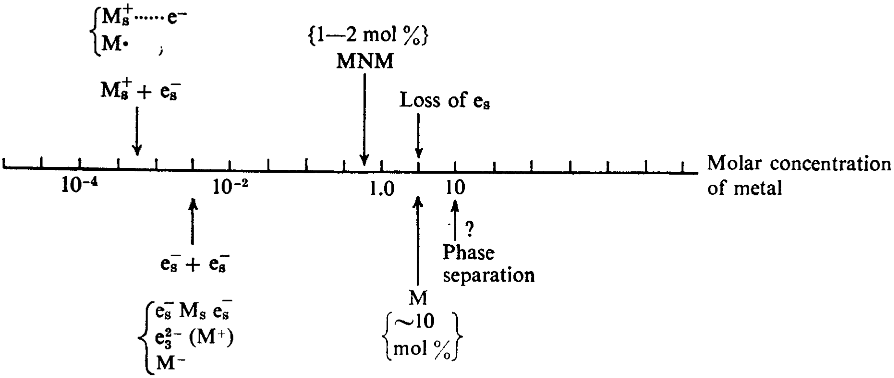

Figure 1 *Concentration effects in alkali-metal ammonia solutions*

2 *F*-Centres

There can be no doubt that de Boer's model for the *F*-centre—an electron trapped at an anion vacancy—is correct (Figure 2). E.s.r. (ENDOR) spectroscopy shows that the excess electron is strongly confined to the vacancy and the first shell of cations,[13–15] but effects caused by slight delocalization or spin polarization can be detected out to the 11th shell by this sensitive technique. The absorption bands for *F*-centres have high oscillator strengths and band maxima that are roughly proportional to the inverse square of the lattice parameters. On an

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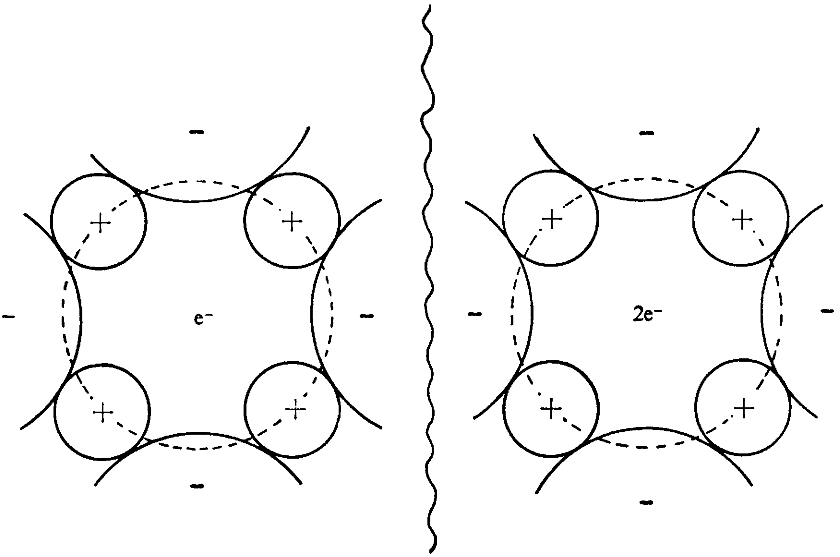
[13] G. Feher, *Phys. Rev.*, 1957, **105**, 1122.

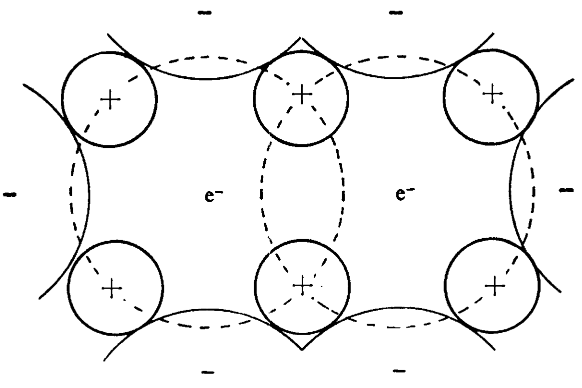
[14] B. S. Goway and F. J. Adrian, *Solid State Phys.*, 1960, **10**, 127.

[15] T. A. Claxton, D. J. Greenslade, K. D. J. Root, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 2050.



F-Centre

F′-Centre



M-Centre

Figure 2 *Cross sections showing structures of F, F′, and M centres in an alkali-halide crystal*

energy (frequency) plot, these *F*-bands are asymmetric, having a marked high-energy tail. Above a low limiting temperature, they broaden almost linearly on heating.

Photolysis in the *F*-band results in bleaching and the formation of a broader absorption on the low-energy side of the *F*-band. These new centres are symbolized *F′*, and are thought to comprise two (paired) electrons at the same vacancy. Another two-electron centre formed in alkali halides doped with relatively high concentrations of metals is the *M*-centre (Figure 2). This has a long-lived triplet state, and hence the use of e.s.r. spectroscopy has resulted in an extremely detailed and precise description.[16] Thus the *D* and *E* terms map the mean separation of the two electrons, showing that they must occupy two adjacent anion vacancies, and the cation hyperfine coupling shows that the spin density on the cations shared by the vacancies is *ca.* twice that on the peripheral cations.[16] These centres also have weak absorption bands on the low-energy side of the main *F*-band. The *F*-centres are the most stable, and centres such as *M* and *F′* only become populated when the concentration of trapped electrons is high, or during photolysis.

3 Metal–Ammonia Solutions

Dilute solutions of the alkali metals in ammonia resemble solutions of 1 : 1 electrolytes. As the concentration of metal is increased conductivity studies reveal the onset of 'ion-pairing' which closely follows that found for normal electrolytes. However, magnetic studies (e.s.r. spectroscopy and static susceptibility) show that shortly after this, spin-pairing to give diamagnetic centres ensues (see Figure 1). This pairing presents major problems, not least because it does not seem to modify the conductivity of the solutions in the expected manner.[17] Further increase in concentration leads to a gradual acquisition of properties typifying liquid metals.[18] There is no well defined switch, and the changes are markedly temperature dependent. In some instances phase separation into solid + liquid or two liquid phases is observed, but not with all metals. This intermediate region (the metal–non-metal region) has properties dominated by microscopic inhomogeneity which gives rise to fluctuations[19,20] characteristic of incipient phase separation. Certain solid phases have well defined properties: thus $Li(NH_3)_4$ and $Ca(NH_3)_6$, for example, have been studied by *X*-ray and neutron diffraction,[21,22] and their structures seem to be reasonably well understood. The ammonia molecules are co-ordinated to the cations in the usual manner and these are well separated from each other with the electron cloud occupying the interstices. However, recent neutron diffraction studies of $Ca(ND_3)_6$ suggest that the ammonia molecules are distorted and have only C_s symmetry.[22]

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[16] H. Seidel, *Phys. Letters*, 1963, **7**, 27.

[17] J. L. Dye, 'Metal–Ammonia Solutions', ed. J. J. Lagowski and M. J. Sienko, Butterworths, London, 1970, pp. 1—19.

[18] J. P. Lelieur, P. Damay, and G. Lepoutre, *J. Phys. Chem.*, 1975, **79**, 2879.

[19] M. H. Cohen and J. C. Thompson, *Adv, Phys.*, 1968, **17**, 857.

[20] P. Chieux, *J. Phys. Chem.*, 1975, **79**, 2891.

[21] R. B. Von Dreele, W. S. Glaunsinger, A. L. Bowman, and J. L. Yarnell, *J. Phys. Chem.*, 1975, **79**, 2992.

[22] P. Chieux, M. J. Sienko, and F. De Baecker, *J. Phys. Chem.*, 1975, **79**, 2996.

