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## Assignment of the OH Bending Frequency in Alcohols

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protons. For this isotope the degeneracy resulting from chemical equivalence is removed by the difference in coupling of the  $\text{CH}_2$  and of the  $\text{CH}_3$  protons to  $\text{Pb}^{207}$ . The role of the absent chemical shift difference is usurped by the splitting difference  $\pm \frac{1}{2}(J_{\text{CH}_3\text{Pb}} - J_{\text{CH}_2\text{Pb}})$  which causes the doubled ethyl satellite pattern shown. It is interesting that the  $\text{CH}_3$  proton coupling to the lead is the larger, although it is the  $\text{CH}_2$  which is attached to the lead.

A Bloch<sup>2</sup> double resonance experiment showed that simultaneous saturation of the  $\text{Pb}^{207}$  resonance collapsed the entire spin structure and permitted a precise determination of the ratio

$$\nu\text{Pb}^{207}/\nu\text{H}^1 = 0.2092198 \pm 10.$$

This result is just outside the stated errors of the combined ratios of Proctor<sup>3</sup>  $\nu\text{Pb}^{207}/\nu\text{Na}^{23} = 0.7901 \pm 0.01\%$ , and  $\nu\text{Na}^{23}/\nu\text{H}^1 = 0.2645 \pm 0.03\%$  of Zimmerman and Williams<sup>4</sup> which give  $\nu\text{Pb}^{207}/\nu\text{H}^1 = 0.2090 \pm 1$ .

All measurements were made at 30 Mc with an NMR super-stabilized, precalibrated, swept frequency spectrometer, which will be described elsewhere.

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<sup>4</sup> J. R. Zimmerman and D. Williams, *Phys. Rev.* **76**, 350 (1949).

## Assignment of the OH Bending Frequency in Alcohols

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(Received November 5, 1956)

A GOOD deal of controversy has arisen in recent years about the frequency of the hydroxyl bending mode in alcohols. As far as the "free" (nonbonded) frequency is concerned, two types of assignments are to be considered:

- (1) A number of authors favor the 1250  $\text{cm}^{-1}$  region (1350  $\text{cm}^{-1}$  in methyl alcohol).<sup>1-4</sup>
- (2) An alternative assignment is the 1000-1100  $\text{cm}^{-1}$  region, with possible overlapping by the strong  $\nu_{\text{C-O}}$  band.<sup>5-8</sup>

An important contribution to this problem was very recently given by Stuart and Sutherland<sup>4</sup> (referred to as S.S. in the following text), who were able to show that one band (1250  $\text{cm}^{-1}$  region) in *n*-primary alcohols, and two bands in branched primary, secondary, and tertiary alcohols were strongly shifted by association, and so could be related to an hydroxyl vibration, namely the in-plane deformation vibration.

Our own results are based upon a systematic study, in

the gaseous state, of ordinary and deuterated alcohols; our data are summarized in Table I (which only gives the position of the bands shifted by deuteration).

In ethyl alcohol, two bands are strongly shifted by deuteration.

The first of these two bands is assigned by S. S. to the OH bending mode; but our results prove that the second band has the same spectroscopic behavior. This second band appears very weak in S. S.'s spectra, where it is overlapped by the strong  $\nu_{\text{C-O}}$  band; but if good resolution is achieved (better than 2  $\text{cm}^{-1}$  in our spectra), it appears as a distinct parallel band with a prominent *Q* branch; surprisingly enough, the corresponding band at 790  $\text{cm}^{-1}$  of the deuterated compound is not mentioned by S. S., although it appears very clear in our spectra as a typical parallel band (this band also appears in the spectrum published by Barrow<sup>9</sup>).

TABLE I.

Alcohol	$\delta_{\text{OH}}$	$\delta_{\text{OD}}$
Ethyl	{ 1243 1030	{ ~890 790
<i>n</i> -propyl	~1128	842
Allyl	~1210	~847
sec-propanol	{ 1253 1073	885
sec-butanol	{ 1243 1084	885
tert-butanol	{ ~1330 ~1143	878

In the secondary and tertiary alcohols studied, two bands disappear on deuteration (and this is in accordance with S. S.'s results obtained by the dilution method), but only *one* band appears in the deuterated compound.

The expected second band should lie in the 700-800  $\text{cm}^{-1}$  region, but it seems to be completely missing.

Owing to the small number of alcohols investigated, a detailed discussion of our results seems to be premature, and we only want to point out the somewhat puzzling aspects of this problem.

- (1) In most cases, two  $\delta_{\text{OH}}$  bands are present, and the classical case of one  $\delta_{\text{OH}}$  (and one  $\delta_{\text{OD}}$ ) band seems to be the exception rather than the general rule.
- (2) Rotational isomerism would explain the doubling of both  $\delta_{\text{OH}}$  and  $\delta_{\text{OD}}$  bands in ethyl alcohol, but additional results are needed to check this hypothesis.
- (3) This explanation does not hold for secondary and tertiary alcohols, where only one  $\delta_{\text{OD}}$  band is present. The doubling of the  $\delta_{\text{OH}}$  band probably arises from some coupling such as Fermi resonance, but the origin of the band responsible for this coupling is still unknown. Such a coupling has been observed in phenols by Mecke and Rossmly.<sup>10</sup>

Further work is in progress, and detailed results will be published in the future.

