# Relative Intensity Measurements in Microwave Spectroscopy*

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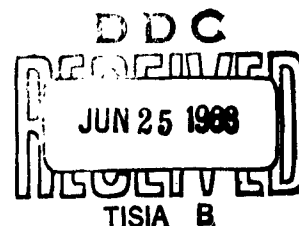Cambridge 38, Massachusetts

## ABSTRACT

A method is described for the measurement of peak intensity ratios of gas phase microwave absorption lines. Large errors associated with multiple reflections in the waveguide have been eliminated by careful design and the use of ferrite isolators. Detector nonlinearities have been neutralized by using a precisely calibrated step attenuator allowing both lines involved in a ratio to be displayed with approximately the same amplitude. Means of minimizing additional sources of error are discussed. Application of the method to a number of problems indicates that ratios accurate to a few percent can be obtained.

Microwave spectroscopy of gases has been an extremely useful and reliable method for the examination of molecular and nuclear properties. Much of its success is due to the capability of making precise frequency measurements under conditions of high sensitivity and resolution. A portion of the spectroscopic information has remained unavailable, however, due to the inability to measure

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relative intensities confidently to even a few percent.  Such
measurements would simplify the assignment of spectra and allow
for the determination of vibrational frequencies and barriers
to internal rotation,                                    measurement
of isotope ratios, and quantitative chemical analysis.

Although many relative intensity measurements are reported,
it is recognized that they have been subject to rather serious
and unpredictable errors.  Furthermore, many investigators have
probably attempted rough intensity estimates during their examina-
tion of a spectrum, but few have been concerned with developing
techniques to make such measurements more reliable.  The present
paper  describes simple modifications of a standard Stark effect
microwave spectrometer which, in combination with suitable operating
procedures, are capable of providing relative intensity data
accurate to within a few percent.

## BACKGROUND

A number of efforts at intensity measurement have been made
utilizing cavity spectrometers,[1-4] one of which was reported to
yield integrated line intensities with an expected accuracy of
4%.[5]  However, the narrow-bandedness of/a cavity and the associated
tuning problems limits its usefulness.  Similarly, methods developed
with bridge spectrometers[6,7] depend on the response of the crystal
detector being square-law, and it is not certain that this condition
is satisfied to the extent necessary for accurate measurements.
Our investigations were directed towards the utilization of a

conventional Stark-modulated spectrometer employing phase-sensitive detection. Previous investigators have recognized that reflections within the waveguide and detector non-linearities seriously handicap intensity measurements with such an instrument. However, the reflection problem had not been adequately investigated and phase-sensitive detection was usually abandoned for the less sensitive method of balancing the modulation frequency component of the crystal detector output with a calibrated signal of opposite phase.[8-10]

The basis of our method was developed by Baird and Bird.[10] They showed that the DC response of the crystal detector can be expressed in terms of the peak value of the microwave electric field, $E$, as

$$i_{DC} = c_1 E + c_2 E^2 + c_3 E^3 + \ldots = \sum_{n=1} c_n E^n \qquad (1)$$

in which the $c_n$'s generally vary from crystal to crystal. If a square-wave Stark field of frequency $v$ is used to modulate the absorption lines there will also be a component at this frequency when absorption is taking place. If the absorption coefficient is small enough ($10^{-4}$ cm$^{-1}$ or less), this component is given by

$$i_m = \frac{-2\alpha d}{\pi} \left( \sum_{n=1} n\, c_n E^n \right) \sin 2\pi v t \qquad (2)$$

in which $\alpha$ is the amplitude absorption coefficient of the transition per unit length, and $d$ is the effective length of the absorption path. Comparison of the two equations indicates that if the

DC crystal current is maintained at the same value during the measurement of two lines, then the ratio of the modulation frequency crystal currents will give the absorption coefficient ratio directly.

## WAVEGUIDE REFLECTIONS

For accurate measurements of intensity ratios, it is essential that the value of/effective path d remain constant. If two or more reflections are present in the waveguide system, their interaction with the microwave power is strongly frequency dependent. Successively reflected waves will add or interfere in varying amounts as the ratio of the wavelength to the distance between reflections changes. Calculations with usual lengths of absorption cells and operating frequencies show that a comparison of two lines only ten megacycles apart can be seriously affected.[11]

A series of standing-wave ratio (VSWR) measurements as a function of frequency was made on various waveguide components to evaluate their reflection properties and, if necessary, reduce them to negligible effect.

Tapered Transitions: When using the typical X-band absorption cell at frequencies above 12kMc it is necessary to place tapered transitions at both ends to match the cell to the smaller dimensions of the higher frequency components. A pair of X to K-band transitions constructed in our laboratory gave frequency-dependent power reflections of 10% or more. The measurements were repeated

using high quality commercial units (7 wavelengths long) and the maximum reflected power was reduced to 0.4%.