For bivalent metals such as Ca and Eu, ion-pairing and spin-pairing set in at a lower concentration. The same is true of solutions of metals in primary amines, ethers, and hexamethylphosphoramide (HMPA). However, solubilities are relatively low in these solvents, and the solutions never exhibit signs of metallic character. Dye and his co-workers have recently shown that solubilities can be greatly increased by complexing the cations with crown ethers (cryptates),[23,24] and it is possible that some solutions of this type may be found to exhibit incipient liquid-metal characteristics.

4 Nature of Solvated Electrons

Kraus[1] originally postulated that the electron in ammonia could be viewed as a solvated anion, and this is still a common viewpoint. However, there are obvious differences: on the one hand anions in protic media are usually hydrogen-bonded to specific solvent molecules, a situation that is impossible for electrons, and on the other hand the electron can be delocalized outside any cavity which it may occupy, again in contrast to most anions.

A. Optical Spectra.—All trapped and solvated electrons are characterized by broad, intense, low-energy bands assigned in a general sense to the $1s \rightarrow 2p$ transition for the centre. The solvent sensitivity of these transitions is marked, being comparable to that found for the c.t.t.s. transitions[25] of halide ions. Indeed, we showed some time ago that there was an approximately linear correlation between $E_{\max}$ for iodide ions in crystals and in various solvents and $E_{\max}$ for *F*-centres and solvated electrons.[26] This correlation, recently extended by Fox *et al.*,[27] is shown in Figure 3. For both systems $E_{\max}$ moves to high energies on cooling, and on increasing the pressure, but the characteristic band-narrowing observed for iodide ions and *F*-centres is not always found for solvated electrons. In particular, the near-i.r. band for dilute metal–ammonia solutions has a width that is independent of temperature over a wide range. This surprising result is discussed further below.

We have previously postulated that the marked solvent sensitivity displayed by the iodide spectrum arises because the electron in the excited state is in an orbital, the periphery of which is strongly interacting with solvent molecules adjacent to the anion.[25,28] Indeed, we compared the excited state for ions like iodide with the ground state for the corresponding solvated electron, the major difference being thought to be the central iodine 'atom'. This would explain in a general sense the similarity in optical properties. In particular the spectral bands in typically protic solvents such as water and the alcohols tend to cluster in the high-frequency region, close to the alkali halide values, whereas those in aprotic

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[23] J. L. Dye, C. W. Andrews, and S. E. Matthews, *J. Phys. Chem.*, 1975, **79**, 3065.

[24] J. L. Dye, C. W. Andrews, and J. M. Ceraso, *J. Phys. Chem.*, 1975, **79**, 3076.

[25] M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, 1958, **54**, 338, 346.

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[27] M. F. Fox and E. Hayon, *Chem. Phys. Letters*, 1974, **25**, 511.

[28] T. R. Griffiths and M. C. R. Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125.

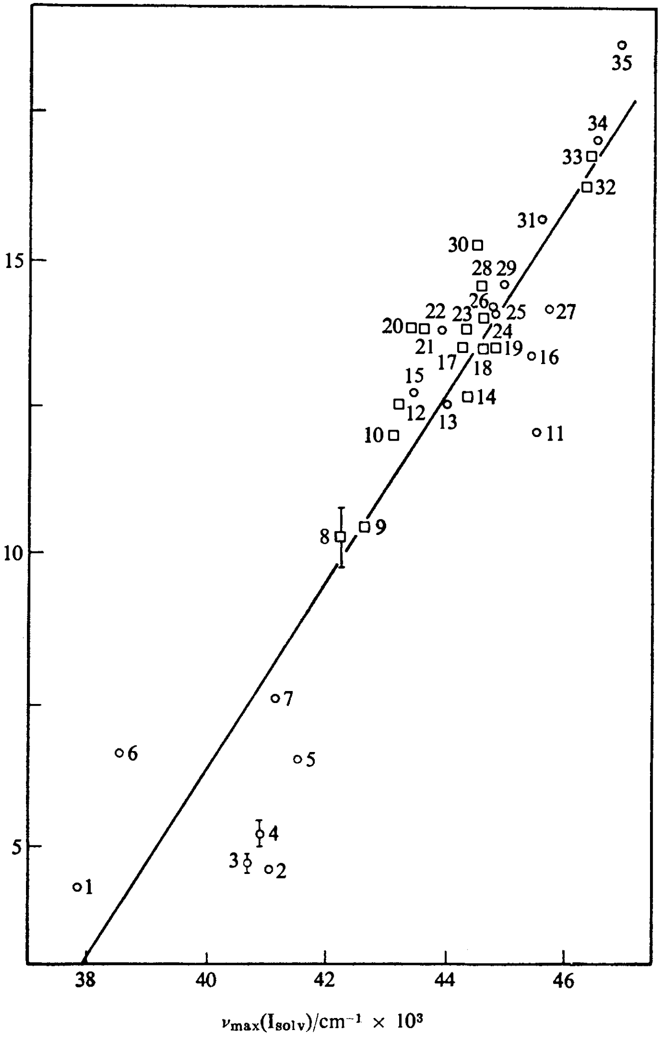

Figure 3 *Plot of* ν_{max} *for* e_s^- *against* ν_{max} *for the first CTTS band for* I^- *in the same solvents and crystals at* 293—298 K.[27] 1 *HMPA*; 2 MeTHF; 3 THF; 4MeOCH$_2$CH$_2$OMe; 5 *isobutylamine*; 6 NH$_3$; 7 NH$_2$CH$_2$CH$_2$NH$_2$; 8 NH$_3$ + H$_2$O; 9, 10, 12 *dioxan* + H$_2$O; 11 Me$_2$CHOH; 13 CsI; 14, 17, 20, 21 Me$_2$CHOH + H$_2$O; 15 RbI; 16 MeCH$_2$CH$_2$OH; 18, 19, 23, 24 EtOH + H$_2$O; 22 H$_2$O; 25 Bu^{t}OH; 26 D$_2$O; 27 EtOH; 28 MeOH + H$_2$O; 29 Bu^{n}OH; 30 6.4M *aqueous* MgCl$_2$; 31 MeOH; 32 12M *aqueous* KF; 33 12M *aqueous* LiCl; 34 *ethylene glycol*; 35 *glycerol*

solvents such as HMPA are at the other extreme. In this sense ammonia behaves like an aprotic medium. Thus, even though e_s^- cannot experience H-bonding in its normal form, there does seem to be a special effect derived from protic media.

We originally endeavoured to explain these optical effects in terms of an average 'radius' defined by the surrounding solvent, and hence envisaged a much larger spherical 'cavity' for anions in ammonia than in water. This is clearly an over-simplification and it now seems more reasonable to assign a major role to the orientation and dipolar character of the protic media, though this may control cavity size.

One important aspect of anion solvation is that, for water and the alcohols, there is direct competition for hydrogen bonds between anion and solvent. Thus most OH groups are relatively strongly bonded to neighbouring solvent molecules, and these bonds need to be broken when an anion is solvated. No such requirement is needed for aprotic solvents. Furthermore, it is not necessary for ammonia either, since at least two of the three protons are not hydrogen bonded and hence are directly available for anion solvation. This explains the observation of a low-field proton resonance shift for ammonia on adding anions despite the weakness of the resulting interactions.[29]

Another significant property of the optical absorption for solvated electrons is that only one band in the low-energy region can be assigned to these species, and this is invariably strongly asymmetric with a marked 'tail' on the high-energy side (Figure 4). We first drew attention to this phenomenon for metal–ammonia solutions some years ago,[4,30] and pointed out that *F*-centre bands displayed the same type of asymmetry. We suggested that other weak higher-energy transitions might be contributing, but that since there was no sign of any resolution this could not be the major reason for the asymmetry. Others have invoked this multiple-band explanation but, in my view, it becomes increasingly less acceptable as the number of different systems showing this asymmetry with no sign of band resolution in the high energy tail increases.

