Interaction of Hydrogen Atoms with Alkali-metal Ions

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WE report a novel interaction between a hydrogen atom and a sodium ion observed during e.s.r. spectroscopic studies of a polycrystalline sample of barium sulphate. γ-Irradiation of precipitated barium sulphate containing trace amounts of water led to the formation of hydrogen atoms which were subsequently trapped at specific lattice sites. When the barium sulphate was precipitated from solutions containing sodium ions the e.s.r. powder spectrum of the vacuum-dried sample, after γ-irradiation and measurement at 77° K, showed the presence of two non-equivalent hydrogen species. The more abundant radical had spin resonance parameters similar to those of hydrogen atoms observed in the gas phase,[1] whilst the second species, characterised by a pair of quartets separated by approximately 500 G, was interpreted in terms of the interaction of a hydrogen atom with a single sodium ion ($I = \frac{3}{2}$) (Figure).

The intensity of the e.s.r. signal from the second radical increased when the barium sulphate was precipitated in the presence of singly charged anions such as nitrate, the concomitant increase in concentration of sodium ions as impurity being required to maintain charge neutrality.

When potassium ions were incorporated into the lattice the analogous $K^+ \cdots H$ species was formed on γ-irradiation. The hyperfine lines were less well resolved than in the sodium case, and it was only possible to obtain the perpendicular hyperfine coupling constant to potassium from the outermost features of the quartets. Precipitation of barium sulphate from deuterium oxide resulted in the formation of the corresponding $Na^+ \cdots D$ radical, lending further support to our assignment.

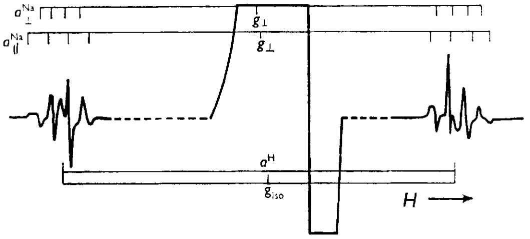

FIGURE. *The e.s.r. spectrum of the* ($Na^+ \ldots\ldots H$) *and "lattice" hydrogen species in γ-irradiated* $BaSO_4$ *measured at* 77°K.

The alkali-metal hydrogen centre is thought to arise from the trapping of a hydrogen atom if not at a sodium site itself, then at a barium or sulphate site close to a sodium ion. The quartet features from this radical decay at about 220° K and there is a parallel increase in intensity of the e.s.r. signal for the first radical, which we will call "lattice" hydrogen. This shows that the ($Na^+ \cdots H$) centre is less stable than the lattice hydrogen centre.

Nevertheless, the ratio of ($Na^+ \cdots H$) to lattice hydrogen is higher than that predicted statistically. We postulate that H_2O or OH^- is incorporated near a sodium ion in the lattice and hence the probability of a hydrogen atom finding a sodium site will be large. The e.s.r. parameters of these centres, obtained at 77° K at X-band frequency, are given in the Table.

Electron spin resonance parameters

Radical	*g*-tensor			Alkali metal hyperfine splittings (G)			Hydrogen hyperfine[a] splittings (G)			a_s^2 on metal
	$g_{\parallel}$	$g_{\perp}$	g_{av}	$a_{\parallel}$	$a_{\perp}$	A_{av}	$a_{\parallel}$	$a_{\perp}$	A_{av}	
"Lattice hydrogen"			2·0015						503·9	
($Na^+ \cdots H$)	2·0012	2·0013	2·0013	21·4	15·1	17·2	513·2	510·7	511·2	0·054
($Na^+ \cdots D$)[b]		2·0032			16·2			$a_{\perp}^{D} = 79$ G		
($K^+ \cdots H$)[b]		2·0016			4·0			~500		~0·05

[a] Corrected to 2nd order.

[b] Only the perpendicular features have been resolved.

The anisotropic hyperfine tensor representing the interaction of the unpaired electron with the sodium nucleus has the form (2B, −B, −B). This we assign entirely to an indirect coupling, and by using a point dipole approximation we calculate a sodium–hydrogen bond length of 1·5 Å. This can be compared with the value of 1·8 Å for sodium hydride in the gas phase.

Since $|a_{\parallel}^{Na}|$ is greater than $|a_{\perp}^{Na}|$ and since the 2B term must be positive, then a_{iso}^{Na} must be positive. This is almost certainly a result of direct delocalisation of the unpaired electron into the 3*s*-orbital on sodium, giving a spin-density of 0·054.

However, the proton coupling shows no evidence for such delocalisation, being in fact slightly greater than that for hydrogen atoms in the gas-phase. A similar lack of sensitivity of the proton hyperfine splitting to electron delocalisation has been observed in other systems and is discussed elsewhere.[2]

Similarly, we derive a value for a_s^2 for the potassium 4*s* orbital of *ca.* 0·05. However, no anisotropy could be detected. This is not surprising in view of the smaller nuclear magnetic moment of potassium compared to sodium, and the expected larger internuclear distance in ($K^+ \cdots H$) leading to a reduced dipolar coupling between the unpaired electron and the alkali-metal nucleus.

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[1] N. Ramsey, "Nuclear Moments", Wiley, 1953; P. Kusch, *Phys. Rev.*, 1955, **100**, 1188; R. Berringer and M. A. S. Heald, *Phys. Rev.*, 1954, **95**, 1474.

[2] P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967.