Stark Electrode: A length of X-band guide was fitted with a brass Stark electrode having squared ends and held in place with Teflon strips. The reflected power varied with frequency with a period equal to that expected from the presence of two reflections, one at either end of the Stark strip. The reflected power varied with frequency with a period equal to that expected from the presence of two reflections, one at either end of the Stark strip. The maximum reflected power was 2%. The corners of the electrode were then cut back giving a pointed taper 4 cm. in length at each end. The maximum reflected power was reduced to 0.5%. Similar reductions were obtained when the ends were cut in either a wedge or fishtail configuration.

Sample Inlets: Sample inlets constructed in X-band guide by drilling 1/4 in. holes in the center of the broad waveguide face and inserting copper tubes flush with the inner surface of the guide wall gave power reflections between 1 and 2%. By using narrow slits (3/32 in. wide and 2 in. long) cut along the no-current line instead, maximum reflections of only 0.5% were obtained.

Crystal Detector: The reflection characteristics of a group of crystal diode detectors and a number of commercially available tunable crystal mounts were measured. It was found that tuning the crystal holder so that the DC crystal output was maxium also

corresponded to the condition of minmum reflection. Over a wide range of frequencies, power reflections from 2 to 30% were found, with 8% being a representative value.

Placing a ferrite isolator (which allows microwave power to be transmitted through it in one direction only) directly before the crystal holder reduced reflections to 0.5% or less, and this value was maintained even when the crystal was severely detuned.

To determine the effect of crystal tuning on the measured height of an absorption line, the peak height was first recorded with the crystal tuned for maximum DC output. The crystal holder was then detuned and the microwave attenuator in the waveguide system adjusted to bring the DC current back to its original level. Variation in line height was 1% or less when an isolator was used, even when the crystal was so detuned that the current was 20% of its in-tune value before attenuator adjustment. Without the isolator, variations in line height as great at 13% were found with even less detuning.

Next, with the isolator in position and the crystal tuned for maximum DC output, peak heights were successively measured using a different crystal each time. In no case was further tuning of the crystal holder necessary to bring the DC current to maximum, but the sensitivity of the five crystals tested (indicated by the maximum current obtainable) varied by as much as 80%. Nevertheless, as long as the DC current was returned to the same value for each measurement, variations in line height

never exceeed 8%. Thus, although the ratio of modulation frequency signal to DC is approximately constant among crystals, the variation is large enough to prohibit substitutions during a measurement.

Jarring the crystal in its holder was found to cause variations in peak heights as large as 4%. Because of this and the above result indicating that the crystal could be operated although highly detuned, no further crystal tuning was performed during relative intensity measurements after the initial tuning, arranged to provide sufficient microwave power for all lines.

Wave Guide System: Our waveguide system was modified to incorporate changes suggested by the above measurements. The original system (including attenuators, wavemeter, "TEE" and vacuum flanges in addition to the components discussed above) had reflection characteristics shown in Fig. 1. Use of isolators,[12] commercial tapered transitions, sample inlet slits, a carefully aligned and tapered Stark electrode, and precisely machined flanges resulted in a system whose reflection characteristics are shown in Fig. 2.

## DETECTION SYSTEM NONLINEARITY

A further source of error is a nonlinear response by the detection system to the modulation frequency signal produced at the crystal as the result of absorption. Our detection system consists of a preamplifier, a phase-sensitive detector, and a recorder. Of the three, only the detector was found to have a nonlinear response. Rather than redesign it, an alternative

method was employed involving the insertion of an accurately
calibrated step attenuator between the preamplifier and detector.[13]
By setting the attenuator to make the larger of a pair of lines
record at the same height as the smaller, the same portion of
the response curve of the detector can be used throughout the
measurement. Calculations based on the response curve are used
to determine to what extent the lines should be made of equivalent
size to maintain the error within acceptable limits. The use
of the attenuator also has the advantage of allowing large ratios
to be measured conveniently without having one line fill the
chart paper while the other is hardly noticeable.

## ADDITIONAL SOURCES OF ERROR

Interference from Stark Lobes and Nearby Lines: Adequate Stark
voltage must be applied to remove all the Stark lobes from lines
being measured,[14] particularly if they are expected to have
different Stark effects. In addition, lobes from neighboring lines
must not interfere. For this reason the region of the line should
be examined by recording it at different Stark voltages until
a value is found where no interference occurs.

Serious errors can also arise if the lines being measured
have a first-order Stark effect and the Stark generator has im-
perfect zero-basing. The peak height of the line will be reduced
under these conditions; the concurrent increase in line width
can sometimes aid in recognizing this situation.

