NASA CR-967

A STUDY OF TRACE CONTAMINANT IDENTIFICATION BY MICROWAVE DOUBLE RESONANCE SPECTROSCOPY

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Prepared under Contract No. NAS 1-6308 by
RESEARCH SYSTEMS INC.
Lexington, Mass.

for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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TABLE OF CONTENTS

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SUMMARY

A microwave double resonance spectrometer has been assembled. It operates with pump frequencies between 12 GHz and 18 GHz and signal frequencies between 26.5 GHz and 40 GHz. The absorption cell consists of a coiled 100' section of X-band guide. Modulation of the double resonance phenomenon is achieved through frequency modulation of the pump radiation, the modulation frequency being 100 KHz.

For each of the five molecules ($CH_3CH_2COH_1$) $CH_3CH_2CH_2Cl$, CH_3CH_2COOH, $(CH_3)_2S$, and CH_2Cl_2 one or two double resonance connections were selected and suitable for the identification of these compounds. The amplitude of the double resonance signals has been studied as a function of the sample pressure for both pure samples and samples diluted in air. In typical cases double resonance signals can be observed in the pressure range from 1 μHg to ∼ 100 μHg. The smallest detectable amount of a gas contaminant was found to be of the order of ∼ .3%.

In mixtures of several gases with rich microwave spectra the double resonance technique affords a rapid and extremely specific method for identifying individual components. There is no ambiguity on account of interference from neighboring and/or overlapping lines with only one double resonance connection required to identify the compound from which it arises.

INTRODUCTION

Acknowledgements

Research Systems, Inc. would like to acknowledge gratefully the following people who made significant contributions to the conception, design and testing of the microwave double resonance system for contaminant identification described in this report: John D. Baldeschwicler,* Avigdor M. Ronn, Claude Woods III, and John Rigden.

The Double Resonance Technique

Microwave spectroscopy came into its own with the development of the Stark-modulated spectrometer by Hughes and Wilson in 1947.(1) Since that time the microwave spectra of many molecules have been studied.

In microwave spectroscopy, radiation is passed through a waveguide cell which contains the gaseous molecule of interest. At microwave frequencies equal to the separation of molecular rotational energy levels, microwave power is absorbed. Absorption frequencies are characteristic of the structure of the molecule.

The sensitivity of the absorption detection is enhanced in the Stark-modulated spectrometer by the introduction of an alternating electric field applied transverse to the direction of the propagating microwave power. The alternating electric field perturbs the molecules through the Stark effect. Thus, the microwave power absorbed by the gas is modulated at the frequency of the applied alternating electric field. Lock-in detection at this frequency provides considerable improvement in signal-to-noise over direct absorption detection.

The microwave double-resonance spectroscopy, radiation of two frequencies is passed simultaneously through the gaseous sample under investigation. Let

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us assume that the molecule being studied possesses rotational energy levels E_1, E_2, and E_3. (See Fig. 1) If there are nonvanishing dipole-moment matrix elements between states 1 and 2 and between states 2 and 3, transitions will occur at frequencies given by $f_1 = 1/h\ (E_2 - E_1)$ and $f_2 = 1/h\ (E_3 - E_2)$. Double quantum transitions can occur if the intensity of either f_1 of f_2 (or both f_1 and f_2) is high enough to produce appreciable power saturation.

A double-resonance microwave technique has been investigated(2,4) which detects double quantum transitions. Such a technique involves two microwave sources operating at frequencies f_1 and f_2. One source, say f_1, is operated at a high power level to give saturation, while f_2 is operated at the usual spectroscopic low power level. After passing through the gaseous sample, f_1 and f_2 are separated by a filtering system which prevents f_1 from reaching the crystal detector.

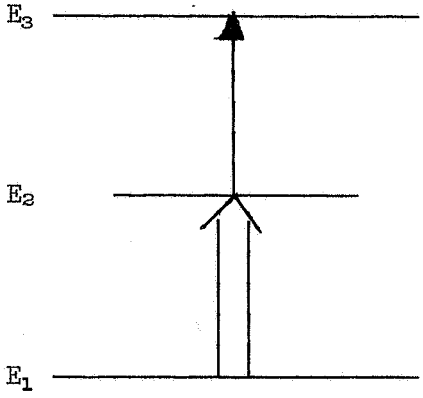


Fig. 1

Two modulation schemes have been used - Stark modulation(3) and source modulation.(2,4) The details of the Stark modulation technique is essentially the same as in a conventional Stark modulated spectrometer and will not be discussed further. In the source modulated system, a low amplitude square wave voltage at a frequency f_m is applied to the high power microwave source at f_1. This modulation reaches the crystal detector only through the double resonance phenomenon. Any single resonance absorption at f_2 is unmodulated and is not observed. Any single resonance absorption at f_1 is modulated but is stopped short of the crystal detector by the filter and hence is not observed. However, the double resonance events are modulated via f_1 and affect the detector via f_2 and are observed.

Lock-in detection at the modulation frequency f_m provides a very sensitive means of detecting microwave absorption. The output of a phase-locked detector is displayed on an oscilloscope or recorder as a function of the frequency f_2.

The double resonance microwave technique employing source modulation has some distinct advantages over the conventional Stark spectroscopic techniques. Chief among these advantages are:

1. The selectivity of the double resonance technique is such that one observed absorption is sufficient to identify a molecule unambiguously.
2. The double resonance spectrometer eliminates the necessity of a high powered square wave generator and the Stark absorption cell.

Proposed Research

The purpose of the research proposal submitted to NASA by Research Systems Inc. was the development and investigation of double resonance microwave spectroscopy as a possible means of contaminant detection. The proposed research consisted of three parts:

1. The development and construction of a double resonance microwave spectrometer.
2. The determination of the optimal experimental conditions for observing double resonance transitions occurring in both pure samples and mixtures.
3. The evaluation of double resonance spectroscopy as a method for contaminant detection.

The proposed double resonance spectrometer was to operate with two microwave sweep oscillatores - one in the R-band (26.5 - 40 GHz.) and one in the P-band (12.5 - 18.0 GHz.). Direct readout at the R-band frequencies was to be provided with an electronic counter. A special sample cell was to be designed and constructed from at least 50' of coiled waveguide.

Five gaseous compounds selected by NASA were to be studied both as pure gases and as mixtures. The samples chosen for analysis were chloropropane, dimethyl sulfide, methylene chloride, propionaldehyde, and propionic acid. A deeper analysis of particular gases were to be made under varying values of such parameters as pressure, temperature, concentration, and microwave power. A comparison of selective portions of data were to be made with data obtained on a conventional Stark modulated spectrometer.

With these findings, an evaluation of the double resonance technique was to be made. The results of the investigation, along with the evaluation, were to be included in a final report.

RESEARCH

Theory

This section is intended to elucidate the fundamental aspects of double resonance spectroscopy and to provide some insight into the origin of the characteristic double resonance line shape. The latter is of particular importance to the experimental results of this research. Therefore, the line shape will be discussed as a function of the gas pressure and pump power. The findings will be compared with the corresponding results for Stark modulation, which are briefly reformulated in Appendix.

The treatment given here is based mainly on the paper by Javan(6) and book by Townes and Schwalow,(5) to which the reader is referred for further details.

Double resonance modulated microwave spectrometer. - In general double resonance modulated microwave spectroscopy makes use of two radiation fields.

$$E = E_0 \cos \omega t$$

$$E' = E'_0 \cos \omega' t$$

impinging upon a gas. For all cases of interest to us $E'_0 >> E_0$ and $|\omega' - \omega|$ is a "large" number. That is, one radiation field is of very high power while the second is much weaker, and the frequencies of the two radiation fields are not close (generally they differ by 1-20 GHz). The field E is called the observing (low power) field and the field E' is generally referred to as the pump field. We are immediately faced with a serious problem in describing our line shape as a function of ω. This is because we may have an infinite number of values of ω' for each ω. Such a situation can be readily handled with a computer(7,8) but we will simplify matters here by limiting ω' to a single discrete value. Then we will investigate the shape of the double resonance signal, as ω, E_0, E'_0 and the sample gas pressure are varied for a fixed ω'. This will give us the general functional dependence of the signal for one value of ω', and this is approximately the dependence of all ω'.

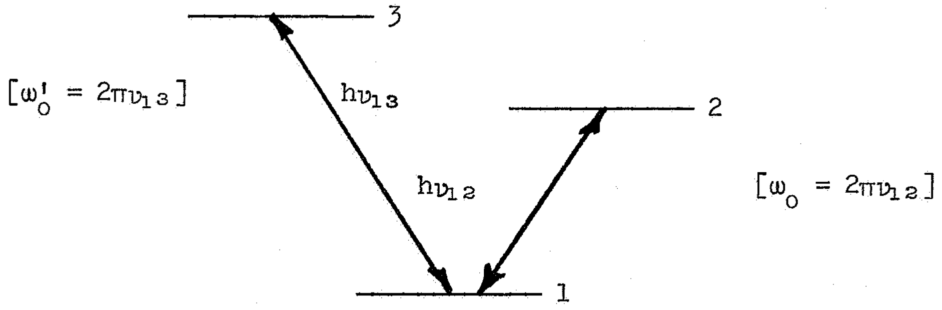
The general idea of microwave double resonance spectroscopy can probably best be stated in the following simple terms:

1. A strong (high power) radiation field E' is used to modulate a molecule gaseous sample.

2. The modulation produced by (1) causes small but readily detectable changes in the absorption of radiation from a second weak field E by the same gaseous system.
3. The signal detected in double resonance spectroscopy consists essentially of the power absorbed from the field E.
4. The field E' (high power) is <u>never</u> directly observed.

Our approach will be to consider first the general assumptions which enter the theory and which depend upon the properties of our molecular system. Second, we will write down an expression for the power absorbed from the radiation field E. Third, we will derive an expression for the signal observed with the spectrometer. The signal depends on the power absorbed from E in a somewhat complex way. Finally, we will consider the pressure and power dependence of the signal observed.

<u>General description of theoretical considerations</u>. - We now assume that we have a gas of molecules with only three quantum states 1, 2, and 3 separated in energy by $(En)_{12} = h\nu_{12}$, $(En)_{13} = h\nu_{13}$, and $(En)_{23} = h\nu_{23}$. Again we take the average lifetime of a molecule to be the same in all three of these states and equal to τ, where τ is the mean time between collisions of the molecules. A diagram of the energy level scheme is given below:



It is not at all obvious that the relative positions of the levels (for example $1 < 2, 3$; $2 < 3$) do not affect the observed signals. However, for the properties considered here the relative positions are not important and the above scheme has been chosen to correspond to reference 6.

The following quantities are defined most of which are anologous to the terms used in describing the ordinary Stark Spectrometer:

n_1, n_2, n_3	the number of molecules per cm^3 in states 1, 2, 3 for the gas at thermal equilibrium
$\omega_0 = 2\pi\nu_{12}$	the resonance frequency of transition 1 → 2
$\omega_0' = 2\pi\nu_{13}$	the resonance frequency of transition 1 → 3
$\mu_{12} =$	dipole moment of the molecular system for the transition from state 1 to 2
$\mu_{13} =$	dipole moment of the molecular system for the transition from state 1 to 3
$E = E_0 \cos \omega t$	weak radiation field with frequency ω near ω_0
$E' = E_0' \cos \omega' t$	strong radiation field with frequency ω' near ω_0'

As before the quantities $\mu_{12}\, E_0/2\hbar$ and $\mu_{13}\, E_0'/2\hbar$ appear frequently so we define

$$x = \mu_{12}\, E_0/2\hbar$$

$$y = \mu_{13}\, E_0'/2\hbar$$

Furthermore it is assumed that

$$|\mu_{12}\, E_0/2\hbar|^2\, \tau^2 \ll 1$$

$$|\mu_{13}\, E_0'/2\hbar|^2\, \tau^2 \gg 1$$

Thus the field E_0' is large enough to "saturate" the 1-3 transition, the field E_0 does not saturate the 1-2 transition.

Power absorbed from the weak field E. - At this point we could write down an expression for the power absorbed from the weak field E at frequency ω by the gas. As mentioned earlier the power absorbed from the strong field E' is never measured and therefore does not concern us directly. The power of the pump field E' does, however, affect the shape of the power absorption curve for the field E (weak field) and thus is of importance indirectly. In essence we wish to know what the power absorption at ω is in the presence of strong power absorption at ω' which occurs simultaneously but is not measured. Shortly we will write a very lengthy formula giving P_ω (absorbed); however, first we give some qualitative arguments about the physical phenomena which occur in the gaseous system.

For weak radiation fields it is generally true that only single quantum transitions can take place in a molecular system due to absorption of radiation. Thus a molecule can absorb a photon from field E and go from state 1 to 2 or absorb a photon from field E' and go from state 1 to 3. Usually (although not always) if the 1-2 and 1-3 transitions are allowed, the direct 2-3 transition is forbidden due to symmetry considerations. However, in the presence of a very large field at E' and a weaker field at E it is possible for a molecule in state 3 to simultaneously emit a photon into the field E' and absorb one from the field E in a single step. If energy level 3 were lower in energy than level one, a direct transition from 3 to 2 would involve absorption of a photon from both fields. Thus the molecule is said to have made a two quantum jump from state 3 to 2 via state 1. We see now that power absorbed from the field E in such a situation will consist of two separate terms. First, power is absorbed from E by molecules in state 1 making a direct single quantum transition from state 1 to 2. Second, power is absorbed from E by molecules in state 3 making an indirect two quantum transition from state 3 to 2. We may write

$$\begin{aligned} P_\omega \text{ (absorbed)} &= P_\omega \text{ (double quantum)} \\ &\quad + P_\omega \text{ (single quantum)} \end{aligned}$$

It turns out that this somewhat simplified physical picture is a reasonably good description of the actual situation.

In order to simplify the following discussion we make one further assumption by restricting the frequency ω' of the pumping field to the single value $\omega' = \omega'_o$. Thus the pumping field is directly on the 1-3 resonance transition at ω'_o and

$$E' = E'_o \cos \omega'_o t$$

We now write an expression for the power absorbed at the frequency ω by the molecular system from the radiation field $E = E_o \cos \omega t$. At the risk of over-emphasis, we again point out that the power absorbed at frequency $\omega' = \omega'_o$ from E' does not concern us in a microwave double resonance experiment.

$$P_\omega \text{ (absorbed)} = P_\omega \text{ (double quantum)} + P_\omega \text{ (single quantum)}$$

$$P_\omega \text{ (double quantum)} = (n_3 - n_2)\, h\nu_{12} \left|\frac{\mu_{12} E_o}{2h}\right|^2 \tau$$
$$\left\{ \frac{1}{2\left[1 + \left(\omega - \omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right)^2 \tau^2\right]} + \frac{1}{2\left[1 + \left(-\omega + \omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right)^2 \tau^2\right]} \right\}$$

$$P_\omega \text{ (single quantum)} = (n_1 - n_2)\, h\nu_{12} \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau$$
$$\left\{ \frac{1}{2\left[1 + \left(\omega - \omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right)^2 \tau^2\right]} + \frac{1}{2\left[1 + \left(-\omega + \omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right)^2 \tau^2\right]} \right\}$$

$$P_\omega \text{ (absorbed)} = \left[\tfrac{1}{2}(n_1 + n_3) - n_2\right] h\nu_{12} \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau$$
$$\left\{ \frac{1}{1 + \left[\omega - \omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2} + \frac{1}{1 + \left[\omega_o - \omega + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2} \right\}$$

In deriving this expression certain terms considered by Javan (reference 6) and called "Interference Terms" have been neglected. This does not lead to any serious problem provided $|\mu_{13} E_o'/2\hbar|^2 \tau^2 \gg 1$.

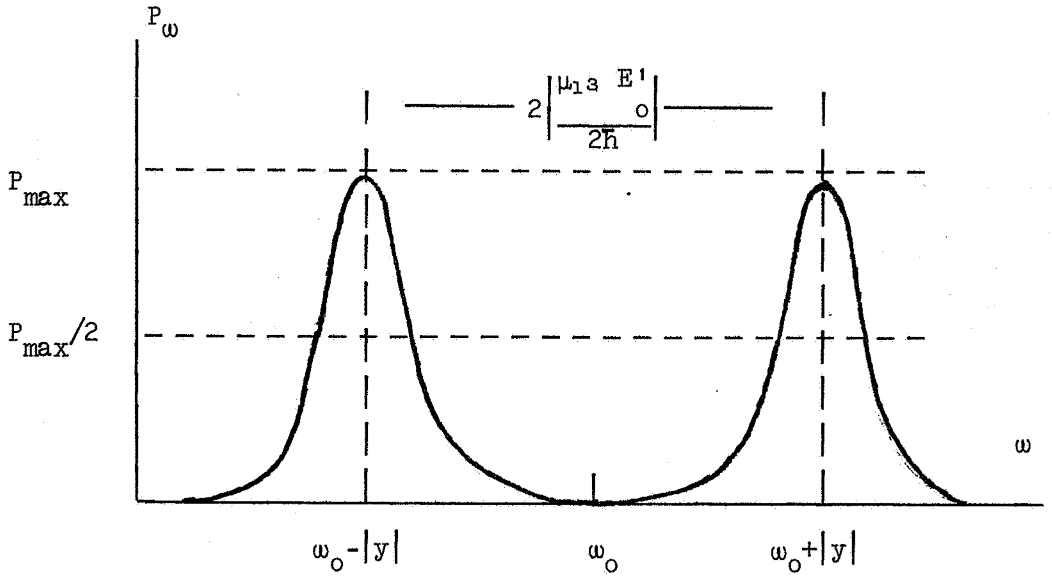
Let us now consider some of the characteristics of the expression for power absorbed in a double resonance experiment.

1. The absorbed power has two maxima:

$$\omega = \omega_o + |\mu_{13} E_o'/2\hbar| = \omega_o + |y|$$

$$\omega = \omega_o - |\mu_{13} E_o'/2\hbar| = \omega_o - |y|$$

2. A plot of P_ω versus frequency has the following form:



3. The maximum height of each peak is calculated as follows:

$$P_\omega\ (\max) = P\ (\omega-\omega_o \pm y)$$

$$= [\tfrac{1}{2}(n_1 + n_3) - n_2]\ h\nu_{12} \left|\frac{\mu_{12}\,E_o}{2\hbar}\right|^2 \tau \left\{1 + \frac{1}{4\left|\frac{\mu_{13}\,E'_o}{2\hbar}\right|^2 \tau^2}\right\}$$

However, we have taken $|\mu_{13}\,E'_o/2h|^2\ \tau^2 \gg 1$ so that we may approximate:

$$P_\omega\ (\max) \cong [\tfrac{1}{2}(n_1 + n_3) - n_2]\ h\nu_{12} \left|\frac{\mu_{12}\,E_o}{2\hbar}\right|^2 \tau$$

4. The full width at half height of each peak is almost exactly $\Delta\omega_{\frac{1}{2}} = 2/\tau$ This can be proved by setting

$$\frac{1}{1 + [\omega-\omega_o + |y|]^2\ \tau^2} = \tfrac{1}{2}$$

and

$$\frac{1}{1 + [\omega - \omega_0 - |y|]^2 \, \tau^2} = \tfrac{1}{2}$$

and solving for ω. Such a derivation ignores the contribution to the linewidth of one peak from the other peak. This is in general quite small and can be neglected. A more rigorous deviation would be to set

$$P_\omega = P_{max}/2$$

and then solve for the four resulting values of ω.

5. From (3) we see that the peak intensity of a double resonance absorption depends

   a. linearly upon the power in the observing field (that is, linearly on E_0^2) and

   b. is <u>independent</u> of pressure because it depends upon the product n_1 τ which is pressure independent (see Appendix for discussion on Stark modulated spectrometer). Note, however, that this is only approximately true since it assumes $1/4|y|^2\tau^2 \ll 1$.

6. The linewidth of <u>each</u> of the two double resonance peaks increases linearly with pressure because $\Delta\omega_{\frac{1}{2}} = 2/\tau$ (see Appendix for discussion on Stark modulated spectrometer).

7. The <u>separation</u> between the two peaks in the double resonance absorption depends linearly on the square root of the power in the <u>pumping</u> field (<u>not</u> on the power in the weak or observing field). That is, the separation $2|y| = 2|\mu_{13}E'_0/2\hbar|$ depends on E'_0.

We may now compare the characteristics for the power absorbed in the single and double resonance cases:

1. The single resonance power absorbed shows a single peak of width $\Delta\omega_{\frac{1}{2}} = 2/\tau$ while the double resonance power absorbed shows two peaks of width $\Delta\omega_{\frac{1}{2}} = 2/\tau$.

2. The <u>maximum</u> peak height for both single and double resonance power absorptions is pressure independent, while the linewidths in both cases are linearly related to pressure.

3. The peak height for both single and double resonance power absorptions increases linearly with the power in the observing or weak field This holds, however, only as long as $|\mu_{12} E_0/2\hbar|^2 \tau^2 \ll 1$.

Dependence of signal strength on power absorbed. - We have restricted our pump field to a single frequency ω' such that

$$E' = E'_0 \cos \omega'_0 t$$

Let us now squarewave modulate E' at 100 kc/sec so that it has the following form:

$$E' = E'_0 \cos \omega'_0 t \qquad 0 \le t < 5 \ \mu\text{sec}$$

$$E' = 0 \qquad 5 \le t \le 10 \ \mu\text{sec}$$

Such a description assumes a 100% amplitude modulation of E' at a rate of 100 k/csec. In practice the double resonance spectrometer makes use of a frequency modulation scheme such that

$$E' = E'_0 \cos \omega'_0 t \qquad 0 \le t \le 5 \ \mu\text{sec}$$

$$E' = E'_0 \cos \delta t \qquad 5 \le t \le 10 \ \mu\text{sec}$$

However, provided $|\delta - \omega'_0| \ge 10$ MHz, $E' = E'_0 \cos \delta t$ is essentially ineffectual at modulating the gaseous molecular sample because E' is too far from the resonance ω'_0 of the 1-3 transition. Thus for all practical purposes $E' = 0$, $5 \le t \le 10$ μsec as far as the gas is concerned.

In the presence of the strong pump field E', the power absorbed at frequency ω is just the double peak expression given earlier for the double resonance experiment. However, when E' = 0 the power absorbed at ω is simply that given by the ordinary expression stated in Stark modulation spectrometers. Thus we have for E' = 0

$$P_\omega = (n_1 - n_2) \frac{2\tau \left|\frac{\mu_{12} E_0}{2\hbar}\right|^2 h\nu_{12}}{1 + (\omega - \omega_0)^2 \tau^2 + 4\left|\frac{\mu_{12} E_0}{2\hbar}\right|^2 \tau^2}$$

Using this expression along with the one given earlier for the double resonance power absorption at ω, we can write down P_ω for the case where E' is modulated in the squarewave fashion described above. We obtain

$$P_\omega = [\tfrac{1}{2}(n_1 + n_3) - n_2]\, h\nu_{12} \left|\frac{\mu_{12}\, E_0}{2\hbar}\right|^2 \tau$$

$$\left\{ \frac{1}{1 + \left[\omega-\omega_0 + \left|\frac{\mu_{13}\, E'_0}{2\hbar}\right|\right]^2 \tau^2} + \frac{1}{1 + \left[\omega-\omega_0 - \left|\frac{\mu_{13}\, E'_0}{2\hbar}\right]^2 \tau^2} \right\}$$

for $0 \leq t < 5$ μsec

$$P_\omega = (n_1 - n_2) \frac{2\tau \left|\frac{\mu_{12}\, E_0}{2\hbar}\right|^2 h\nu_{12}}{1 + (\omega-\omega_0)^2 \tau^2}$$

for 5 μsec $\leq t < 10$ μsec

with the assumptions

$E' = E'_0 \cos \omega_0 t$ $\qquad$ $0 \leq t < 5$ μsec

$E' = 0$ $\qquad$ 5 μsec $\leq t <$ μsec

$$4\left|\frac{\mu_{12}\, E_0}{2\hbar}\right|^2 \tau^2 \ll 1 .$$

To simplify the following discussion let us define

$P_\omega \equiv P_\omega$ (DR) $\qquad$ $0 \leq t < 5$ μsec

$P_\omega \equiv P_\omega$ (SR) $\qquad$ $5 \leq t < 10$ μsec

Note that both P_ω (DR) and P_ω (SR) are independent of time (τ is a constant depending on the temperature, pressure, etc.) even though P_ω is not.

The power absorbed in a double resonance spectrometer where the strong field is modulated as above is therefore a squarewave. In order to determine the signal observed by the spectrometer, we must analyze this squarewave into its Fourier components. This is because the electronics used in a double resonance (or a Stark) spectrometer are not sufficiently broadbanded to pass the entire squarewave undistorted. It is well known that a squarewave has only odd harmonics of the basic (100 kc/sec) component, a 300 kc/sec component, a 500 kc/sec component, etc. We will assume that the amplifiers used reject all but the 100 kc/sec component so that we need obtain only the 100 kc/sec part of the Fourier Transform.

