Electron Spin Resonance Studies of the Hydroxyl Radical in γ-Irradiated Ice

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ATTENTION was recently drawn[1] to the difficulty of accommodating the electron spin resonance parameters assigned to the hydroxyl radical in ice.[2] In particular, the magnitude and sign of the proton isotropic hyperfine coupling constant of +41·3 gauss were questioned and it was suggested that a value of about −25 gauss would be expected. Also it was shown that the anisotropic coupling was far too small for unperturbed hydroxyl radicals. This paradox has been further accentuated by the results of Radford[3] for the hydroxyl radical in the gas phase. These results together with those of McMillan *et al.*[2] are listed in the Table.

The aim of our work was to discover possible alternative interpretations of the solid-state spectra and to this end we have studied the electron spin resonance spectra at *X*- and *Q*-band of γ-irradiated powders and single crystals of ice and deuterium oxide at 77° K. In particular, dilute "solutions" of radicals thought to be hydroxyl have been prepared in crystals consisting largely of deuterium oxide in order to reduce the widths of the proton hyperfine lines. These hyperfine lines then appeared as relatively narrow satellites on either side of the triplet assigned to OD.

In this communication we only wish to report the major features of our results: a variety of details, some of which remain obscure, will be reported later. Our major disagreement with earlier workers is that a prominent feature at low field, usually assigned to other radicals, is assigned to the hydroxyl radical. Furthermore, our results completely eliminate the suggestion[2] that one of the principal *g*-factors occurs at 2·0127.

Comparison of the present hyperfine data with those obtained from radicals in the gase phase[3] and with theoretical predictions (see Table) shows that within a fairly large experimental error there is now good agreement and there is no need to postulate any major environmental distortion of the electronic structure.[1] However, in order to understand the *g*-tensor, which has principal values close to 2·0023, one must postulate a large environmental splitting of the normally doubly-degenerate π^*-level. In ice this is presumably due to hydrogen bonding and would not normally lead to an axially-symmetric proton hyperfine coupling tensor. Using the method of McConnell and Strathdee[4] with an OH bond length[5] of 0·97 Å and the value of the oxygen screening constant obtained from the self-consistent-field atomic wave-function,[6] we have calculated the anisotropic hyperfine coupling to be $A_z - A_{iso} = +31{\cdot}9$, $A_x - A_{iso} = -8{\cdot}9$, and $A_y - A_{iso} = -22{\cdot}9$ gauss, for the external magnetic field along the OH bond, along the axis of the *p*-orbital of the unpaired electron and at right angles to these directions respectively. Moreover, one would not ordinarily

TABLE

Ref.	g-*Factors*		*Hyperfine coupling constants* (*gauss*)		
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	A_{iso}
a	2·0127 ± 0·001	2·0077 ± 0·001	+53·3	+35·3	+41·3
b	2·05 ± 0·01	2·008 ± 0·001	0 ± 7	−43 ± 2	−29 ± 4
c			+5·0 ± 0·3	−42·6 ± 0·3	−26·7 ± 0·2
d			+5·2	−42·7	−26·7

a Results of McMillan *et al.* (ref. 2).
b Our experimental data.
c Calculated from Radford's gas-phase data (ref. 3).
d Calculated assuming the gas-phase value for A_{iso} (ref. 3) and using the method of McConnell and Strathdee (ref. 4) with $A_{\parallel} = A_z$ and $A_{\perp} = \frac{1}{2}(A_x + A_y)$.

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[1] M. C. R. Symons, *J. Chem. Soc.*, 1963, 570.
[2] J. A. McMillan, M. S. Matheson, and B. Smaller, *J. Chem. Phys.*, 1960, **33**, 609.
[3] H. E. Radford, *Phys. Rev.*, 1962, **126**, 1035.
[4] H. M. McConnell and J. Strathdee, *Mol. Phys.*, 1959, **2**, 129.
[5] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. **11**, ed. L. E. Sutton, The Chemical Society, London, 1958.
[6] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.

expect to find $g_x = g_y$. Nevertheless, our present analysis of the spectra of single crystals does suggest that $g_x \doteqdot g_y$ $(=g_\perp)$ and that $A_x \doteqdot A_y$ $(=A_\perp)$. Interpretation is rendered difficult because there are many magnetically non-equivalent sites for hydroxyl radicals in ice, and hence for many orientations of a single crystal in the magnetic field the spectrum closely resembles that of the powder.

If our postulate of axial symmetry is correct, then there must be some mechanism whereby the field which causes the splitting of the π^*-level fluctuates sufficiently rapidly to give apparent axial symmetry. Ways in which this might happen will be discussed later.

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