Neighboring lines can affect the height of the line being

measured and corrections must be made for their presence. Generally, with lines of equal height, the ratio of their separation to the line width must be greater than five for their effect upon one another to be negligible. On the other hand, lines which are non-resolvably close may still be separated enough to give a resultant line whose peak height is not the sum of the peak heights of the two components. Verdier[15] has given correction formulas to be applied in such cases, and they have been used successfully in our experiments.

Saturation: If the sample pressure is too low and the microwave power density too great, saturation of the absorption lines will occur. This results in a decrease in peak height accompanied by an increase in line width. Since saturation is different for different rotational transitions, and may be different for the various components and vibrational levels of the same transition, ratios should be measured at a series of power levels to insure that saturation is not affecting the results.

Changes in Sample Composition: Problems associated with changes in the sample gas during the time of measurement are often encountered. Variations in line height and width accompanied by changes in pressure are often noted due to the release of gases which had previously been adsorbed on the waveguide walls, thus diluting the gas. Care must also be taken to insure that the sample does not decompose, or react chemically with residues of previously introduced samples. Heating the waveguide to

80-100°C followed by several repeated fillings of the cell before
starting measurements usually aids in obtaining a stabilized sample.
Pickup: Probably the greatest uncertainty in the measurement of
intensity ratios is encountered in determining the base line of
the recorder trace. Drifting, sporadic irregularities, a high
noise level and irregular sweep rates can all contribute to a
non-linear base line, but the most complicating effect of all
is the presence of pickup signals at the modulation frequency
which are detected and displayed but are not the result of absorp-
tion. With weak lines, the response to the pickup signal may be
even greater than the response to a line which would otherwise
have an acceptable signal to noise ratio. This problem is a
persistent one with Stark effect spectrometers, and since both
the magnitude and phase of the pickup relative to the absorption
signal constantly changes, it is difficult to account for. How-
ever, several steps were taken which reduced it considerably,
usually to negligible proportions.

There are at least three mechanisms by which pickup from
the Stark modulation generator enters the system. These are
direct radiation due to inadequate shielding, transmission through
AC power lines, and ground loops among the spectrometer components.

One effect of pickup is a variation in the zero level of
the recorder with Stark voltage when no microwave power is trans-
mitted through the waveguide. Subsequent transmission of power
causes a further increase in recorder deflection. Fig. 3 shows

the components and cable shields in the ground loop responsible
for this pickup. An equivalent circuit is shown in Fig. 4. Here
$R_s$ is the shield resistance of the cable carrying the modulating
square-wave, $C_f$ is the capacitance of the/waveguide flange, and
insulated
$R_{ab}$ is the ground-path resistance from a point on the guide just
after the flange to the detector side of the preamplifier. $R_d$
is the resistance along the path completing the loop, and $R_x$
is the crystal impedance.

The square-wave cable carries currents up to about one ampere
and the presence of a finite $R_s$ causes a voltage drop across it
and therefore across $R_{ab}$ at the preamplifier input. This accounts
for the variation in detected signal as a function of square-
wave voltage without any microwave power. With power, $R_x$ is
decreased as the power increases and the larger voltage drop
across $R_{ab}$ results in an increase in the pickup signal. The pick-
up can be reduced by making $R_{ab}$ as small as possible or by pro-
viding additional resistance at some other point in the ground loop.
The former was accomplished by removing the cable from the crystal
holder to the preamplifier and connecting them together with a
single coaxial connector and adapter. Impedance was introduced
in the loop by using a second insulated wave-guide flange before
the crystal holder. Additional resistance was obtained by winding
a portion of the cable from the preamplifier to the current meter
around a ferrite toroid. The bifilar nature of this winding does
not affect the desired signal carried by the cable, but does place
an added impedance in the cable shield.[16]

Modulation voltage reaching the repeller of the klystron will also cause recorder deflections as a function of microwave power and Stark voltage. Both frequency modulation and amplitude modulation of the microwave power occurs, the latter when operating on sloping portions of the klystron mode or reflections. This was almost entirely eliminated by placing a braided copper ground strap in parallel with the power cable from the klystron power supply to the klystron, thereby reducing the voltage drop across part of the ground loop, and by utilizing ferrite windings in other parts of the loop.

Finally, tuned traps are inserted in the AC power lines to the klystron power supply and the Stark generator, and adequate shielding is provided for the latter.

A procedure useful when measuring lines in the presence of a nonlinear base line is to sweep over the region of the line placing a frequency marker at its peak. The sample gas is then quickly pumped from the absorption cell, and the region is again recorded using the marker to identify the line's position on the base line.

