

V. MICROWAVE SPECTROSCOPY

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A. ZEEMAN EFFECT

Absorption plots of σ Zeeman components of the $5_{23}-6_{16}$ rotational transition of H_2O have been obtained which demonstrate clearly the τ dependence of the molecular magnetic moment. Figure V-1 shows the lower frequency σ components as observed on a slow-sweep, Stark-modulation spectrograph. Figure V-2 is a plot of expected absorption-component structure for an arbitrary difference in magnetic moment for the two states involved in the transition, assuming that the lower state has the larger g value. The individual components have not been resolved, since with a half-width at half-intensity of approximately 220 kc/sec the line width is too great. The asymmetry is clearly in agreement with the calculated intensity pattern, indicating that $g(5_{23}) > g(6_{16})$. In the present case, the maximum is split 2.39 Mc/sec from the undisplaced line in a field of 4900 g, yielding an effective g value of 0.531. Since the components are unresolved, this g value has no precise interpretation. Work is continuing to determine the true g values of both rotational levels by a process of curve fitting and other means.

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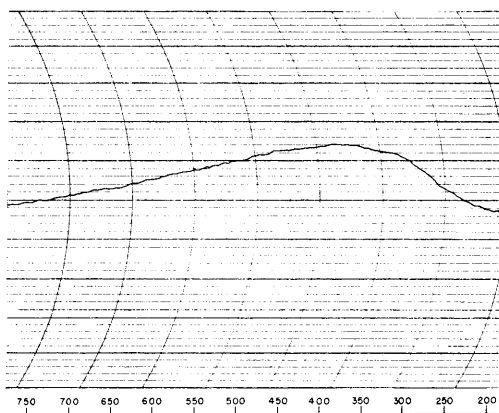


Fig. V-1

Absorption pattern observed for low-frequency σ components of $5_{23}-6_{16}$ transition in H_2O .

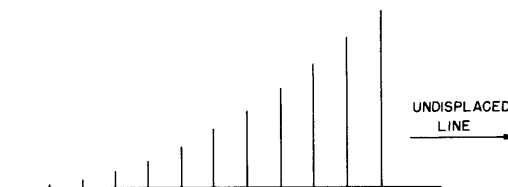


Fig. V-2

Intensities of individual σ Zeeman components for $5_{23}-6_{16}$ rotational transition.

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B. PARAMAGNETIC RESONANCE

The apparatus for use in this work as described in the Quarterly Progress Report of October 15, 1951, has been completely modified during the last six months to increase its sensitivity and stability.

One of the principal changes was the introduction of a magnetic field control servo. In this, the voltage induced in a synchronous flip coil is subtracted from a fraction of that produced by a 30-cycle generator (on the same shaft) to produce an error signal. After amplification and phase detection in a Brown converter, this signal controls the magnetic field by means of a dc amplifier and electronic field current supply for the motor generator supplying the magnet current. The response of these highly inductive components is speeded by the use of an inner dc feedback loop from the magnet current back to the input of the dc amplifier. This allows a stable loop gain of about 80 for the complete ac feedback loop, with a corresponding decrease in drift. This stabilized field can now be swept at a very uniform rate by sweeping the reference-signal amplitude with a helipot across the reference generator. At present field marker pips are provided manually with the aid of an auxiliary null-comparator circuit using 4-decade resistance boxes to allow setting precisely to one gauss.

To increase the sensitivity of the apparatus, we have adopted a modification of a method used by Beringer (R. Beringer, J. G. Castle: Phys. Rev. 81, 82, 1951) in which a 47-cycle oscillating field of amplitude small compared to the absorption line width is superimposed on the slowly sweeping field. This gives a 47-cycle component of crystal current proportional to the derivative $d\chi''/dB$ of the imaginary part of the susceptibility of the sample. This eliminates the crystal modulator of the previous apparatus which chopped the entire carrier rather than tagging only the desired signal with a certain frequency. This 47-cycle component of crystal current is amplified and phase-detected to give a deflection proportional to $d\chi''/dB$. The $d\chi''/dB$ signal may also be integrated electronically to give χ'' itself, if this quantity is more easily interpreted.

At present we are engaged in perfecting the integration arrangement to remove baseline shifts and in testing the performance of the apparatus on various samples which have been studied previously with the other apparatus. The accompanying specimen charts demonstrate the versatility of the sweep scheme in handling patterns from 5 gauss to 4000 gauss in width.

The irregularity in the pattern from the free radical (Fig. V-3) indicates that the field servo does leave a small amount of rapid, irregular fluctuations in the field, although it does take out the slower variations. The sharpness of this absorption line and the stability of the field has allowed the homogeneity of the field to be studied. It appears that, with the pole piece separation required for low temperature work, the field changes by about 15 gauss over the width of the cavity. This is greatly reduced

with a smaller gap.