Fourier transform of power absorbed. - We have

$$P_\omega = P_\omega \text{ (DR)} \qquad 0 \leq t < 5$$

$$P_\omega = P_\omega \text{ (SR)} \qquad 5 \leq t < 10$$

Let us change variables of time from t to $\bar{x}$ where

$$\bar{x} = \pi t/5$$

giving

$$P_\omega (\bar{x}) = \begin{cases} P_\omega \text{ (DR)} & -\pi \leq \bar{x} < 0 \\ P_\omega \text{ (SR)} & 0 < \bar{x} < \pi \end{cases}$$

The Fourier series of $P_\omega (\bar{x})$ may be written

$$P_\omega (\bar{x}) = a_o/2 + \sum_{n=1}^{\infty} (a_n \cos n\bar{x} + b_n \sin n\bar{x})$$

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} P_\omega (\bar{x}) \cos n\bar{x} \, d\bar{x}$$

$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} P_\omega (\bar{x}) \sin n\bar{x} \, d\bar{x}$$

By direct substitution it can readily be shown that

$$a_o = P_\omega (DR) + P_\omega (SR)$$

$$b_o = 0$$

$$a_1 = 2/\pi \, (P_\omega (SR) - P_\omega (DR))$$

$$b_1 = 0$$

Since we are assuming the electronics of our spectrometer to reject all harmonics higher than the first one. The signal seen on the double resonance apparatus is just proportional to $P_\omega (\bar{x})$ where

$$P_\omega (\bar{x}) = a_o/2 + a_1 \cos \bar{x}$$

or

$$P_\omega \left(\frac{\pi t}{5}\right) = \tfrac{1}{2} (P_\omega (SR) + P_\omega (DR)) + \frac{2}{\pi} (P_\omega (SR) - P_\omega (DR)) \cos \frac{\pi t}{5}$$

with t in microseconds. The term $\frac{1}{2} (P_\omega (SR) + P_\omega (SR))$ merely appears as a constant D.C. level on the spectrometer and can be neglected for ordinary capacitively coupled amplifiers. We are thus left with a double resonance signal

$$S_\omega \text{ (double resonance)} \sim \frac{2}{\pi} (P_\omega (SR) - P_\omega (DR)) \cos \frac{\pi t}{5} .$$

The signal S_ω amplified by the electronics of a double resonance modulated microwave spectrometer is therefore a 100 kc/sec cosine wave whose amplitude is just proportional to

$$P_\omega\,(SR) - P_\omega\,(DR)\ .$$

If phase sensitive detection locked to the 100 kc/sec modulation frequency is used after the amplifiers, the signal S_ω is proportional only to the signed amplitude of $\cos \pi t/5$. That is

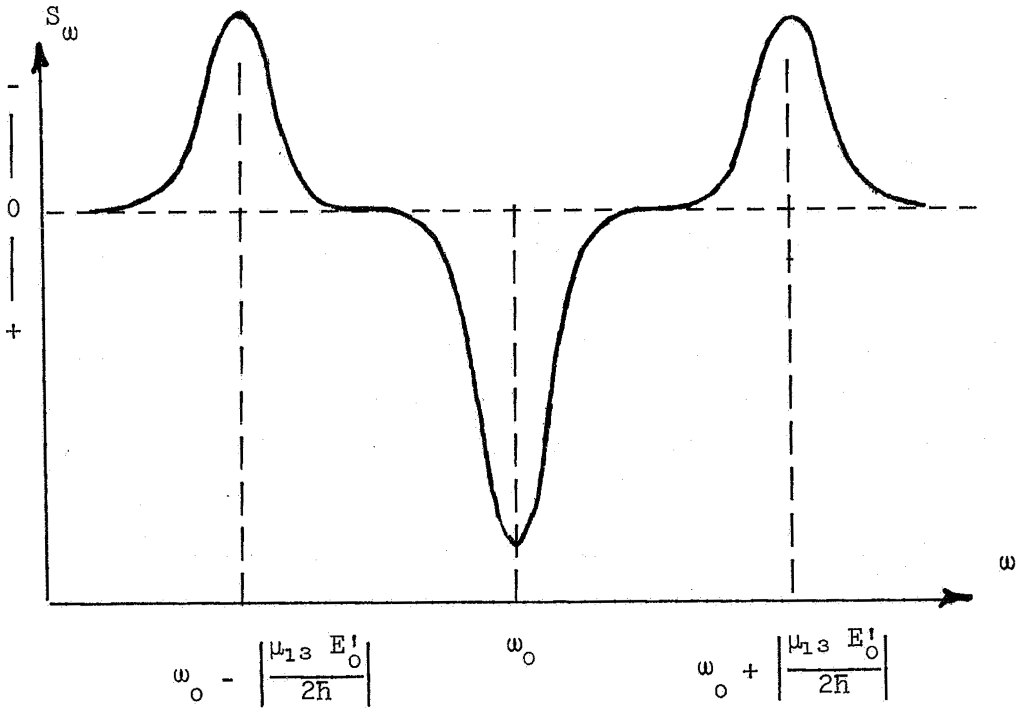
$$S_\omega \sim P_\omega\,(SR) - P_\omega\,(DR)\ .$$

The word signed is important for a phase detector preserves information concerning whether $P_\omega\,(SR) - P_\omega\,(DR)$ is positive or negative.

General line shape. - We have shown

$$S_\omega \sim P_\omega\,(SR) - P_\omega\,(DR)\ .$$

For both $P_\omega\,(SR)$ and $P_\omega\,(DR)$ positive (which is generally, though not always true) S_ω has the following shape:



We note that the line shape is just the superposition of two separate curves of opposite sign. One is a double peaked curve ($-P_\omega$ (DR)) and the other is a single peak curve ($+ P_\omega$ (SR)). The analytic form for S_ω is given by:

$$S_\omega \sim P_\omega\,(SR) - P_\omega\,(DR) = (n_1 - n_2)\,\frac{2\tau\left|\dfrac{\mu_{12} E_o}{2\hbar}\right|^2 h\nu_{12}}{1 + (\omega-\omega_o)^2\,\tau^2}$$

$$- \left[\tfrac{1}{2}\,(n_1 + n_3) - n_2\right] h\nu_{12}\left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau \left\{\frac{1}{1 + \left[\omega-\omega_o + \left|\dfrac{\mu_{13} E'_o}{2\hbar}\right|\right]^2 \tau^2} + \frac{1}{1 + \left[\omega-\omega_o - \left|\dfrac{\mu_{13} E'_o}{2\hbar}\right|\right]^2 \tau^2}\right\}$$

Power and pressure dependence of S_ω. - Now that an expression has been derived for S_ω in the case of a double resonance modulated microwave spectrometer it is possible to consider the pressure and power dependence of this line shape. Let us rewrite S_ω as

$$S_\omega \sim h\nu_{12}\left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau \left\{\frac{2\,(n_1 - n_2)}{1 + (\omega-\omega_o)^2\,\tau^2} - \frac{\left[\tfrac{1}{2}\,(n_1 + n_3) - n_2\right]}{1 + \left[\omega-\omega_o + \left|\dfrac{\mu_{13} E'_o}{2\hbar}\right|\right]^2 \tau^2} - \frac{\left[\tfrac{1}{2}\,(n_1 + n_3) - n_2\right]}{1 + \left[\omega-\omega_o - \left|\dfrac{\mu_{13} E'_o}{2\hbar}\right|\right]^2 \tau^2}\right\}$$

Furthermore, let us make the rather drastic assumption $\frac{1}{2}\,(n_1 + n_3) \simeq n_1$. This will simplify the following discussion somewhat and should not affect the general trend of the results which are obtained. In this case S_ω becomes

$$S_\omega \sim h\nu_{12} \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau \, (n_1 - n_2) \left\{ \frac{2}{1 + (\omega-\omega_o)^2 \tau^2} - \frac{1}{1 + \left[\omega-\omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2} - \frac{1}{1 + \left[\omega-\omega_o - \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2} \right\}$$

Let us first consider the term outside of the brackets

$$h\nu_{12} \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 \tau \, (n_1 - n_2) \ .$$

This term has the following properties:

1. It depends linearly on the power in the observing field (i.e., depends linearly on E_o^2); however, note we always assume $\mu_{12} E_o/2\hbar \ll 1$.
2. It is <u>independent</u> of pressure because $\tau \, (n_1 - n_2)$ is independent of pressure (see earlier discussion).

Finally we consider the properties of the bracket term

$$\frac{2}{1 + (\omega-\omega_o)^2 \tau^2} - \frac{1}{1 + \left[\omega-\omega_o + \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2} - \frac{1}{1 + \left[\omega-\omega_o - \left|\frac{\mu_{13} E_o'}{2\hbar}\right|\right]^2 \tau^2}$$

1. It consists of three peaks with maxima occurring at:

$$\omega = \omega_o - \left|\frac{\mu_{13} E_o}{2\hbar}\right|$$

$$\omega = \omega_o$$

$$\omega = \omega_o + \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|$$

2. The width of each peak at half maximum is $\Delta\omega_{\frac{1}{2}} = 2/\tau$ and is thus linearly dependent upon pressure ($p = c/\tau$ where c is a constant).
3. The peak heights of each of the three peaks is most emphatically not pressure independent. This result is the most important one which has been derived and is the most drastic departure from the results obtained for single resonance Stark spectrometers. Let us, therefore, consider this in more detail. The maximum amplitudes for each of the three peaks are readily seen to be:

For $\omega = \omega_o - \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|$

$$P_1 \equiv \frac{2}{1 + \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2} - 1 - \frac{1}{1 + 4\left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2}$$

For $\omega = \omega_o$

$$P_2 \equiv 2\left(1 - \frac{1}{1 + \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2}\right)$$

For $\omega = \omega_o + \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|$

$$P_3 \equiv \frac{2}{1 + \left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2} - \frac{1}{1 + 4\left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2} - 1$$

Note $P_1 = P_3$. We see now that each peak height depends upon the parameter

$$\left|\frac{\mu_{13}\, E'_o}{2\hbar}\right|^2 \tau^2$$

which is essentially a measure of the amount of saturation achieved at the pumping (or high power) frequency $\omega' = \omega_o'$. Furthermore, this parameter is a linear function of the power in the pumping field (depends upon $E_o'^2$); however, since $\tau = c/p$, $|\mu_{13}\, E_o'/2\hbar|^2\, \tau^2$ depends upon the square of one over the pressure (1/p). Thus, if p is double, τ is halved and $|\mu_{13}\, E_o'/2\hbar|^2\, \tau^2$ is divided by four.

In order to get a practical feeling for the effect of pressure and power on the peak heights let us consider the behavior of these peak heights for typical pressures, fields, and μ_{13} 's. We take

$$\mu_{13} = 0.7 \text{ Debye} = 0.7 \times 10^{-18} \text{ esu-cm}$$

$$\tau = 5 \times 10^{-7} \text{ sec } (p \simeq 10\mu \text{ of Hg})$$

$$2\hbar = 2.1 \times 10^{-27} \text{ erg-sec}$$

$$E_o' = 5.7 \text{ volts/cm}$$

This E_o' corresponds to a power level of 100 millivolts in a cross-sectional area of 2.32 cm² (X-Band waveguide). The power P and field E_o' are related through the equation

$$P = \frac{c}{8\pi}\, \frac{(E_o')^2}{A}$$

where c is the velocity of light and A is the cross-sectional area for propagation of the field (see reference 1, pp. 340, 377). All units are c.g.s. Using the relations

1 erg = 1 stat coulomb-stat volt
1 stat coulomb/cm - 1 stat volt
1 stat volt - 300 volts

it can easily be shown that

$E_o' = 8.7 \times 10^{-3}\, \sqrt{P/A}$
P in ergs/sec
A in cm²
1 milliwatt = 10^{-3} joules = 10^4 ergs

The values chosen for τ and μ_{13} are typical empirical values found in the microwave range by use of standard Stark modulation spectroscopy.

Define:

$$\delta = |\mu_{13}\ E_o'/2\hbar|^2\ \tau^2$$

Using the values above for μ_{13}, τ, etc. we get

$$\delta = \frac{(0.7 \times 100^{-18})^2 \left(\frac{5.7}{300}\right)^2 (5 \times 10^{-7})^2}{(2.1 \times 10^{-27})^2}$$

or $\delta \simeq 10$, for Power = 100 milliwatts.

As shown earlier, the peak heights for the double resonance line shape are:

$$\text{For } \omega = \omega_o \pm |\mu_{13}\ E_o'/2h| :$$

$$P_1 = P_3 = 2/(1+\delta) - 1/(1+4\delta) - 1 .$$

$$\text{For } \omega = \omega_o :$$

$$P_2 = 2\ (1 - 1/1 + \delta) .$$

Thus:

$$P_1 = 2/11 - 1/41 - 1 = -0.84$$

$$P_2 = 2\ (1 - 1/11) = 1.82$$

Thus we have values for P_1 and P_2 for a pressure of 10 μ of Hg ($\tau = 5 \times 10^{-7}$ sec) and a pumping radiation field of 100 milliwatts. Using the exact same procedure as above, we can readily calculate values for δ as the pressure is changed and thus get values for P_1, P_2 with E_o' a constant. The following tables give P_1, P_2, δ versus pressure for $E_o' = 5.7$ v/cm (Power of 100 milliwatts).

TABLE I. - DEPENDENCE OF PEAK HEIGHT ON PRESSURE AND CONSTANT POWER

Pressure (μ of Hg)	δ	P_1	P_2	Power (milliwatts)
10	10	-0.84	1.82	100
20	2.5	-0.52	1.42	100
40	0.63	-0.03	0.76	100

It is not particularly valid to carry this Table to values of δ much less than 1 because much of the preceding treatment depends upon the approximation:

$$\delta = \left| \frac{\mu_{13}\, E'_0}{2\hbar} \right|^2 \tau^2 \gg 1 \ .$$

The trend of the results, however, is quite clear: The peak *heights* of the double resonance signals decrease (in a *roughly* linear fashion) with increasing pressure. This is *in addition to* the broadening which also occurs for these peaks since $\Delta\omega_{\frac{1}{2}} = 2\tau$. Thus for double resonance modulated microwave spectroscopy we find that the *linewidth* increases linearly with increasing pressure and the *peak height* decreases with pressure. This is in contrast to the Stark modulated spectrometer where the *linewidth* increased linearly with increasing pressure but the *peak height* was independent of pressure.

To offset the decrease in peak height with increasing pressure, the power in the pumping field can be increased as the pressure is increased. In Table II are given the values of power needed to keep δ = 10 as the pressure is increased.

TABLE II. - DEPENDENCE OF PEAK HEIGHT WITH INCREASING PRESSURE AND PUMP POWER

Pressure (μ of Hg)	-δ	Peak Height		Power (milliwatts)
		P_1	P_2	
10	10	-0.84	1.82	100
20	10	-0.84	1.82	400
40	10	-0.84	1.82	1600

We note immediately that a drastic increase in power is necessary to offset the effect of increasing pressure on the peak height. It is important to note that the widths of the three peaks still increase linearly with pressure even if the power of the pumping field is increased. There is apparently no way to offset this pressure broadening phenomenon.

It is of some interest to ask why the peak height of a double resonance signal depends upon pressure when in fact no such problem arises for a Stark modulated spectrometer. The answer turns out to be quite simple. In a Stark spectrometer the modulation scheme is one where an alternating (zero based) electric field is applied to a molecular gas. The effect on the gas is to cause the center frequency of absorption to alternate between ω_0 and $\omega_0 + \equiv$ where $\equiv$ is the Stark shift. The crucial point to note here is that $\equiv$ is in almost all cases and to a very good approximation independent of pressure. In the double resonance case the modulation scheme is one which has an effect on the gas proportional to $|\mu_{13} E_0'/2\hbar|^2 \tau^2 = \delta$. For large δ the modulation effect is great, while for small δ there is relatively little if any modulation. However, δ depends critically on the pressure due to the presence of τ^2. As pressure increases τ decreases and thus the modulation decreases. Such a situation is analogous to the case in a Stark modulated spectrometer where the Stark shift $\equiv$ is very small because the molecule under study has a small dipole moment. In this case the lines are said to be "incompletely" or "under" modulated. In the Stark spectrometer such an under modulation depends upon the dipole moment and is pressure independent. In the double resonance case the under modulation depends upon both the dipole moment μ_{13} and the pressure τ.

Summary on pressure broadening of a Stark modulated spectrometer. - Signal $\sim [(n_1 - n_2)\ \tau]\ 21 \times 1^2\ h\nu/1 + (\omega-\omega_0)^2\ \tau^2$. This is in the absence of saturation.

Half width: $\dfrac{1}{1 + (\omega-\omega_0)^2\ \tau^2} = \frac{1}{2}$, $(\omega-\omega_0)^2\ \tau^2 = 1$, $\omega = \omega_0 \pm \dfrac{1}{\tau}$.

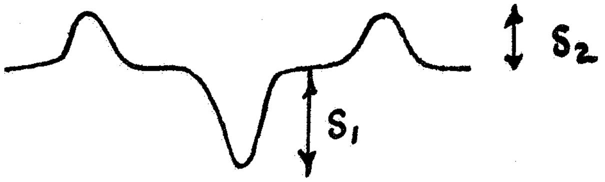
Full width at half height: $\Delta\omega = 2/\tau$. τ, the lifetime, is inversely proportional to pressure. If double pressure, τ goes down by a factor of 2.

Result:

1. Maximum signal height is independent of pressure.
2. Line width is directly proportional to pressure.

Double resonance modulated spectrometer. - Assume the two pump frequencies in the square wave are ω_1' and ω_2'. For simplicity take $\omega_1' = \omega_0'$ (resonance frequency of the pump) but $|\omega_2' - \omega_0'| \gg 1$.

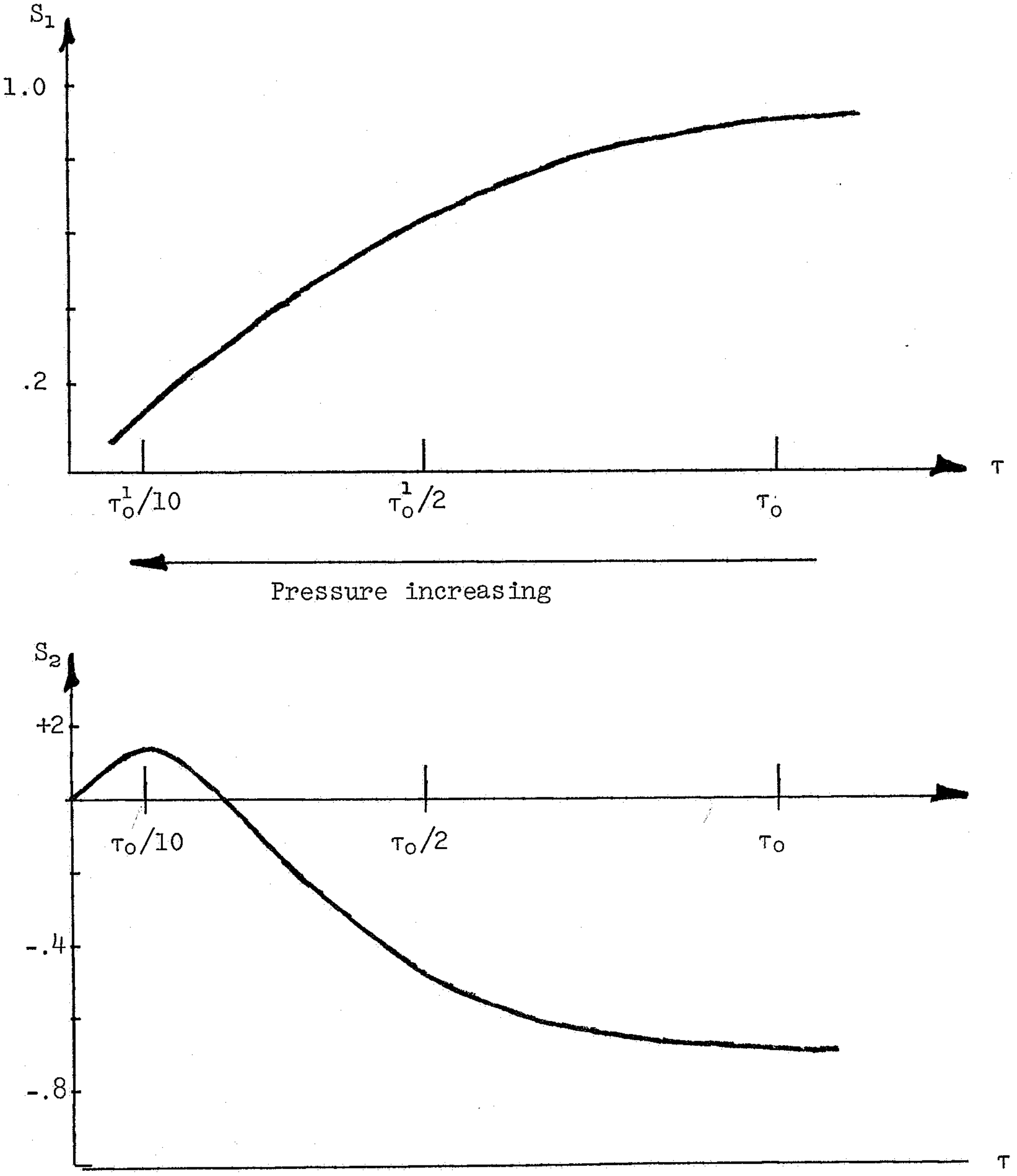
In this case the line shape is



This is for $|y|^2\ \tau^2 \gg 1$, where $y = \mu\ E_0'/2\hbar$. τ is molecule lifetime. Here E_0' is the amplitude of the pump field and the power of the pump field is

$$P_{pump} \sim (E_0')^2$$

1. The full width at half height for all three peaks is $2/\tau$. Thus the line width is directly proportional to the pressure. This is the same as the ordinary Stark modulated case.
2. Take $|y|^2\ \tau_0^2 = 10$. The signal heights vary as the pressure changes because the signal heights in this case depend upon $|y|^2\ \tau^2$. The following results are approximate as we vary the pressure.



S_1 and S_2 as functions at the life time τ

Results:

1. Signal height decreases roughly linearly with increase in pressure.
2. Line width is directly proportional to pressure.
3. To offset II - 1 (decrease in signal with increased pressure) the power must be increased by a factor of 100 for every factor of 10 increase in pressure.

Instrumentation

The first objective of this contract was the fabrication of a laboratory model, source modulated double resonance microwave spectrometer. The double resonance microwave spectrometer is pictured in Fig. 2.

The design and development of the double resonance spectrometer was strongly influenced by its projected use. That is, the instrument was developed for applications to trace contaminant detection and identification. Commercially available subunits are employed in the design of the instrument whenever possible. By this method, the first test experiments were performed just four months after receipt of the contract.

The double resonance microwave spectrometer can be considered in terms of three subsystems: the microwave system, the electronic system, and the vacuum system. To facilitate the description of the instrument, each of these subsystems will be discussed individually.

Microwave system - The diagram Fig. 3 indicates the final working microwave configuration. Since the microwave system is an assembly of commercially available units no attempt to describe in detail the electronic workings of the subunits will be made.

Two microwave sources are required for a double resonance absorption. Absorption frequencies are dictated by the characteristic molecule under investigation. This has been covered in the previous sections of this report.

The first microwave source or irradiating signal frequency oscillator is a Hewlett Packard type 690A. This unit is a conventional backward wave oscillator capable of a broadband sweep covering the frequency range of 26.5 GHz to 40 GHz. For use in our experiments a recurrent Δf of approximately 30 mc/sec. at any pre-selected frequency within the 26.5 GHz to 40 GHz is generally all that is required. Although the source is capable of generating approximately 5 milliwatts of power only 2 to 3 mw are needed to produce an absorption in this range. The use of two microwave frequencies immediately indicates a double search operation which obviously suggests an extremely laborious and time-consuming procedure. Therefore, the ability to measure one of the two microwave frequencies and select a Δf sweep over this region would greatly simplify the experiments. The commercially available system for this requirement is provided by a Hewlett Packard sweep oscillator stabilization system type K03-8690.