Miscellaneous Errors: There are other effects which can lead to erroneous or misinterpreted intensity ratios. For example, the expression for the peak intensity ratio, R, of two lines due to the same asymmetric rotor rotational transition in two different vibrational states is[17]

$$R = \frac{\alpha_1 d_1}{\alpha_2 d_2} = \frac{d_1}{d_2} \frac{g_1}{g_2} \left(\frac{A_1 B_1 C_1}{A_2 B_2 C_2}\right)^{\frac{1}{2}} \frac{|\mu_{1j}|_1^2}{|\mu_{1j}|_2^2} \frac{\nu_1^2}{\nu_2^2} \frac{\Delta\nu_2}{\Delta\nu_1} \frac{f_1}{f_2} e^{-W_r/kT} \quad (3)$$

in which the subscripts 1 and 2 denote the two lines and

> d = effective length of the absorption cell
>
> g = nuclear statistical spin weight of the lower rotational level involved in the transition
>
> A,B,C = rotational constants
>
> $|u_{1j}|$ = dipole moment matrix element
>
> $\nu$ = resonance frequency
>
> $\Delta\nu$ = half-width
>
> f = fraction of molecules in the particular vibrational state
>
> $W_r$ = the difference in rotational energy of the lower level involved in the transition for the two vibrational states.

Generally we would want our intensity ratio to give the relative populations of the two vibrational states, i.e., $R = f_1/f_2$, directly. As indicated by the above expression, however, a number of other quantities might be unequal for the two lines.

The ratio of the effective length of the absorption cell at the two frequencies can be other than unity due to the waveguide reflections discussed above. However, even in the absence of reflections, d is a function of frequency:

$$d = d_0 \left(1 - \frac{\nu_c^2}{\nu^2}\right)^{-\frac{1}{2}} \qquad (4)$$

Here $d_0$ is the physical length of the cell, $\nu_c$ is the cut-off frequency of the waveguide, and $\nu$ is the operating frequency. Fortunately, for frequencies not close to cut-off, this is a slowly varying function and usually no correction is necessary.

A difference in statistical weights can be accounted for by group-theoretical methods if the symmetry of the molecule is known. Differences in rotational constants and energies will always be present but the fractional change is usually negligible or can be calculated. The correction for the difference in resonant frequency can easily be made.

The square of the dipole moment matrix element may be written as

$$|u_{1j}|^2 = \frac{\mu^2 S}{2J+1} \qquad (5)$$

where S is the transition strength and $\mu$ is the molecular dipole moment active in the transition. This dipole moment may be different for the two transitions. Additionally S may be quite sensitive to changes in the asymmetry parameter of the molecule for certain transitions in near-symmetric tops.[18]

Finally, the half-widths of the two lines studied may be unequal. The major contribution to the line width under the usual conditions employed in microwave spectroscopy is pressure broadening associated with inter-molecular collisions. If these are considered as dipole-dipole interactions, the line width will be proportional to the square of the dipole moment. Thus any contribution to R from the line width factor will be partly compensated by the change in dipole moment matrix elements. Unfortunately, no accurate experimental determinations of these line width effects are available and, although they are expected to be within the limits of experimental error, care should be taken to insure that they are not affecting the results.

## MEASUREMENT PROCEDURE

The microwave spectrometer is operated in its usual manner except for the insertion of a ferrite isolator before the crystal holder and the calibrated step attenuator leading to the detector. The klystron is first tuned to the frequency of one of the lines to be measured. The line is positioned on the flat part of the mode, the crystal mount is tuned to give maximum DC current, and the line is recorded. The klystron is then brought to the frequency of the second line and the klystron voltages are again adjusted to give a flat mode. The microwave attenuators are used to bring the DC current to the same level as for the first line and, without retuning the crystal or changing any detection system controls, the line is recorded. From this preliminary investigation an estimate may be made of the intensity ratio, and the measurement is repeated using the step attenuator to make the lines sufficiently equal in height. Preliminary measurements are also made to investigate the effects of changes in sample composition, power saturation, and Stark lobe interference. The final measurement of the ratio is performed by recording the lines alternately, each single measurement of one of the lines consisting of a number of sweeps over it, the results of which are averaged.

## APPLICATIONS

A number of relative intensity measurements were made for which the results could be compared to those obtained by a different and independent method.

Internal Barrier in $CH_3CHF_2$: Molecules in which free rotation
of a methyl group about a single bond is hindered by a three-
fold potential barrier provide such an opportunity. The presence
of the barrier splits each torsional level into a nondegenerate
sublevel of symmetry species A and a doubly degenerate one of
species E. The rotational constants in each of these sublevels
are different so that, for certain ranges of the barrier height
and structural constants, a splitting of the rotational transi-
tions is easily observed in the microwave spectrum. A measure-
ment of this splitting allows the barrier height to be calculated.
The result is usually considered accurate to between 2% and 5%.

Alternatively, the relative populations and, therefore,
the energy difference between two torsional levels can be de-
termined from the relative intensities of a rotational transition
in the two different levels. Using a suitable potential energy
curve, the height of the hindering barrier can be calculated.