The increased sensitivity is shown by the trace of the 0.01 molar MnCl_2 solution (Fig. V-4). This concentration is only one tenth that of the most dilute sample which could be studied with the previous apparatus. Since a rather rapid sweep and broad bandpass was used in this trace, it is clear that another factor of 10 can be expected.

The chrome alum trace (Fig. V-5) demonstrates the convenience of the very long linear sweep which this field control arrangement makes possible.

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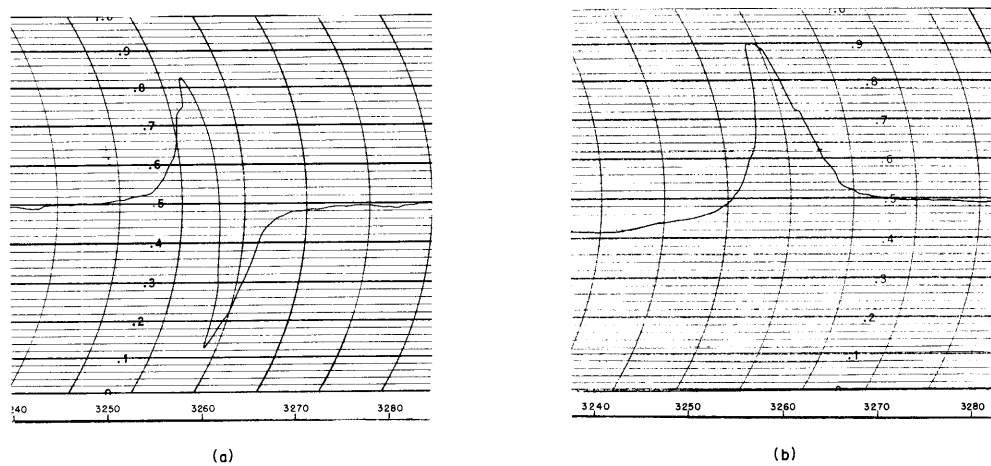


Fig. V-3

$d\chi''/dB$ and χ'' for the organic free radical Diphenyl-trinitrophenyl-hydrazyl.

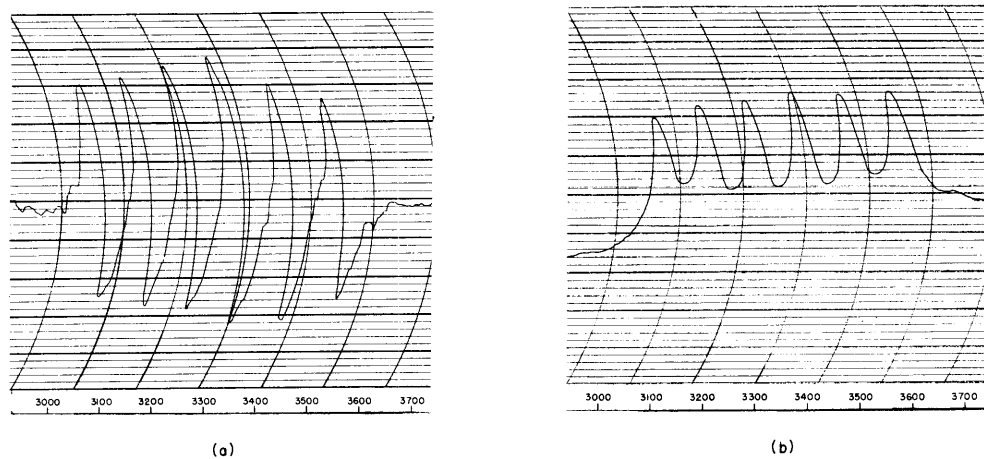


Fig. V-4

$d\chi''/dB$ and χ'' for 0.01 molar MnCl_2 solution.