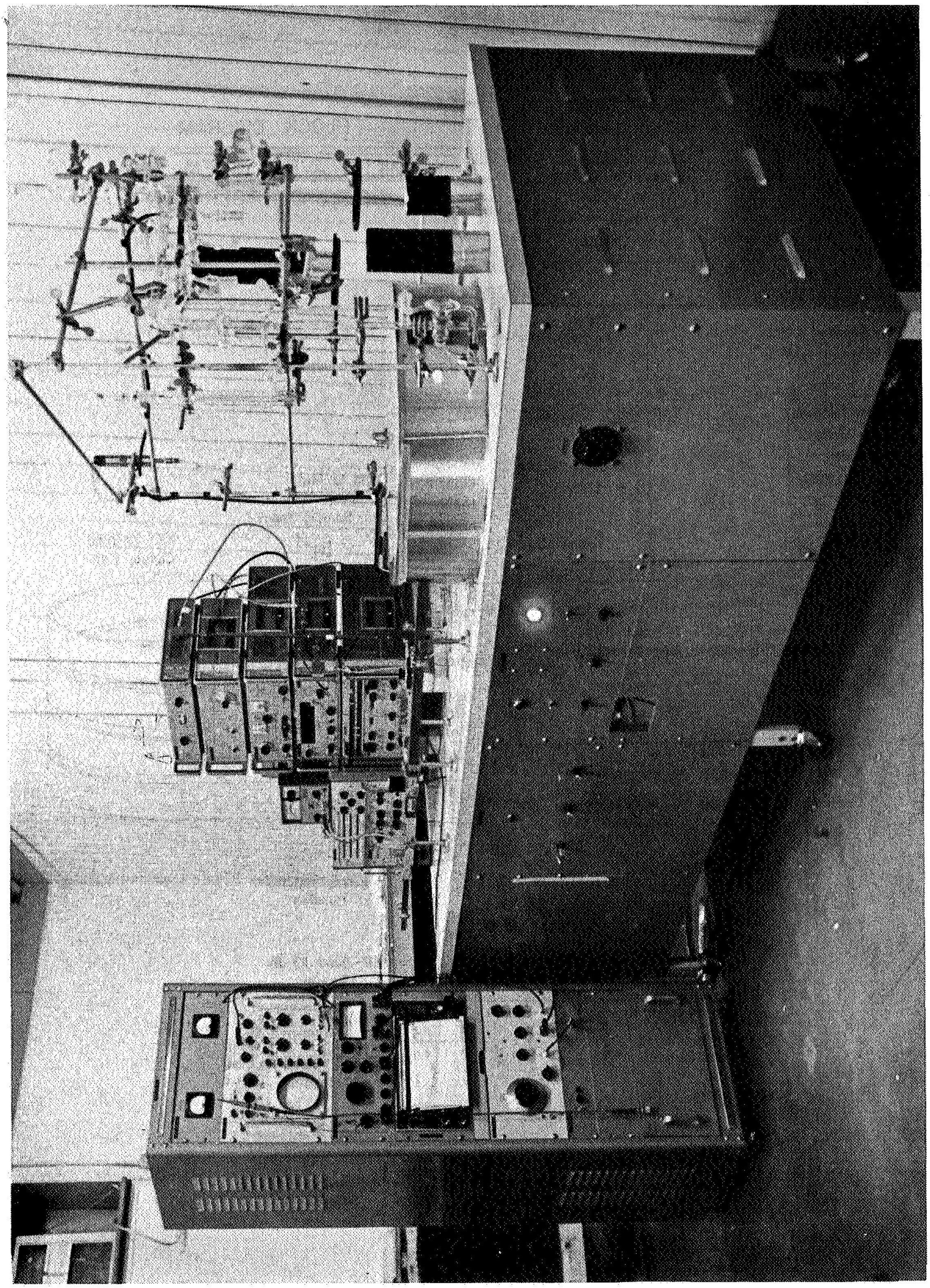
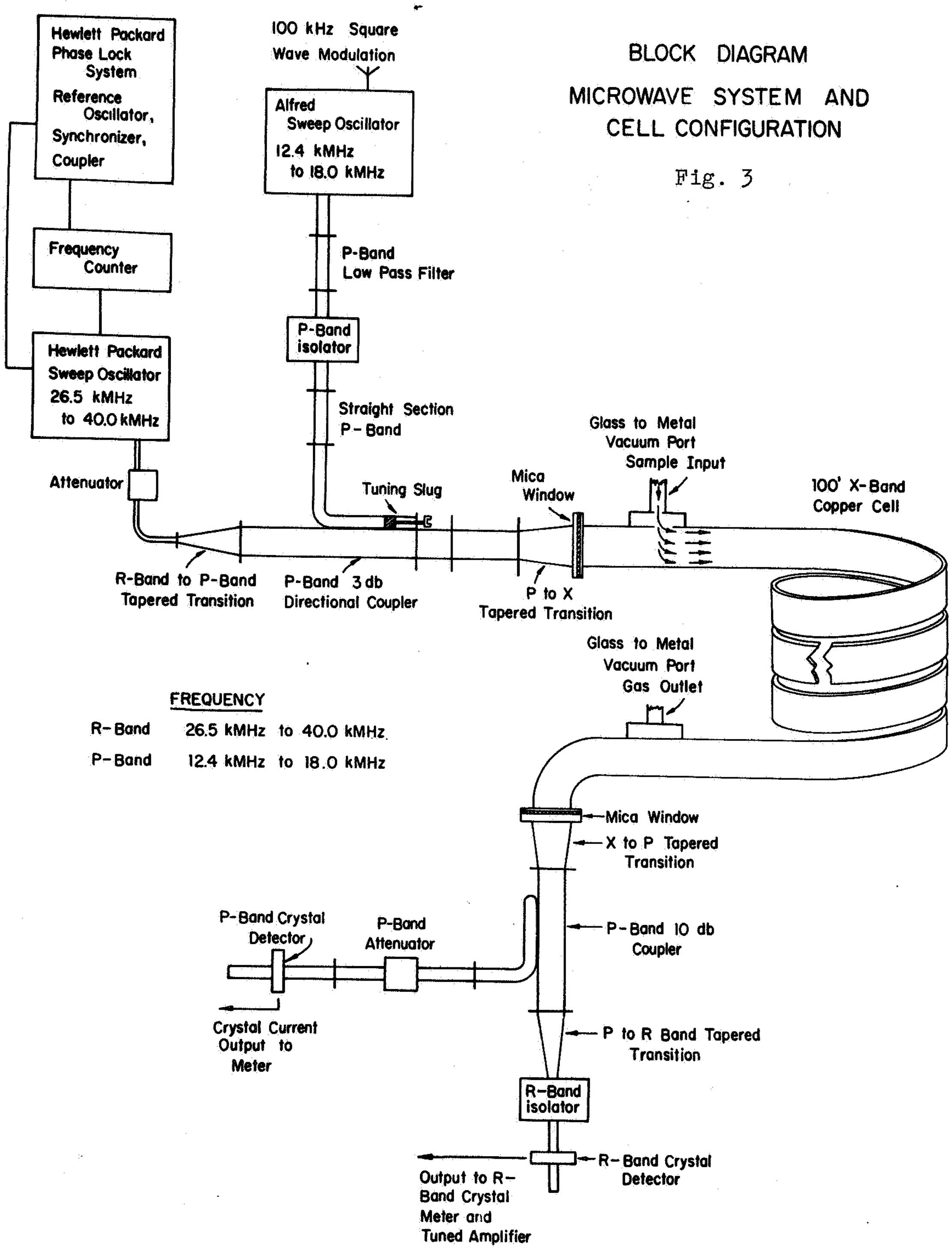


Fig. 2

Double Resonance Microwave Spectrometer



BLOCK DIAGRAM

MICROWAVE SYSTEM AND CELL CONFIGURATION

Fig. 3

This system provides the means of swept-frequency, phase locked operation in the irradiating frequency range of 26.5 GHz to 40 GHz with a direct frequency readout supplied by a modified HP 5245L counter with type 5252A prescaler, shown in Fig. 4.

The R-Band microwave phased locked system consists of the following units:

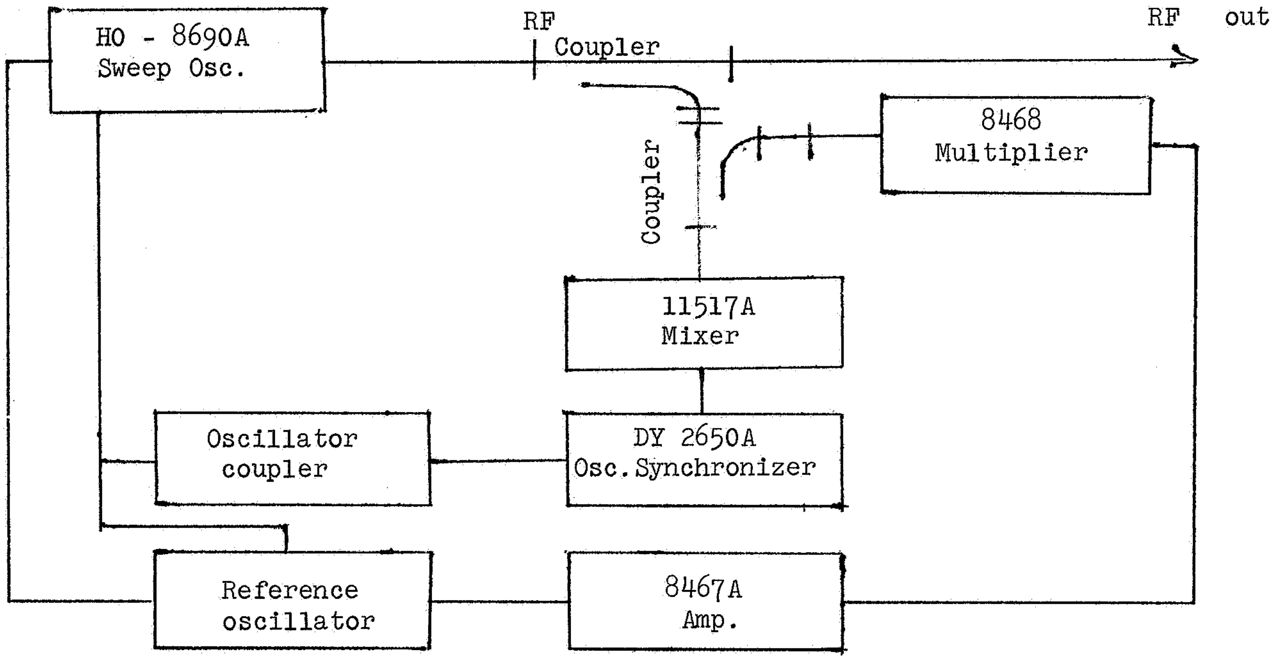


Fig. 4

The output as obtained from the R.F. source is passed through a flap attenuator for controlling the power used. An R-band to P-band tapered transition (R-band = 26.5 GHz to 40 GHz) (P-band = 12.4 GHz to 18 GHz) is next connected to a 3db P-band directional coupler. This is followed by a P - X band tapered transition separated from the 100' X-band sample cell by a mica window. The mica window permits the microwaves to pass through into the sample cell with essentially no attenuation, thus providing a method to contain the gaseous sample in the cell.

A second microwave source (in this case the pumping frequency) is supplied by an Alfred sweep oscillator type 650. This unit also contains a conventional backward wave oscillator covering the frequency range of 12.4 GHz to 18 GHz.

The reason for this selection was the versatility of this instrument. Changing the microwave regions (bands) is done by simply plugging in selected backward wave oscillators available from the manufacturer. This source provides the pump power and is frequency modulated. Frequency modulation is obtained by applying a symmetrical low voltage square wave (100kc) coupled through a phone jack in the rear of the instrument to the helix voltage of the BWO. The depth of frequency modulation is adjustable by selecting the peak to peak voltage of the applied 100kc square wave. Swept frequency capability is also provided in this unit; however, the mode of operation required for the pumping frequency is fixed frequency with maximum power. Microwaves from this unit are passed through a P-band low pass filter. This unit prevents harmonics of the pump frequency from coupling into the system. A P-band isolator is added to prevent the higher frequency (R-band) from feeding into the P-band source. From this point the signal is fed into the coupling arm of the P-band 3db coupler. The R-band and the P-band microwaves are mixed and passed into the 100' sample cell, shown in Fig. 5.

Since the directional coupler does not provide an ideal method of coupling two frequencies, reflections at discrete R-band frequencies resulted in a loss of R-band power. This was greatly reduced by substituting a brass tuning slug for the absorbing material in the coupling arm.

The microwaves after passing through the gaseous sample of interest contained in the 100' X-band cell are then coupled through a X-P-band tapered transition, P-band 10db coupler, and P-R-band tapered transition. This section rejects the P-band microwaves. Additional filtering is provided by an R-band isolator. The isolator also reduced any reflections which could be produced at this point.

Finally the R-band absorption power is detected by a crystal. A monitoring of the pump power (P-band) is achieved by sampling this frequency from the coupling arm of the P-band 10db coupler and detecting the power as received at the P-band crystal detector and measuring this power with a standard current meter.

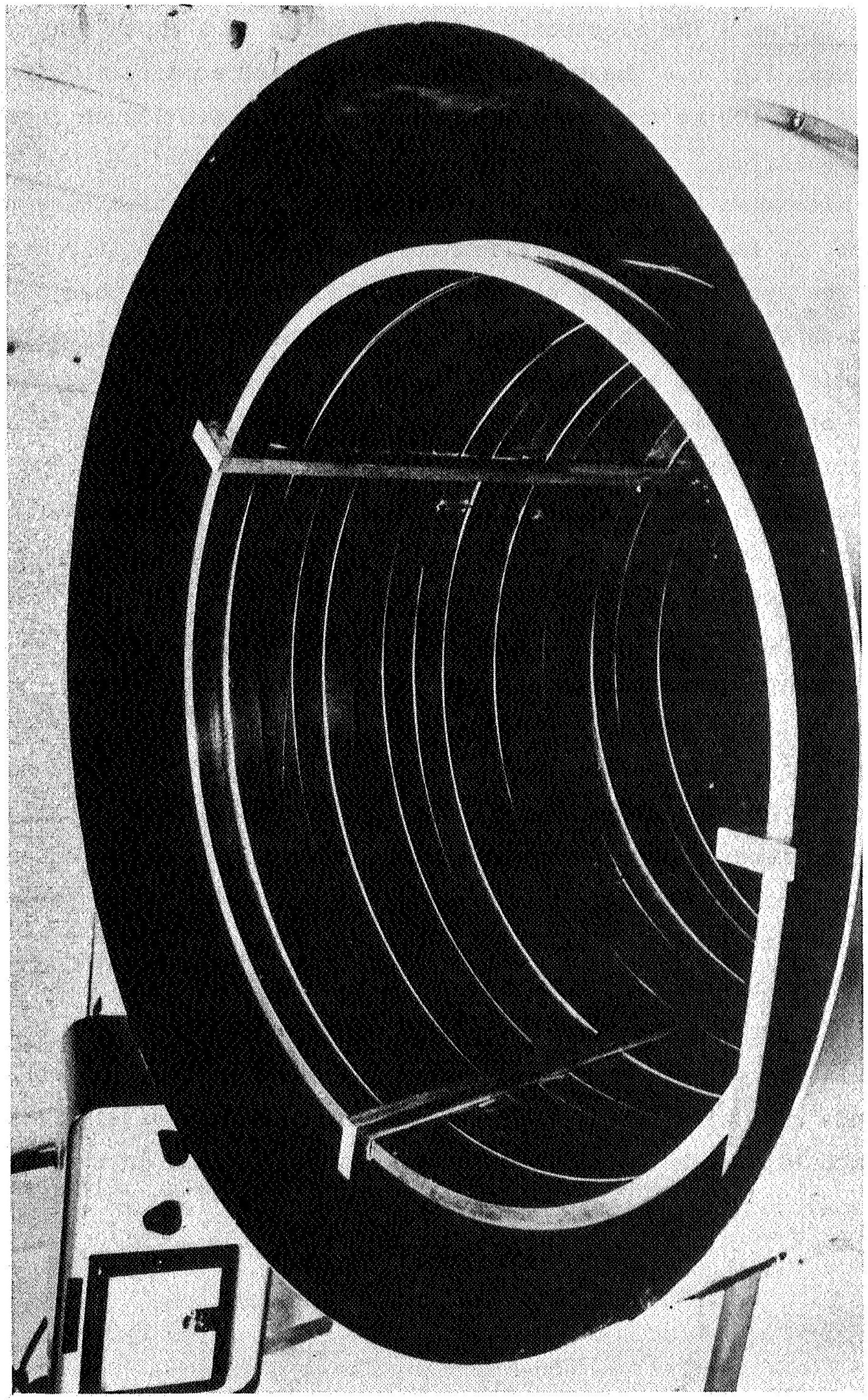


Fig. 5

100' X-Band Sample Cell

Electronic System.- The electronic system is shown in a block diagram on the following page, Fig. 6. The system is an assembly of commercial units with the exception of the 100 kc tuned network, pre-amplifier, and 100 kc crystal oscillator sync unit.

Since the microwave absorption signal received by the crystal detector is of low amplitude, it is necessary to eliminate interferences and to reduce the noise level of the system by using selective amplification. For this purpose, a network tuned to the 100 kc signal frequency is coupled to the crystal detector. This unit operates as a filter attenuating the unwanted frequencies by the Q factor of the network. The pre-amplification of the signal is performed by a specially designed unit shown in the schematic, Fig. 7. The input stage of this unit is a high gain tuned cascade amplifier. This is followed by a second tuned stage coupled to an emitter follower output for impedence matching to a lock-in detector. Provision for a (4) decade selection of the amplification factor is made by a rotary switch. The maximum gain available is greater than 10^5. The absorption signal is then passed through the Princeton lock-in detector. This unit is essentially a detection system capable of operating with an extremely narrow equivalent noise band width. Its function is to select only the 100 kc carrier [containing the absorption line as amplitude modulation] and to recover the signal after transposition to zero frequency.

Time constant filtering can be selected as either 6db or 12db per octave. The demodulated signal is then traced on a strip chart recorder.

A dual beam Tektronix oscilloscope is used to monitor the detected signal and R-band crystal current simultaneously. The reference signal (100 kc) for the phase sensitivity detection is provided by a Hewlett Packard square wave oscillator. This unit also supplies the low voltage square wave signal used for frequency modulating the P-band sweep oscillator described in Section 1 (microwave system).

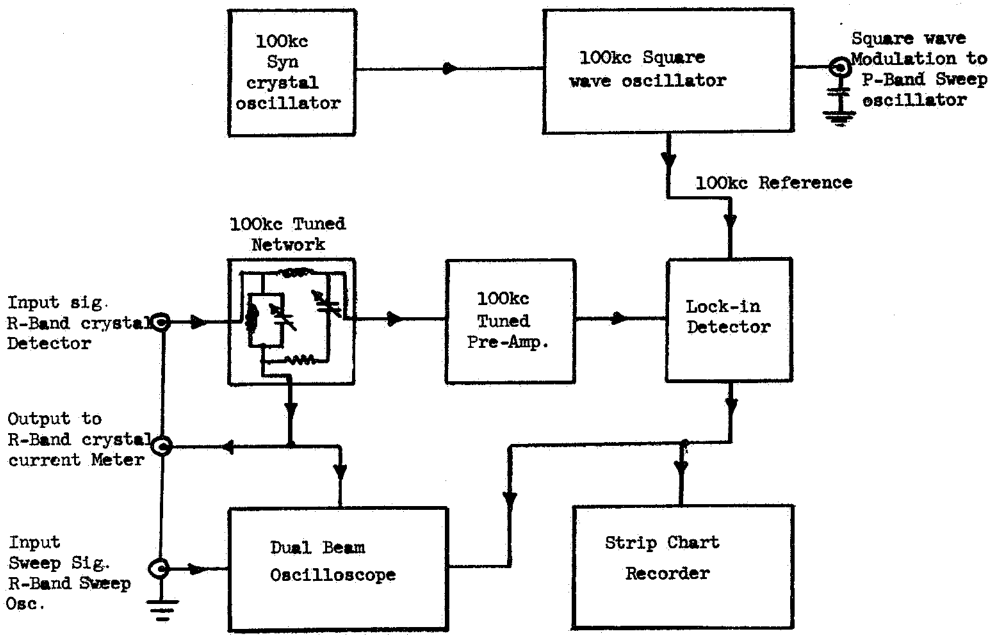
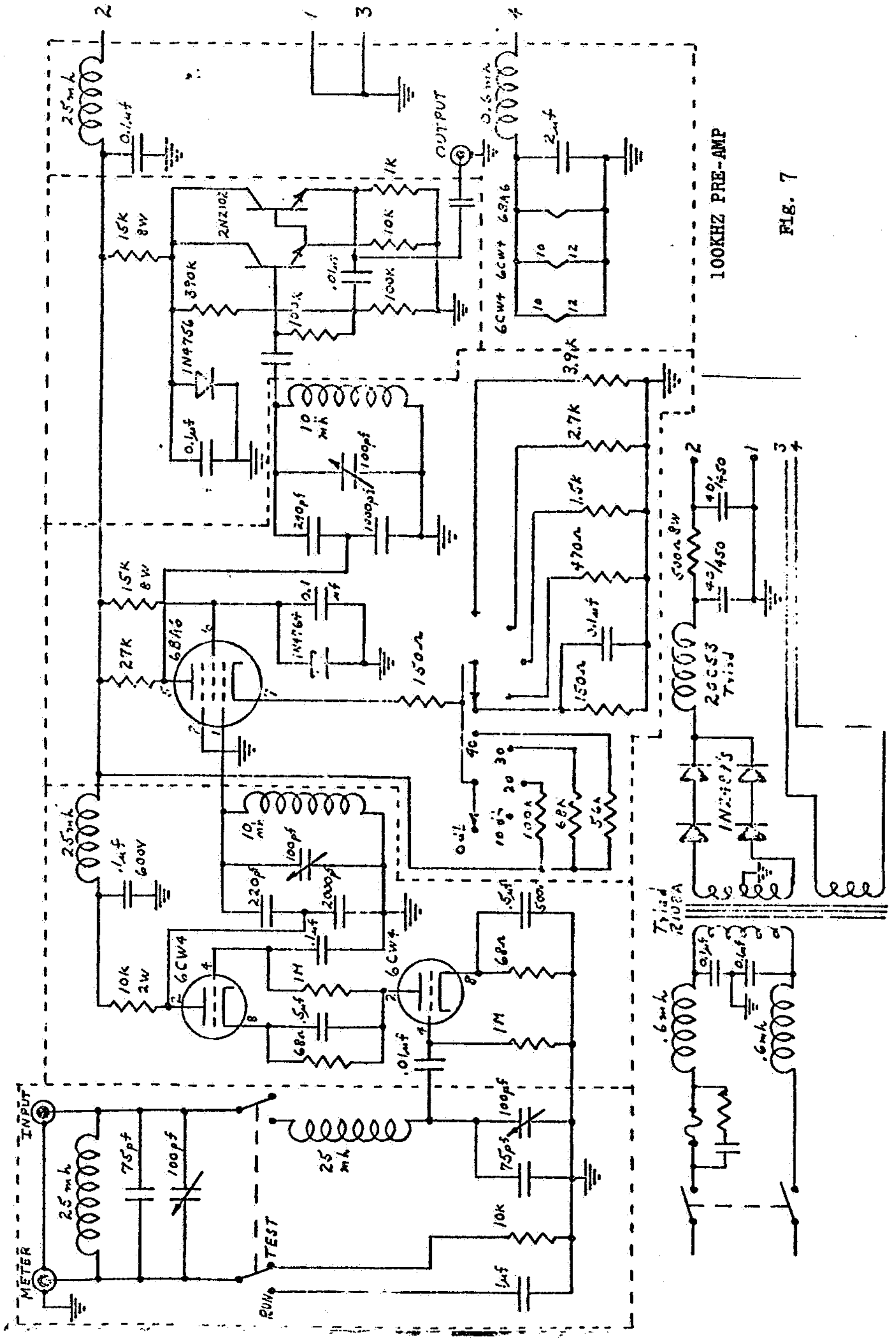


Fig. 6

Block Diagram - Electronic System



100KHZ PRE-AMP

Fig. 7

Vacuum system. - The vacuum system provides the means of evacuating the sample cell and handling the gaseous samples which were studied. The main components of the vacuum system are a fore pump, an oil diffusion pump, liquid nitrogen traps, gas entry ports, and pressure gauges. A schematic diagram of the vacuum system is shown in Fig. 8.

The demands of the vacuum system are more severe for a double resonance microwave spectrometer than for a conventional microwave spectrometer. The more stringent demands arise because of the differences in the sample cells. Part of the advantage of the double resonance technique is the increased path length through the sample that the technique allows. In the conventional microwave spectrometer, the length of the sample cell is limited to about 10 feet. This limitation is due to the additional attenuation of the Stark septum and its supporting teflon insulation.