An alternative approach is to postulate a range of cavity sizes (static or dynamic). We showed that simple theories for the '$1s \rightarrow 2p$' transition for electrons more or less confined in a cavity leads naturally to the observed band-shape.[31] Thus, for *F*-centres, for which Mollwo's correlation $\lambda^{F}_{\max} = 600a^2$ (when a is the lattice parameter) holds reasonably well, we found that if the vacancies are allowed to breathe in and out equally the experimental asymmetries are nicely reproduced. If it is assumed that a similar relationship between $\lambda_{\max}$ and the cavity size holds for solvated electrons, a similar range of cavity sizes will lead naturally to the observed asymmetry.[31] This theory can be extended to cover asymmetric modulations with the same conclusion. Catterall[32] has shown that the simple theory reproduces the complete absorption band for dilute metal–ammonia solutions reasonably well if a Gaussian distribution of radius parameters is used. A comparable fit can be obtained with the same pattern of distributions using the 'polaron' model[32] (Figure 4). It can be argued that bandwidths for some e_s^- centres are too great for such a model to be applicable.

[29] M. C. R. Symons and J. Davies, *J.C.S. Faraday II*, 1975, **71**, 1037.
[30] H. C. Clark, A. Horsfield, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 2478.
[31] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 3759.
[32] R. Catterall, *Nature*, 1971, **229**, 10.

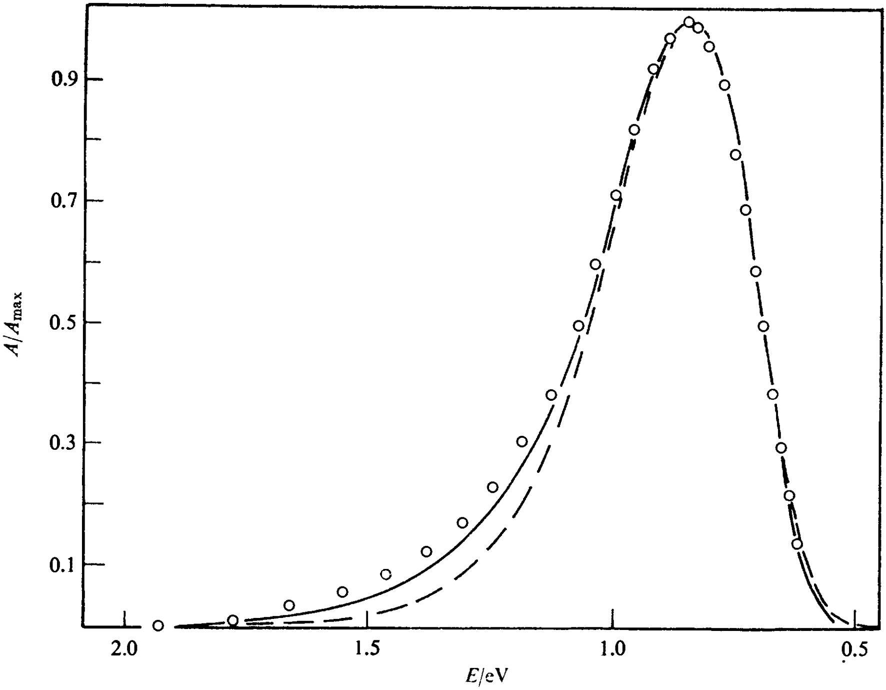

Figure 4 *Absorption band for a dilute solution of sodium in ammonia* (O) *together with curves calculated using the square well model* (- - - -) *and the polaron model* (——)[32]

However, widths for the first c.t.t.s. absorption for iodide ions in the same solvents are equal or even greater. These widths almost certainly reflect the same phenomenon of a range of rapidly interchanging solvent shells, probably with about the same number of solvent molecules in the first shell, but with various conformations, distances, and degree of hydrogen-bonding to other solvent molecules. Obviously, local lattice modes will also contribute, as in *F*-centres.

Thus we do not think that the characteristic asymmetry and width for e_s^- species presents a serious problem, even though some current theoretical calculations fail to reproduce them.[33] Very recent picosecond flash-photolysis studies of dilute metal–ammonia[34] and –methylamine[35] solutions have shown that there is a momentary bleaching of the whole band for e_s^- during the duration of the pulse. (There is then an immeasurably rapid return showing that the lifetime of the excited 2*p* state is *ca.* 2×10^{-13} s.) This was taken as evidence against an 'inhomogeneous broadening'. Certainly for rigid samples partial bleaching of a

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[33] N. R. Kestner and J. Jortner, *J. Phys. Chem.*, 1973, **77**, 1040.
[34] D. Huppert, W. S. Struve, P. M. Rentzepis, and J. Jortner, *J. Chem. Phys.*, 1975, **63**, 1205.
[35] D. Huppert, P. M. Rentzepis, and W. S. Struve, *J. Phys. Chem.*, 1975, **79**, 2850.

band in the region of the energy of the light pulse can be observed,[36] but no such effect has ever been seen for liquids and we suspect that equilibration between the different conformations envisaged would occur sufficiently fast to give rise to the observed overall bleaching.

In the particular case of e_{am}^- there remains the problem that the band-width and -shape are not strongly temperature dependent. This may be to do with the structure of the solvent itself. The hydrogen bonds present no doubt contract, but at least two-thirds of the NH groups remain unbonded. If the 'cavity' size is largely determined by the hydrogen bonds and by repulsions between $(NH)_{free}$ groups, it seems quite possible that there is little or no tendency for a large contraction on cooling.

B. E.s.r. Spectra.—E.s.r. spectroscopy is not directly very helpful in the task of understanding the nature of solvated electrons in fluid solutions. This is because the expected electron–nuclear hyperfine interactions are so rapidly averaging that only a very narrow singlet is obtained. The residual width is still informative but, for such narrow lines, extracted kinetic data are not very reliable. There is a small shift to low *g*-values ($g \approx 2.0015$), implying slight occupancy of vacant orbitals on solvent molecules, but again this is too small to give reliable structural information. Interesting results were found on addition of a range of 1 : 1 electrolytes,[37] the outstanding factor being that the e.s.r. spectrum, which was shifted to lower *g*-values and broadened, was far more sensitive to anions than to cations. This result is curious since, for both cations and anions, the lowest-lying vacant orbital is the outer *s* AO, momentary occupation of which will contribute to the width (by hyperfine coupling) but not to the *g*-shift. We have suggested that, despite the negative charge, the weakly solvated anion makes the electron more welcome than the strongly solvated cation, and hence that species such as I^{2-} are momentarily formed and are responsible for the shifts and broadening.[37] This suggestion has received strong support from a ^{127}I n.m.r. study,[38] and the results may have a bearing upon the possibility that the spin-paired species, discussed below, comprises two electrons in the same solvent shell.

Results for solids are more informative. We consider first electrons trapped in solids after exposure to high-energy radiation, before turning to the apparently simpler, but actually more complex situation found for frozen metal solutions.

It was shown some time ago that ionizing radiation produced a violet species in frozen alcohols[39] that was tentatively identified with excess electron 'colour centres'. (A similar absorption had previously been detected in alcoholic solutions of hydrogen peroxide exposed to u.v. light.[40]) The fact that crystalline alcohols do not give this colour centre strongly supports the view that ejected

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[36] A. Namiki, M. Noda, and T. Higashimura, *Chem. Phys. Letters*, 1973, **23**, 402; S. L. Hager and J. E. Willard, *J. Chem. Phys.*, 1974, **61**, 3244.

[37] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4342.

[38] D. E. O'Reilly, *J. Chem. Phys.*, 1969, **50**, 4320.

[39] R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, 1959, **30**, 695.

[40] M. C. R. Symons and M. G. Townsend, *J. Chem. Phys.*, 1956, **25**, 1299.

electrons, unable to react efficiently with the medium, were trapped at vacancies present in the glasses but almost absent in the crystals.