The barrier height in $CH_3CHF_2$ has been previously determined
by splitting measurements to be 3180 cal/mole.[19] The ground
and first excited state lines of the $1_{11}-2_{12}$ transition at
24,474.4 and 24,425.7 Mcs, respectively, were used for in-
tensity measurements. The A and E components are degenerate
in the ground state and are split by only 0.02 Mcs in the excited
state. This splitting is too small to necessitate any correction
for its presence. No important sample decomposition was evident
and since the lines were very strong, no difficulty was encountered

in determining the base line. Ten measurements of the ratio of the ground state intensity to that of the excited state gave an average value of 2.93 with a standard deviation of 2.8%.

The energy of a torsional level is given by

$$E_v = \frac{9Fb}{4} \qquad (6)$$

in which b is an eigenvalue of the Mathieu equation which is satisfied by the torsional motion and F is a function of the molecular structure. The intensity ratio R (ground state/excited state) gives the Boltzmann ratio of the population as

$$R = e^{(E_{v_1} - E_{v_0}) / kT} \qquad (7)$$

where the subscripts 1 and 0 denote the first excited and ground states, respectively. Combining the equations gives

$$\Delta b = b_1 - b_0 = 4kT \ln R/9F \qquad (8)$$

$\Delta b$ is then related to a parameter, $S^{20}$ from which the barrier height is calculated as

$$V = \frac{9SF}{4} \qquad (9)$$

Following this procedure a barrier height of 3205 cal/mole is obtained from the intensity measurement. From eq. 8 the fractional error in $\Delta b$ is given by the fractional error in R divided by ln R. The uncertainty in S corresponding to a given uncertainty in $\Delta b$ depends on the magnitude of $\Delta b$ and can be obtained by inspection of the referenced tables. In this case a 2% error in R results in a 3.2% error in $V_3$. The barrier measured

is therefore 3205 ± 105 cal/mole in excellent agreement with
the 3180 cal/mole, value obtained from the splitting measurements.

Internal Barrier in Propylene Oxide: The barrier to methyl group
rotation in propylene oxide has been determined from splitting
measurements to be 2560 ± 70 cal/mole.[21] Relative intensity
measurements were made of the $O_{00}$-$1_{11}$ transition in which the
ground state line at 23,975.20 Mc is split unresolvably by 0.1 Mc.
Applying the approrpiate correction factor given by Verdier
indicates that the observed intensity of the line must be divided
by 1.97 and not by 2 before comparing it to the intensity of
the A or E line of the first excited state. These two lines,
at 23,955.64 Mc and 23,960.29 Mc respectively, are separated by
4.7 Mc which causes the measured intensity of either to be too
high by 0.5% due to the presence of the other. Additional cor-
rections totaling 2% had to be made for the presence of another
neighboring line and a Stark lobe. Thirteen measurements of the
ratio gave a corrected value of 2355 calories. Due to the weakness
of the lines and the consequent difficulty in determination of
the base-lines, the uncertainty in the ratio is estimated to be
4%. This leads to an uncertainty of 8.5% or 200 cal/mole in the
barrier.

Isotope Ratio in Methyl Formate: A sample of C-13 enriched methyl
formate was prepared and the ratio of the C-12 to the C-13 species
in the mixture was determined from a measurement of the relative
intensities of lines due to the same transition in each of the two
species. The lines studied are given in Table 1.

Although the $1_{01}-2_{02}$ lines are split due to the internal barrier of the methyl group, no correction was necessary since the splitting is almost identical for both isotopic species. Thus, for the ratio of E line intensities which was determined, the additive effect of the A lines is the same for both. A similar situation prevails for the $1_{11}-2_{12}$ transition where the transitions are unresolvably but equally split (0.4 Mc).

An average of six measurements of the $c^{12}/c^{13}$ ratio from the $1_{01}-2_{02}$ transition gave a value of 0.635 with 2.8% standard deviation. The major contribution to this deviation was sample decomposition resulting in a decrease of peak height with time. Eight measurements of the $1_{11}-2_{12}$ transition gave a value of 0.636 with the same deviation. A mass spectrographic determination of the ratio was independently made by Dr. William Kirchhoff who obtained a value of 0.644 with 3% uncertainty.

Quadrupole Components in Ethyl Chloride: The relative intensities of three of the quadrupole components of the $1_{10}-2_{11}$ transition in ethyl chloride were measured(Table 2).

Nine measurements of the II/I ratio gave an average value of .492 with 1% standard deviation - 3.3% higher than the value of .509 indicated by Table 2. The discrepancy here is due to the necessity of making a large empirical correction to the measured height of Line II due to the proximity of the larger Line I. The reverse correction was much smaller and Verdier's formula could be used.

