

**688.** *Unstable Intermediates. Part XXX.\* Solvated Electrons: Line Shapes of Electronic Absorption Bands*

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It is postulated that the marked asymmetry observed for the absorption bands of *F*-centres, metal-ammonia solutions, irradiated organic glasses, and related systems is characteristic of electrons which are not an integral part of a single molecular system, but are associated with cavities in the media. The band-width can be simply related to the distribution of cavity radii.

ATTENTION has been called<sup>1</sup> to the marked asymmetry of the near-infrared absorption band of metal-ammonia solutions when plotted linearly in energy, compared with the nearly symmetrical bands obtained on a wavelength plot. A similar but less marked asymmetry is found for *F*-bands in alkali-halide crystals at elevated temperatures,<sup>2</sup> and for a variety of other solids thought to contain trapped electrons.<sup>3,4</sup> This is not a general feature of electronic transitions in molecules, although relatively minor deviations from symmetry are sometimes observed.<sup>5</sup>

The aim of this Paper is to suggest that this line-shape is an essential characteristic of systems containing electrons trapped at cavities in fluid or solid media, and to show that

\* Part XXIX, M. C. R. Symons, *J.*, 1965, 2276.

<sup>1</sup> M. C. R. Symons, *Quart. Rev.*, 1959, **13**, 99.

<sup>2</sup> H. Rabin and M. Reich, *Phys. Rev.*, 1964, **135**, A, 101.

<sup>3</sup> M. J. Blandamer, L. Shields, and M. C. R. Symons, *J.*, 1964, 4352.

<sup>4</sup> M. J. Blandamer, L. Shields, and M. C. R. Symons, *J.*, 1965, 1127.

<sup>5</sup> C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 92.

any model for such systems which requires that the electron be strongly confined to the cavities can adequately account for the asymmetry. In such cases, the band-width can be used to obtain an estimate of the relative range of cavity sizes in different media.

Other interpretations seem to us to be less satisfactory. It is always possible to break down such spectra into a series of symmetrical bands but it is hard to believe that the exacting requirements needed in order that no extra peaks or shoulders be observed are fulfilled in all these instances. Another explanation, possibly relevant to the asymmetries observed for certain transition-metal complexes,<sup>5</sup> is that the bands consist of broad overlapping vibronic components which necessarily terminate on the low-energy side with the  $0 \rightarrow 0$  transition. Such a model, using a small number of discrete quantised vibrational levels, is hardly likely to pertain to a diffuse solvent shell of the type presently under consideration.

## RESULTS

A variety of spectra thought to be due to trapped or solvated electrons are given in Figures 1 and 2. Band maxima with corresponding half-widths at half-height ( $\Delta\nu_{\pm}$ ) for these and many other spectra are listed in the Table, together with some calculated radii (see below).

Optical absorption spectra and derived parameters \* for trapped electrons

Matrix	Temp.	$E_{\max}$ (ev)	$\delta E^+$	$\delta E^-$	$a'_{\max, \dagger}$ (Å)	$\delta a'^+$ (Å)	$\delta a'^-$ (Å)	Ref.
LiF .....	R.T.	4.97	0.41	0.34	2.80	0.10	0.11	a
NaCl .....	R.T.	2.70	0.29	0.26	3.81	0.19	0.19	b
KCl .....	R.T.	2.23	0.20	0.18	4.19	0.18	0.18	b
KBr .....	R.T.	1.95	0.23	0.14	4.48	0.24	0.17	b
RbCl .....	R.T.	1.97	0.17	0.16	4.46	0.18	0.19	c
CsBr .....	R.T.	1.80	0.18	0.14	4.65	0.21	0.20	b
KI .....	R.T.	1.76	0.19	0.15	4.71	0.23	0.21	b
5M-KOH-H <sub>2</sub> O .....	77°K	2.12	0.63	0.37	4.29	0.52	0.44	d
10M-KOH-H <sub>2</sub> O .....								
2 M.T.H.F. ....	77°K	0.94	0.46	0.25	6.45	1.16	1.08	d
MeOH † .....	77°K	2.50	0.68	0.35	3.95	0.44	0.31	e
EtOH † .....	77°K	2.42	0.79	0.20	4.02	0.53	0.18	e
Na-NH <sub>3</sub> .....	-78°C	0.818	0.211	0.136	6.93	0.69	0.55	f
Na, K-NH <sub>3</sub> .....	-70°C	0.868	0.228	0.174	6.74	0.68	0.69	g
Li, Na, K, Cs-NH <sub>3</sub> ...	-65°C	0.811	0.230	0.133	6.94	0.72	0.74	h
Na, K-NH <sub>3</sub> .....	-65°C	0.843	0.233	0.144	6.83	0.73	0.58	g
Li, Na, K, Cs-NH <sub>3</sub> ...	-55°C	0.792	0.241	0.138	7.03	0.79	0.73	h
	-45°C	0.773	0.258	0.141	7.08	0.84	0.73	h
Na, K-NH <sub>3</sub> .....	-31°C	0.793	0.253	0.173	7.04	0.84	0.76	g

\* Superscript + and - refer to energies at half-height on high and low energy sides of optical absorption bands. † Radius of potential well corresponding to energy of absorption maximum.

