III. MICROWAVE SPECTROSCOPY*

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A. SPIN-LATTICE RELAXATION

In order to relate experimentally observed relaxation times to the spin-phonon transition probabilities, it is necessary to solve the system of rate equations:

$$\frac{dN_i}{dt} = \sum_{j \neq i} (W_{ij}N_j - W_{ji}N_i)$$

with the constraint $\sum_i N_i = 1$. Here, N_i is the fraction of particles in the i^{th} level, and W_{ij} is the lattice-induced transition probability from state j to i.

In matrix notation, this system of equations represents an eigenvalue problem:

$$\frac{dN}{dt} = WN$$

where $W_{ii} = -\sum_j W_{ji}$. The solution is N = DC, where C is a column matrix such that $C_i = \exp(\lambda_i T)$, and D is a square matrix whose columns are the eigenstates

$$(W - \lambda_i I)\, D_i = 0$$

The proper normalization of the eigenstates is given by the initial conditions. With the solution written in this form, matrix techniques can be used to show the general properties of the relaxation:

(a) The eigenvalues are real and negative, hence the populations of the levels simply decay to thermal equilibrium and do not oscillate.

(b) The steady-state solution is a Boltzmann distribution.

These properties will be shown for a four-level system with $E_4 > E_3 > E_2 > E_1$. Let S be a diagonal matrix with elements

$$S_{ij} = \exp\left(\frac{E_1 - E_j}{2kT}\right) \delta_{ij}$$

If we use the fact that

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$$W_{ij} = W_{ji} \exp\left(\frac{E_j - E_i}{kT}\right)$$

then $\overline{W} = S^{-1}WS$ is a symmetric matrix, and so its eigenvalues are real. Since the secular equation is invariant under a similarity transformation, the λ's must also be real.

The constraint $\sum_i N_i = 1$ requires that only three of the rate equations be independent. Hence, $\|W\| = 0$ and $\lambda = 0$ is a root of $\|W-\lambda I\| = 0$. If we call this root λ_4, the corresponding eigenstate D_4 is the steady-state solution $WD_4 = 0$.

The system of equations for the elements of D_4 is easily solved. The result is the Boltzmann distribution

$$D_{i4} = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_{i=1}^{4} \exp\left(-\frac{E_i}{kT}\right)}$$

That the remaining eigenvalues are negative can be seen by writing the reduced secular equation in the form:

$$\lambda^3 + P\lambda^2 + q\lambda + r = 0$$

where

$$P = -\mathrm{tr}(W) = \sum_{ij} W_{ij}$$

$$q = \sum_{i>j} (W_{ii}W_{jj} - W_{ij}W_{ji})$$

$$r = \begin{vmatrix} W_{41} & W_{21} & W_{31} \\ W_{42} & W_{22} & W_{32} \\ W_{43} & W_{23} & W_{33} \end{vmatrix} \sum_{i=1}^{4} \exp\left(\frac{E_1 - E_i}{kT}\right)$$

The quantities P, q, and r are positive, so by Descartes' rule of signs, $\lambda_i \leq 0$ for i = 1, 2, 3.

The results presented here can easily be extended to any multilevel problem for which the rate equations apply.

J. R. Shane

B. MICROWAVE PHONONS AND THEIR ABSORPTION BY F-CENTERS

Microwave phonons have been produced, and their interaction with paramagnetic impurity centers in quartz has been studied. Phonon packets were produced by the

piezoelectric effect at the end surface of a quartz rod placed in the electric field of a re-entrant cavity. These packets propagated down the rod, were reflected from the opposite end, and were detected at the generating surface by the inverse effect. The amplitude envelope of the echoes consisted of a series of maxima and minima, or beats, caused by interference effects arising from a slight nonparallelism of the end surfaces superposed on an exponential decay. From the decay, the average lifetime of the coherent phonons was found to be 10^{-5} sec. The t = 0 intercept of the envelope measured the square of the fraction of the microwave power converted into acoustic power, which was found to be a factor of 10^{-5} smaller than the computed value of 10^{-4}. We attribute this discrepancy to interference effects arising from roughness of the end surfaces, or to lattice damage at the generating surface which would decrease the piezoelectric effect.

