

IV. MICROWAVE SPECTROSCOPY

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A. MOLECULAR-BEAM MICROWAVE SPECTROSCOPE*

A resonant cavity was added to the molecular-beam spectroscopy in order to allow more efficient matching of the microwave power into the sodium chloride beam.

The inner dimensions of this cavity (see Fig. IV-1) are: $a = 3.850$ inches, $b = 5$ inches, $c = 28$ inches. It has a loaded Q of 5000 and is critically coupled to the input. The two end surfaces of the cavity ($a \times b$) are open to permit entrance of the two beams. Mode stability is obtained by means of damping slits, D , in the top and bottom surfaces and by excitation of the proper mode by means of the antenna system described earlier (1). This antenna excites the surface, A , which is a distributed iris consisting of a copper-plated perforated steel plate, $1/16$ inch thick, with $3/16$ inch round holes, whose centers are $5/16$ inch apart and staggered. The neoprene

spacers in the damping slits D can be compressed by the mounting screws, S , and thus a tuning range of 0.05 per cent is obtained. Across the side surfaces, A and B , a homogeneous electric field, E , can be applied for Stark modulation, since the bars, C , are isolated. Surface B is shown in Fig. IV-2. The six dark lines are created by the 12 molecular beams coming from the two sources that were shown earlier (2).

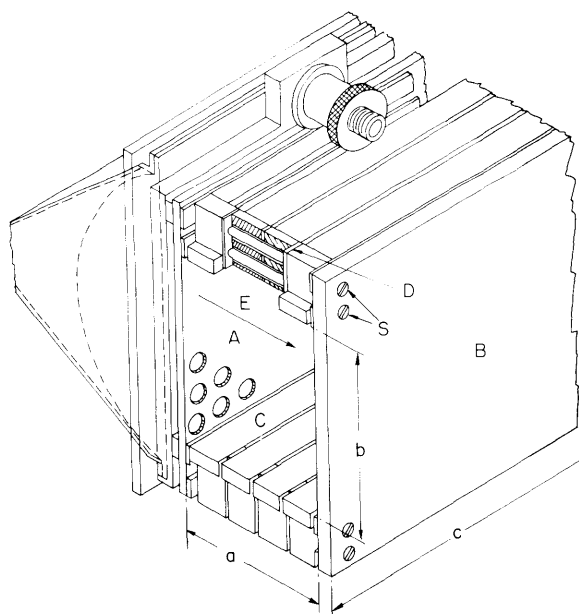


Fig. IV-1. Perspective view of large K-band cavity.

The cavity was installed and preliminary measurements have been made. This system was further improved by adding an i-f amplifier of wider passband and better noise figure than the earlier model had, and by adding a 2K50 klystron that operates at 26,050 mc, which was kindly selected by the Bendix Red Bank Division. A calibrated K-band noise

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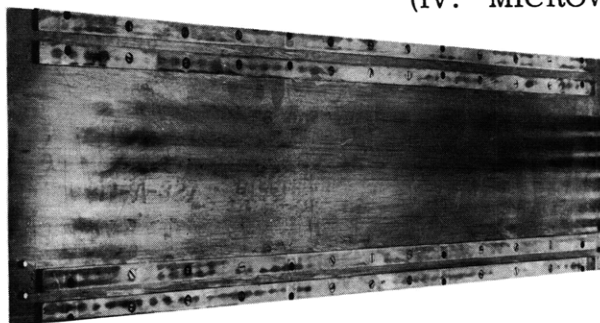


Fig. IV-2. Collimation of molecular beam as shown by sodium chloride plated on one side wall.

source that will soon be available will enable us to obtain the noise figure of the system by direct measurement. This noise figure, together with the study of the molecular trajectories made by H. G. R. Venkatesh (see Sec. IV-B), will allow a more reliable calculation of the expected signal-to-noise ratio than has hitherto been possible.

M. Peter

References

1. M. Peter, Ph.D. Thesis, Department of Physics, M.I.T., May 16, 1955.
2. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., Jan. 15, 1957, p. 22; see Fig. IV-1.

B. MOLECULAR BEAMS OF ALKALI HALIDES

A first step in the development of a technique for the study of molecular energy states, especially the close splittings from nuclear quadripole interaction with orbital electrons, is to secure beams of sufficient intensity, predominantly in one quantum state. A detectable signal from induced emission from excited states could then be obtained.

Toward this end, the dispersal of a "white" beam of sodium chloride molecules in an electrostatic field was investigated, taking into account the angular divergence. The field was produced by a lattice of charged rods. The field has the property of being exponentially cut off at the fringes of the lattice. Analytical expressions have been obtained for the fringe fields and the core field, and for the accelerations and displacements of the molecules in several quantum states. Of the nine tables being prepared for the numerical evaluation of the formulas, the last two give the accelerations, the actual trajectories, and the directions of emergence of the molecules in different quantum states.

In the calculation of the trajectories the charts for energy of the molecule versus the field intensity, calculated from quantum theory by Strandberg and Peter

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(to be published), are of the most vital use.