We later suggested[41] that the electrons, initially only weakly trapped at these vacancies, were subsequently stabilized by a reorientation that directed the protons of the hydroxy-groups towards the centre of the vacancy. Thus, when the OH protons were replaced by deuterons, the e.s.r. singlet narrowed by a factor of about three, showing that its width is dominated by an unresolved envelope of hyperfine features from the OH protons.

This hypothesis was strongly supported by the work of Smith and Pieroni,[42] who showed that on irradiation of alcohols at 4.2 K narrow e.s.r. lines comparable to those from ethers were obtained. These broadened irreversibly to the width obtained at 77 K on slight warming. Further support for this concept has recently been obtained from optical studies.[43,44] When alcohols were irradiated at 4.2 K only a near-i.r. absorption was detected, comparable to that for electrons in ethers. On warming, this was lost and the normal band in the visible region was irreversibly obtained (Figure 5). Similar results for protic solvents have been

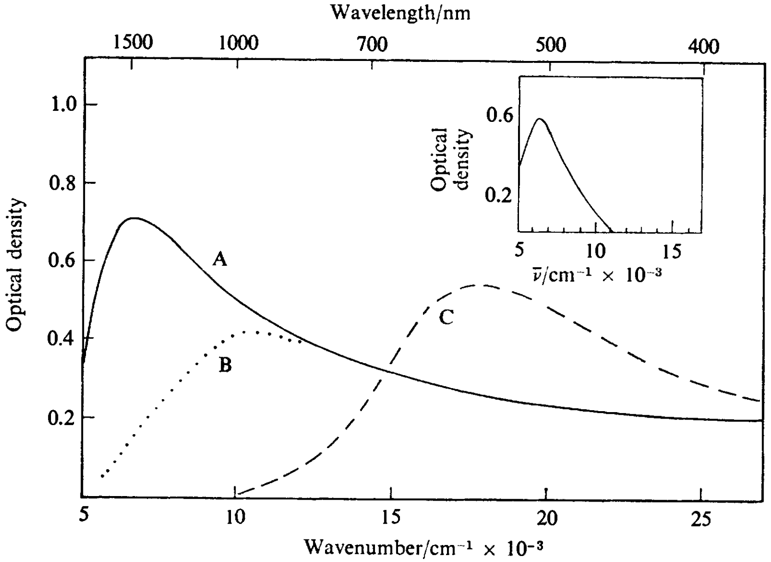

Figure 5 *Optical spectrum for* e_t^- *in ethanol,* A *at* 4 K *after radiolysis at* 4 K; B *after photolysis* (λ = 1700 nm) *at* 4 K. (*Subtraction of* B *from* A *gives the insert spectrum.*) C *after warming to* 77 K[43]

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[41] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1127.

[42] D. R. Smith and J. J. Pieroni, *Canad. J. Chem.*, 1967, **45**, 2723.

[43] H. Hase, T. Warashina, M. Noda, A. Namiki, and T. Higashimura, *J. Chem. Phys.*, 1972, **57**, 1039.

[44] H. Yoshida and T. Higashimura, *Canad. J. Chem.*, 1970, **48**, 504.

obtained at room temperature using picosecond pulses.[45,46] These show that the time required for reorientation of solvent molecules to give the polarized traps is very short: (*ca.* 10.7 ps for MeOH, 23 ps for EtOH, and <3 ps for H_2O at 20 °C).[46] Of course, ethers and ammonia, which only have a band in the 'shallow-trap' region show no short-term optical effects of this sort.

Apart from an isolated, but most interesting, result of Bennett *et al.*,[47] further information about the proton interaction causing these broad lines is scanty. However, in an important paper, Kevan *et al.*[48] have shown that poorly defined features separated by *ca.* 5 G from the main line found under certain conditions, and thought to be resolved proton structure, almost certainly arise because of concerted proton 'spin-flips' well known for trapped hydrogen atoms.[49] In fact their studies show in an indirect sense that the isotropic proton coupling must be considerably less than 5 G, and about 2 G seems to be the best present estimate.

It would be of great interest to obtain the coupling to ^{17}O in these centres, but this would require considerable enrichment, and I know of no such studies as yet. However, we have detected hyperfine features from ^{14}N in the e.s.r. spectrum assigned to trapped electrons in irradiated pyrolidine.[50] The wing lines were very broad, but these were probably nine lines indicating four equivalent ^{14}N nuclei. The isotropic coupling was *ca.* 5.6 G, and the anisotropic coupling was relatively small.

We now turn attention to problems encountered with frozen metal solutions. When metal–ammonia solutions are frozen, phase separation to give crystalline ammonia and colloidal metal particles normally occurs. In our original attempts to prevent this[30] we used potassium iodide as a structure breaker, and obtained blue solids having a single symmetrical e.s.r. feature with a width between points of maximum slope (ΔH_{MS}) of *ca.* 4.6 G and a *g*-value of 2.0020. However, in subsequent work[51] on similar systems, we found that this result was difficult to reproduce. For relatively concentrated solutions (*ca.* 0.4 mol l^{-1}) of metal and a range of electrolytes we have now observed a broad, 35 G feature together with a remarkably narrow line of 0.035 G width (ΔH_{MS}) (Figure 6). The broad feature accords well with expectation for the e_s^- spectrum in the absence of solvent exchange. Hyperfine coupling to many ^{14}N nuclei is then responsible for the width but, unfortunately, there was no sign of resolution.

The surprising aspect of these results is the presence of an extremely narrow component (Figure 6). This represents only a minute percentage of the total electron concentration, and, in view of the clear tendency of these systems to

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[45] J. H. Baxendale and P. Wardman, *Chem. Comm.*, 1971, 429; *J.C.S. Faraday I*, 1973, **69**, 586.

[46] W. J. Chase and J. W. Hunt, *J. Phys. Chem.*, 1975, **79**, 2835.

[47] J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc.* (*A.*), 1967, 1393.

[48] B. L. Bales, M. K. Bowman, L. Kevan, and R. N. Schwartz, *J. Chem. Phys.*, 1975, **63**, 3008.

[49] H. Zeldes and R. Livingston, *Phys. Rev.*, 1954, **96**, 1702.

[50] W. T. Cronenwett and M. C. R. Symons, *J. Chem. Soc.* (*A.*), 1968, 2991.

[51] R. Catterall, W. T. Cronenwett, R. J. Egland, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2396.

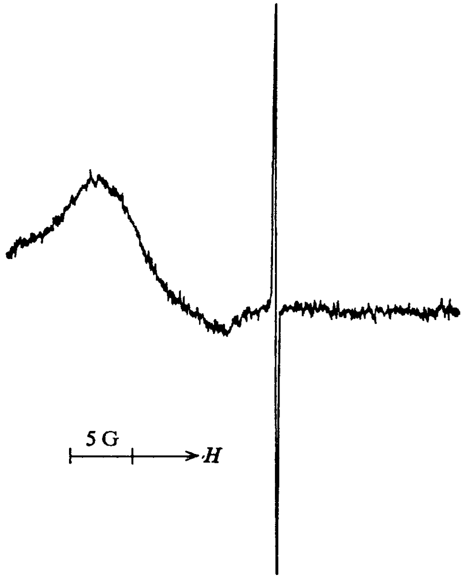

Figure 6 X-*band e.s.r. spectrum for a solution of potassium* (0.4 mol l^{-1}) *in ammonia containing* KBr (1.0 mol l^{-1}) *at* 77 K

undergo some phase separation on freezing, it is not clear how much weight should be placed upon its significance. Similar, very narrow components have recently been detected in frozen metal solutions in HMPA.[52] It is possible that these narrow, liquid-like features are associated with small regions that remain fluid even at 77 K. This seems unlikely, in which case, the 0.035 G centre must be such that rapid electron migration between many solvent molecules occurs in order to avoid hyperfine broadening. We have suggested[51] that this occurs *via* reactions such as

$$e_s^-(\alpha) + e_2^{2-} \rightleftharpoons e_2^{2-} + e_s^-(\alpha) \qquad (1)$$

which occur with spin conservation. Alternatively one might say that these are microscopic regions of a metal-like phase which, because of its size and composition, gives rise to a very narrow line. Until more is known about the composition of these interesting solids it is perhaps unsafe to base a great deal upon the significance of this feature.