The absorption of phonons by spins produced in the natural quartz by gamma irradiation from a Co^{60} source was detected as a partial saturation of the spin electron paramagnetic resonance. The partial saturation, S/S_o, was found to be 0.75 at 1.7°K, 0.75 at 4.2°K, and 0.92 at 20°K, the error in S/S_o falling between 2 per cent and 5 per cent. These values for S/S_o were independent of the difference between the microwave and phonon frequencies within 20 mc. From microwave saturation measurements, the order of magnitude of the spin-lattice relaxation time T_1 was found to be greater than 3 sec at 1.7°K, and equal to 0.3 sec at 4.2°K, 3×10^{-4} sec at 20°K, and 3×10^{-6} sec at 77°K. The spin-resonance absorption, which was measured as a function of microwave power, saturated in such a manner as to indicate partial inhomogeneous broadening, and cross relaxation took place between the closely spaced, narrow (approximately 1 gauss wide) lines of the spectrum. These two effects prevented quantitative determination of the spin-phonon transition probability.

P. H. Carr

C. THE EVOLUTION OF BEAM-MASER APPARATUS IN THE MICROWAVE SPECTROSCOPY LABORATORY

Since the pioneering experiments by Johnson and Strandberg (1) and by Strandberg and Dreicer (2), interest in molecular-beam microwave spectroscopy has been acute in this laboratory. The concurrent, now classic, experiments of Gordon, Zeiger, and Townes (3) lent further impetus to this interest which Peter and Strandberg (4) channeled into maser spectrometry. Their work was directed toward beam spectroscopy of the alkali halides, yet gaps in experimental method and theoretical understanding compelled them, at that time, to embrace widely divergent interests, such as information theory applied to microwave spectroscopy and mode control in microwave cavities of large volume. From this earlier work, Venkates (5) was led to the studies on ammonia-maser spectroscopy which formed the basis of his doctoral thesis. When these studies were

completed our laboratory was left with apparatus that we decided to refine so that a maser spectrometer facility would be readily available. We are able to report that this evolutionary process has been completed with the development and operation of a handy single-beam maser and with the construction of a twin-beam maser. The functions of both of these instruments are quite flexible and conveniently arbitrary.

This high-resolution equipment demonstrated its value when a need arose recently for the frequencies of the hyperfine-split 1,1 inversion line of ammonia to be accurately specified. Our single-beam maser was set up for this purpose, and the split line was easily resolved within a few kilocycles at 23 kmc.

Experience during the past few years has shown that within the bounds of cautious insight and good engineering, ammonia-beam masers are remarkably insensitive to details of their construction. Once it is working, a maser works easily, and further modifications to the basic design are simply optimization procedures for extraction of maximum signal-to-noise with minimum effort.

The apparatus described in this report is the result of evolution in the Laboratory. The basic design is simple, compact, inexpensive, and, in its way, foolproof. Based on these attractive properties, a new twin-beam maser, more streamlined and sophisticated than its single-beam predecessor, has been constructed. It is intended that the facility represented by this apparatus will lend itself to studies of oscillator noise, frequency standards, and stimulated-emission spectroscopy in general.

The Single-Beam Maser

Venkates' original maser (5) was modified and reworked until it took the present form, which now permits disassembly, assembly, and operation within an hour and a half. The photograph shown in Fig. III-1 illustrates the single-beam maser assembly. From top to bottom the major components of the maser are arranged as follows: microwave cavity, state-selector and cold-trap, effuser, baffles, and diffusion pump. With

