

III. MICROWAVE SPECTROSCOPY

Prof. M. W. P. Strandberg
 Dr. M. Peter
 A. Annacone
 Y. Chou
 S. A. Collins, Jr.

J. G. Ingersoll
 B. Josephson, Jr.
 J. D. Kierstead
 S. Krongelb
 D. M. Lazarus

R. D. Mattuck
 J. J. McNicholl
 K. Spaulding
 H. G. R. Venkates
 G. J. Wolga

A. MOLECULAR-BEAM MICROWAVE SPECTROSCOPE*

The electronic components for observing the alkali-halide beam, described in the Quarterly Progress Report of July 15, 1956, page 12, were assembled. The experimental problem is to obtain the same favorable noise figure of 17 db, which was used to observe the NH_3 emission, as reported in the Quarterly Progress Report of April 15, 1956. We must also have a very stable source at a microwave frequency that is different from that previously used, i.e., the NH_3 3-3 frequency. An automatic-frequency control system for stabilizing the 2K33 klystron was assembled. The stabilized klystron now shows a short-time frequency stability of 100 cps. The stability and frequency of the signal is checked against a signal obtained from a harmonic converter driven by a multiplier chain from a 1-mc crystal. Elements of this multiplier chain were developed by members of the laboratory as a part of a general program undertaken for the purpose of advancing frequency stabilization and measurement techniques. As the next step, a phase stabilization system, which will allow longer integration times for high-resolution measurements, will be assembled.

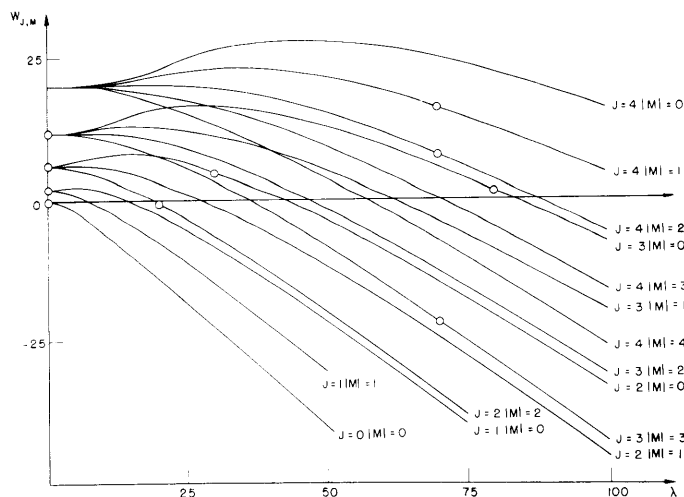


Fig. III-1. High-field Stark effect in rigid linear rotors.

*This work was supported in part by Contract DA36-039 sc-73014.

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A check of the noise figure of the system is obtained by using a microwave bridge circuit. One arm of the bridge includes the beam interaction region; the second arm includes a cell filled with a suitable test substance. The actual test substance is iodine cyanide, which was prepared by Dr. C. F. Davis, of this laboratory. In order to obtain better understanding of the focuser that was described in the Quarterly Progress Report of Jan. 15, 1956, the Stark effect for rigid linear molecules for arbitrarily high fields was calculated. In Fig. III-1, the reduced energy $W = E/hB$ is plotted against the reduced field $\lambda = F\mu/hB$. A formula which is asymptotically valid for the high-field case is

$$W_{(J, M)} = -\lambda + \sqrt{2} (2J - |M| + 1) \lambda^{1/2} + \frac{1}{4} [M^2 + 2|M|J - 2J^2 + |M| - 2J - 2] \\ + \frac{\sqrt{2}}{64} [-4|M^3| + 6M^2J + 6|M|J^2 - 4J^3 + 3M^2 + 6|M|J - 6J^2 + 3|M| - 6J - 2] \lambda^{-1/2}$$

Drawings for a source that is twelve times larger than that presently available were completed, and this source is being made in the Laboratory machine shop.

M. Peter

B. PARAMAGNETIC RESONANCE

A program of study of F-center paramagnetic resonance in alkali-halide crystals was initiated. Single crystals of NaCl, KCl, LiF, NaF, and KBr were irradiated and colored by exposing them to 1.1 and 1.3 mev gamma rays from the Co^{60} source of the Department of Food Technology, M.I.T. Irradiation of 1-5 hours is sufficient to produce intense coloration. From an initial survey of the problem, resonances have been obtained from NaCl, KCl, and LiF. Investigation is proceeding with the NaF and KBr samples. Preliminary experimental results follow.