An alternative field in a different experiment is being investigated. Two significant properties of the Strandberg-Peter charts for electric dipolar molecules are important: the vanishing of the force on the molecules at certain fields, and the linearity of the energy-field relation for a wide range of fields.

H. G. R. Venkatesh

C. VERSITRON

We are testing materials for use in the Versitron study. For this purpose, equipment has been built to measure the relaxation times (T_1 's) of paramagnetic salts. These are observed simply as the exponential decay after a saturation (magnetron) pulse. Although this technique is applicable only to materials with T_1 that is long compared with a magnetron pulse, they are the ones required for Versitron operation.

Data and oscilloscope pictures were taken on dilute ammonium chrome alum at liquid helium temperature. Based on the resonance recovery to thermal equilibrium, the relaxation time is roughly 4 msec.

Two electromagnets are being designed. These will have pole diameters of 10.5 inches and operating fields as high as 13 kilogauss. The field coils will be separate and removable to facilitate adjustment and repair. Models have been built and tested.

C. F. Davis, Jr.

D. INTERACTIONS BETWEEN TORSIONAL AND OVER-ALL ROTATIONS IN SYMMETRIC-TOP MOLECULES

The experimental investigation of the effects of hindered internal torsion on the spectrum of symmetric-top molecules was resumed and completed (1, 2). Measurements of the $J = 1 \rightarrow 2$ rotational transitions were made on a conventional Stark spectroscopy by using a 1N26 crystal driven as a harmonic generator by a 2K33 klystron. The satellite lines resulting from the $n = 0, 1, 2$ internal torsional states were observed and were found to be in good agreement with Kivelson's theoretical treatment (3). The required empirical constants were determined from $J = 0 \rightarrow 1$ measurements. The variation in dipole moment with torsional state, which was indicated by the second-order Stark effect measurements on the $J = 0 \rightarrow 1$ spectrum, was confirmed by the first-order Stark effect observations on the $J = 1 \rightarrow 2$ spectrum.

S. Krongelb

References

1. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., July 15, 1955, p. 19.
2. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., Oct. 15, 1955, p. 23.
3. D. Kivelson, J. Chem. Phys. 22, 1733 (1955).

E. PARAMAGNETIC RESONANCE

Work on irradiated alkali halides has been extended to very lightly irradiated samples. This is possible because of the high sensitivity realized in the spectrometer. The advantages of this approach to the problem are that light irradiation minimizes the extent of crystal damage and that possible interactions between the paramagnetic centers are minimized by the increased average separation of centers. The first of these, decreased crystal damage, means that the spectrum of each absorbing center will add more nearly coherently (in the magnetic field domain) and thus the complicated structure of the resonance can be resolved.

Measurements were made on lightly irradiated lithium fluoride and sodium fluoride. The lithium fluoride spectrum can be fitted quite well to the case in which 19 resonances are superposed, spaced by an amount comparable to the individual linewidth, and in which the relative magnitude of the lines can be determined from quantum statistics. Such a spectrum arises from quantum mechanical considerations if we include only nearest nuclear neighbor interactions and assume a contact type of hyperfine interaction $\vec{A}\vec{I} \cdot \vec{J}$. A perturbation treatment of this problem was carried out to second order in the energy.

Greater resolution was achieved with sodium fluoride, for which a very extensive and complicated spectrum was observed. A previous report (Quarterly Progress Report, Jan. 15, 1957, p. 25) gave results for heavily irradiated samples of sodium fluoride. With the very lightly irradiated samples the original spectrum of 17 or 19 lines splits into hundreds of lines which are grouped in a regular manner, and extends over a wider range of magnetic field with the spectrum center corresponding very nearly to $g = 2$. In addition, a definite angular dependence of the spectrum was observed. The angle being varied, θ , is between the crystalline electric field for the cubic crystal and the dc magnetic field. The spectrum is invariant to rotations of $\theta = \pi/2$. Further experimental work is in progress. A theoretical understanding of these phenomena is being sought from crystalline-field effects which would involve spin-orbit coupling, higher-order tensor interactions of the usual magnetic types, and an exact treatment of the perturbation Hamiltonian for the hyperfine interaction.

The operating range of the spectrometer has been extended to low temperatures, in that high-frequency modulation at 6 kc can be used from room temperature down to liquid helium temperature. A solid quartz cavity coated with silver and fed from a dielectric loaded waveguide has enabled the reduction of physical dimensions sufficiently to allow double dewar operation. Experiments were successfully run at liquid helium temperature.

G. Wolga

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F. ATOMIC RECOMBINATIONS

A paramagnetic resonance system similar to one already in use (Quarterly Progress Report, April 15, 1956, p. 20), but using a permanent magnet to establish the field, is being set up. It will be used to study the recombination of oxygen atoms by observing the atomic oxygen resonance as a function of time. By this means, both volume and surface effects in the recombination process will be studied.