The sample cell was fabricated from X-band waveguide and designed for this contract. This is a coil 100 feet long. Diffusion through the coiled sample cell is very slow even for large pressure gradients. If a sample is introduced at one end of the cell, several minutes are required to reach pressure equilibrium.

For these reasons, the vacuum system was designed so that the sample cell could be evacuated from each end simultaneously. Also, samples could be introduced to the cell from each end simultaneously. Pirani gauges (Model GP-001) made by Consolidated Vacuum were placed near each end of the sample cell. By monitoring the pressure at each end of the cell, it could be determined when the pressure had equilibrated.

A fore pump with high pumping speeds is mandatory. The fore pump used in this system is Model H-14 made by Central Scientific Co., Inc. and has a pumping speed of 4.94 cu.ft./min. An even higher pumping speed would be desirable. A single-stage diffusion pump provides an ultimate vacuum of 10^{-6} Torr.

The Pirani gauges are reliable over a short-time basis, but, due to aging of the filament and interaction with the gaseous samples, they should not be relied on exclusively. For relative pressure measurements, however, the Pirani gauges are very convenient. For more precise pressure measurements, a mercury pressure gauge has been incorporated into the vacuum system.

VACUUM SYSTEM
GAS HANDLING AND PRESSURE MONITORING

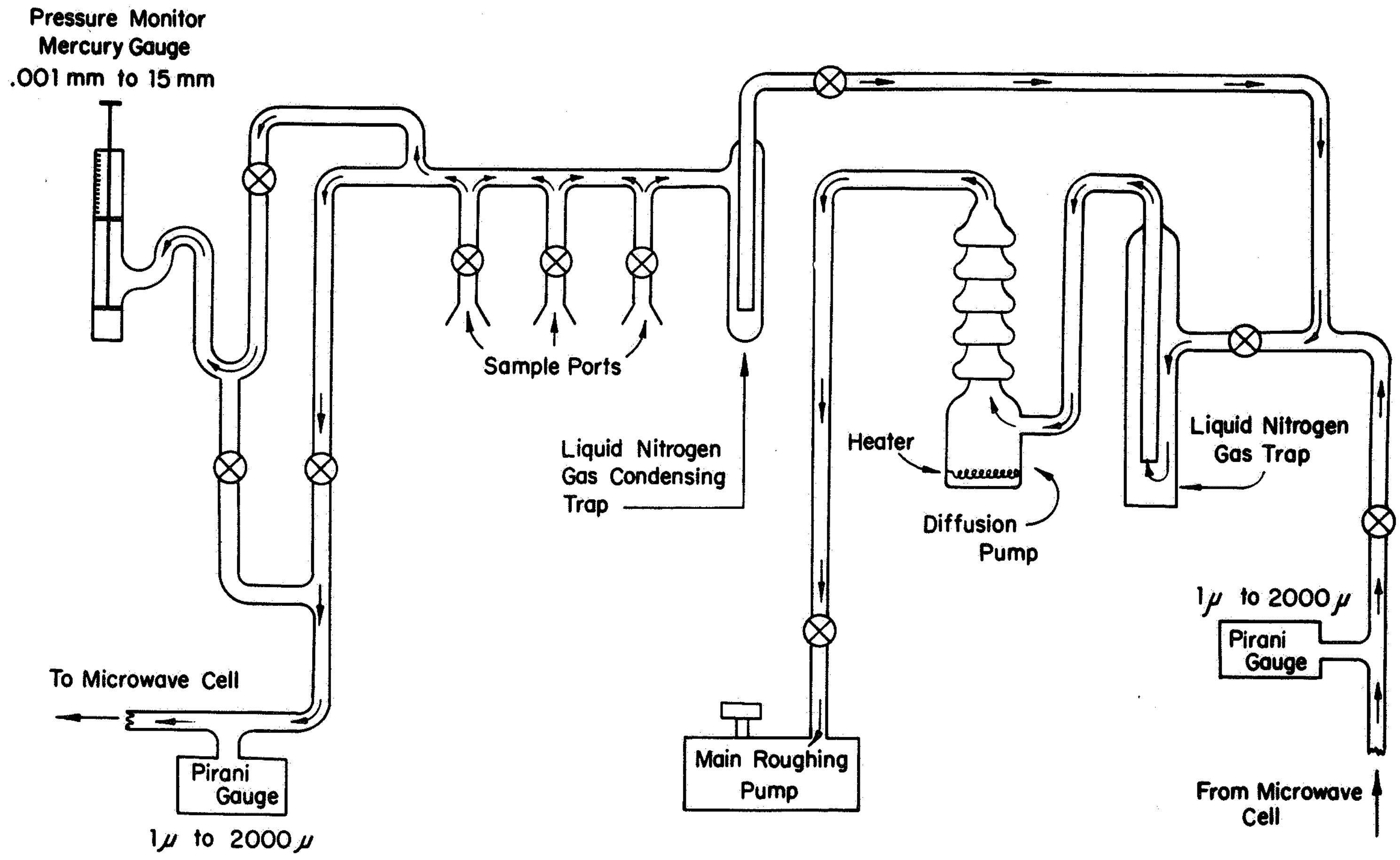


Fig. 8

Measurements

The major goal of this research effort is to determine whether the double resonance technique can be applied successfully for the identification of a gaseous compound when contained as a trace contaminant in an atmosphere or when representing a constituent of a complex mixture of gases. Clearly, before this problem can be tackled the following questions have to be answered: First: what are the pump and signal frequencies at which a double resonance is obtained for the gases in question? Second: how sensitive is the double resonance signal amplitude against pressure variations and in what pressure range can the double resonance be observed? Third: how does the double resonance signal change with temperature?

To answer these three questions the five contract molecules were first studied when present in the absorption cell as pure samples.

To obtain an estimate of the minimum detectable concentration of a gas when contained in an atmosphere, experiments were conducted on samples diluted with air. This work is described in the second section.

The third section finally reports double resonances obtained when three or four gases are simultaneously contained in the absorption cell.

In contrast to these experiments, which are concerned with data characteristic of the molecules under investigation. The last section reports on parameters inherent in the instrument: The ultimate sensitivity of the double resonance spectrometer is estimated and experimental comparisons with Stark spectra are reported. The effect of the limitation in the available pump power on the double resonance signal amplitude, and hence sensitivity, has been examined also.

The following sub-sections are concerned with basic information about the five contract molecules. Each section is headed by a short resume of general spectroscopic properties of the particular compound. This information is needed for the subsequent selection of double resonances. Besides the trivial requirement that the double resonance connections must fall within the frequency ranges of the spectrometer, the most important factors in selecting a suitable double resonance are: The intensity and shape (fine structure) of the signal line, the dipole moment matrix element of the pump line, and the microwave power available at the frequency of the pump line. The transmission properties of the waveguide system had also some influence on the selection of double resonance connections.

In studying the pressure dependence of the double resonance signal amplitude the latter was defined as the difference between the peak height of the center line and the average height of the double quantum peaks. The pressure quoted in this work were the readings taken from a commercial Pirani pressure gauge. Since the characteristics of this instrument changed frequently and somewhat uncontrollably an uncertainty of ± 20 μHg should be allowed on the absolute pressure values quoted.

Propionaldehyde.(9) - Propionaldehyde (Fig. 9) exists in two rotameric conformations which are separated from each other by an energy of ≈ 900 cal. The more stable conformation is the cis-form in which the heavy atom skeleton, C-C-C = O, is planar. The dipole moment has approximately equal components in the a and b direction of the principal axis system. (μ_a = 1.11 D, μ_b = 1.85 D, μ_c = 0, μ total = 2.52). The two dipole moment components in conjunction with the asymmetry and several low lying vibrations give rise to a very dense microwave spectrum for the cis-form.

The less stable conformation is a gauche form, in which the methyl group is rotated by ~ 130° out of the C-C = O plane. This rotation causes the moments of inertia about the b- and c- axis to become similar to each other. Hence the microwave spectrum becomes typical of a (accidentally) near prolate rotor, i.e., the spectrum consists of groups of μ_a -R-branch transitions separated from each other by ~ (B + C).

Selection of double resonances: The greater number and higher intensity of the microwave lines arising from the cis-conformation of CH_3CH_2COH suggests to use a pair of connected cis-lines for the investigations on this compound. The frequency range of our spectrometer together with consideration of the intensity of the signal line, the dipole matrix element of the pump line, and the pump power available lead to the selection of the following double resonances:

$$2_{02} \rightarrow 2_{11} = \nu_{pump} = 13474.9 \text{ MHz}$$

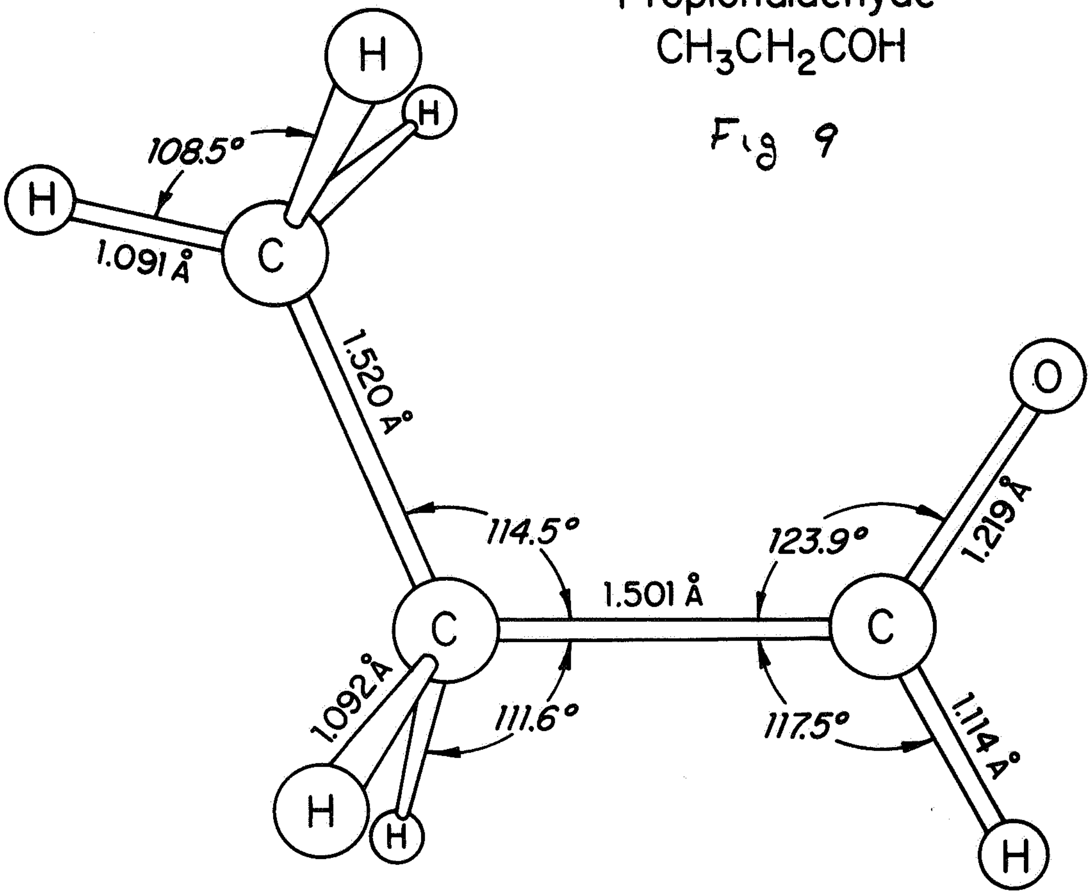
$$2_{11} \rightarrow 3_{12} = \nu_{signal} = 33347.0 \text{ MHz}$$

$$3_{03} \rightarrow 3_{12} = \nu_{pump} = 15778.6 \text{ MHz}$$

Recorder traces of the double resonance signal obtained with either of the two pump transitions are shown in Fig. 10. It can be seen from these traces, that the double resonance $\nu_p = 2_{02} \rightarrow 2_{11}$, $\nu_s = 2_{11} \rightarrow 3_{12}$ is stronger than the double resonance obtained when using the $3_{03} \rightarrow 3_{12}$ transition as pump line. This result is anomalous in so far as the $3_{03} \rightarrow 3_{12}$ transition has a higher dipole moment matrix element than the $2_{02} \rightarrow 2_{11}$ transitions. The discrepancy was explained by observing that there is much more pump power available at 13475 MHz than there is at 15779 MHz.

Propionaldehyde
CH_3CH_2COH

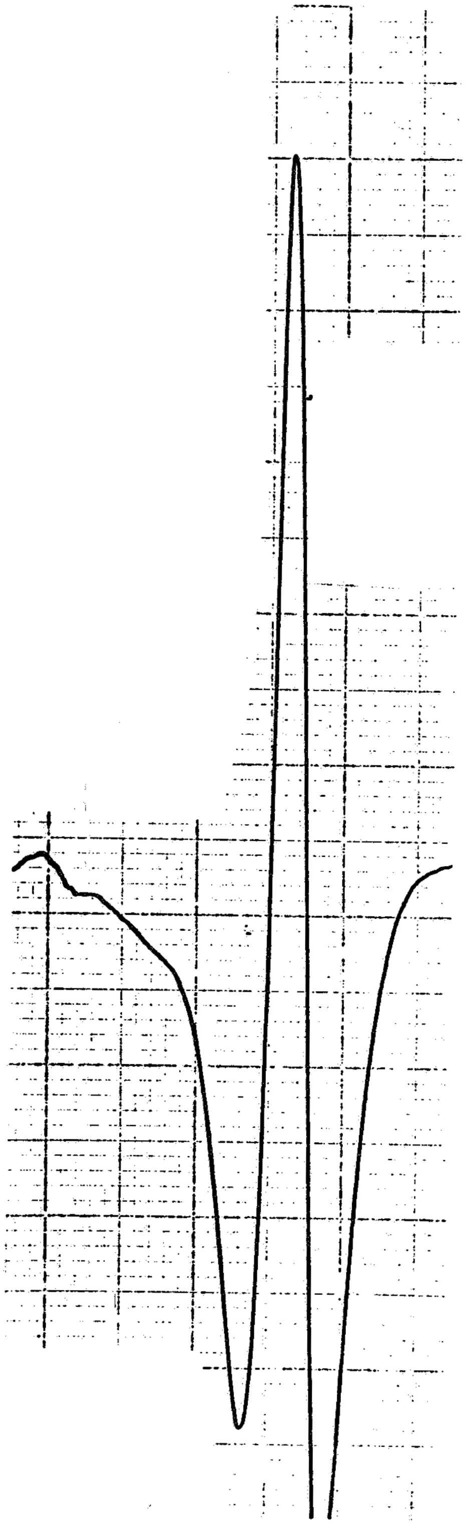
Fig 9



S.S. Butchers & E.B. Wilson
JCP, 40, 1671, 1964

Fig. 9
Propionaldehyde
CH_3CH_2COH

Propionaldehyde



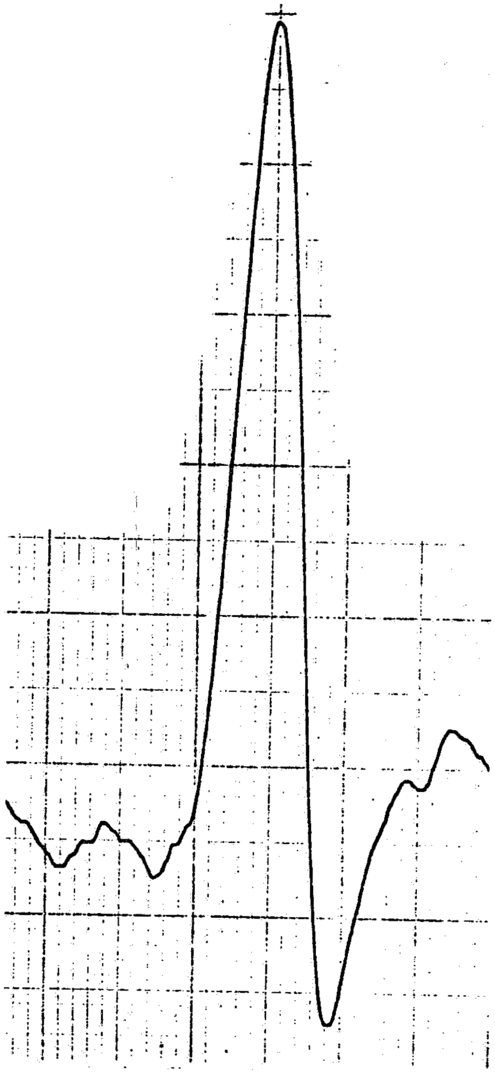


Fig. 10

Double resonances of propionaldehyde

$\nu_S = 2_{11} \rightarrow 3_{12} = 33347.0$ MHz

$\nu_P = 2_{02} \rightarrow 2_{11} = 13474.9$ MHz

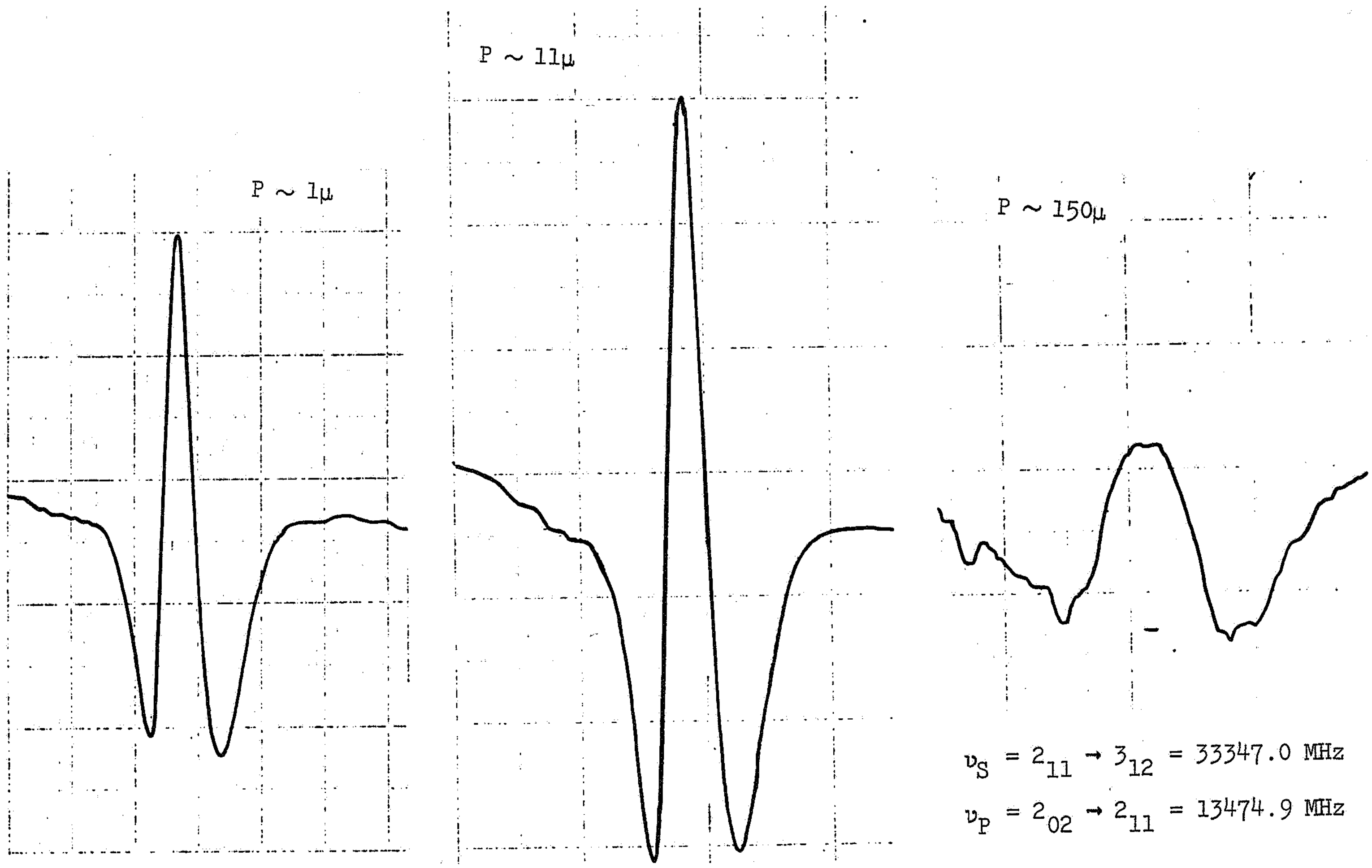
$\nu_S = 2_{11} \rightarrow 3_{12} = 33347.0$ MHz

$\nu_P = 3_{03} \rightarrow 3_{12} = 15778.6$ MHz

Pressure dependence: As indicated before, it is necessary to investigate the pressure dependence of the double resonance signal amplitude in order to determine the pressure range in which a double resonance of propionaldehyde can be obtained. Consequently, a pressure study was undertaken at room temperature, Fig. 11, shows three traces corresponding to the lowest, optimum, and highest pressure at which CH_3CH_2COH can be identified. The overall pressure dependence at room temperature is shown graphically in Fig. 12. Unfortunately no equivalent diagram could be obtained for the overall pressure dependence at dry ice temperature due to erroneous readings on the commercial pressure gauge used.

As is seen from Fig. 12, propionaldehyde can be observed between 2 μ and 150 μ with the optimum signal occurring at a pressure of 25 μHg.

Line Shape: Theoretically, a splitting of the double resonance line into a closely spaced doublet could occur due to the interaction of the hindered internal rotation of the methyl-group with the overall rotation of the molecule. However, even at very low pressure no such splitting can be observed. This result is explained by the height of the potential barrier (2.2 k cal/mole) which reduced the splitting between the A/E components of the observed ground state transition to less than 0.1 MHz.

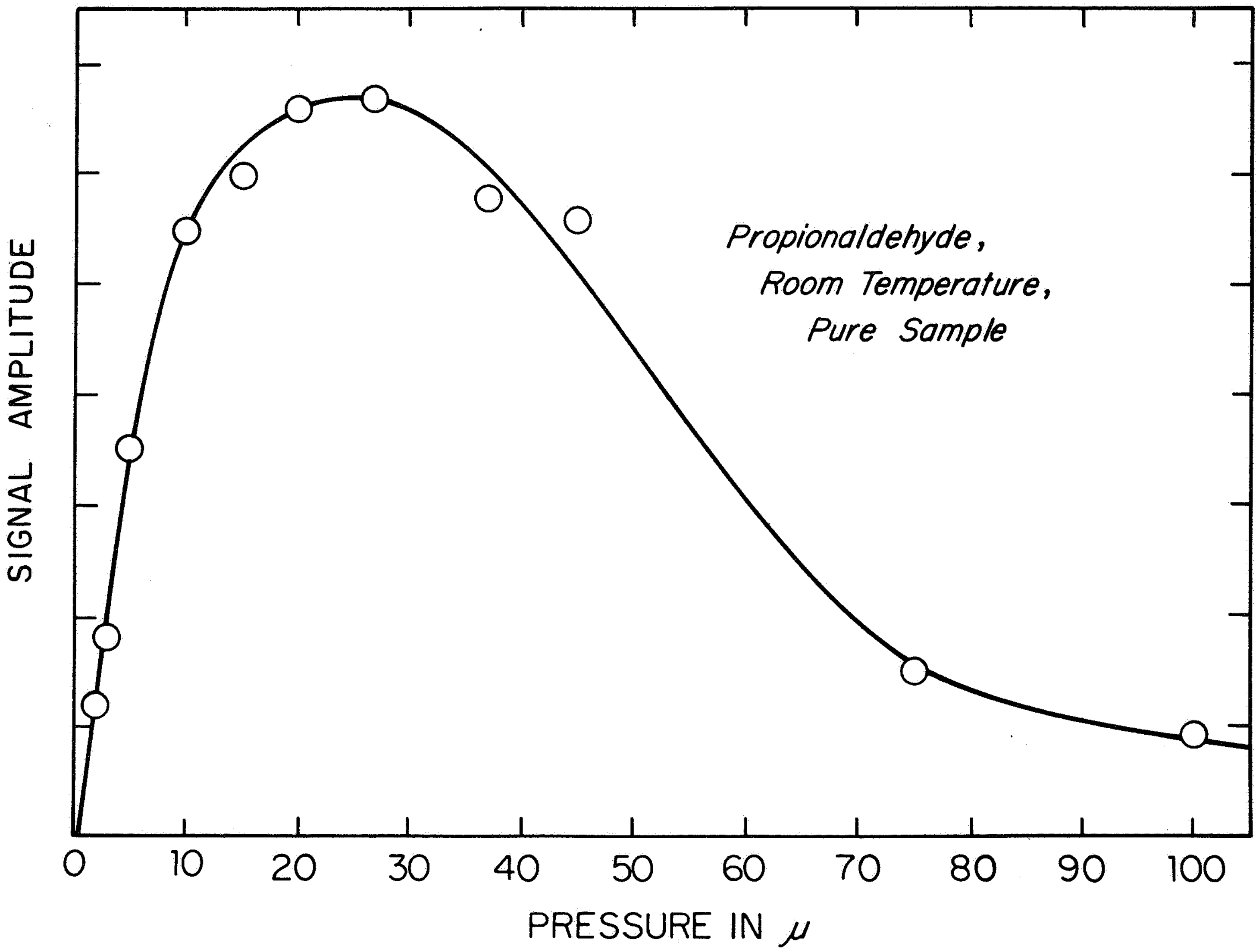


$\nu_S = 2_{11} \rightarrow 3_{12} = 33347.0$ MHz

$\nu_P = 2_{02} \rightarrow 2_{11} = 13474.9$ MHz

Fig. 11

Double resonances of propionaldehyde for three selected pressure values.



