

## Letters to the Editor

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### Environmental Effect on Atomic Hydrogen Hyperfine Structure in Acids\*

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**P**ARAMAGNETIC resonance absorption lines of atomic hydrogen have been observed<sup>1</sup> in  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  after irradiation with  $\text{Co}^{60}$  gamma rays at 77°K. In the course of re-examining some samples showing very intense lines in these acids relatively weak satellite lines have been observed. Figure 1 shows the high-field atomic hydrogen line and these satellites for irradiated  $\text{HClO}_4$  at a microwave frequency of about 23 050 Mc/sec. The main line can be readily power-saturated, causing the ratio of satellite to main line intensity to increase. The low-field hydrogen line as well as the pair of hydrogen lines in irradiated  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  show essentially similar satellites.

The spacing of satellite to main line is field-dependent, and within our present accuracy of measurement corresponds to the proton magnetic resonance frequency. For example, the high-field  $\text{HClO}_4$  central line of Fig. 1 appeared at a measured field of 8482.8 gauss with the satellites spaced at  $\pm 12.9$  gauss. At the microwave frequency of 23 050 Mc/sec this corresponds to a spacing in frequency units of  $\pm 35.1$  Mc/sec and is, within our experimental error, the same as the proton magnetic resonance frequency at this field, 36.12 Mc/sec. The low-field hydrogen line appeared at 7980.6 gauss with  $\pm 11.95$  gauss or  $\pm 34.5$  Mc/sec separated satellites which compares favorably with the proton frequency of 33.98 Mc/sec for this field. The results for the other two acids were similar. Observations were also made with a spectrometer operating at a nominal frequency of 9000 Mc/sec. The satellites could just be resolved in the three acids, and in the one preliminary measurement made on the high-field line in  $\text{H}_2\text{SO}_4$  appearing at 3428.8 gauss and 8945 Mc/sec the satellites were spaced at  $\pm 4.6$  gauss or  $\pm 12$  Mc/sec to be compared with a proton resonance frequency of 14.60 Mc/sec.

These lines seem to originate from the flipping of nearby proton spins in conjunction with the flipping of the electron spin as a consequence of a weak magnetic

dipole-dipole coupling. Calculations made by George Trammell using this model gave a reasonable intensity ratio of center to satellite line for a reasonable distance to neighboring proton. The intensity ratio varies essentially as the inverse sixth power of the distance making an accurate calculation of the distance possible. The final value awaits the evaluation of several integrals. The observed intensity ratio in  $\text{HClO}_4$  at low power levels is roughly 35:1 which gives a preliminary value for this distance of 1.8 Å. This ratio may represent a single

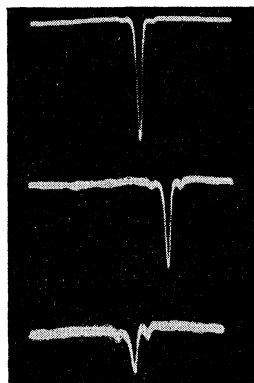


FIG. 1. The high-field atomic hydrogen line in  $\text{HClO}_4$  at 23 050 Mc/sec. and 8483 gauss with progressively increasing microwave power from top to bottom.

proton at this value or more than one at greater distances. Although these results are highly preliminary, we are inclined to interpret the ratio as representing the effect of more than one proton distributed more or less randomly in the chemical sample at distances usually greater than 1.8 Å. It should be pointed out that the satellite separation is strikingly insensitive to variation in this distance, and an averaging over a distribution of distances as well as over all angular orientations of a powdered sample does not give a smudging of the satellites.

In addition to the saturation effect illustrated for  $\text{HClO}_4$  in Fig. 1,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  showed another interesting effect. The satellite on one side of the central line was always much weaker than on the other side. The weak-satellite side was always the trailing side for the direction of the magnetic field sweep in the field-modulated spectrometer. In other words, in these two acids the strength of the satellite depends on how recently a moderate amount of power has been applied to effect the main transition. We presume this means that the thermal relaxation time is longer than in  $\text{HClO}_4$ , and by varying the sweep rate we may vary the relative intensity of the trailing-side satellite.

These experiments, along with more detailed calculations on the satellite transition probabilities, are continuing and will be reported in greater detail later. We are particularly grateful to George Trammell for his help.

\* This work was performed for the U. S. Atomic Energy Commission.

<sup>1</sup> Livingston, Zeldes, and Taylor, Phys. Rev. 94, 725 (1954).

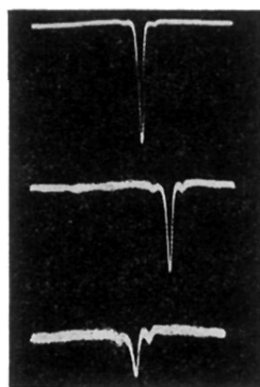


FIG. 1. The high-field atomic hydrogen line in  $\text{HClO}_4$  at 23 050 Mc/sec. and 8483 gauss with progressively increasing microwave power from top to bottom.