‡ Results on high-energy side are dubious because of possible presence of second band.

(a) Ref. 2. (b) C. J. Rauch and C. V. Heer, *Phys. Rev.*, 1957, **105**, 914. (c) H. Rabin and M. Reich, *J. Chem. Phys.*, 1964, **40**, 3634. (d) This work. (e) R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, 1959, **30**, 695; 1961, **35**, 49. (f) H. C. Clark, A. Horsfield, and M. C. R. Symons, *J.*, 1959, 2478. (g) R. C. Douthit and J. L. Dye, *J. Amer. Chem. Soc.*, 1960, **82**, 4472. (h) M. Gold and W. L. Jolly, *Inorg. Chem.*, 1962, **1**, 818.

*Dependence upon Lattice Parameter.*—The basis of any theoretical interpretation of the asymmetric shape of *F*-bands must be the fact that the band maxima are dependent primarily on the lattice parameter rather than any property of the individual ions. Mollwo<sup>6</sup> first showed that the simple equation

$$\lambda_{\max} = 600 a^2 \quad (1)$$

relating wavelength ( $\lambda$ ) to lattice parameter ( $a$ ) held remarkably well for very many *F*-bands, and it has recently been shown that bands for trapped electrons in many solids other than alkali halides may be reasonably included in such a correlation.<sup>7</sup> [Ivey<sup>8</sup> has since shown that the relation

$$\lambda_{\max} = 703 a^{1.84} \quad (2)$$

<sup>6</sup> E. Mollwo, *Z. Physik*, 1933, **85**, 56; *Nachr. Akad. Wiss. Göttingen, Math.-phys. Kl.*, 1931, 99.

<sup>7</sup> M. J. Blandamer, R. Catterall, L. Shields, and M. C. R. Symons, *J.*, 1964, 4357.

<sup>8</sup> H. Ivey, *Phys. Rev.*, 1947, **72**, 341.

fitted the data known in 1947 somewhat more accurately, but equation (1) will be used here since it leads to the simple theoretical expression derived for these systems (equation 3)]. *F*-bands are quite narrow at very low temperatures but broaden markedly with increasing temperatures and also the band maximum moves to lower energies.<sup>9</sup> At least in part, the former can be understood in terms of an increase in the range of vibrational modes of the ions surrounding the cavity, leading, under the Franck–Condon restriction, to an increase in the range of effective lattice parameters governing  $h\nu_{\max}$ , and hence to a broader band. The shift then reflects the net expansion of the crystal and hence of the mean volume of the cavity. If, as would be expected for small changes in  $a$ , there is an equal probability of the cavity expanding

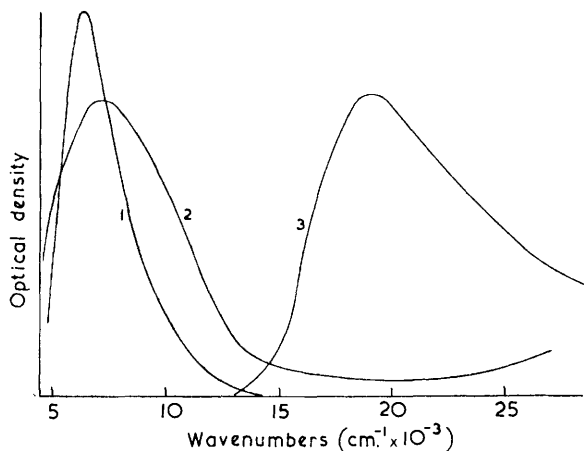


FIGURE 1

FIGURE 1. Absorption spectra assigned to trapped or solvated electrons in (1) liquid ammonia at room temperature (R. Catterall, unpublished results); (2) vitreous methyl-2-tetrahydrofuran at 77°K; and (3) vitreous ethanol at 77°K.

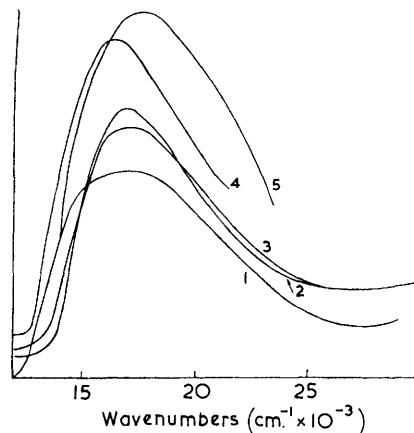


FIGURE 2

FIGURE 2. Absorption spectra assigned to trapped or solvated electrons at 77°K in (1) 10M-KOH in 33–35% w/w ammonia in water solution; (2) 10M-KOH in water; (3) 10M-NaOH in water; (4) 20M-CsOH in water; and (5) 10M-RbOH in water.

or contracting [leading to new lattice parameters  $(a + \delta a^+)$  and  $(a - \delta a^-)$ , respectively], then we can write, from (1)

$$\lambda_{\max. \pm} = F(a \pm \delta a^{\pm})^2 \quad (3)$$

where  $F$  is a constant for this class of transition.

