Preparation and Properties of the H_2S Negative ion

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WE have shown previously[1] that when potassium or sodium atoms are deposited on ice at 77°K, the valence electron of the alkali-metal atom is transferred to an assembly of water molecules to become a trapped electron. The electron is located in an orbital which is not confined to one water molecule but is associated with several.

We now report the results of a similar study of the reaction between potassium or sodium atoms and hydrogen sulphide or deuterium sulphide at 77°K. The deposits in every case were a deep yellow–brown colour. The optical absorption spectra (Fig. 1), obtained by a reflectance technique with a spectrometer fitted with traversing photomultipliers,[2] were all identical, with a broad maximum (possibly twin peaks) from about 7000—10,600 Å, and a narrower peak at 4000 Å. A further region of continuous absorption commencing at about 3000 Å and increasing strongly towards shorter wavelengths was clearly indicated on a photograph of the spectrum, but quantitative measurements were not made on this region.

Electron spin resonance (e.s.r.) spectra of the deposits were recorded: those of products from the reaction of potassium with H_2S and with D_2S being shown in Fig. 2. The following comments may be made:

(1) Identical spectra were obtained when sodium was used instead of potassium, indicating that, as in the water–alkali metal systems, the valence electron has been transferred completely from the alkali-metal atom.

(2) The spectrum of the product from D_2S is asymmetric and typical of a paramagnetic centre with an axially symmetric *g*-tensor. In contrast, the spectrum of the D_2O system was symmetric, indicating an isotropic *g*-tensor.

(3) A comparison of the spectra of the D_2S and H_2S systems shows that there is a hyperfine interaction with two equivalent protons or deuterons. A similar comparison of the spectra of electrons trapped in H_2O and D_2O has indicated hyperfine interaction with six protons. (In our earlier publication[1] we reported interaction with only four protons. Markedly better spectra obtained in more recent work show clearly that there are six.[2])

(4) When the spectrum of the D_2S system was recorded at two hundred times the original sensitivity, weak satellite lines were observed, which are attributed to a hyperfine interaction with naturally occurring ^{33}S-atoms.

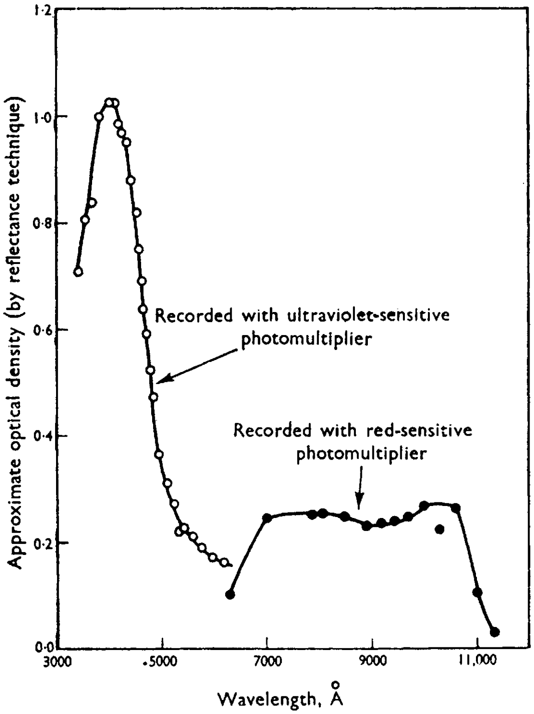

FIGURE 1.—*Optical absorption spectrum of* H_2S^-.

We conclude from these features that, whereas in ice the orbital of the unpaired electron extends over several molecules of water, in solid H_2S or D_2S it is confined to only one molecule to form the negative ions, H_2S^- or D_2S^-. This marked difference between the behaviour of water and of hydrogen sulphide is understandable because (i) the sulphur atom has low lying $3d$-orbitals which can accommodate the extra electron, whereas the oxygen atom does not, and (ii) the molecules in solid H_2S have a lower dipole moment and are almost completely unassociated,[3] and thus are less likely to form assemblies which can trap electrons, as in ice.

The e.s.r. constants of H_2S^- and D_2S^- are:

$$g_{11} = 2{\cdot}0023 \pm 0{\cdot}0005$$
$$g_{\perp} = 2{\cdot}0164 \pm 0{\cdot}001$$
$$A(\mathrm{H})_{\perp} = A(\mathrm{H})_{11} = 7{\cdot}7 \pm 0{\cdot}3 \text{ oersted}$$
$$A(^{33}\mathrm{S}) = 60 \pm 2 \text{ oersted (in } D_2S).$$

The principal values of the g-tensors of H_2S^- and D_2S^- are similar to those attributed to negative ions formed by γ-irradiation of pentyl disulphide[4] or electron irradiation of L-cysteine dihydrochloride[5] at 77°K. Complete agreement would not be expected because in these latter compounds the unpaired electron is probably located in a molecular orbital involving both sulphur atoms.

