types however there is no sign of convergence at $n = 2$, which explains the failure of the Onsager-Fuoss theory for calcium chloride and lanthanum chloride.

For potassium chloride the terms beyond Δ_2 are negligible; for calcium chloride at 0.005 molar the values are: $\Delta_1 = -0.019$, $\Delta_2 = +0.037$, $\Delta_3 = -0.016$, $\Delta_4 = +0.016$, $\Delta_5 = -0.010$, ... (the units being cm.^{2} sec.$^{-1}$ × 10^{-5}). For lanthanum chloride at 0.003 molar they are: $\Delta_1 = -0.033$, $\Delta_2 = +0.074$, $\Delta_3 = -0.071$, $\Delta_3 = +0.093$, $\Delta_5 = -0.096$, ...

A fuller account of this work will appear shortly.

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ANISOTROPY IN THE PARAMAGNETIC RESONANCE SPECTRUM OF PEROXYLAMINE DISULFONATE ION[1]

Sir:

In an earlier report[2] of the hyperfine splitting in the paramagnetic resonance absorption spectrum of $(C_6H_5)_3C^{13}$ attention was called to the fact that observations in liquid solutions fail to reveal important features of the phenomenon. We have since observed the paramagnetic resononce spectrum of the free radical ion peroxylamine disulfonate ($NO(SO_3)_2^{=}$) in dilute solid solution in single crystals of diamagnetic potassium hydroxylamine disulfonate. In liquid solution the ion exhibits an absorption spectrum of three equally spaced equal intensity lines. The three lines result from the hyperfine interaction between the nitrogen nucleus (spin one) and the electron.[3] The interval between adjacent lines is 13 oersteds. In the single crystals (containing about 0.25 mole per cent. of the paramagnetic ion) the spectrum is highly anisotropic. The crystals, whose structure is under investigation by Professor Lindsay Helmholz and Mr. Merton Brooks, are monoclinic. When the external magnetic field is perpendicular to the two-fold axis of the crystal and makes an angle of about 45° with the "*c*" axis, three lines of equal intensity with interval 27 oersteds—more than twice the interval observed in liquid solutions—are seen. When the crystal is rotated by 90 degrees around the two-fold axis from the above orientation, the interval shrinks to six oersteds. At most other orientations the spectrum is complex, consisting of four or five lines. An explanation of the details of the dependence of spectrum on orientation of the crystal awaits completion of the crystal structure determination.[4] Nevertheless, sufficient information is available to permit the drawing of certain conclusions concerning the distribution of the unpaired electron in the molecule.

Interpretation of the experimental results depends on the fact that the hyperfine interaction consists of two parts, one isotropic, the other anisotropic. The former depends only on the nonvanishing component of the wave function at the nucleus, the latter only on the non-spherically symmetric components distant from the nucleus. If the electronic wave function of a free radical is expanded in atomic functions only s components contribute to the isotropic interaction, non s components to the anisotropic interaction. When the frequency of molecular tumbling is high compared with the frequency associated with the hyperfine interaction, only the isotropic part of the splitting is observed, the non-isotropic part averaging to zero.[5,6,7]

Thus the observed splitting in liquid solutions of $(C_6H_5)_3C^{13}$ demonstrates the existence of methyl carbon 2s component in the electronic function.[8] Experiments in single crystals are required for estimation of the non "s" components. In the peroxylamine disulfonate, both nitrogen 2s and 2p components are important. Their amplitudes will be estimated at another time.

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RECEIVED APRIL 24, 1953

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[1] Assisted by the joint program of O.N.R. and A.E.C.

[2] S. I. Weissman and J. C. Sowden, THIS JOURNAL, **75**, 503 (1953).

[3] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952); J. Townsend, S. I. Weissman and G. E. Pake, *ibid.*, **89**, 606 (1953).

[4] The magnetic observations suggest that two orientations of the peroxylamine disulfonate ion with respect to the crystal axis occur.

[5] See for instance, A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, **205**, 1935 (1951); N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **71**, 466 (1947); H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[6] In the cases here described the hyperfine frequency is in the neighborhood of 10^8 sec.$^{-1}$.

[7] The result is readily demonstrated for the case in which the external magnetic field is strong and spin orbit interaction is small. It is probably correct in the absence of these restrictions.

[8] The square of the amplitude of this component is probably between 0.05 and 0.10.