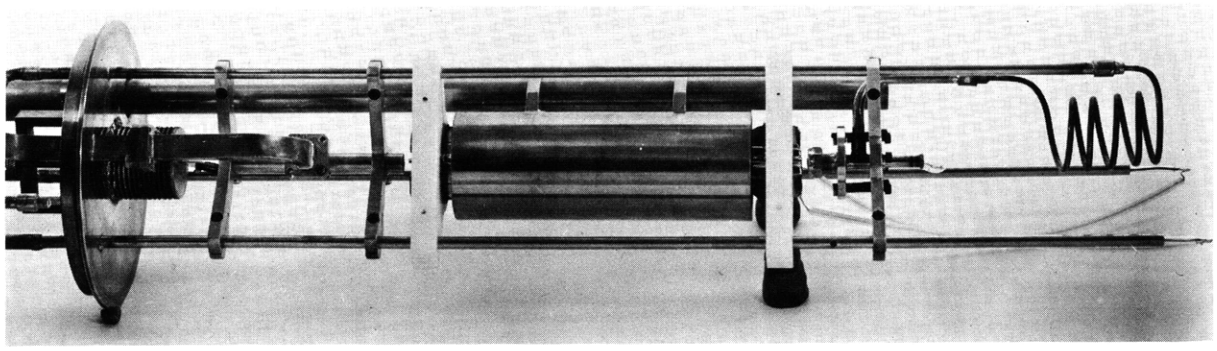

Fig. III-1. The maser assembly.

this arrangement the beam source is nearest to the diffusion pump, and back-scattered molecules issuing from the effuser with trajectories outside of the entrance aperture of the state selector are quickly pumped away. Except for the diffusion pump and its baffles, all of these components are part and parcel of the top plate. In this way, those components that must be optically aligned are removable as a unit for servicing.

Component alignment is ensured by a parallel tripod arrangement of three stainless-steel tubular supports that are fitted into the top plate, which is a sturdy piece of brass machined to mate with an O-ring flange on the vacuum chamber. Two of the supports are used, in effect, as an optical bench, and the third is actually a feed line to the effuser. It extends through the top plate down to the effuser, and the ammonia is conducted through it. The first two supports, in addition to their function as an optical bench, contain glass-insulated high-voltage leads that connect to the state selector. These high-voltage leads conduct coaxially through two legs of the tripod, and extend through the top plate, eventually encountering Kovar-to-glass vacuum seals.

The vacuum system consists of a Megavac roughing pump, a 4-inch diffusion pump, and an upright cylindrical tank that forms the vacuum chamber supporting the diffusion pump at the bottom and the maser proper at the top. The maser simply hangs down into the vacuum chamber, and the top plate and O-ring flange seal at least to 10^{-6} mm Hg. An ionization gauge and a thermocouple gauge connect to the side of the vacuum chamber to enable testing of the entire vacuum system that can be made independent of the relatively complex top-plate assembly.

The cylindrical microwave cavity is mechanically tuned — an easily effected arrangement because the mode configuration is TM_{010}. This mode is characterized by longitudinal surface currents and, consequently, a tuning vane inserted in a slot cut lengthwise in the cavity perturbs the frequency but not the Q. Thus tuning is accomplished by means of a Sylphon bellows variably constrained to press from within the vacuum chamber against a tuning vane lever. The cavity has a single iris, and the maser signal is observed in reflection.

The state selector is a quadrupolar arrangement of four highly polished vanes with an aperture varying parabolically to match the smaller diameter of the effuser to the larger diameter of the cavity. Teflon is used in judicious quantities to support and insulate the vanes. Jacketed by a cylindrical cold trap, the Teflon-insulated state selector can be called upon to support more than 32 kv before electrical breakdown occurs.

A stainless-steel dewar extends parallel to the tripod supports through the top plate. The cold trap clamps to this dewar and is cooled by conduction; the state selector is cooled, in turn, by radiation. During operation of the maser, the dewar is conveniently and economically filled from the top of the entire assembly.

A piece of Varian klystron grid stock is used as an effuser. Mounted on an adjustable

platform, it can be tilted and shifted around for correct alignment of the molecular beam. In order to facilitate the alignment procedure, a window is provided directly behind the effuser, and when illumination is introduced through it along the beam axis, the effuser, the state selector, and the cavity can be brought visually into line from stem to stern.