Propionaldehyde,
Room Temperature,
Pure Sample
SIGNAL AMPLITUDE
PRESSURE IN μ
0
10
20
30
40
50
60
70
80
90
100

Fig. 12

Propionic acid.- Propionic Acid, Fig. 13, CH_3CH_2COOH, is not only chemically, but also spectroscopically closely related to the propionaldehyde described in the previous section. It is strongly believed that CH_3CH_2COOH exists in the vapor phase in two rotameric forms. However, so far only the cis-form (all heavy atoms co-planar) has been identified in the microwave spectrum. The dipole moment of this form is approximately parallel to the b axis of the inertial tensor and its magnitude is 1.46D. The μ_b selection rule in conjunction with the asymmetry of $X \sim -.72$ allows for many transitions. There are, furthermore, four low lying vibrations which give rise to ten (10) detectable satellite spectra. The overall spectrum is, therefore, very rich and contains ~ 1500 assigned lines between 12 and 40 GHz.

Selection of double resonances: Although there exists a great number of lines there are only a few double resonance connected transitions within the frequency range of the spectrometer. Since the absolute intensity of the lines is considerably smaller than in propionaldehyde, it was necessary to select transitions with J-values larger than $J = 3$ in order to obtain a reasonably good double resonance. The final choice was:

1) $6_{15} \rightarrow 6_{24} = 17269.0 = \nu_p \qquad 6_{24} \rightarrow 6_{33} = 30436.6 = \nu_s$

2) $6_{15} \rightarrow 6_{24} - 17269.0 = \nu_p \qquad 5_{25} \rightarrow 6_{15} = 28186.3 = \nu_s$

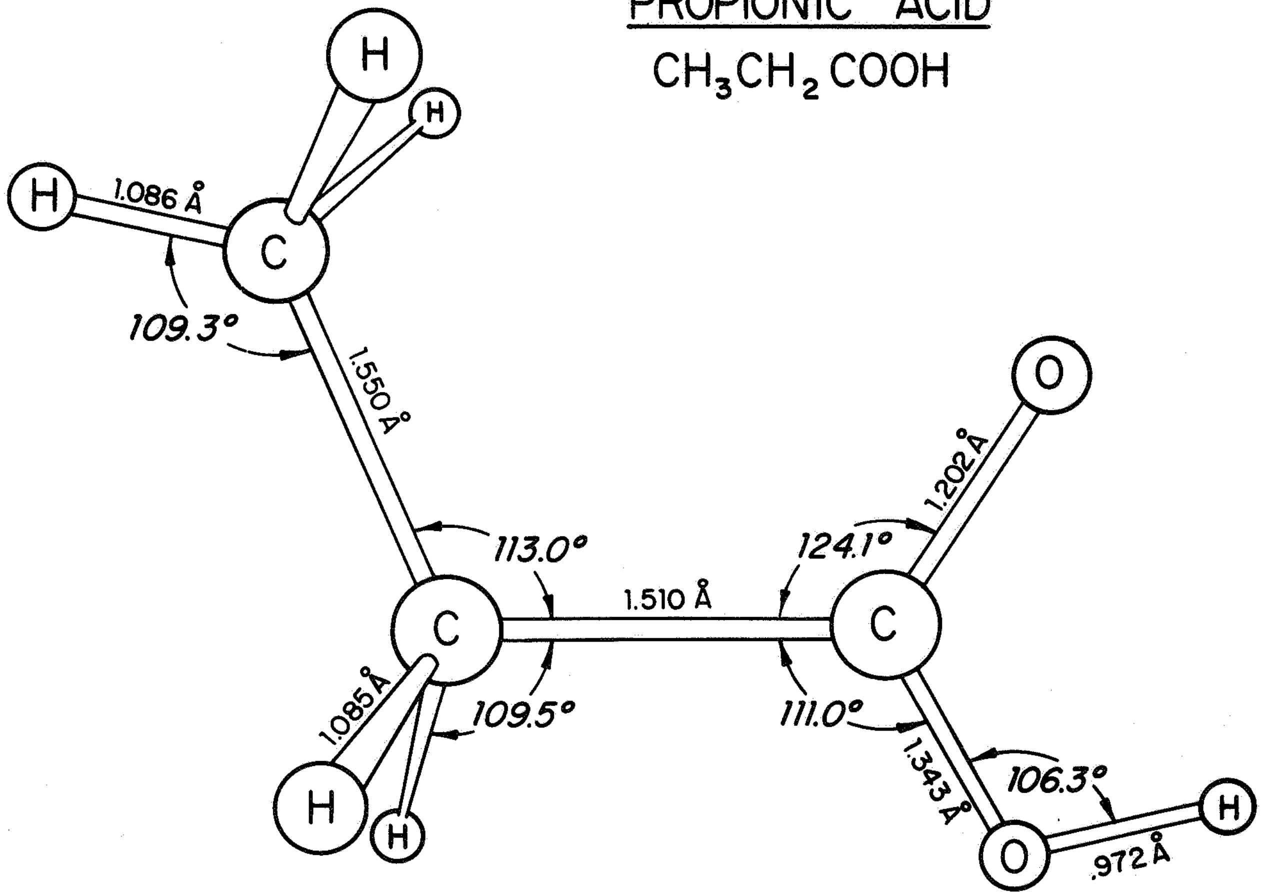
These two double resonances are shown in Fig. 14. Note that the pump transition is the same for both signal lines.

Pressure dependence: In order to determine the optimum pressure condition for the detection of CH_3CH_2COOH the signal strength of the R-branch transition at 28186.3 MHz was studied for different pressures. Three characteristic recorder traces obtained in this investigation are shown in Fig. 15 and the overall pressure dependence is summarized in Fig. 16. It is apparent that propionic acid can be observed under pressures varying from 1 μHg to 150 μHg with the optimum pressure occurring ~ 10 μ - 15 μHg. Since propionic acid solidifies at -22°C it is not possible to observe microwave lines at dry ice temperature.

A very serious drawback in the investigation of CH_3CH_2COOH was its

PROPIONIC ACID

CH_3CH_2COOH



O.L. Stiefvater
(unpublished)

Fig. 13

$\nu_S = 6_{24} \rightarrow 6_{33} = 30436.6$ MHz

$\nu_P = 6_{15} \rightarrow 6_{24} = 17269$ MHz

$\nu_S = 5_{24} \rightarrow 6_{15} = 28186.4$ MHz

$\nu_P = 6_{15} \rightarrow 6_{24} = 17269$ MHz

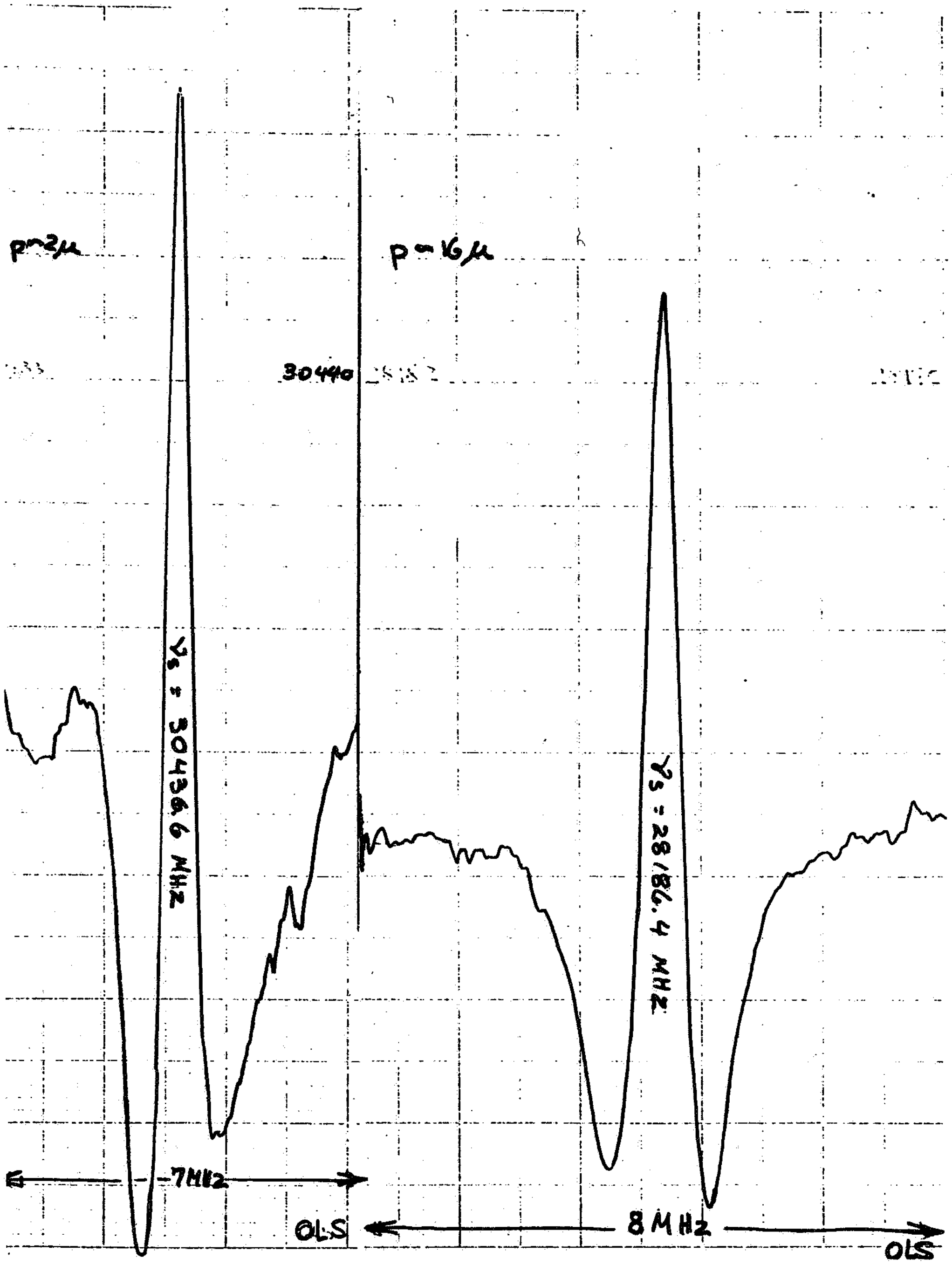


Fig. 14

Double resonances of propionic acid.

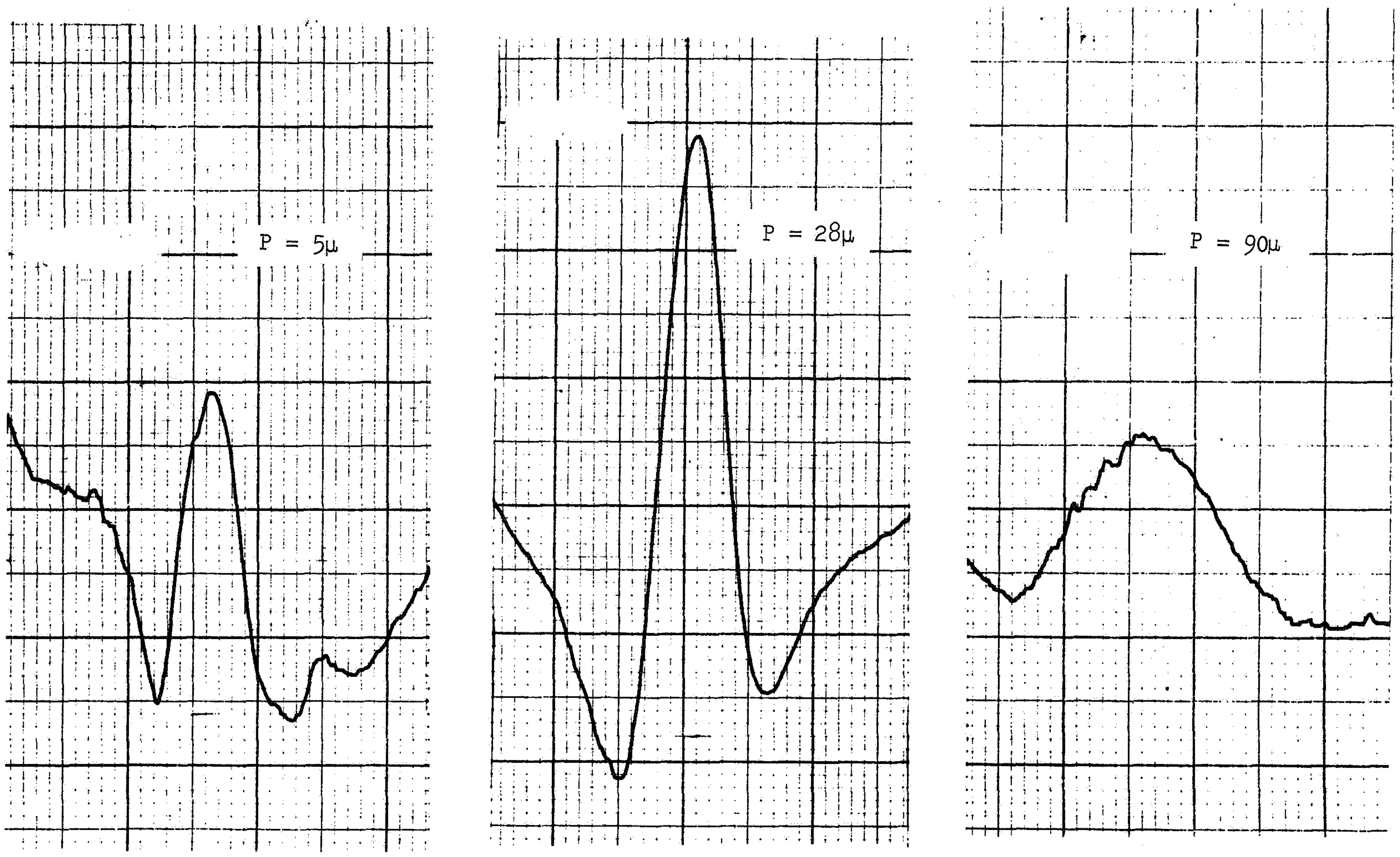


Fig. 15

Propionic acid double resonance signal for limiting pressure values.

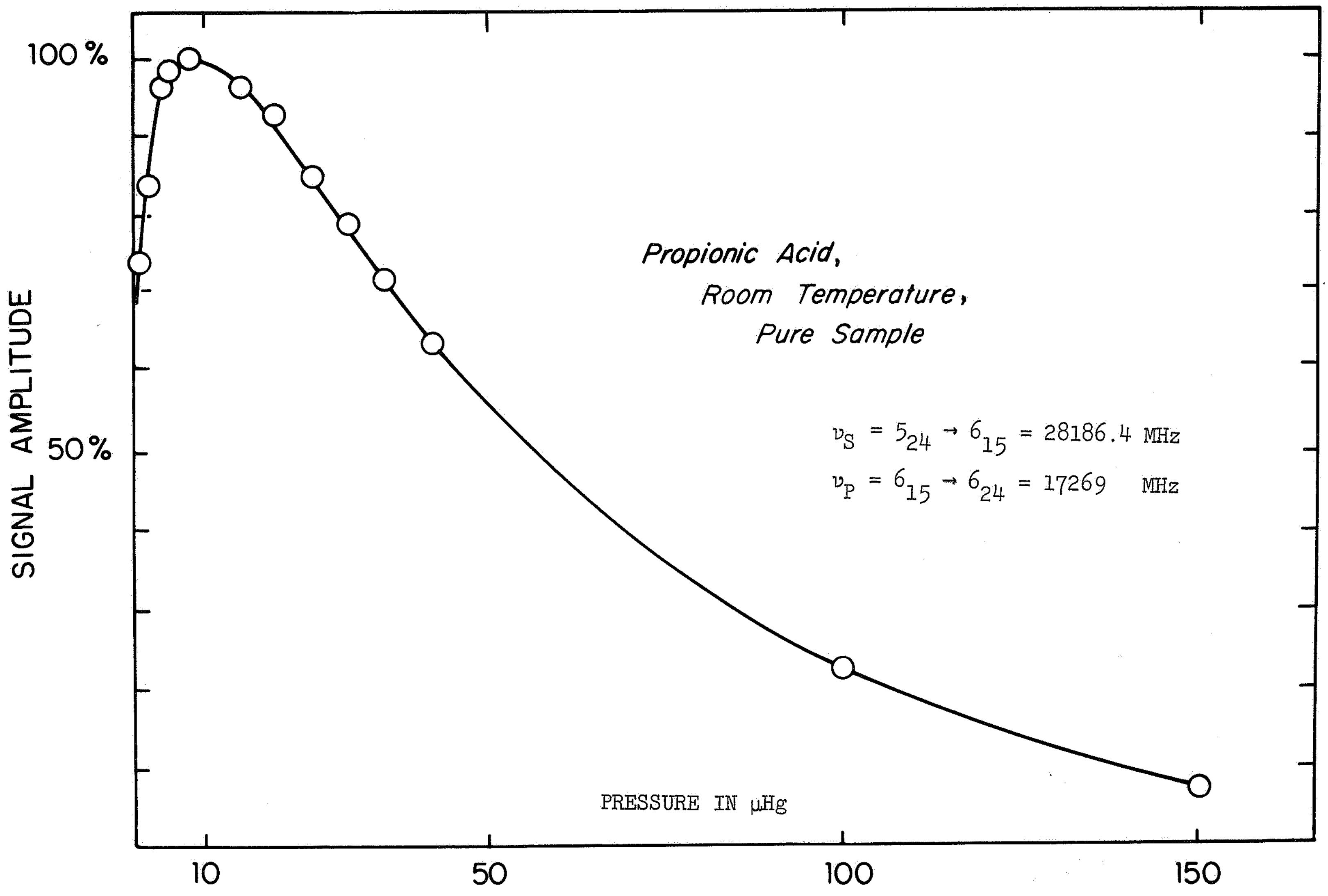


Fig. 16

Double resonance signal amplitude as function of sample pressure.

adsorption on the walls of the waveguide cell. For this reason an additional uncertainty of at least 10 μHg in the pressure values should be allowed on top of the uncertainty due to the variations of the characteristics of the Pirani gauges used in this work.

Line shapes: The only complication in the shape of propionic acid lines could arise from the internal rotation of the methyl-top. However, due to the barrier height of 2.3 K ca./mole this hindered rotation does not affect the ground state lines, they are all singlets. It is, therefore, possible to obtain symmetrical double resonance line shapes.

N-Chloropropane.-(10) In the gas phase, normal propyl chloride (Fig. 17), $CH_3CH_2CH_2Cl$, exists in two rotameric conformations, a trans-form (in which the heavy atoms form a staggered planar chain) and a gauche form (in which the CH_2CO-group is rotated by ~ 120° from the transconfiguration). Unlike propionaldehyde and propionic acid the two rotamers are of roughly equal energy.

The microwave spectrum of the nearly symmetric transform shows only μ_a -R-branch transitions spaced by ~ 4.5 GHz. The gauche spectrum is stronger due to the statistical weight of two, and richer due to the higher asymmetry of this conformation.

In addition to the existence of two rotameric forms there are two isotopic species of the chlorine atom (Cl^{35} ~ 75%, Cl^{37} ~ 25%). The interaction of the chlorine nuclear quadrupole moment with overall rotation produces a fine structure in the microwave lines of this compound. There is in addition, the low lying skeletal torsion and the methyl torsion. These three facts make the spectrum of $CH_3CH_2CH_2Cl$ rich and complex.

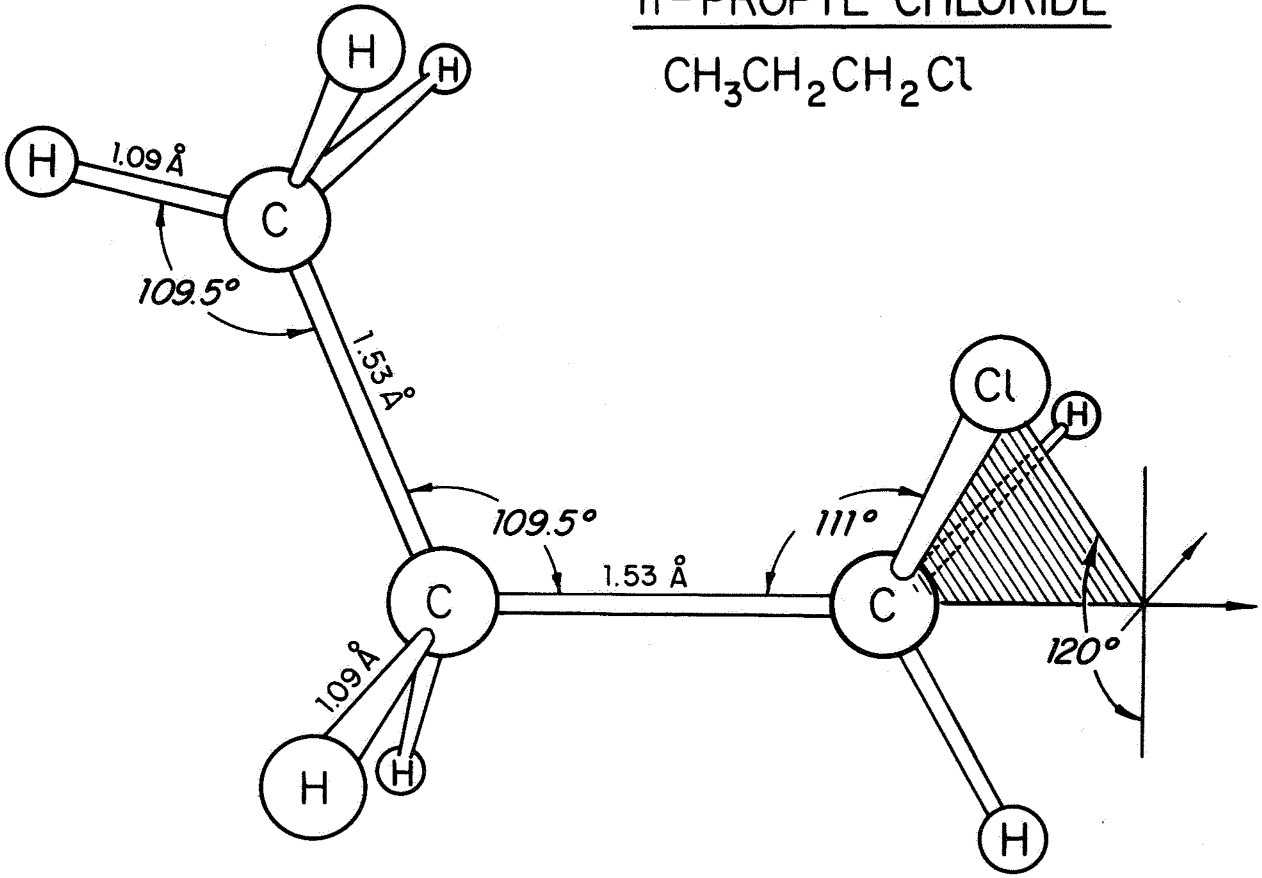
Selection of double resonances: The sparsity and spacing of the transitions arising from the trans-conformation of n-propyl chloride makes it advisable to select a double resonance in the stronger and richer gauche-spectrum for the identification of this compound. However, the table of observed gauche lines given in the original paper does not contain any connected low J transitions coinciding with the frequency ranges of our spectrometer. It was, therefore, necessary to repredict the spectrum of gauche - $CH_3CH_2CH_2Cl$ for the frequency range from 12 GHz to 40 GHz. In this calculation the rotational constants of the more abundant Cl^{35} -species were used and the effect of the quadrupolar nucleus on the rotation spectrum were omitted for simplicity. A critical examination of the predicted transitions indicated that the double resonance connections listed in TABLE III ought to be the most favorable cases for our purposes and shown in Fig. 18.