If the unpaired electron in H_2S^- or D_2S^- were located in a pure $3d$-orbital on the sulphur atom, a negative shift in the g-factor would occur as found, for example, in the case of the isoelectronic titanium (Ti^{3+}) ion.[6] The observed positive shift in $g_{\perp}$ suggests that the free electron orbital has some $3p$-character. The $3s$-orbitals additionally contribute about 6% to the orbital as indicated by the coupling constant of 60 oersted to the ^{33}S nucleus,[7] and the hydrogen $1s$-orbitals also contribute about 1·5% each to the orbital as indicated by the 7 oersted hyperfine splitting of the two protons. We therefore conclude that the unpaired electron orbital is a hybrid of $3s$, $3p$, and $3d$ sulphur orbitals. This implies that the bonding orbitals are also hybrids of the same orbitals, as concluded for the bonding orbitals of neutral H_2S by Barrus and Gordy[8] from a study of its microwave spectrum. The fact that g_{11} is very close to the free-spin value suggests that the orbital of the unpaired electron possesses axial symmetry, but from our present results we cannot determine its orientation with respect to the molecular axes.

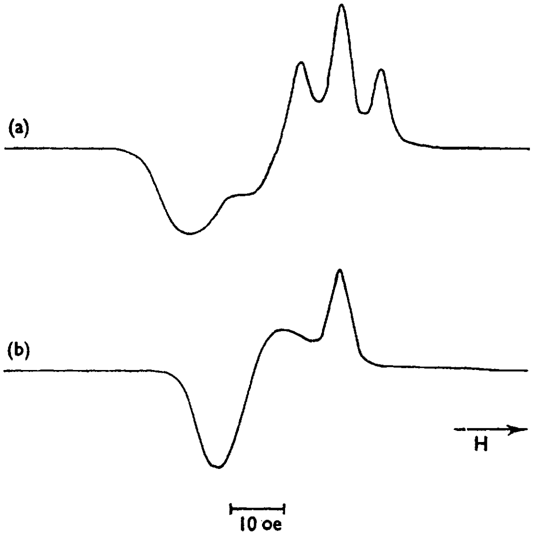

FIG. 2.—*First derivative spectrum of the products from the reaction of* (*a*) $K + H_2S$, *and* (*b*) $K + D_2S$.

When the H_2S and D_2S deposits were illuminated with light from a tungsten lamp, neither their colour nor their e.s.r. spectra decayed. This is in marked contrast to the behaviour of trapped electrons in ice, whose deep blue colour and paramagnetism were rapidly lost on illumination. The excited states of H_2S^- resulting from absorption at 9000 Å and 4000 Å must therefore be stable. In contrast, illumination with light from a mercury lamp (predominant wavelength, 2536 Å) resulted in a progressive diminution of e.s.r. signal strength. It is therefore likely that the absorption commencing at about 3000 Å (corresponding to about 100 kcal. mole^{-1} or 4·3 *e*v) results in photodetachment of the unpaired electron and consequently gives a measure of the adiabatic ionization potential of H_2S^-.

If a sample of either H_2S^- or D_2S^- is warmed there is no change in the e.s.r. spectrum until a temperature of 100—110°K is reached when it changes irreversibly. The change is accompanied by an approximately ten-fold decrease in the concentration of unpaired electrons. This second spectrum, which is identical for both H_2S and D_2S systems, consists of a single asymmetric line with the following principal values of the *g*-tensor:

$$g_1 = 2{\cdot}002 \pm 0{\cdot}001$$
$$g_2 = 2{\cdot}033 \pm 0{\cdot}001$$
$$g_3 = 2{\cdot}053 \pm 0{\cdot}001.$$

These values are close to those observed for RS· radicals,[9] and for radicals at the ends of polymeric sulphur chains.[10] They suggest that some degree of polymerization has occurred to give a free radical with the unpaired electron located mainly in a 3*p*-orbital of a terminal sulphur atom.

It may be noted that there is an abrupt phase change in solid H_2S at 103°K.[11,12] Below this temperature there is a high degree of order in the positions of both hydrogen and sulphur atoms, but above it there is disorder in the positions of the hydrogen atoms. The chemical reaction of H_2S^- with hydrogen sulphide probably occurs when this rearrangement of the positions of the hydrogen atoms of neighbouring molecules is able to take place.

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