Hyperfine Structure in the Paramagnetic Resonance of the Ion $(SO_3)_2NO^{--}$†

J. TOWNSEND, S. I. WEISSMAN, AND G. E. PAKE
Washington University, St. Louis, Missouri

(Received September 26, 1952)

Paramagnetic resonance spectra of the free-radical ion $(SO_3)_2NO^{--}$ in dilute solutions were observed in fields up to 50 oersteds and at frequencies up to 120 Mc/sec. The observed pattern of absorption lines agree well with that calculated for an *s*-electron coupled to a N^{14} (spin 1) nucleus. The zero-field splitting is 54.7±0.5 Mc/sec.

THE present results represent a continuation of the work reported earlier under the same title.[1] Resonance absorption lines were studied at low values of magnetic field to further verify the mechanism of hyperfine splitting by the N^{14} nucleus, and to measure more accurately the zero-field splitting, $\Delta\nu$.

The ion was studied in the form of solutions of tetraphenyl stibonium peroxylamine disulfonate in pyridine. The concentrations were in the neighborhood of 0.1 *M*, giving absorption lines about one oersted wide between points of maximum slope. These solutions decompose rather rapidly after an interval of a few hours, and it was found, during the course of the experiments, that the decomposition could be delayed by the addition of a small amount of a base, such as NaOH.

The magnetic fields were produced by a pair of Helmholtz coils aligned with the earth's field, and calibrated by means of a polycrystalline sample of the free radical tris-*p*-nitrophenyl methyl, whose *g* value has been compared with that of the proton at low fields, and has been found to be independent of field.[2] The detector used is a variation of the transitron circuit,[3] used with magnetic field modulation and a phase-sensitive detector.

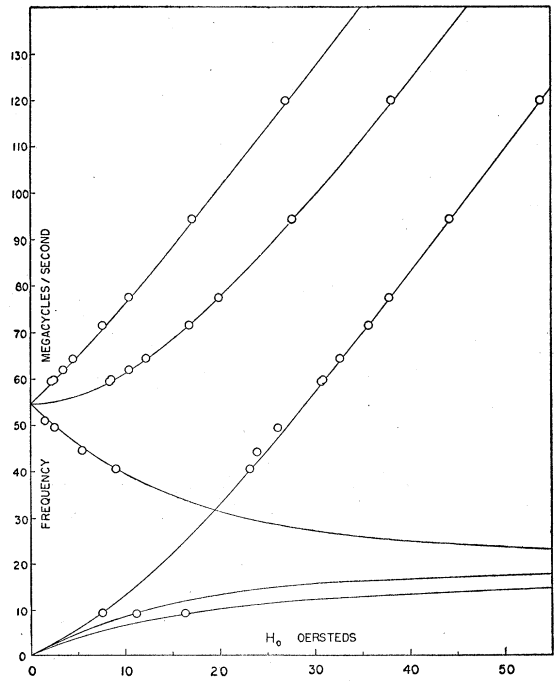

FIG. 1. Resonances of the peroxylamine disulfonate ion. The curves are calculated according to the Breit-Rabi formulas using $\Delta\nu$=54.7 Mc/sec.

The centers of the observed resonances are plotted in Fig. 1. The three points at 9.21 Mc/sec were obtained previously.[1] The curves are computed from the Breit-Rabi formulas[4,5] and fitted to the data using the single adjustable parameter $\Delta\nu$, whose value was found to be 54.7±0.5 Mc/sec. The six curves given are those for transitions in which $\Delta m=\pm1$, the π-transitions, which are expected when the rf magnetic field is perpendicular to the static field,[5] as was the case in this experiment. The σ-transitions, $\Delta m=0$, induced if the rf and steady fields are parallel, would lie along two additional curves not shown. The σ-transitions, as expected, did not appear. It was impossible to make measurements of the relative intensities of these transitions, due to the decomposition of the solutions.

The bumps appearing on the sides of the 9.21-Mc/sec resonance curves in reference 1 have not been explained. Similar bumps, as many as six in number and of very low relative intensity, have appeared on the 9000-Mc/sec resonance spectrum when the sensitivity was increased.

The value of $\Delta\nu$ for this hyperfine splitting may be compared with the results of Beringer and Castle[6] for NO and of Hutchison, Pastor, and Kowalsky[7] for dilute solutions of diphenyl picryl hydrazyl. These measurements correspond to respective zero-field splittings of 44.7 Mc/sec and 42 Mc/sec. Such data, of course, impose a condition on the wave function of the unpaired electron.

Part of the equipment used was provided through a grant-in-aid from the Research Corporation.

† Assisted by the joint program of the Office of Naval Research and Atomic Energy Commission. This work has been reported by one of the authors (G.E.P.) at the American Physical Society Meeting, Columbus, Ohio, March, 1952.

[1] Pake, Townsend, and Weissman, Phys. Rev. **85**, 682 (1952).

[2] N. A. Schuster, thesis, Washington University (1951) (unpublished).

[3] H. W. Knoebel and E. L. Hahn, Rev. Sci. Instr. **22**, 904 (1951).

[4] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

[5] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948). The notation of this paper is followed here.

[6] Robert Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).

[7] Hutchison, Pastor, and Kowalsky, J. Chem. Phys. **20**, 534 (1952).