The signal amplitude of the n-propyl chloride double resonance transition was studied for different sample pressures at room temperature and dry ice temperature. Three typical recorder traces corresponding to the low pressure limit of detectability, the optimum pressure and the high pressure limit are reproduced in Fig. 19. Fig. 20 and Fig. 21 summarize the overall pressure dependence as obtained in these experiments.

It is apparent from these figures that n-propyl chloride can be detected

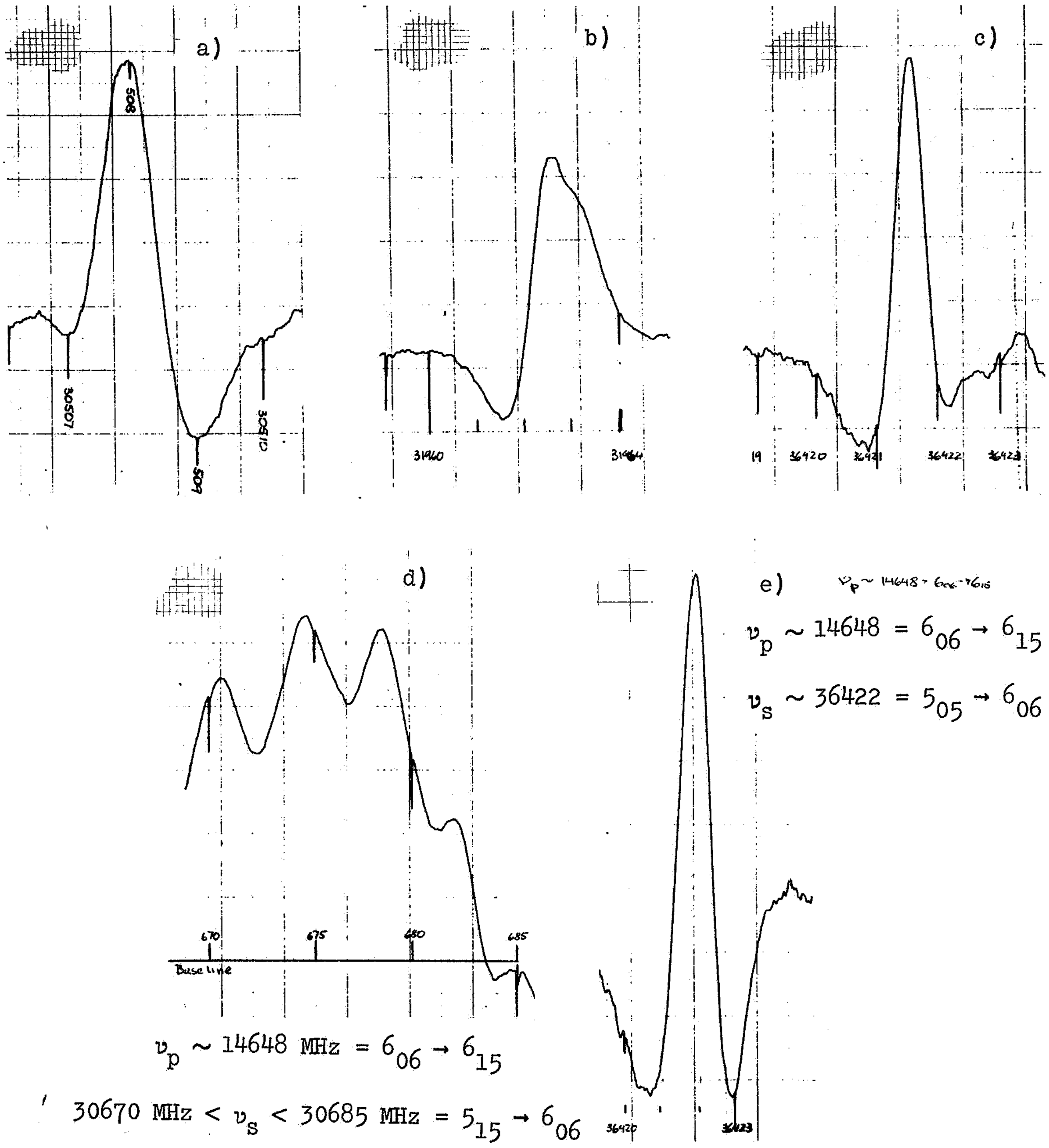
n-PROPYL CHLORIDE

$CH_3CH_2CH_2Cl$



T.N. Sarachman,
JCP, <u>39</u> 469, 1963

Fig. 17



$\nu_p \sim 14648 = 6_{06} \to 6_{15}$

$\nu_s \sim 36422 = 5_{05} \to 6_{06}$

$\nu_p \sim 14648$ MHz $= 6_{06} \to 6_{15}$

30670 MHz $< \nu_s <$ 30685 MHz $= 5_{15} \to 6_{06}$

Fig. 18

Observed double resonances of n-propyl chloride.

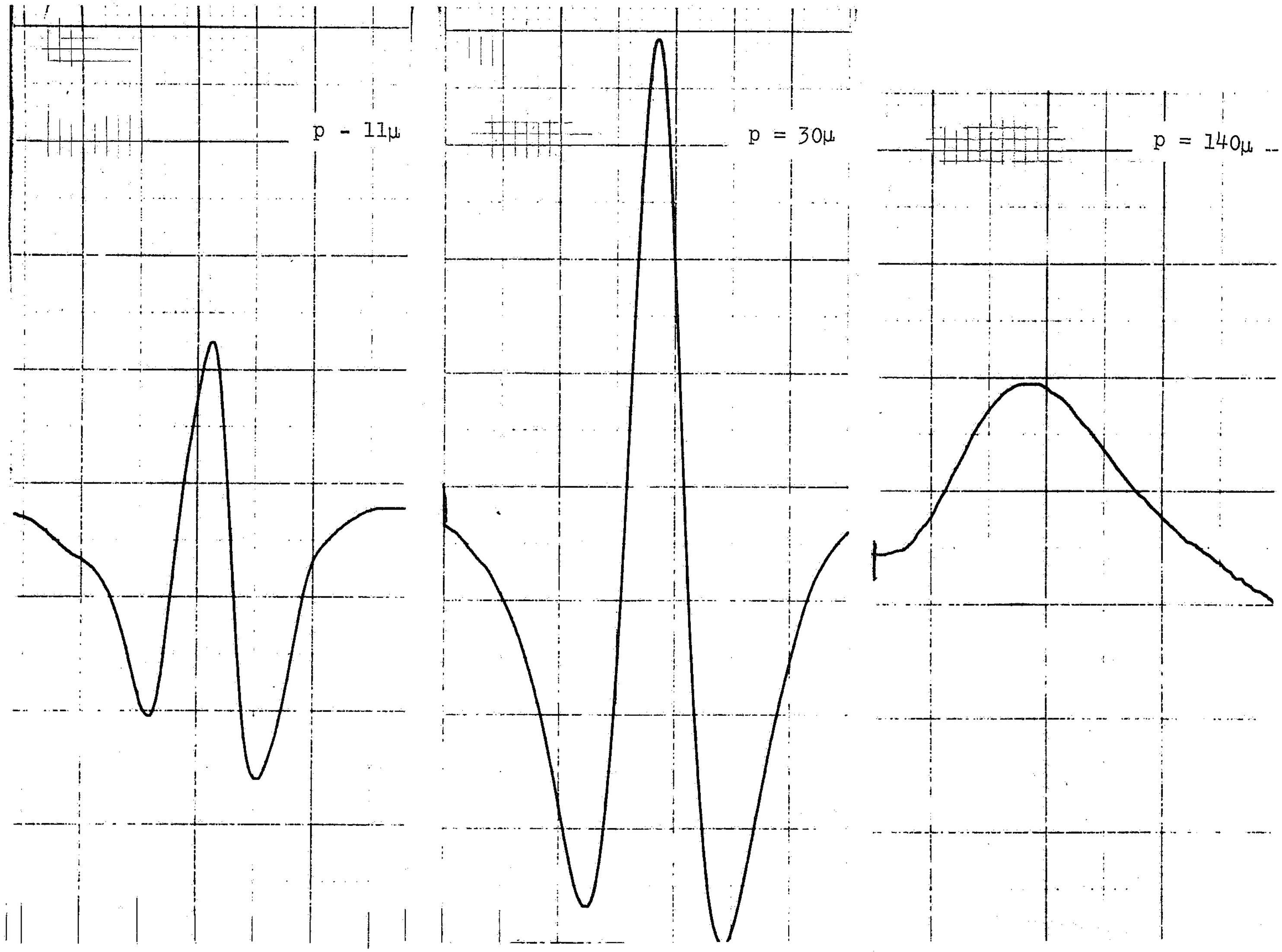


Fig. 19

n-Propyl chloride. Double resonance signal
for limiting pressure values.

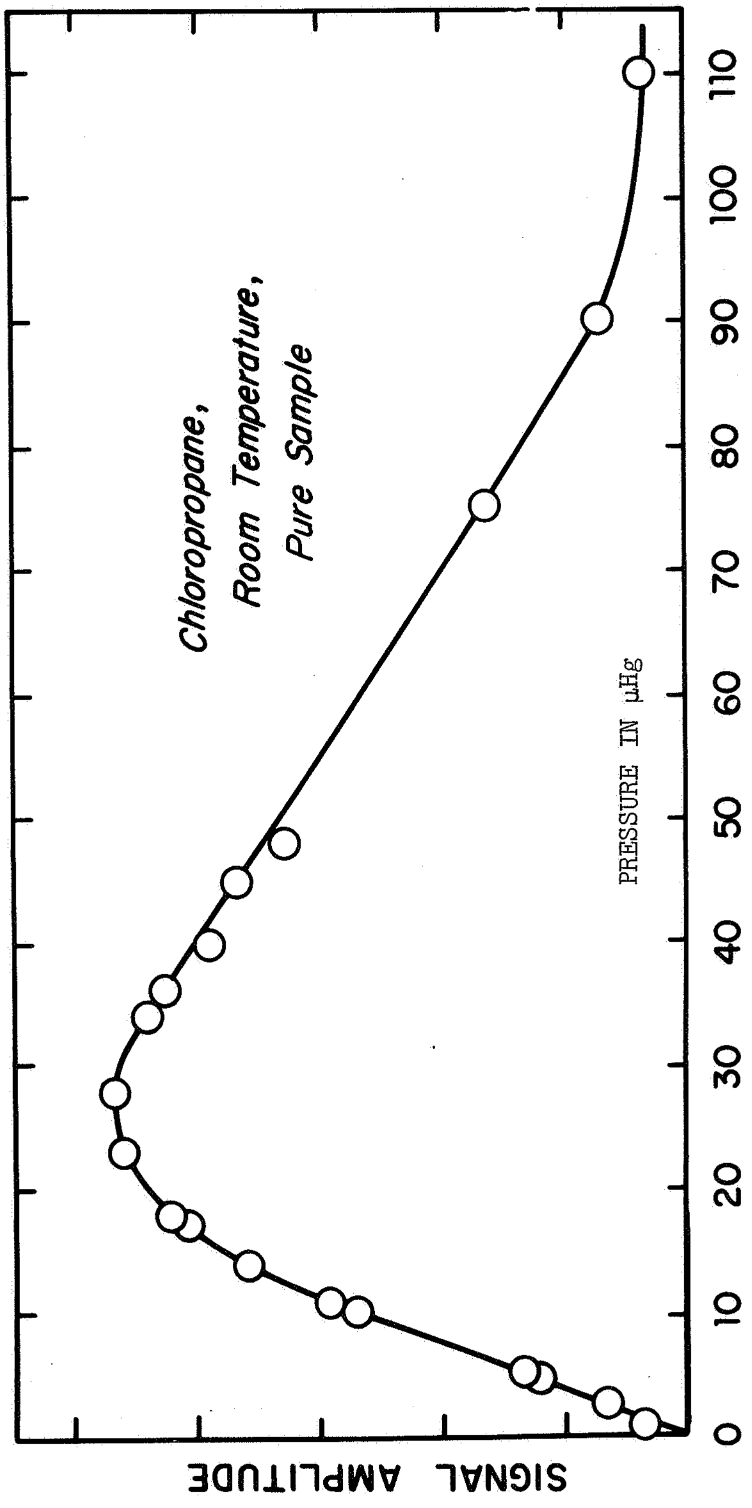

Chloropropane,
Room Temperature,
Pure Sample
SIGNAL AMPLITUDE
PRESSURE IN μHg
0
10
20
30
40
50
60
70
80
90
100
110

Fig. 20

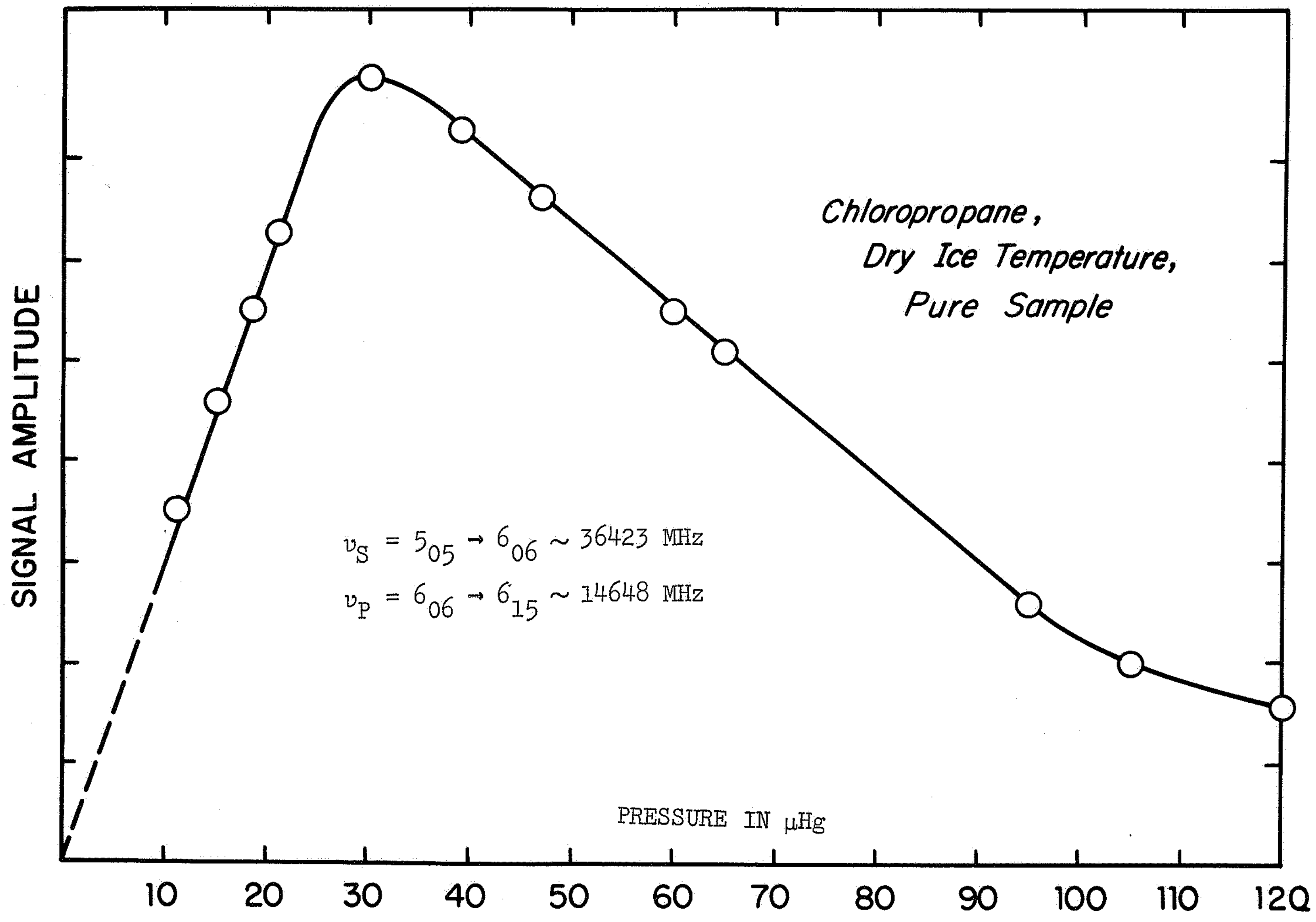


Fig. 21

n-Propyl chloride. Double resonance signal amplitude as function of sample pressure. Dry ice temperature.

TABLE III. PREDICTED DOUBLE RESONANCES FOR N-PROPYL CHLORIDE

Pump Line			Connected Signal Line			
Transition	Frequency* MHz	Dipole Selection Rule	Transition	Frequency* MHz	Dipole Selection Rule	Fig. 18
$5_{05} \rightarrow 5_{14}$	12775	μb	$4_{04} \rightarrow 5_{05}$	30509	μa	a
			$4_{13} \rightarrow 5_{14}$	31964	μa	b
			$5_{05} \rightarrow 6_{06}$	36423	μa	c
			$5_{15} \rightarrow 6_{15}$	38297	μa	-
$6_{06} \rightarrow 6_{15}$	14648	μb	$5_{15} \rightarrow 6_{06}$	30678	μb	d
			$5_{05} \rightarrow 6_{06}$	36423	μa	e
			$5_{14} \rightarrow 6_{15}$	38297	μa	-

*These are the predicted absorption frequencies for a rigid asymmetrical rotor without quadrupole fine structure.

in the pressure range from 5 μHg to 120 μHg with the optimum signal occurring for pressures around ~ 30 μHg. The optimum pressure, as well as the overall pressure dependence of the signal amplitude, appear to be temperature independent. The absolute enhancement of the signal when changing from room temperature to dry ice is of the order of 5 to 10.

Methylene chloride.(11) - Compared to the propane derivatives described in the previous sections, methylene chloride, CH_2Cl_2 (Fig. 22) is a comparatively small and rigid molecule. It is a nearly prolate symmetric top with its dipole moment of 1.62D oriented along the b- axis of the inertial tensor. The existence of two isotopic species of Chlorine occurring with a natural abundance of 3:1 gives rise to two different sets of microwave lines with the Cl^{35} spectrum being the stronger one. Many of the microwave lines of methylene chloride are split into multiplets, frequency triplets. This fine structure is due to the interaction of the nuclear quadrupoles of the two equivalent chlorine atoms with the overall rotation of the molecule.

Selection of double resonances: Unfortunately the microwave papers on methylene chloride (CH_2Cl_2) do not list any pair of connected transitions usable for double resonance experiments. A choice had, therefore, to be made between recalculating the entire spectrum up to, say J = 12 (as had to be done for n-propyl chloride) and calculating only a few low J lines known to have common energy levels and double resonance connections suitable for our spectrometer. For simplicity the latter procedure was tried yielding the following double resonance possibilities:

$$\nu_s = 35067.0 \text{ MHz} = 0_{00} \rightarrow 1_{11}$$

$$\nu_p = 15911.9 \text{ MHz} - 1_{11} \rightarrow 2_{20}$$

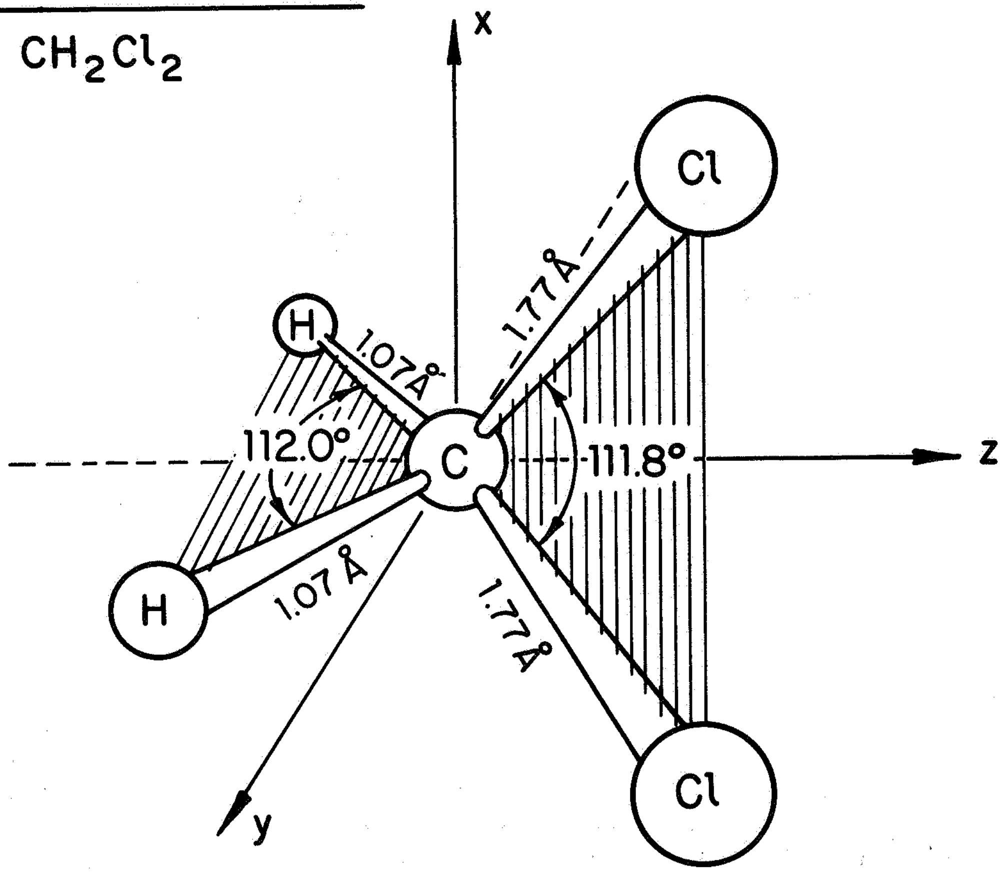
$$\nu_s = 29193.5 \text{ MHz} - 2_{02} \rightarrow 2_{11}$$

Subsequent experimental examination showed (Fig. 23) that both double resonances could indeed be obtained, the first one giving a better signal to noise ratio. This $(1_{11} \rightarrow 2_{20}) \rightarrow (0_{00} \rightarrow 1_{11})$ double resonance was considered strong enough for our purposes and was consequently used throughout the following stages of this research.