Hence, a value for  $\delta a^{\pm}$  can be obtained. For a given temperature it is found that  $\delta a^+ \sim \delta a^-$ , and the values are not markedly dependent upon the nature of the host crystal (Table). Thus, for *F*-centres, the characteristic asymmetry could well be a direct consequence of relationship (1).

*Relation between Lattice Parameters and Square-well Radii.*—There are numerous examples of the utility of describing the spectra of electrons in cavities in terms of a  $1s \rightarrow 2p$  transition of an electron in a spherical well.<sup>7</sup> The energy of this is related to the square-well radius  $a'$  by

$$h\nu(1s \rightarrow 2p) = 1.04h^2/8ma'^2 \quad (4)$$

Hence, an effective lattice parameter  $a'$  can be estimated, which can be equated approximately to the sum of the cavity radius and that of the surrounding solvent molecules.<sup>8</sup> Here we do not wish to discuss the merits and disadvantages of this particular theory, but, in view of its simplicity, to use it to discuss the spectra of trapped electrons. We stress that the use of more sophisticated theories, provided they lead, as they must, to a dependence upon the lattice parameter of the sort given in (1) or (2), would be equally satisfactory.

<sup>9</sup> G. E. Stungis, J. J. Markham, and G. A. Noble, *J. Chem. Phys.*, 1964, **40**, 3634.

*Electrons in Fluid and in Rigid Solvents.*—In these systems, the cavity size is not known directly, so we use the effective lattice parameter  $a'$ .<sup>8</sup> For electrons in fluid solvents, under equilibrium conditions, we expect cavities to be approximately spherical and to have radii close to the mean. However, in contrast with *F*-centres, the number of solvent molecules associated with a given electron will be continuously changing, as will their relative orientations, and hence a range of different cavities will be present at a given time. This will be expected to contribute to the band-width rather more than vibrational factors. This conclusion is well borne out by results for metal-ammonia solutions, as compared with those for *F*-centres.

The situation for rigid solvents is again different, since the electron will be far less able to define the size or the form of the cavities. For irradiated glasses, the cavities are already present prior to irradiation, having been incorporated from the liquid state. Little is known about these imperfections, but one would certainly expect to find the far greater range of cavity sizes reflected in the width of the optical absorption band. This conclusion is borne out by the results given in the Table for electrons in ethers, but the estimated results for methanol and ethanol glasses are somewhat less than for metal-ammonia solutions. This is partly an artifact of the crude model used, and partly, a result of the difference in temperature, and size of the solvent molecule. The latter factor is brought out by the marked increase in  $\delta a^{\pm}$  as the size of the alkyl group of the alcohols increases. Also, results of electron spin resonance studies of the alcohol centres have been interpreted in terms of a partial tightening and reorientation of the hydroxyl groups around the cavity when the electron is trapped. Similarly, results for electrons in hydroxide glasses suggest that the cavities are quite well defined, in accord with the postulate<sup>3</sup> that the electrons are trapped at hydroxide-ion vacancies. Partial replacement of water by ammonia, while not greatly modifying the cavity site, ought nevertheless to lead to a greater range of sites and hence to a broader band. This effect is clearly seen in curve 1 of Figure 2 and it is to be noted that there is no major shift towards the infrared in this instance.

All these results are in accord with the original concept that the asymmetry stems from a variety of cavities having  $\delta a^{+} \sim \delta a^{-}$ .

*Application.*—The postulate that the band asymmetry is a necessary property of trapped or solvated electrons can be applied to other systems where the species responsible for the colour is less well defined.

(a) It has been postulated<sup>10</sup> that a broad band in the 700  $\mu$  region detected during pulsed radiolysis of water at room temperature is due to aquated electrons. The spectra show a marked asymmetry with broadening on the high-energy side, in accord with this postulate.

(b) The nature of the coloured species in metal-molten salt solutions is still poorly understood. Recently, the absorption spectra of lithium, sodium, and potassium in molten lithium chloride-potassium chloride eutectics have been reported.<sup>11</sup> The smooth structureless absorption spectrum is independent of the nature of the added metal and is symmetric about the maximum absorption when plotted as a function of wavelength. This is the behaviour anticipated from an electron trapped at an anion site.

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<sup>10</sup> E. J. Hart and J. W. Boag, *J. Amer. Chem. Soc.*, 1962, **84**, 4090; *Nature*, 1963, **197**, 45.

<sup>11</sup> J. Greenberg and I. Warshawsky, *J. Amer. Chem. Soc.*, 1964, **86**, 3572.