1. Lithium Fluoride

Investigation revealed a very intense center line with a resolved hyperfine spectrum of 18 lines, giving a total of 19 resolved lines, in agreement with the results of Schneider (1). His analysis attributes the hyperfine structure to the six nearest neighbor lithium ions with nuclear spin 3/2. The main center line has a full width at half-power of 41 gauss, assuming a Lorentzian line shape. The hyperfine lines are separated 20-30 gauss and are symmetrically distributed about the center line. They appear to be unequally spaced, but this conclusion must be investigated further. Work with lithium fluoride continues.

2. Sodium Chloride

A resonance was observed in Sodium chloride, there is also evidence of a partially resolved hyperfine structure on the line. The strong center line has a full width at half-power of 21 gauss, assuming a Lorentzian shape. Three hyperfine lines symmetrically located on either side of the center line were resolved. It is possible that the high density of F-centers of this particular sample (judging from the intense coloration) might have masked additional hyperfine structure. The observed linewidth is much narrower than that previously reported. Kip and others (2) observed a full width at half-power of 162 oersteds. They did not report any structure on their line. Further investigation with less densely colored samples is planned.

3. Potassium Chloride

A single resonance with uncertain indication of hyperfine structure was obtained. The line has a full width at half-power of 7 gauss. The observed width is again much narrower than was previously reported (2, 3), which was approximately 54 oersteds. Further investigation with different potassium chloride samples continues.

4. Program of Future Work

A systematic investigation of the general properties of the resonances in the various alkali halides will continue. Samples of varying F-center concentrations will be prepared to see the effect of concentration on linewidth and hyperfine structure. A careful analysis of the line shape will be made and evaluated. The effect of saturation on the resonances will be studied by variation of the incident microwave power density. In particular, the effect of power variation on the linewidth and hyperfine structure will be studied. It is hoped that this work will yield information on the relaxation times T_1 and T_2 .

G. J. Wolga

References

1. E. E. Schneider, (abstract), *Phys. Rev.* 93, 919 (1954).
2. A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* 91, 1066 (1953).
3. C. A. Hutchison, Jr., and G. A. Noble, *Phys. Rev.* 87, 1125 (1952).

C. FREE RADICALS IN IRRADIATED CARBON BLACK

Workers in the field of rubber technology have noticed that carbon black which has been irradiated with high-energy particles, on being mixed with rubber, provides a higher amount of bound rubber than that produced by unirradiated carbon black. An

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explanation which postulated the creation of free radicals in the carbon black was proposed. The radicals result from broken carbon linkages as a consequence of the radiation. To test this hypothesis, a paramagnetic-resonance study of irradiated carbon black was made. Since the free radicals contain an unpaired electron, and, consequently, a nonzero magnetic moment, they should show paramagnetic resonance with a g -factor close to the free-electron value. The results of this investigation support the hypothesis. A single, weak resonance absorption, with a half-width of approximately 20 gauss and a g -value close to the free-electron value, was observed and it showed the density of radicals to be $\approx 1 \times 10^{14} \text{ cm}^{-3}$. A control sample of unirradiated carbon black did not show a resonance.

Samples of carbon black (1) irradiated with high-energy electrons from the High Voltage Engineering Corporation's Van de Graaf generator were examined immediately and at varying times after irradiation. The strength of the absorption appeared to decrease with time after irradiation; however, there is a leveling-off of this decrease so that the signal strength after a week's time is roughly equal to that obtained after four or five hours. This leveling-off might arise from two types of radicals, one of which recombines soon after formation.

The peak absorption was compared with a known absorption in the oxygen molecule ($J = K = 1$; $\Delta M = 1 \rightarrow 0$) and from this the radical density was determined.

The resonant absorption described above is probably not the same as that described by Uebersfeld (2) and Castle (3). The difference may result from our measurements being made at atmospheric pressure rather than in vacuum.

G. J. Wolga

References

1. The samples were obtained from and irradiated by Dr. E. H. Immergut, of Dunlop Research Center and Visiting Fellow, Department of Chemistry, M.I.T.
2. J. Uebersfeld, *Ann. phys.* (Mars - Avril 1956).
3. J. G. Castle, Jr., *Phys. Rev.* 92, 1063 (1953).