S. Krongelb

G. MICROMODULATOR

It was pointed out (Quarterly Progress Report, Jan. 15, 1957, p. 26) that g -factor anisotropy causes inhomogeneous broadening in polycrystalline samples of diphenyl trinitrophenylhydrazyl and that this yields a linewidth (> 3 gauss or 9000 mc) that is too great for oscilloscope display in a conventional Stark modulation microwave spectroscopy. A method of circumventing this difficulty has been developed. It consists of linearly sweeping the dc magnetic field in synchronism with the klystron sweep. Since the line-shape factor is a function of $H(t) - 1/\gamma_e \nu(t)$, where $H(t)$ is the magnetic field, γ_e is the electron gyromagnetic ratio, and $\nu(t)$ is the klystron frequency, the normalized line-shape factor, $g(H - \nu/\gamma_e)$, can be arbitrarily compressed in the time domain for display purposes.

It can be shown that the absolute intensity of a Stark-modulated absorption can be determined if the following product is known:

$$C = C_{\text{display}} \times C_{\text{demodulator}} \times C_{\text{amplifier}} \times C_{\text{crystal}} \times E_o^2$$

where the various C 's describe the transfer functions of the spectroscopy components, and E_o is the amplitude of the electric vector emitted by the klystron. C can be determined from measurements with the micromodulator, and by using the following equation (which is derived from first-order theory):

$$C = \frac{(\ell - s/\gamma_e)^2}{\epsilon H_m V_r} \left\{ \left[\frac{kc}{\pi^3 (\gamma_e \hbar)^2} \right] \left[\frac{T}{N_o} \right] \left[\frac{ab}{\nu^2 \sqrt{1 - (c/2 a \nu)^2}} \right] \right\} \int_0^\infty V_s(t) dt$$

where

ℓ = magnetic field sweep rate (gauss/sec)

s = klystron sweep rate (cps/sec)

γ_e = electron gyromagnetic ratio

ϵ = transfer constant of integrator inserted between demodulator and RC filter

H_m = amplitude of modulating magnetic field

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V_r = amplitude of demodulator reference voltage

k = Boltzmann constant

$\hbar$ = Planck's constant/ 2π

T = temperature ($^{\circ}\text{K}$)

N_o = total number of hydrazyl molecules

a, b = waveguide dimensions in centimeters

ν = klystron frequency

$V_s(t)$ = hydrazyl resonance display in oscilloscope units

Note that since the only line-shape information entering the derivation of this equation is the normalization of the shape factor to unity, broadening caused by field inhomogeneity and the polycrystalline nature of the sample have no effect on the result.

Remaining aspects of the investigation include consideration of the effects of reflection in the guide, attenuation in the Stark cell and phase shift in the hydrazyl, perfection of the electronic integrator, construction of a prototype micromodulator that will include a new magnet, and testing the device on several known resonances in ammonia.

R. D. Mattuck

H. TRAVELING-WAVE CAVITY

Use of a traveling-wave cavity results in an electromagnetic energy density step-up proportional to the Q of the cavity and makes it possible to utilize the points of pure circular polarization found in a traveling wave. The present form of the cavity is constructed of rectangular waveguide bent in the H -plane into a circular ring. Coupling to the main waveguide is achieved through Bethe coupling; ideally, it should yield an infinite directivity.

In order to set up a traveling wave in the cavity, the two degenerate modes that exist, because of the cylindrical symmetry of the cavity, must remain exactly degenerate. This is achieved if the directivity of the coupling hole is perfect. For this purpose, several tuning screws are introduced into the cavity to compensate for any imperfection in coupling which might destroy the exact degeneracy of the two modes.

The cavity has been analyzed theoretically and experimentally and will be utilized in resonance studies of paramagnetic materials in the solid state.

J. J. McNicholl

I. PERMANENT MAGNETS

Three permanent magnets are now in service. One magnet, with a gap of 1.5 inches, has been aligned for optimum homogeneity by making a point-by-point plot of the magnetic field with a proton probe. An extremely accurate plot was made possible by using a positioner, constructed for the purpose, to hold the proton probe as it was

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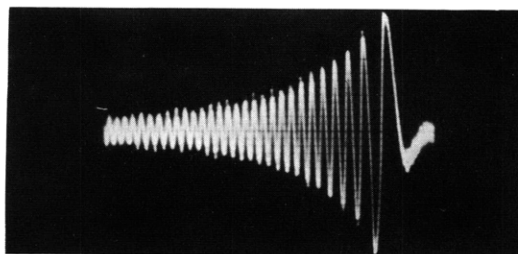


Fig. IV-3. Proton resonance.

moved through the field.

Inhomogeneity estimated to be 10 milligauss over a water sample $1/4$ inch in diameter and $3/8$ inch long was obtained in a region 1.5 cm in diameter at the center of the gap. An inhomogeneity of 0.2 gauss was obtained in a region 3 cm in diameter at the center of the gap.

Figure IV-3 shows a proton resonance obtained in a field of 4290 gauss by using a transitron oscillator (1). Sinusoidal field modulation at 50 cps and peak amplitude of approximately 5 gauss was employed. The number of "wiggles" observed is indicative of the homogeneity of the field.

B. Josephson, Jr.

References

1. W. F. Knoebel and E. L. Hahn, Rev. Sci. Instr. 22, 904 (1951).
2. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).