The Twin-Beam Maser

The twin-beam maser really consists of two independent masers mounted side by side on a common top plate, sharing a common vacuum chamber. Each of them differs but little from the single-beam maser described above. The principal difference is that a dewar of much larger capacity is located in such a way as to service both cold traps symmetrically. This, together with new features of component clamping, and so on, makes it possible to remove any single component without disturbing its neighbors.

Auxiliary Equipment

To perform the function of reducing the pressure from a tank of compressed ammonia to a value near 1 mm Hg in an easily controlled way, an inlet manifold is required. The present manifold admits ammonia through a pressure-reduction valve into a cylinder of approximately 2 inches diameter and 12 inches length. This cylinder is so arranged that it can be bathed in liquid nitrogen and the noncondensed gas pumped off. The purified ammonia can then be revaporized and conducted to a needle valve, beyond which a thermocouple gauge meters gas flow that is then direct to the effuser inlet at the maser. The manifold is made entirely of metal and has small bellows-sealed valves throughout.

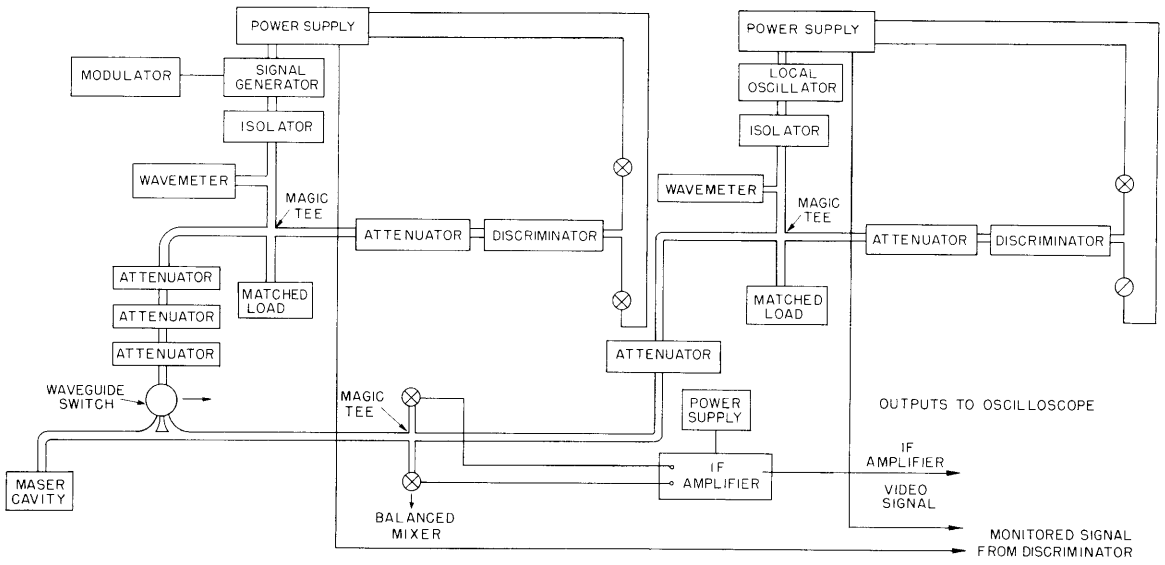

Fig. III-2. Block diagram of microwave circuit.

The detection scheme (Fig. III-2) is balanced-mixer superheterodyne. The additional stabilized klystron ("Signal Generator" in Fig. III-2), with provision for frequency modulation, can be used to sweep over the spectral region that is of interest. If it is desired, the resulting beat frequencies can be displayed on an oscilloscope. In the case of simultaneous operation of two or more of the masers the detection bandwidth can be narrowed for better signal-to-noise ratio by the use of audio filters or other schemes. It is interesting to note that when we beat one of our ordinary dc-bridge-stabilized klystrons against the single-beam maser operated as an oscillator at the 3,3 transition of ammonia, a reasonably steady audio beat note is clearly visible against the background of klystron noise.

This brief report has been concerned with the summary of progress on the development of molecular-beam maser spectroscopy apparatus in this laboratory. Specific devices have been discussed and, in this sense, it is a final report. But in the sense that this laboratory continues to be actively concerned with absorption and emission microwave spectroscopy, it is an interim report.

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