C. **N.m.r. Spectroscopy.**—The rapid solvent exchange that washes out all proton, ^{14}N, and alkali-metal hyperfine features from the e.s.r. spectrum for e_{am}^- is fortunately just the requirement that allows n.m.r. spectroscopy to give some information about the hyperfine coupling. The shift, which occurs because of the population difference between the two electron states in the magnetic field, usually called a Knight shift, is an average over all nuclei because of rapid

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[52] R. Catterall and P. P. Edwards, *J. Phys. Chem.*, 1975, **79**, 3018.

exchange. It is possible[53] to convert these shifts into values for the total isotropic hyperfine coupling, although difficulties arise because relatively concentrated solutions have to be used in which there is extensive spin-pairing. Nevertheless reasonable extrapolations have been made, which show that the total coupling to ^{14}N is *ca.* +110 G and to ^{1}H is *ca.* −15.8 G.[53] This shows that the electron spends some 20% of its time in the nitrogen 2*s* orbital [using $A^{\circ}(^{14}N) = 550$ G],[54] but almost no time in the 1*s* hydrogen orbital. This extraordinary result is discussed further below. No further progress can be made unless some estimate of the number of solvent molecules under the influence of the electron at a given instant can be made.

The n.m.r. shift for metal nuclei[55] showed a strong concentration dependence, tending to zero for dilute solutions. This shows that e_s^- is indeed quite separate from the parent cations but that ion-pairing results in a small spin density in the outer *s*-atomic orbitals of the cations.

Information from amine solutions is fragmentary, but for HMPA solutions we have been able to show that the proton coupling is again negative, whilst that to ^{14}N is positive but much smaller than that for ammonia. Surprisingly, the coupling to ^{31}P was zero within the limits of our experiment.[56]

All these results should first be considered in terms of the radical anion concept.[57,58] Clearly, in so far as the excess electrons fail to avoid solvent molecules, they must occupy that virtual MO of the solvent that has the appropriate symmetry. (Since, on this theory, there must be very rapid electron transfer, it may be more appropriate to consider MO's of the parent unrelaxed molecules rather than those for the relaxed anions.) For $\cdot NH_3^-$ we confidently predict a large isotropic coupling to ^{14}N and a comparable large, positive coupling to the protons.[59] For example, the radical anion $F_3\dot{N}O^-$, recently reported,[60] has $A_{iso}(^{14}N) = 147$ G. By analogy with phosphoranyl radicals we might expect a coupling of *ca.* half this value for $\cdot NH_4$ or $\cdot NH_3^-$. This expectation for ^{14}N fits in well with the Knight shift data, but not the small negative ^{1}H coupling. Thus, for example, the $\cdot PH_4$ radical exhibits a coupling of nearly 200 G to two of its protons.[61] It is often stated that the negative coupling can be understood by reference to π-organic radicals such as $\cdot CH_3$ or $\cdot C_6H_6^-$, but this is an incorrect analogy. Certainly the planar $\cdot NH_3^+$ radical has a negative proton coupling, but pyramidal $\cdot NH_3^-$ should give a large positive coupling on any argument.[59] Thus we need to discover some other reason for this negative coupling.[62]

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[53] R. Catterall, ref. 17, p. 105.
[54] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals', Elsevier, Amsterdam, 1967.
[55] D. E. O'Reilly, *J. Chem. Phys.*, 1964, **41**, 3729.
[56] R. Catterall, L. P. Stodulski, and M. C. R. Symons, ref. 17, p. 151.
[57] T. R. Tuttle and P. Graceffa, *J. Phys. Chem.*, 1971, **75**, 843.
[58] B. Webster, *J. Phys. Chem.*, 1975, **79**, 2809.
[59] T. A. Claxton, I. S. Ginns, M. J. Godfrey, K. V. S. Rao, and M. C. R. Symons, *J C.S. Faraday II*, 1973, **69**, 217.
[60] K. Nishikida and F. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 7166.
[61] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004.
[62] M. D. Newton, *J. Phys. Chem.*, 1975, **79**, 2795.

A model which adopts the other extreme places the electron in a cavity defined by solvent molecules but does not allow much delocalization on to these molecules. However, the e.s.r. results for solid alcohols show that the hydroxyl protons 'penetrate' into this cavity and the same may apply to the ammonia protons. In this case a strong spin-polarization effect can be envisaged of opposite sign to that for π-radicals. This is because the 1*s* level for the excess electron combines with the 1*s* hydrogen orbital, thus forcing the σ-electron close to the proton to favour the opposite spin (*cf.* the situation envisaged for $H\dot{C}O$ radicals[54]), and hence the other σ-electron becomes polarized with positive spin. This will confer a negative isotropic coupling to the protons and a positive isotropic coupling to the nitrogen nuclei to approximately equal extents if the σ-orbitals are approximately sp^3-hybridized. Thus this model is satisfactory for the protons but predicts too small a coupling to ^{14}N. I therefore propose a combination of these two processes in order to explain the final result. Since we do not know the number of solvent molecules involved, I will illustrate the type of interaction envisaged by reference to what is, I hope, a reasonable guess. It is assumed that the isotropic coupling to ^{14}N is a good measure of the spin density and hence that the electron is distributed *ca.* 20% on the ammonia molecules and 80% in the cavity. (This is a lower limit for the NH_3 spin density, but for the undistorted molecules the 2*p* character is expected to be small.) Delocalization is expected to involve those molecules directly defining the cavities together with those to which these primary molecules are hydrogen bonded. Since each ammonia molecule is normally bonded to two others in the liquid, we suggest six primary and twelve secondary molecules as a physically reasonable situation. Then delocalization might give a coupling of, say, *ca.* 12 G and 3 G for the ^{14}N coupling on each primary and secondary solvent molecule respectively.

This numerology is aimed at the task of reconciling the apparently contradictory results for ^{14}N and ^1H. It seems that, using this approach, it can be done.

For HMPA it seems necessary to say that the extent of real delocalization of the unpaired electron on to surrounding molecules must be smaller. This is because the electron is expected to occupy a σ^*-orbital having considerable 3*s* character on phosphorus for $HMPA^-$ and yet the Knight shift is negligible. Certainly, after the anion has distorted to its equilibrium structure, $A_{iso}(^{31}P)$ is expected to be *ca.* 600 G by analogy with similar phosphoranyl radicals.[63] This will be still larger prior to distortion. Hence, if this is correct, the electron has to be strongly confined to the central cavity, together possibly with the annular regions between and around surrounding molecules. Spin polarization would then contribute a negative coupling from the CH_3 proton which will, on average, be directed towards the cavity, but this will not be expected to affect the phosphorus coupling appreciably.

There is, however, an alternative picture that will allow considerable delocalization, namely the use of the empty 3*d* manifold on phosphorus. In my

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[63] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

view, if these were available, the electrons would move on to all solvent molecules and the material would acquire semiconductor or metallic properties. Certainly, results for phosphoranyl radicals give no indication that $3d$ orbitals are involved.[63]

5 Electron–Cation Interactions

A large number of possible structures present themselves for electron–cation interactions, and these are not mutually exclusive. I start by considering metal–ammonia solutions, but move quickly to amines, ethers, and HMPA for which more specific information is available.