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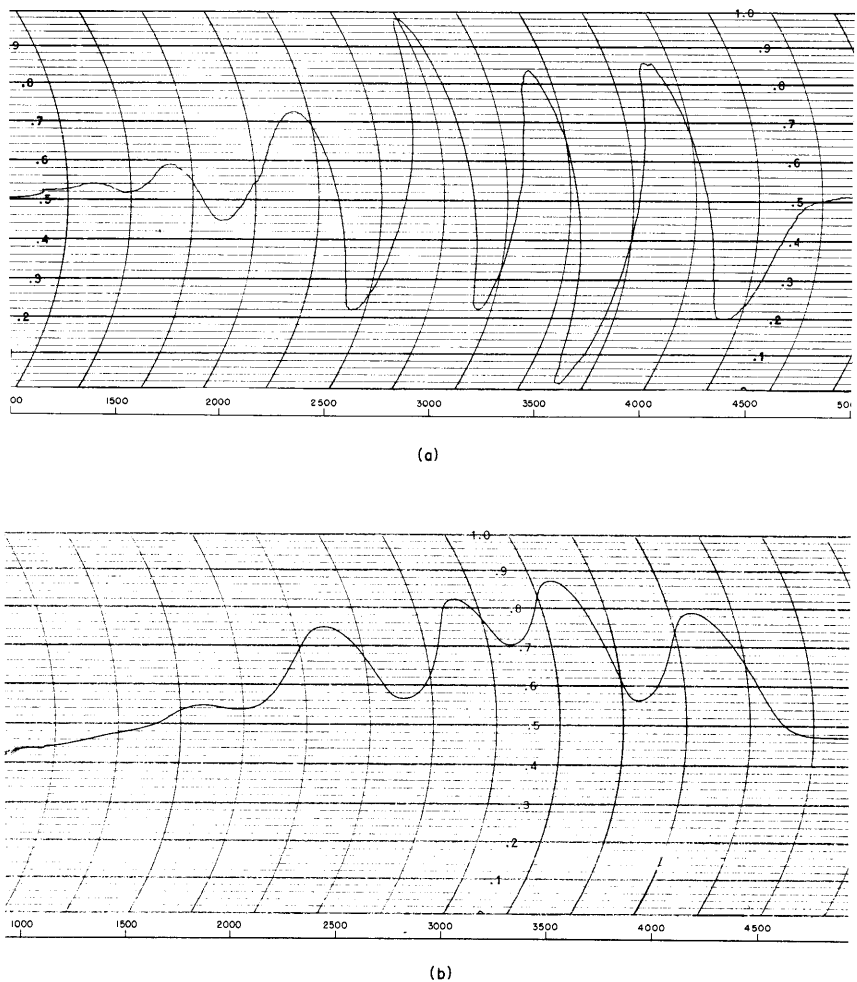


Fig. V-5

$d\chi''/dB$ and χ'' for rubidium chrome alum crystal.

C. THE MICROWAVE SPECTRUM OF METHYL ALCOHOL

The Stark effect of CH_3OH is being studied in the region of 40,000 Mc/sec to 50,000 Mc/sec. A series of lines with second-order Stark effect has been found and is assumed to be due to the $J_{\tau} = 0_0 \rightarrow 1_{-1}$ transition. Accurate Stark measurements are being made in order to calculate and compare the Stark coefficients of this series.

One of the fundamental vibrations of methyl alcohol is that of torsional motion of the hydroxyl group with respect to the methyl group. Depending on the potential due to the methyl group, the hydroxyl group will either oscillate in one of three identical minima or perform a hindered rotation relative to the methyl group. Many of the absorption lines in the microwave spectrum are due to changes in the rotational state of the molecule and/or to changes in this internal rotational state.

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Microwave absorption lines of this molecule were first discovered by Hershberger and Turkevich (1) and were divided by Dailey (2) according to their Stark effect patterns. Coles (3) remeasured these lines and their Stark components and was able to establish J values for a series of nine lines. Dennison and Burkhard (4) have identified this series as the $J \rightarrow J, K = 1 \rightarrow 2, \tau = 2 \rightarrow 1$ transition.

A much more extensive study has been carried out by Hughes, Good and Coles (5), who have listed about 85 lines between 16,000 Mc/sec and 39,000 Mc/sec, as well as lines of $C^{13}H_3OH$ and $CH_3O^{18}H$. Approximate J values and Stark patterns are given for most of the lines in their report. Edwards, Gilliam and Gordy (6) have measured 27 lines in the region 35,000 Mc/sec to 50,000 Mc/sec, but these are in general unidentified.

Calculations of the energy of an asymmetric rotator show that the transition $J_{\tau} = 0_0 \rightarrow 1_{-1}$ (corresponding to the $J = 0 \rightarrow 1, \Delta K = 0$ transition of the limiting symmetric rotator) should give an energy difference in the range 40,000 Mc/sec to 50,000 Mc/sec. This calculation depends only on the rotational constants determined from infrared observations and so can be accepted with little doubt. However, many other strong lines occur in this region due to near degeneracies of higher order J transitions. Identification in the absence of additional information would seem impossible.

By inspection of the Stark effect of the lines in this region, they may be separated into a group with first-order Stark effect (symmetrical components), and one with second-order Stark effect (a single component). Of this latter group, a series of lines has been found which are assumed to be due to the $J_{\tau} = 0_0 \rightarrow 1_{-1}$ transition. The line at 49,867.2 Mc/sec, assigned by Edwards, Gilliam and Gordy (6) to this transition, has a first-order Stark effect and thus would appear to be improperly identified.

Accurate line and Stark component measurements are being made at the present time in order to compare the spacing of the lines in the series and the Stark coefficients of each of the lines.

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References

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