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### On the Interpretation of the Electron Spin Resonance Spectra of Solutions of Hydrocarbons in Sulfuric Acid\*

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(Received November 29, 1956)

RECENTLY Yokozawa and Miyashita<sup>1</sup> have reported that solutions of perylene in concentrated sulfuric acid exhibit electron spin resonance absorption. They did not describe the nature of the spectrum beyond a statement that the spectroscopic splitting factor is close to that of diphenylpicrylhydrazyl.

We have found that dilute solutions of anthracene and tetracene as well as perylene in concentrated sulfuric acid exhibit electron spin resonance absorption and that the spectra consist of characteristic well resolved hyperfine patterns. Each spectrum resembles in a striking way the spectrum of the corresponding hydrocarbon negative ion. In the case of anthracene the spectra of the solution in sulfuric acid and of the negative ion in tetrahydrofuran are almost indistinguishable in shape. They differ only in extension in field, the spectrum of the sulfuric acid solution being 31.5 oersteds long as compared with 26.1 oersteds for the negative ion. The spectrum of the solution in sulfuric acid is shown in Fig. 1. It may be compared with the spectrum



FIG. 1. Derivative of resonance absorption ( $dX''/dH$ ) vs field ( $H$ ) of a dilute solution of anthracene in sulfuric acid.

of anthracene negative ion which has been published previously.<sup>2</sup>

The spectrum of the solution of perylene in sulfuric acid consists of nine equally spaced groups of lines. Similarly, the spectrum of perylene negative ion contains nine groups. The length of the spectrum of the

solution in sulfuric acid is 28.7 oersteds, of the negative ion 26.0 oersteds. The two spectra are shown in Fig. 2.

In like manner, the spectrum of a solution of tetracene in sulfuric acid (Fig. 3), while better resolved, resembles that of the negative ion. It is 29.0 oersteds in length compared with 24.7 oersteds for the negative ion.<sup>3</sup>

Attempts to prepare the paramagnetic compounds by electrolytic oxidation in phosphoric acid and by reaction with lead tetraacetate have failed. However, the long known reaction of antimony pentachloride with each of the hydrocarbons in carbon tetrachloride solution<sup>4</sup> yields a paramagnetic precipitate of the same color as the solution of the hydrocarbon in sulfuric acid.

The spin resonance spectra of the crystalline compounds produced by reaction with antimony pentachloride are typical exchange narrowed lines. Solutions

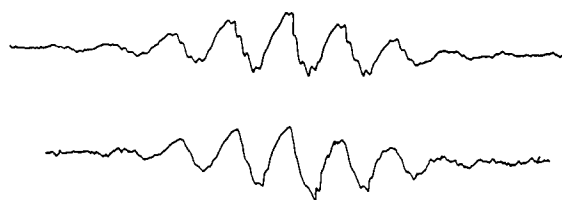


FIG. 2.  $dX''/dH$  vs  $H$  of perylene in sulfuric acid (above) and of perylene negative ion (below).

of the crystals in phosphorus oxychloride have resonances extending approximately over the range of the spectra in sulfuric acid, but with only a trace of the hyperfine structure of the latter.

The behavior of the solutions in sulfuric acid and of the complexes with antimony pentachloride suggest

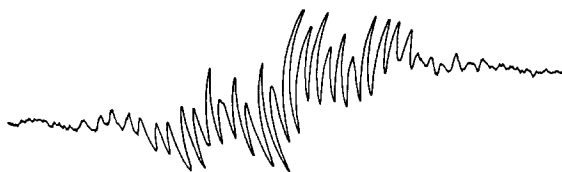


FIG. 3.  $dX''/dH$  vs  $H$  of tetracene in sulfuric acid.

that singly charged positive ions are responsible for at least part of the observed paramagnetism. Weiss<sup>5</sup> has presented evidence for the formation of positive ions of conjugated hydrocarbons. Further, Kainer and Hausser<sup>6</sup> have isolated paramagnetic salts formed in the reaction between aromatic amines and antimony pentachlorides. The analytical data correspond to salts of the form  $A SbCl_4$  where  $A$  is the aromatic amine. In addition, we expect on theoretical grounds that the distribution of unpaired electrons over the various carbon atoms would be the same in the uninegative ion and unipositive ion of a given alternant hydrocarbon. This expectation results from the demonstration<sup>7,8</sup> that the magnitude of the atomic coefficients in the highest occupied molecular orbital and the lowest unoccupied orbital of an alternant hydrocarbon are the same. While it is true