A. Metal–Ammonia Solutions.—The $1s \rightarrow 2p$ transition is hardly modified by the ion-pairing process clearly indicated by conductivity and Knight shift experiments. Thus e_s^- probably retains most of its character and a loose form of ion-pairing is indicated. This agrees with the small total cation spin densities shown by the Knight shifts. Transient atom formation is ruled out, and a centrosymmetric 'monomer' unit, resembling the units formed in the metallic region, also seems improbable since the band in the 6500 cm^{-1} region is apparently lost during the onset of metallic character.[64]

In order to obtain a view of the electrons from the standpoint of the cations, we studied solutions of europium in ammonia.[65] Europium reacts to give Eu^{2+} which has a characteristic optical and e.s.r. spectrum. Electron–cation interactions are expected to be stronger for bivalent cations, but the optical spectrum nevertheless obeyed Beer's Law and was quite unaltered on going into the ion-pairing region, as was the $1s \rightarrow 2p$ transition for the electrons. Dilute solutions exhibited separate e.s.r. spectra for both species. These broadened rapidly with increase in concentration but there was no diminution in the intensity of the Eu^{2+} signal so that Eu^+ or Eu^0 formation can be ruled out. Marked broadening of the e_s^- resonance is to be expected as a result of cross-relaxation with the Eu^{2+} species in the ion pair. These results again accord with the concept of solvent-shared ion-pair formation[65] for metal ammonia solutions.

B. Solutions in Amines and Ethers.—The fact that a band in the visible region in addition to the i.r. band is detected for most metal–amine solutions was originally interpreted in terms of a diamagnetic species absorbing in the visible region and a paramagnetic species in the i.r. region.[66] Subsequent work has shown that the visible band is best assigned to the diamagnetic species M^- and the i.r. band to solvated electrons and related species. The M^- species is envisaged as a genuine $ns^2,np^6,(n+1)s^2$ anion.[23,24] The suggestion that such species, solvated as anions, might be significant was made at Colloque Weil I in 1963,[67] and was subsequently

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[64] T. A. Beckman and K. S. Pitzer, *J. Phys. Chem.*, 1961, **65**, 1527.

[65] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 1965, 3763.

[66] G. W. A. Fowles, W. McGreggor, and M. C. R. Symons, *J. Chem. Soc.*, 1957, 3329.

[67] M. C. R. Symons, 'Metal Ammonia Solutions', ed. G. Lepoutre and M. J. Sienko, Benjamin, New York, 1964, pp. 15—21.

used to explain certain properties of metal–ammonia solutions.[68] However, it is now clear that genuine M^- ions are probably not formed in ammonia, but are present in metal–amine and –ether solutions, and are responsible for the cation-dependent visible bands exhibited by these solutions. The concept has been strongly supported by the work of Dye *et al.*,[23,24] in particular by their isolation of a solvent-free solid, $Na^+(Crypt)Na^-$. Their results demonstrate the presence of Na^- beyond reasonable doubt. It is probable that solvent-shared or solvent-separated ion pairs contribute to the i.r. band for metal–amine solutions, and in this case some evidence for their presence comes from e.s.r. spectroscopy.

Vos and Dye[69] found that solutions of rubidium and caesium in methylamine have e.s.r. spectra that exhibited broad, poorly resolved hyperfine components from the metal nuclei. Shortly after this, Bar-Eli and Tuttle[70] showed that solutions of potassium in ethylamine gave a well resolved quartet spectrum from hyperfine coupling to ^{39}K ($I = \frac{3}{2}$). The splitting fell markedly on cooling, the estimated spin density on potassium falling from *ca.* 16% to 5% of the free-atom value on cooling from 48 to -36 °C.

We have found that for a variety of amines including ethylamine a narrow singlet can be detected in addition to this quartet (Figure 7).[71,72] This is strongly favoured on dilution and is clearly assignable to the solvated electron, e_s^-. Addition of a potassium salt gave initial loss of the singlet and then rapid broadening of the quartet. This broadening was assigned to the cation exchange,

$$K^+ + K^+e^- \rightleftharpoons K^+e^- + K^+ \qquad (2)$$

and the loss of the singlet to constraining the ion-pairing equilibrium to favour the ion pairs.

Thus we now have a slow equilibrium involving e_s^- and ion pairs, but clearly the term 'ion pair' must cover either a species with very temperature-sensitive properties or at least two different species in rapid equilibrium. We favoured the latter hypothesis because of a differential line-broadening effect but this is not a compelling conclusion.[73] Nevertheless, since the ion-pair unit is apparently favoured in ammonia it is reasonable to suggest that a rapid equilibrium,

$$M_s^+\text{—}e_s^- \rightleftharpoons \cdot M_s \qquad (3)$$

is responsible, the $\cdot M_s$ species being favoured at high temperature. It is important to note that the $\cdot M_s$ centre is not simply an alkali-metal atom interacting weakly with its surroundings. The situation has been compared[74] with that found for silver atoms. When these are matrix isolated from the gas phase into polar solvents such as water the *A*- and *g*-values are close to those for gas-phase atoms.

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[68] S. Golden, C. Guttman, and T. R. Tuttle, *J. Amer. Chem. Soc.*, 1965, **87**, 135; *J. Chem. Phys.*, 1966, **44**, 3791.

[69] K. D. Vos and J. L. Dye, *J. Phys. Chem.*, 1964, **68**, 121.

[70] K. Bar-Eli and T. R. Tuttle, *J. Chem. Phys.*, 1964, **40**, 2508.

[71] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 1965, 6656.

[72] R. Catterall, M. C. R. Symons, and J. W. Tipping, *J. Chem. Soc. (A)*, 1966, 1529.

[73] T. R. Tuttle, *J. Phys. Chem.*, 1975, **79**, 3071.

[74] M. C. R. Symons, *J. Phys. Chem.*, 1971, **75**, 3904.

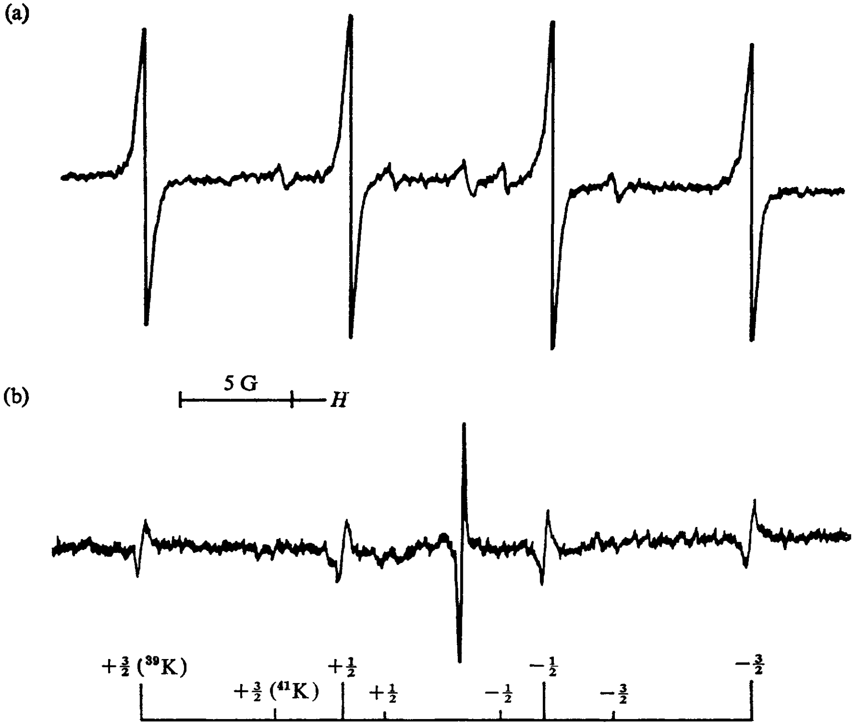

Figure 7 *X-band e.s.r. spectra for solutions of potassium in ethylamine* (a) 10^{-5} M; (b) 10^{-6} M

However, when electrons ejected by ionizing radiation are captured by aquated Ag^+ ions the hyperfine coupling is reduced by *ca.* 30% and g is shifted to low values. A comparable negative g-shift is found for the metal–amine species. Thus the species resembles a cross between a solvated cation and an atom.