Seven measurements of the III/I ratio gave an average value of 1.91 with a standard deviation of 1.5% in agreement with the value of 1.905 obtained from Table II.

Stark Lobes in OCS: Dr. James Boggs examined saturation of the J = 1-2 line of OCS at 24,325.91 Mc. He measured the intensity ratio of the M=0 lobe to that of the M=1 lobe for which a value of 0.667 is expected. The experimental ratio was 0.664. Additionally, if the intensities of the lobes extrapolated to zero power are plotted as a function of pressure for the region in which saturation occurs, the ratio of the slopes for the M=0 and M=1 lobes depends on the relative sizes of their dipole moment matrix elements. A ratio of 0.750 is predicted and 0.759 was obtained experimentally.

Additional Measurements: Relative intensity measurements have also been applied to a study of the ring-puckering vibration in cyclopentene, the results of which are published elsewhere.[22] In addition, the application of intensity measurements to ketene and its deutero derivatives has resulted in the determination of the three lowest fundamental frequencies of these molecules and a recalculation of their thermodynamic properties.[23]

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11. A plot of reflectivity versus frequency for a waveguide containing two small reflections which absorb no power will be sinusoidal with a period equal to $V^2/2\ell v \lambda_g$ where V is the propagation velocity, $\ell$ the distance between reflections, $v$ the frequency, and $\lambda_g$ the guide wavelength.

12. In addition to the isolator positioned directly before the crystal holder, a second isolator was placed immediately ahead of the tapered transition leading to the absorption cell to minimize any interaction between reflectors within the cell and possible reflectors, such as the attenuators, wavemeter, and "TEE", which are before it.

13. A Daven Co. Model No. T-256-E step attenuator was used, providing a total of 38 db attenuation in 2 db steps. In choosing a particular unit, care should be taken to match the attenuator's impedance to that of the preamplifier and detector. Additionally, the attenuator should have a negligible amount of phase shift throughout its range, since this would appear as a change in amplitude under phase-sensitive detection.

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16. This procedure was suggested by Mr. Langdon Hedrick of the Tektronix Company. Using a toroid 2 in. in diameter (Ferroxcube No. 400T750) it was possible to wind 15 turns using small diameter coaxial cable. The inductance of this assembly was measured to be 425 $\mu$H corresponding to a resistance of 270 ohms at our modulation frequency of 100 kc.

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Table 1.  Methyl formate transitions[a]
(Frequencies in Mc)

| Transition | $HC^{12}OOCH_3$ | $HC^{13}OOCH_3$ | Int. Ratio |
|---|---|---|---|
| $1_{01}-2_{02}$ | 24,298.40 A | 24,115.85 A | |
| | 24,296.60 E | 24,114.02 E | 0.635 |
| $1_{11}-2_{12}$ | 22,827.91 A,E | 22,653.03 A,E | 0.636 |
| | | Mass spectral value: | 0.644 |

[a] R. F. Curl, Jr., J. Chem. Phys. 30, 1529 (1956).

Table 2. Quadrupole components in ethyl chloride[a]

| Line | F-F' | Frequency (Mc) | Relative Intensity (Theory) | (obs) |
|------|------|----------------|-----------------------------|-------|
| I | 3/2-5/2 | 21,433.90 | 1 | 1 |
| II | 3/2-3/2 | 21,436.33 | .509 | .492 |
| III | 5/2-7/2 | 21,466.23 | 1.905 | 1.91 |

[a] R. S. Wagner and B. P. Dailey, J. Chem. Phys. 26, 1588 (1957). Values of relative intensities are taken from C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Company, New York, 1955, App. I.