Pressure dependence: An investigation into the pressure dependence of the double resonance signal amplitude was performed in the early stages of this project. After the incorporation of the phase-lock unit and the resulting improvement in signal/noise of the double resonance system, this pressure dependence was re-investigated and the results obtained earlier were confirmed. Three typical traces obtained in the second run are shown in Fig. 24

METHYLENE CHLORIDE

CH_2Cl_2

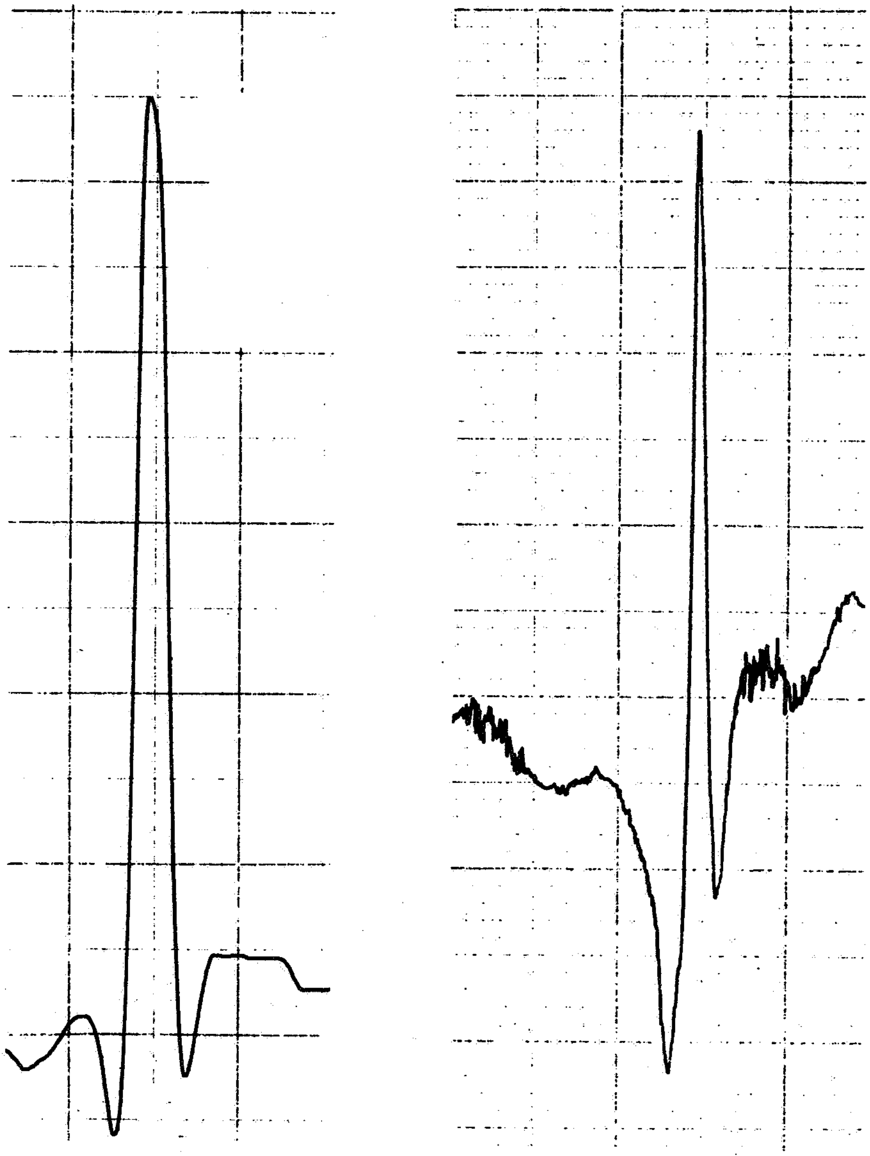


R.G. MYERS & W.D. GWINN
JCP <u>20</u>, 1420, 1952

Fig. 22

Methylene Chloride

1



$\nu_S = 0_{00} \rightarrow 1_{11} = 35067.0$ MHz

$\nu_P = 1_{11} \rightarrow 2_{20} = 15911.9$ MHz

$\nu_S = 2_{02} \rightarrow 2_{11} = 29193.5$

Fig. 23

Double resonances of

Methylene Chloride

$\nu_S = 0_{00} \rightarrow 1_{11} = 35067.0$ MHz

$\nu_P = 1_{11} \rightarrow 2_{20} = 15911.9$ MHz

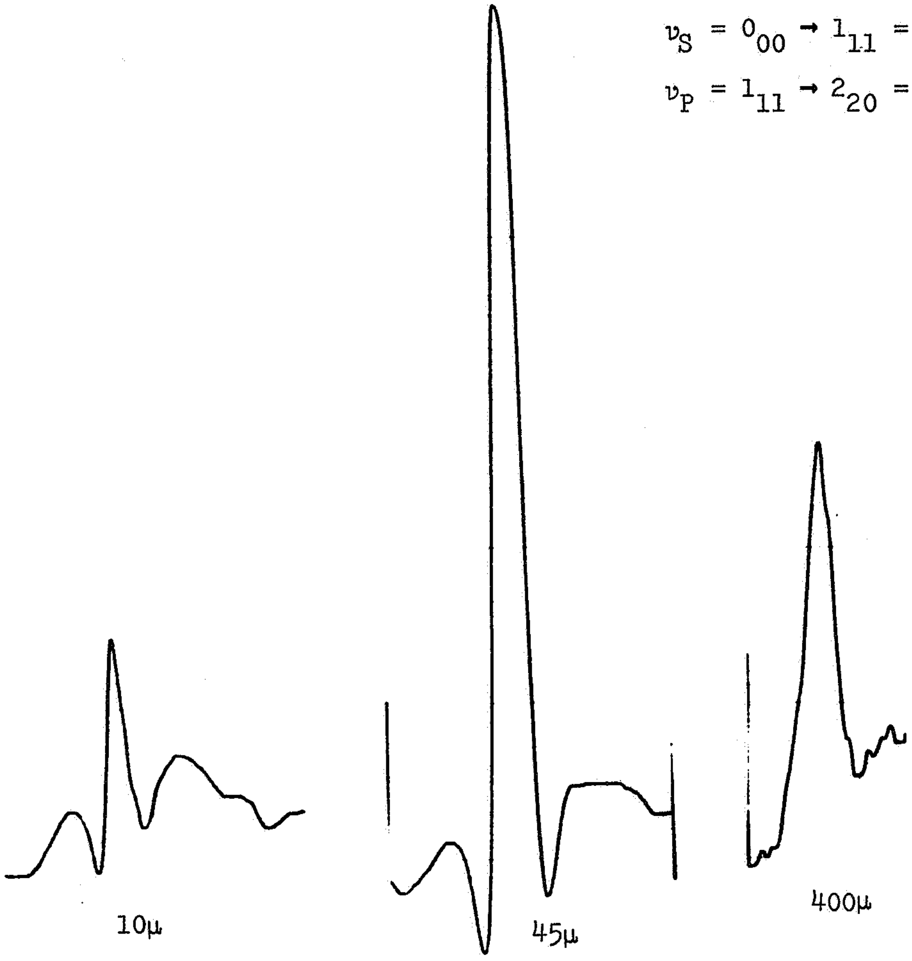


Fig. 24

Methylene Chloride. Double resonance signals for three selected gas pressures.

and the overall behaviour is summarized in Fig. 25.

One striking feature of this curve is that the optimum double resonance signal occurs at ~ 50 μHg, whereas the three previous molecules had the optimum pressure range at ~ 25 μHg. Secondly: the CH_2Cl_2 double resonance can be detected up to considerably higher pressures than was the case for the three propane derivatives.

Line shapes: As can be seen from the traces reproduced in this section there is no detectable fine structure in the $0_{00} \rightarrow 1_{11}$ transition used as double resonance signal line. This result is in agreement with the results of reference 1 according to which the quadrupole interaction is negligible in this transition. The absence of fine structure lends additional support to the selection of the $0_{00} \rightarrow 1_{11}$ transition as the signal line and enables a balanced double resonance line shape to be obtained.

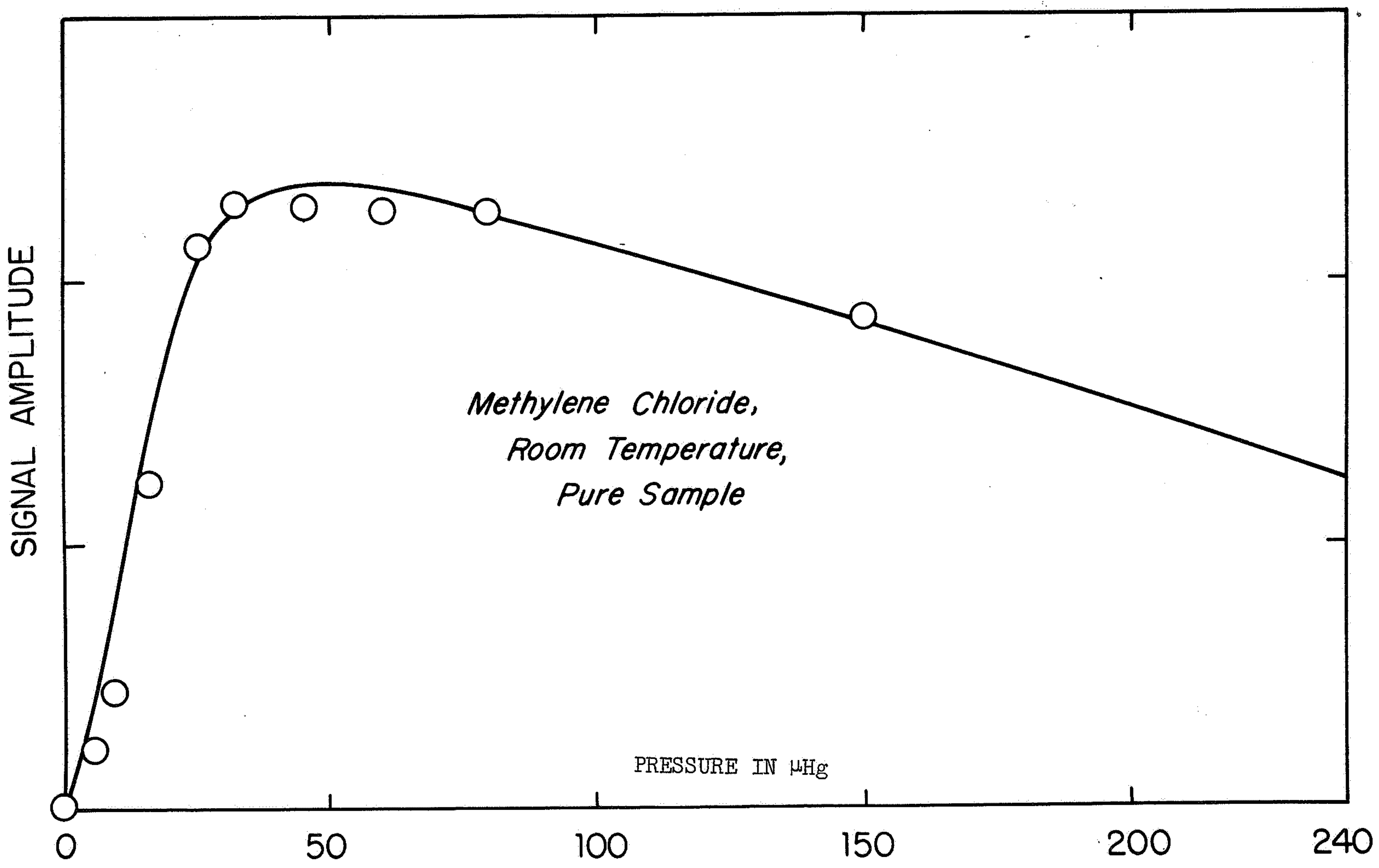


Fig. 25

Methylene chloride double resonance signal amplitude as a function of sample pressure.

Dimethyl sulfide.(12) - Dimethyl sulfide, the structure of which is shown in Fig. 26, concludes the group of five molecules to be investigated under this research contract.

$(CH_3)_2S$ is a prolate asymmetric rotor, and its dipole moment of 1.50D coincides with the b- axis of the inertia tensor. The values of the rotational constants are such as to allow low J, R and Q branch transitions in the 12 GHz - 40 GHz range.

Although small, dimethyl sulfide is a spectroscopically interesting molecule becasue of the presence of two equivalent methyl groups which exhibit hindered internal rotation. The interaction of these internal motions with each other and with the overall rotation cause the microwave lines to split into multiplets (triplets and quartets).

Selection of double resonances of dimethyl sulfide offers at least two low J double resonances compatible with the frequency range of our spectrometer; they are:

$$\nu_s = 2_{12} \rightarrow 3_{03} = 30543.2 \text{ MHz}$$

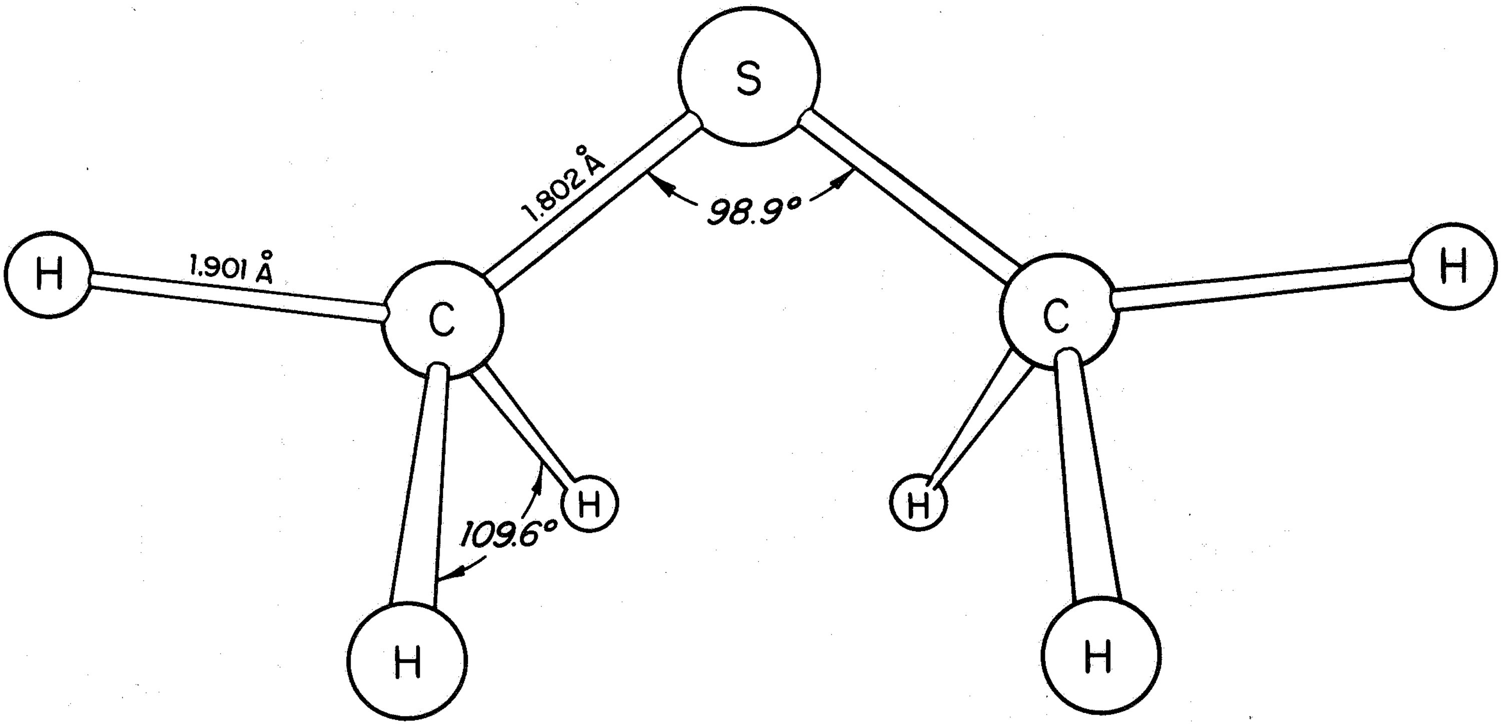
$$\nu_p = 3_{03} \rightarrow 3_{12} = 17875.2 \text{ MHz}$$

$$\nu_s = 3_{12} \rightarrow 3_{21} = 29058.5 \text{ MHz}$$

As can be seen from Fig. 27 both these double resonances could be obtained with a good signal to noise ratio, the $(3_{03} \rightarrow 3_{12})$ $(3_{12} \rightarrow 3_{21})$ double resonance being the stronger one. This result agrees with what one would expect on the basis of established theory. Since the dimethyl sulfide double resonance lines were considerably stronger than the double resonances observed in any of the other four molecules a search for more intense high J connections was considered unnecessary.

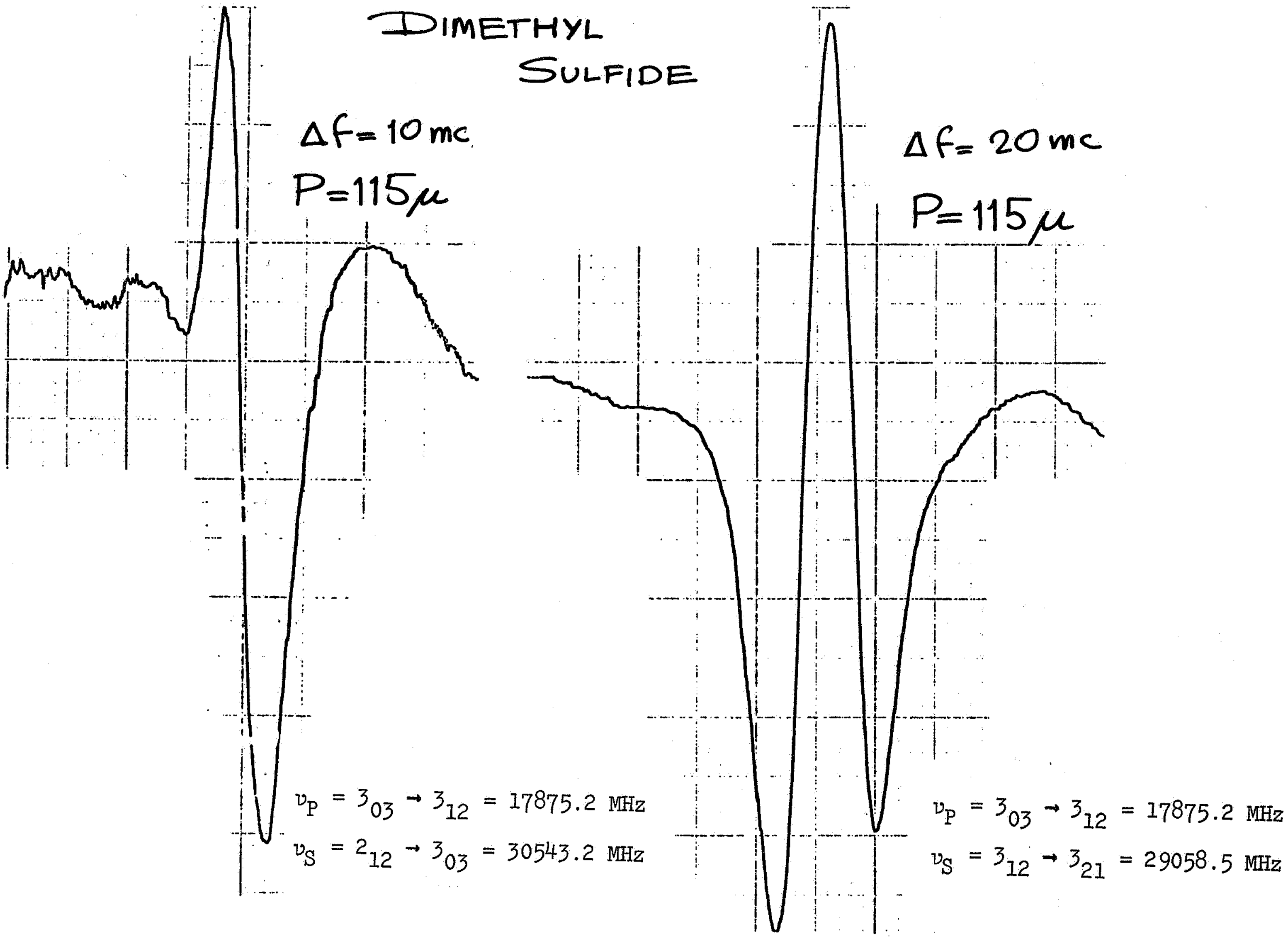
Pressure dependence: The investigation of the double resonance signal strength as function of the sample pressure was made for both room temperature and dry ice temperature. Three traces, corresponding to the optimum pressure and the high and low pressure limits, are included for both temperatures, Fig. 28 and Fig. 29. (The apparent constancy in the signal amplitude on the three traces of the dry ice run is due to a change in the sensitivity settings of the spectrometer.) The pressure curve for temperature is shown in Fig. 30.

DIMETHYL SULFIDE
$S(CH_3)_2$



Pierce & Hayashi
JCP, <u>35</u> 479, 1961

Fig. 26



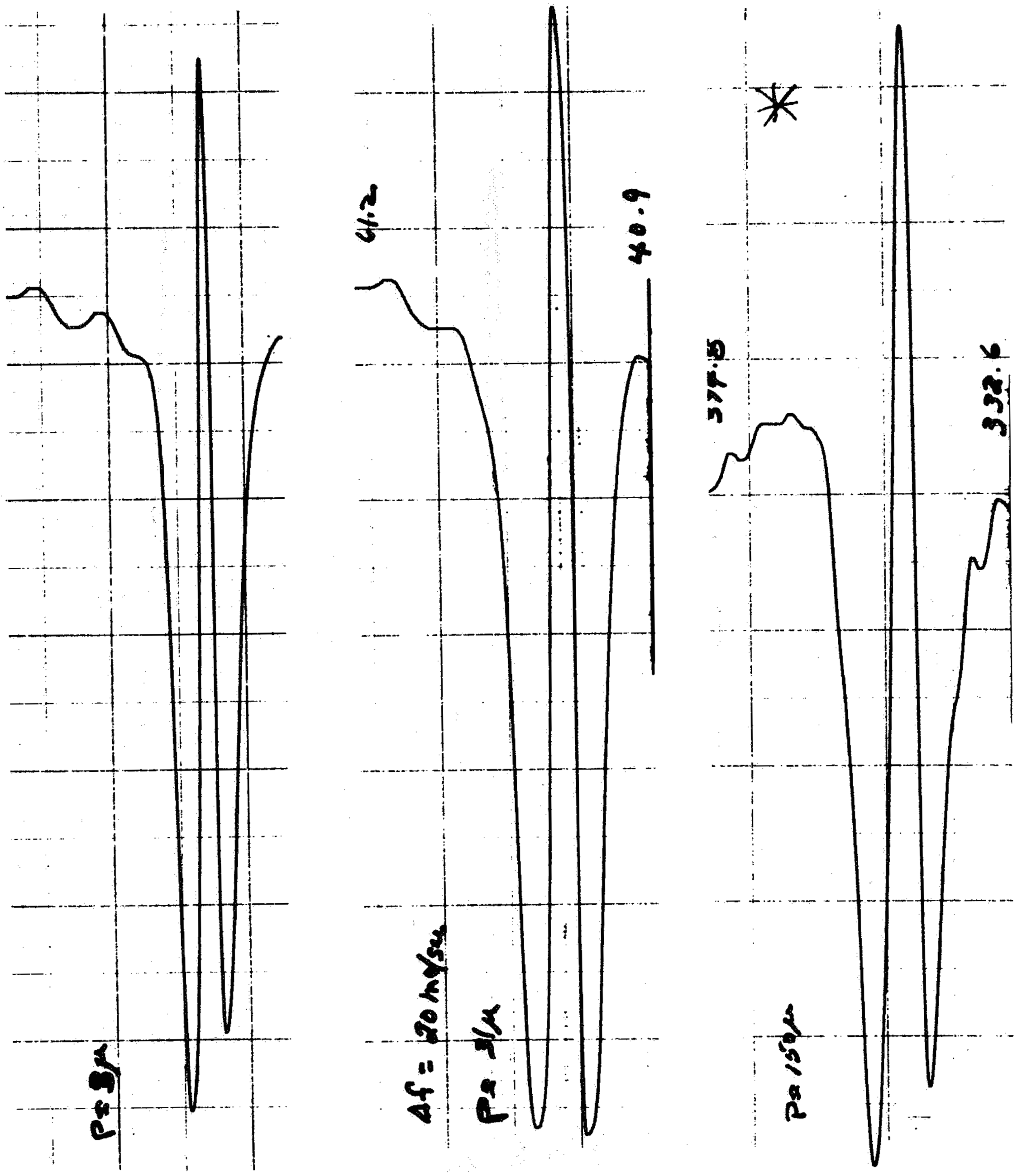
$\nu_P = 3_{03} \rightarrow 3_{12} = 17875.2$ MHz
$\nu_S = 2_{12} \rightarrow 3_{03} = 30543.2$ MHz

$\nu_P = 3_{03} \rightarrow 3_{12} = 17875.2$ MHz
$\nu_S = 3_{12} \rightarrow 3_{21} = 29058.5$ MHz

Fig. 27

Double resonances of dimethyl sulfide.

Pressure dependence,
Dry Ice



P = 3μ   P = 31μ   P = 150 μ

Fig. 28

Dimethyl sulfide. Double resonance signals for optimal and limiting pressure values. Dry ice temperature.