C. Hexamethylphosphoramide.—This view is reinforced by the recent results of Catterall and Edwards,[75] who have succeeded in freezing solutions of alkali metals in HMPA containing various electrolytes to give blue glasses having e.s.r. features comparable to those for the liquid metal–amine solutions (Figure 8). (In these cases the liquid-phase spectra are narrow singlets.) Two major paramagnetic components were detected, the 'solvated atom' $\cdot M_s$, having *ca.* 70% spin density in the outer s-orbital and a g-value shifted to high field of the free-atom value, and a broad singlet with a cation-dependent width indicative of unresolved hyperfine features. It is tempting to identify the broad singlet with solvent-separated ion pairs, in which case the two separate components of

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[75] R. Catterall and P. P. Edwards, *J. Phys. Chem.*, 1975, **79**, 3010.

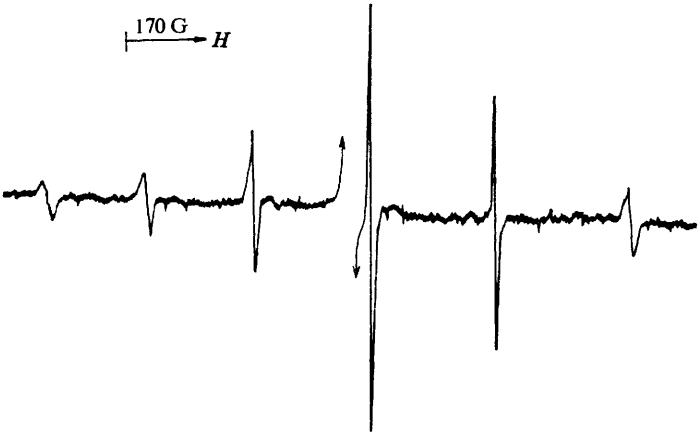

Figure 8 *X-band e.s.r. spectrum for a solution of rubidium in HMPA at* 77 K[75]

equilibrium (3) are detected. It is curious that the average of these is not detected in the liquid phase. This must mean that the ion-pairing equilibrium is fast on the e.s.r. scale for HMPA, just as it is for ammonia.

A complicating factor is that in addition to the intense features for one specific type of 'solvated atom' ($\cdot M_s$) there were other, less intense sets of metal hyperfine lines with coupling constants ranging from *ca.* 36 to 80% of the free-atom values.[75] In no case is any anisotropy observed nor can hyperfine features from solvent nuclei be detected. (The linewidth trends seen in Figure 8 have been shown to stem from a very small statistical range of coupling constants around the average for each species.[75]) The *g*-shifts show no clear trend with the coupling constants, so it is difficult to say whether or not loss of *s*-orbital density is compensated by gain in *p*-orbital density. The remaining spin density probably resides primarily on the weakly co-ordinated oxygen atoms. Studies using HMPA labelled with ^{17}O would be of interest. The presence of a range of distinct species can only be explained in terms of precise structural differences. The most obvious explanation is that the metals have a range of solvation numbers. This is supported by the fact that sodium forms only one secondary species but this number increases to four for caesium. Even Cs^+ is likely to have a variable solvation number because of its size and the relatively weak bonds, so the even weaker bonding in the 'atom' could easily allow several solvates even though one is preferred.

We can now return to the results for metal–amine solutions. Our attempts to detect the 'solvated-atom' species in the frozen solids were unsuccessful,[76] but it is reasonable to suppose that, had good glasses been obtained, the results would have resembled those for HMPA. If this is correct, our suggestion[72] that the marked temperature dependence of $A_{iso}(M)$ arises because of rapid equilibria

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[76] R. Catterall, I. Hurley, and M. C. R. Symons, *J.C.S. Dalton*, 1972, 139.

between two or more species, one with a very low spin density on the metal (the 'ion pair') and another with a high spin density (the solvated atom), would seem to be strongly supported. However, a more direct link is most desirable.

D. γ-Irradiated Glasses.—The most notable aspect of results for irradiated glasses rich in alkali-metal cations is the complete absence of species of the $\cdot M_s$ type. Radical anions, such as $\cdot NO_3^{2-}$ from NO_3^- or CO_2^- from HCO_2^-, are often formed, which interact specifically with neighbouring cations, but I know of no case in which the electron becomes localized largely on the cation itself. Specifically, such centres are not found in aqueous electrolyte glasses, or in frozen solutions of electrolytes in amines or HMPA. This is in sharp contrast with the behaviour of Ag^+ ions, which give $\cdot Ag_s$ centres in high yield in these media.[77–79]

This means that when $\cdot M_s$ units are formed in the liquid phase, there is considerable relaxation of the metal–ligand bonds so as to accommodate the excess electron. However, the ligands must remain, or the units would be normal atoms. In the solid state this seems to be impossible for the alkali-metal ions. The silver(I) ions can presumably capture the electron prior to such relaxation.

An important corollary follows from e.s.r. results for irradiated aqueous glasses that are very concentrated in electrolyte, such as the *ca.* 10M alkali-metal hydroxide glasses. The e.s.r. spectrum for the electron centre in these systems is a singlet that acquires most of its width from hyperfine coupling to a range of protons. The important result is that no matter precisely where these electrons are trapped, be it at an anion vacancy as we have proposed[80] or less precisely at a 'hole' in the glassy system, it cannot avoid being very close to a number of cations. Nevertheless, the contribution of cation hyperfine coupling to the widths of the lines is extremely small.[80] This is in marked contrast to the results for *F*-centres, for which the first shell of cations contributes a huge width increment, and even the second shell makes an appreciable contribution. Thus the electron successfully avoids entering the outer *s*-orbitals of the cations, which implies, in my view, a remarkable degree of localization. It would be of some interest to see if similar amine glasses exhibited the same degree of localization.

6 Spin-pairing

The phenomenon of spin-pairing, so prominent in metal–ammonia solutions, is certainly a precursor to the onset of incipient metallic character, but it may be a side-track rather than a necessary intermediate stage. Thus for compounds such as $Li(NH_3)_4$ or $Ca(NH_3)_6$, which have magnetic and resistivity properties 'normal' for metals such as barium,[81,82] we have spin-pairing at the bottom of the conduction band with slight unpairing at the top. The conduction resonance

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[77] L. Shields, *Trans. Faraday Soc.*, 1966, **62**, 1042.
[78] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1329, 1336.
[79] B. L. Bales and L. Kevan, *J. Chem. Phys.*, 1971, **55**, 1327.
[80] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4352.
[81] W. S. Glaunsinger and M. J. Sienko, *J. Chem. Phys.*, 1975, **62**, 1883.
[82] T. D. Plenty and M. J. Sienko, *J. Phys. Chem.*, 1975, **79**, 2986.

results show that there is less metal *p* character than for the pure metals and the electrons are probably squeezed out of the atomic orbitals of the cations into the considerable free space around and between the large spherical solvated cations.