Fig. 1. Reflection
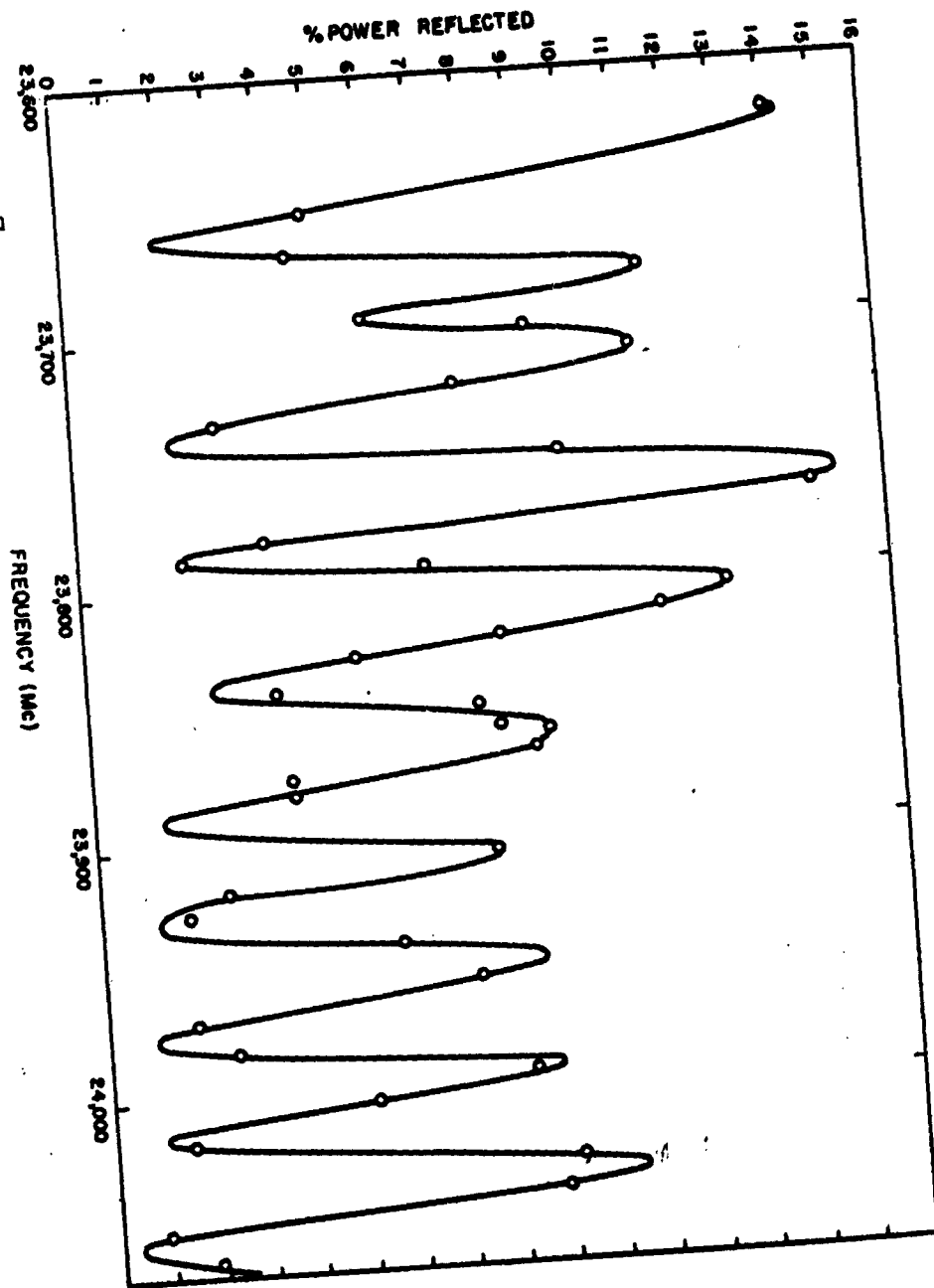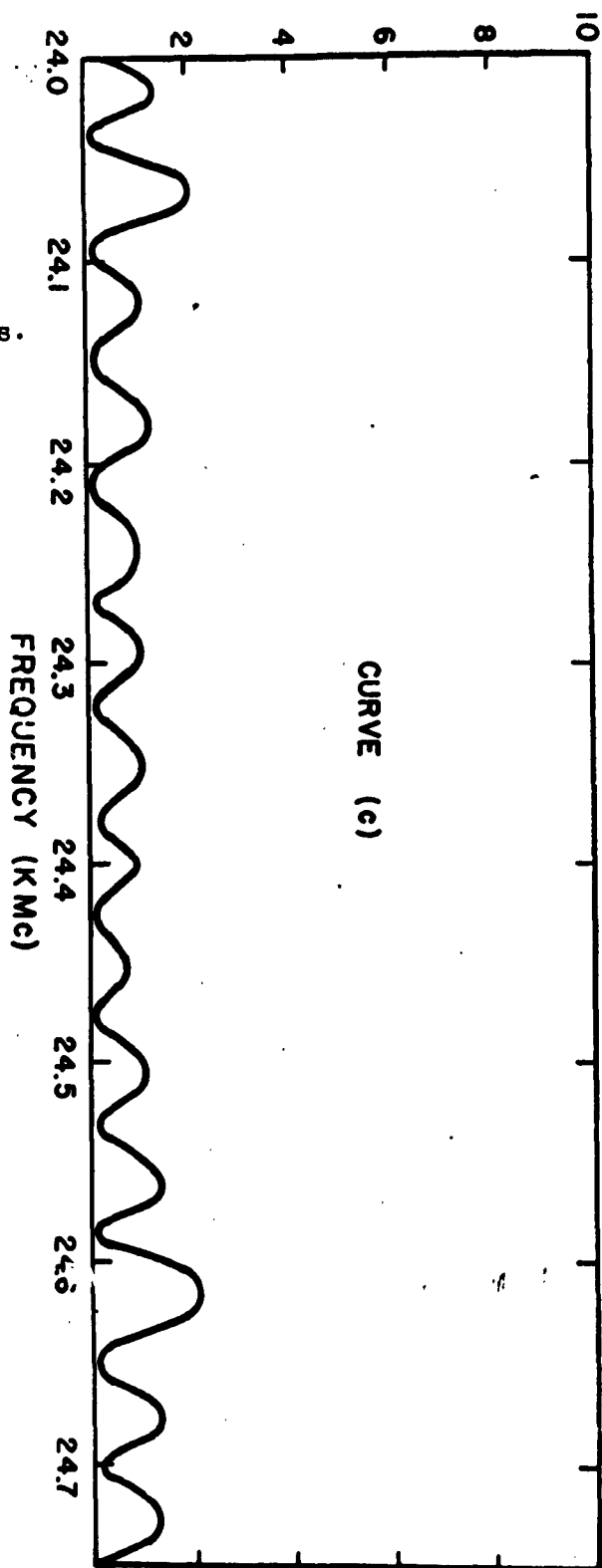characteristics
of waveguide
system before
modification.