This is a far cry from the 'blue' species in very dilute solutions. For solutions in ammonia at least, the spin-paired species seems to resemble the single solvated electrons far more than it resembles the 'metal'. Thus its optical absorption differs only slightly from that for e_{am}, and it has a lifetime that is much longer than that for the contact time between e_s^- and a given cation. Such considerations have led to two alternative modes of pairing which resemble in many ways the *M*- and *F′*-centres of alkali halide crystals. As with these crystals, there is no reason why they should be mutually exclusive. Thus the e_2^{2-} model, favoured by Catterall and Symons,[83] resembles the *F′*-centre in having two electrons paired in a single cavity. It is probable that one or more cations are often 'paired' with this entity, and it may be that their presence is essential to stability. (Thus the onset of spin-pairing occurs much earlier for calcium and europium solutions, as does that of ion-pairing.) Arguments in favour of this species are:

(i) the reduction in the number of 'cavities' required per electron;

(ii) the fact that several recent calculations support the possibility of their formation;

(iii) the fact that when spin-pairing occurs for europium solutions there is no change in the optical and e.s.r. spectrum for the Eu^{2+} ions;

(iv) the fact that electrons interact with anions more than cations when electrolytes are added.[37]

The other model that seems satisfactory resembles the *M*-centre and is often written as $e_s^-\ M^+\ e_s^-$. In principle, a good test for this model would be to study its triplet state. In practice, this would be impossible in the liquid state because of the extremely rapid non-radiative relaxation of the excited singlet state expected by analogy with e_s^- units. There is not a lot to choose between these models, both of which may be involved in the pairing process, as in alkali halide crystals. However, I favour the *F′*-centre model because of the long lifetime that the spin-paired centre appears to require. Since ion-pairing is rapid, so also should be the formation of $e_s^-\ M^+\ e_s^-$ units, whereas e_2^{2-} centres, once formed, could well have long lifetimes.

The 'long-range spin-exchange' concept developed by Dye[17] and by Catterall and Mott[84] is more difficult to envisage. Thus normal e_s^- units are involved, but it is suggested that these form units in which spin-pairing occurs because of a favourable long-range exchange process. This leaves the optical band unmodified (which is not strictly correct) and the conductivity should continue to resemble a 1 : 1 electrolyte. The theory also accommodates the lack of pressure dependence for spin-pairing.[85] There are, however, conceptual difficulties that do not seem

[83] R. Catterall, *Phil. Mag.*, 1970, **22**, 779.

[84] R. Catterall and N. F. Mott, *Adv. Phys.*, 1969, **18**, 665.

[85] K. W. Böddeker, G. Land, and U. Schindewolf, ref. 17, pp. 219—228.

to have been explained by this theory. It seems to me that if the solutions are to remain essentially homogeneous then to explain the onset of pairing in the 10^{-3}—10^{-2} mol l^{-1} region one either needs a very large effective radius for the electrons to give the overlap needed for 'pairing' or one needs to postulate the formation of specific paired units. The former situation would rapidly lead to special magnetic and electrical properties and would require that the system move smoothly to the metallic state. If there is a definite tendency for two electrons to pair over a long distance, one must ask, why do they pair? Exchange energy would inevitably be small and triplet states should be favoured or at least be strongly populated. Also the units should be extremely loosely held and hence rapidly separate into two separate e_s^- units. This should lead to uncertainty in spin lifetime, which is not found. Once the metal concentration is high enough, clustering could certainly give rise to regions such as those envisaged, and this surely occurs in the metal–non-metal region, at much higher concentrations.

As stressed above, spin-pairing to give M^- units could explain many of the properties of metal–ammonia solutions. However, since these centres are now well characterized in amine and ether solvents, and since ammonia solutions have no corresponding cation-dependent absorption bands, it seems that this cannot be correct. On balance, therefore, I still favour the e_2^{2-} (F'-centre) model, but clearly the problem is far from being solved.

One might expect, by analogy with F'- and M-centres in alkali halides, that spin-paired centres would also be formed in glasses capable of trapping electrons. However, direct evidence is scanty. Probably the best case can be made for electrons in aqueous alkali hydroxide glasses. We originally showed that the optical absorption for e_t^- in these glasses could be bleached with light on the high-energy side of the visible band and that a weaker, broad absorption was built up in the near i.r. region.[80] On warming, this was lost and there was a slight return of the normal e_t^- band. These observations have been extended by Kevan *et al.*[86] who uphold our suggestion that e_2^{2-} (F') centres are responsible for the new absorption band. [The situation is obscured by the observation that thermal decay of trapped hydrogen atoms leads to a slight gain of e_t^- centres:[87]

$$\cdot H_t + OH^- \rightarrow e_t^- + H_2O \qquad (4)$$

but this occurs at a different temperature and is too minor an event to account for the gain in e_t^- when the i.r. band is lost.]

It might be supposed that the formation of e_2^{2-} centres in rigid solvents would be opposed by the rigidity of the medium. However, since electrons are able to induce orientational polarization even at 77 K,[42–44] there seems no reason why a second electron should not be able to induce the extra polarization needed to stabilize two charges. This is supported by our observation[88] that when O_2^- ions are formed from trapped dioxygen in alcohols at 77 K $g_{\parallel}$ is nearly equal to

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[86] L. Kevan, D. Renreke, and R. J. Fraiauf, *Solid State Comm.*, 1968, **6**, 469.

[87] D. Zimmerman and M. C. R. Symons, *Internat. J. Radiat. Phys. Chem.*, 1976, **8**, 395.

[88] G. Eastland and M. C. R. Symons, unpublished result.

that obtained when NaO_2 is dissolved in that alcohol and the solution frozen to 77 K. Since the magnitude of $g_{\parallel}$ is controlled by the extent of hydrogen-bonding along the x- and y-axes (when z is the molecular axis) this means that virtually complete solvation has been induced to occur in the rigid glass at 77 K. The same should apply to e_2^{2-} units.

Before leaving the topic of the spin-paired species we draw attention to the fact that the fast decay process responsible for the short lifetime of the aquated electron has a rate that requires the presence of two electrons in the rate-determining step. This suggests that e_{aq}^- is stable in itself, but that formation of an e_2^{2-} unit of some sort leads to rapid and irreversible decomposition:

$$e_2^{2-} + 2H_2O \rightarrow H_2 + 2OH^- \qquad (5)$$

Meisel *et al.*[89] have searched unsuccessfully for an optical feature associatable with the e_2^{2-} unit, but if, as implied, this is only an intermediate in a fast decomposition it is unlikely to build up to detectable concentrations. Also, by analogy with metal–ammonia solutions, its optical absorption could be almost indistinguishable from that for e_{aq}^-, thus making its detection by pulse-radiolysis or flash-photolysis methods almost impossible.

These results do suggest that spin-pairing in water involves a discrete unit, since it is difficult to see why two 'paired' electrons separated by a large distance should facilitate process (5).

7 Conclusions

Clearly, a wide range of species is formed when electrons are solvated, especially if there are metal cations present with which they can interact. The solvated or trapped electron appears to need some sort of central cavity, at least in hydroxylic solvents, and in such solvents it seems to be strongly confined to these cavities. They may be somewhat more delocalized in ammonia, but are probably not different in kind.

In ammonia loose ion pairs are formed, but not solvated atoms ($\cdot M_s$). Electron-pairing is extensive and the units involved, possibly e_2^{2-}, closely associated with cations, are relatively stable and long-lived. In contrast, most amines, ethers, and HMPA give $\cdot M_s$ units and M^- anions. The $\cdot M_s$ species are in rapid equilibrium with some unit in which the electrons are only very weakly coupled to the cation, but must nevertheless be very close. These units may be the same as the 'ion pairs' formed in ammonia. Methylamine and ethylenediamine give solutions which have properties in between these two classes.

Concentrated solutions of metals in ammonia experience local microscopic fluctuations in concentration, and even phase separation in the concentration region in which metallic properties first become detectable. Other recent work on concentrated solutions and on the compounds $Li(NH_3)_4$ and $Ca(NH_3)_6$ includes X-ray and neutron scattering,[21,22] ultrasonic absorption studies,[90] and pressure–temperature dependence of conductivities.[91]

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[89] D. Meisel, G. Czapski, M. S. Hall, and W. A. Mulac, *Internat. J. Radiat. Phys. Chem.*, 1975, **7**, 233.

[90] D. E. Bowen, *J. Phys. Chem.*, 1975, **79**, 2895.

[91] S. Hahne and U. Schindewolf, *J. Phys. Chem.*, 1975, **79**, 2922.