Fig. 2. Reflection
characteristics of
modified waveguide
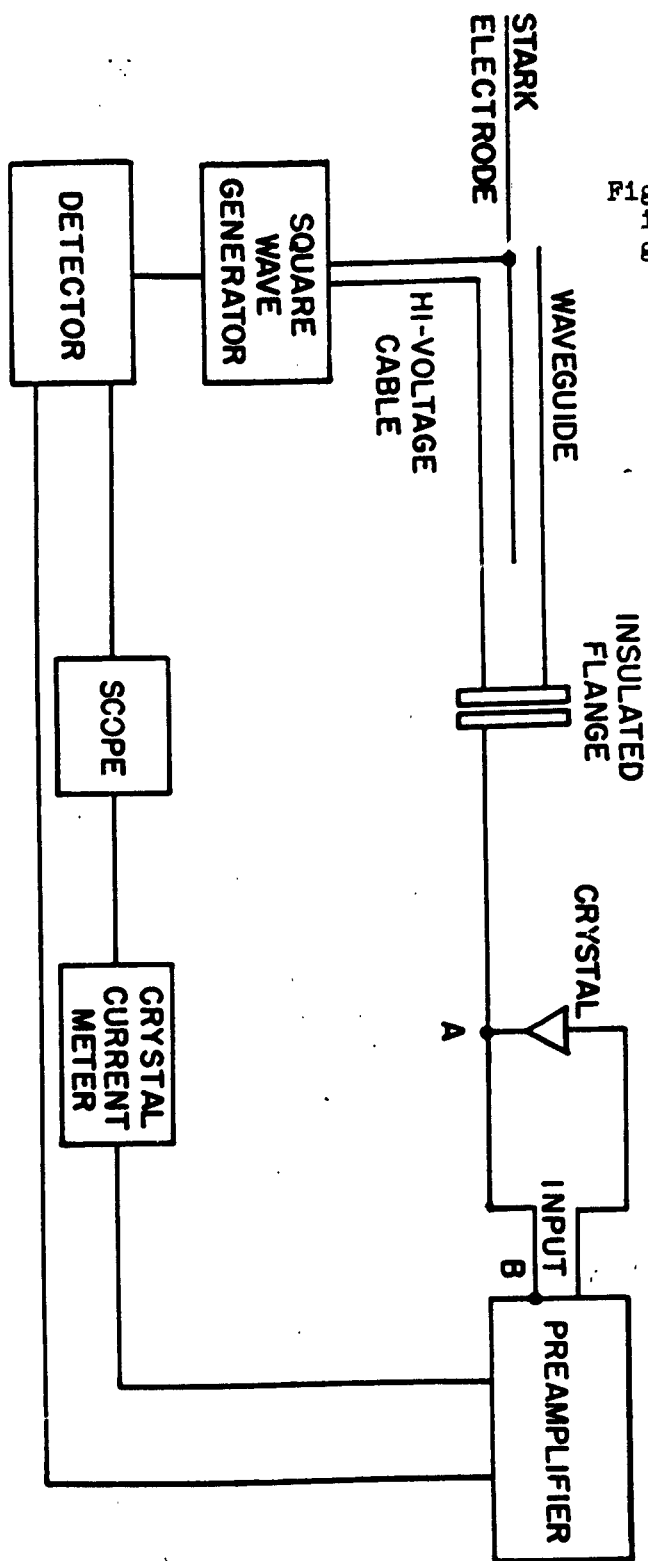system with isolators.

CURVE (c)

FREQUENCY (KMc)

Fig. 3. Components involved in pickup ground loop.

Fig. 4. Equivalent circuit
of ground loop of
Fig. 3.