DIMETHYL SULFIDE

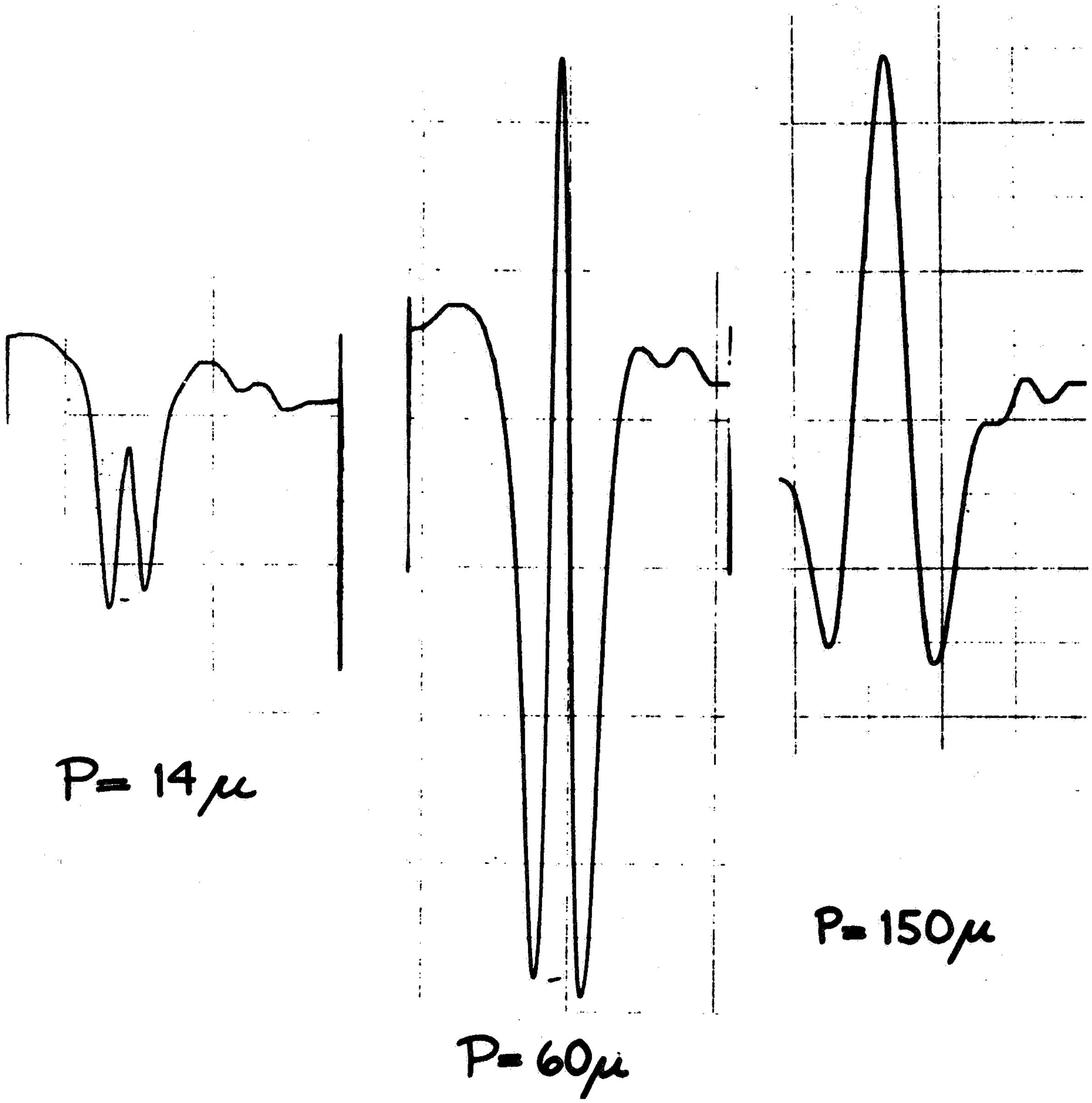


Fig. 29

Dimethyl sulfide. Double resonance signals for optimal and limiting pressure values. Room temperature.

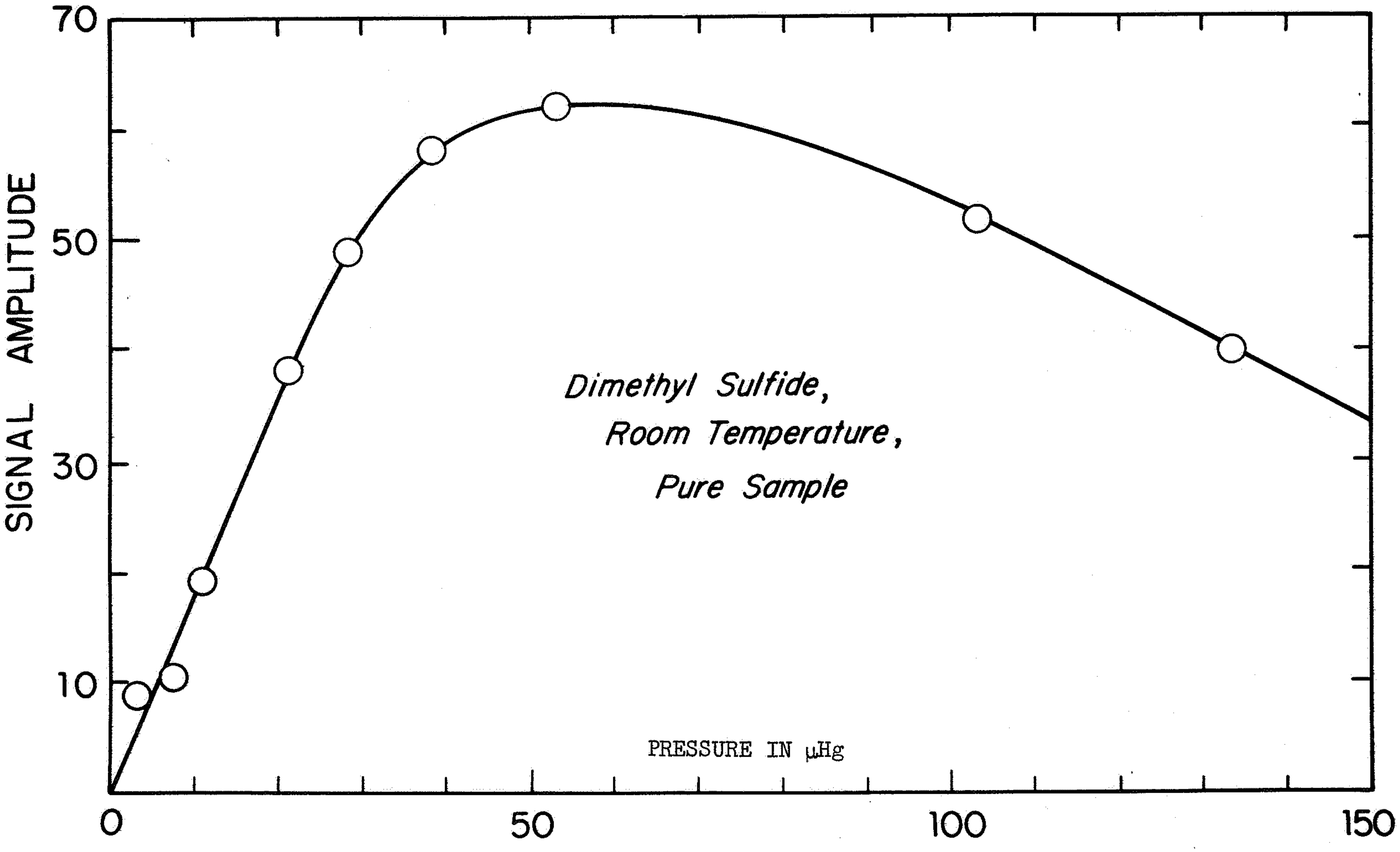

70
50
30
10
SIGNAL AMPLITUDE
Dimethyl Sulfide,
Room Temperature,
Pure Sample
PRESSURE IN μHg
0
50
100
150

Fig. 30

The pressure behaviour of dimethyl sulfide resembles the one in methylene chloride insofar that the optimum signal occurs around 50 μHg and that the signal strength decreases more slowly than for the propane derivatives when the sample pressure is increased. As a consequence, $(CH_3)_2S$ can be observed at pressures up to 400 μHg.

Line shapes: At high and intermediate pressures a balanced double resonance signal can be obtained for $(CH_3)_2S$. When the pressure is decreased below 10 μHg, the line starts splitting up into a closely spaced multiplet. As has been mentioned above, this splitting is due to the internal rotation of the two methyl groups. In the $3_{12} \rightarrow 3_{21}$ transition used here, the separation between the multiplet components is of the order of .5 MHz.

Summary. - Before proceeding to diluted samples and mixtures it seems convenient to summarize the results obtained on the five contract molecules. The frequency, pressure, and temperature data obtained on the pure samples are listed in TABLE IV.

TABLE IV. SUMMARY OF DATA OBTAINED ON PURE SAMPLES

Molecule	Selected Double Resonances ν_p MHz	 ν_s MHz	Pressure Min.	 Opt.	 Max.	Room Temp.	Dry Ice
CH_3CH_2COH	$2_{02} \rightarrow 2_{11}$ = 13474.9	$2_{11} \rightarrow 3_{12}$ = 33347.0	2	25	150	yes	yes
CH_3CH_2COOH	$6_{15} \rightarrow 6_{24}$ = 17269.0	$5_{24} \rightarrow 6_{15}$ = 28186.3	1	15	150	yes	no
$CH_3CH_2CH_2Cl$	$6_{06} \rightarrow 6_{15}$ = 14648.	$5_{05} \rightarrow 6_{06}$ = 36422.	5	30	120	yes	yes
			5	30	120	yes	yes
CH_2Cl_2	$1_{11} \rightarrow 2_{20}$ = 15912.	$0_{00} \rightarrow 1_{11}$ = 35067.	10	50	400	yes	---
$(CH_3)_2S$	$3_{03} \rightarrow 3_{12}$ = 17875.	$3_{12} \rightarrow 3_{31}$ = 29058.5	10	50	400	yes	yes

Measurements diluted samples. - The experiments reported in this section are mainly intended to furnish information about the smallest quantity of gas detectable by the double resonance technique.

The easiest approach to the problem in hand is to progressively dilute one of the samples in air and then to check, down to which degree of dilution the double resonance signal can still be detected by our spectrometer. Unfortunately, however, not all five contract molecules were suitable for this simple procedure. Propionic acid, for example, has been found to be so heavily absorbed on the walls of the waveguide that a large amount of the sample had to be admitted to the cell before a stable pressure was obtained. In view of this it was considered pointless to prepare a diluted sample of this compound. The gas concentration in the cell might have turned out to be as much as ten times smaller than in the originally prepared sample. A similar (but by far not as pronounced) behavior had been observed on n-propyl chloride. For this reason the research effort was centered on diluted samples of $(CH_3)_2S$, CH_3CH_2CHO, and CH_2Cl_2. The double resonance transitions characteristic for these molecules (see Table IV) were observed for different pressures on samples diluted in air to 1:10, 1:100, and 1:300. The pressure curves resulting from these experiments are shown in Figs. 31 to 33. Recorder traces of the signals obtained on the most diluted samples studied are also reproduced along with the corresponding traces of the pure samples (Fig. 34).

Inspecting Figs. 31 to 34, the following qualitative changes due to dilution are obvious:

1. The signal/noise ratios do not decrease proportionally to the degree of dilution. They appear to change more slowly.
2. In propionaldehyde, there occurs a shift of the optimum pressure range to higher values, and the peak of the signal versus pressure curve broadens out when going from the pure to the 1:100 diluted sample. No further broadening is observed, however, when changing from 1:100 to a 1:300 diluted sample.
3. In CH_2Cl_2 and $(CH_3)_2S$ no shift or broadening of the optimum pressure range can be distinguished.

A quanitative explanation of these results necessitates an exact calculation of the apparent double resonance signal as a function of all the parameters contributing to the line shape and is, therefore, beyond the scope of

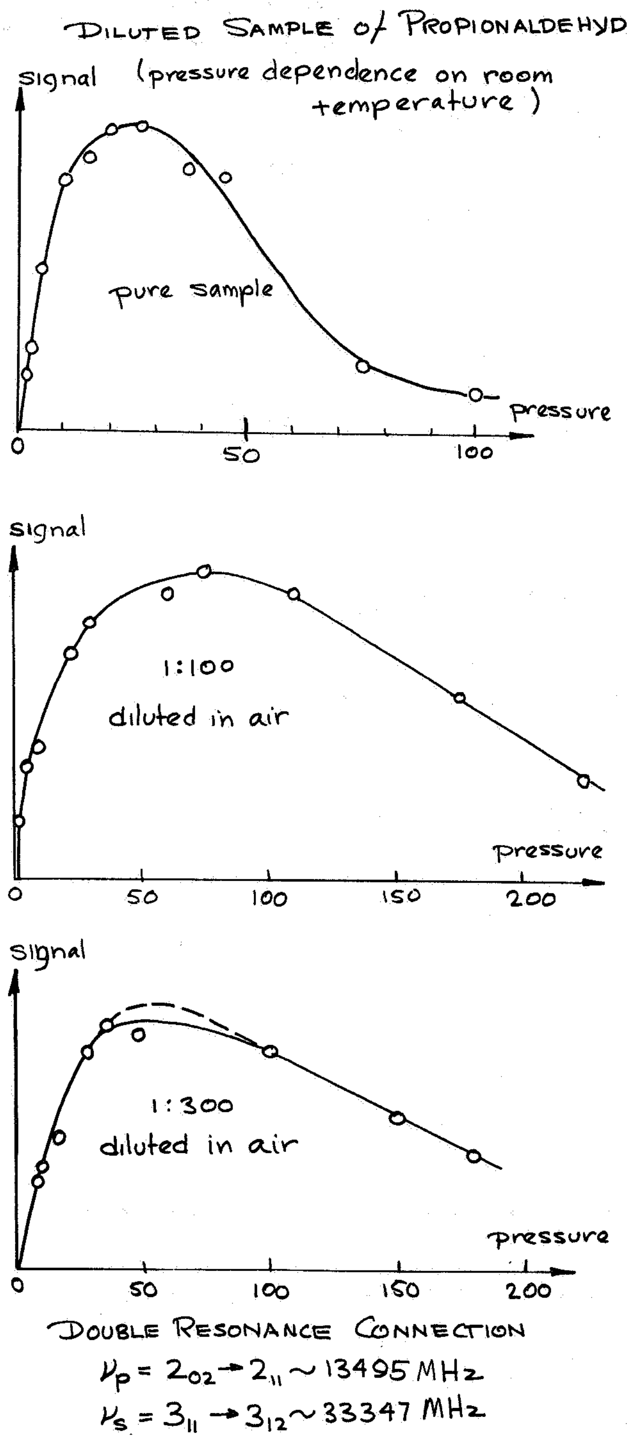


Fig. 31

Propionaldehyde. Pressure dependence of double resonance signal amplitude for pure sample and samples diluted in air.

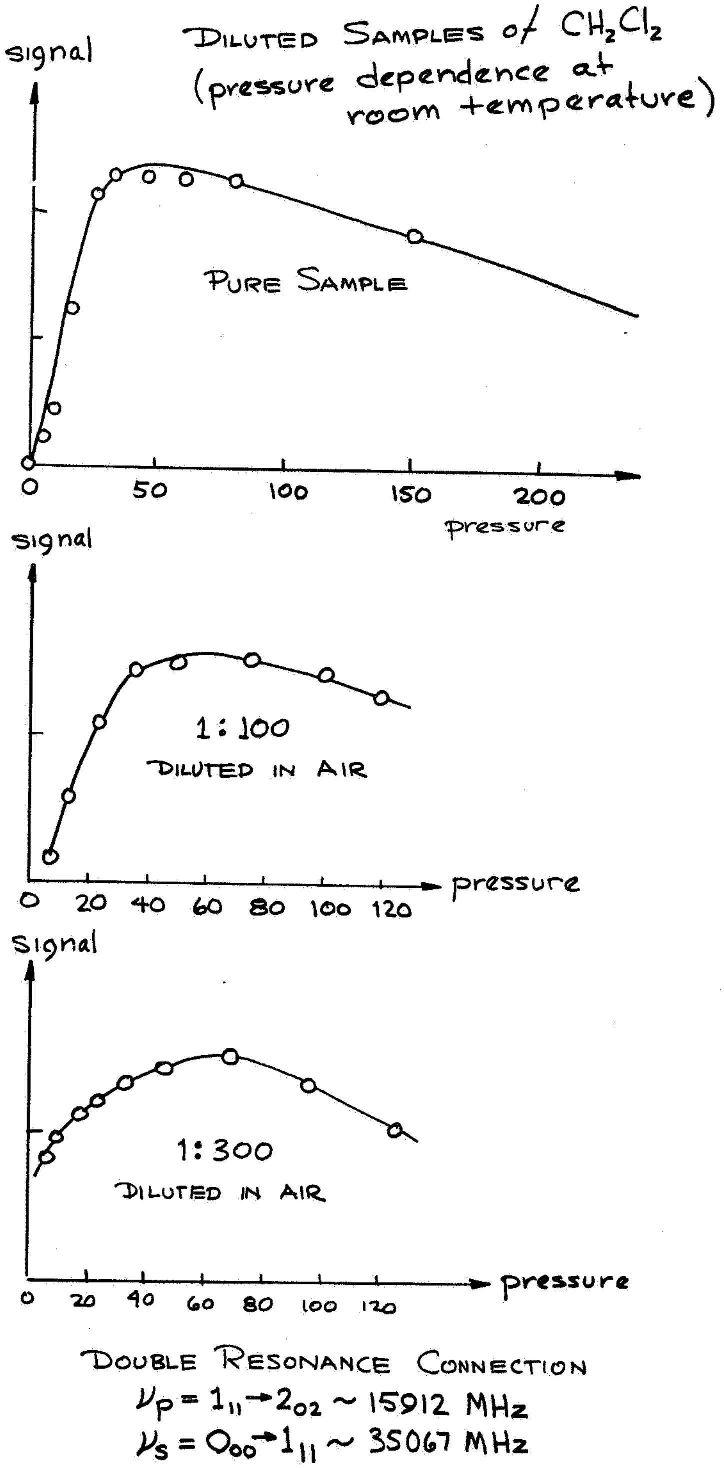


Fig. 32

Methylene Chloride. Pressure dependence of double resonance signal amplitude for pure sample and samples diluted in air.

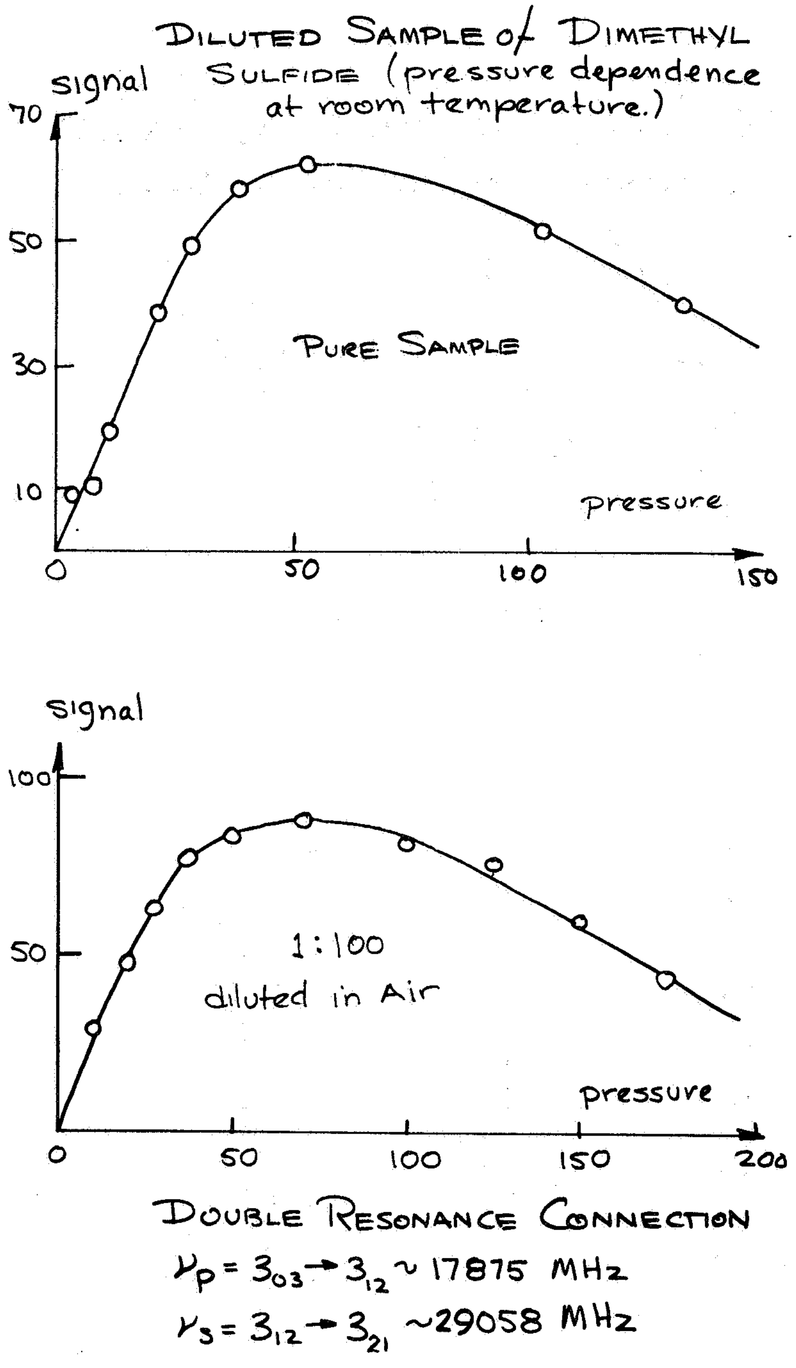


Fig. 33

Dimethyl sulfide. Pressure dependence of double resonance signal amplitude for pure sample and samples diluted in air.

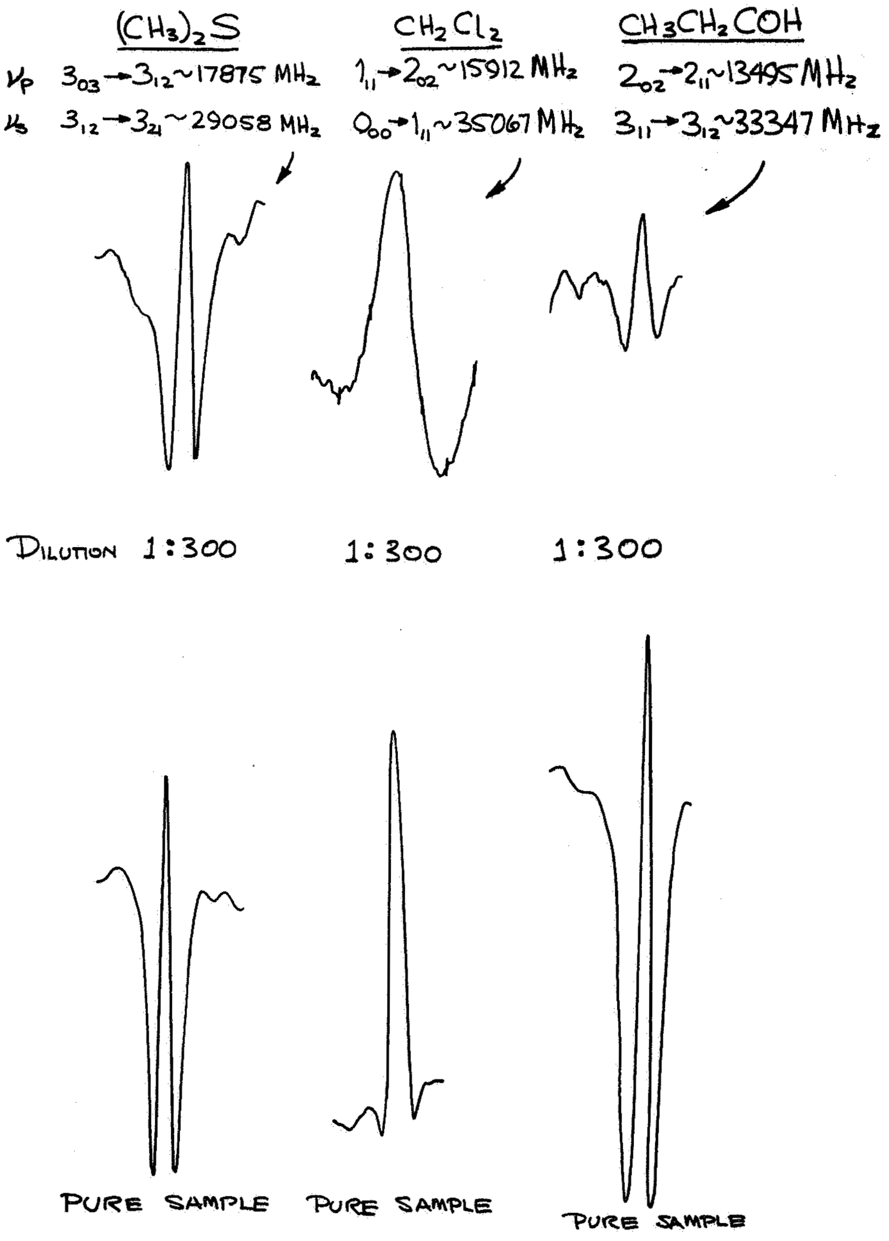


Fig. 34

Comparison between double resonance signals of pure samples and samples diluted in air.

this report. Let it suffice here to indicate that much of the effect can be qualitatively understood by remembering that diluting a sample can have a profound effect on the Van de Waals forces acting on the molecules under investigation.

On the bases of the experiments reported, the question raised at the beginning of this section has to be answered as follows: With the instrument at our disposal double resonance lines can be picked up from samples which are 1:300 diluted in air.

The above quoted value for the threshold of detectability could be pushed down by a factor of > 5 if some technical refinements were made to the spectrometer. If, in addition, a preconcentration technique was used, the threshold of detectability could be reduced to the order of 10 μHg.

Measurements mixtures of pure samples. - After the basic investigations on pure samples and the studies on diluted samples there is enough information available for testing the effectiveness of the double resonance technique for identifying the components of a mixture of gases.

In planning this experiment, one has to make sure that the total pressure obtained when mixing the gases is not higher than the highest pressure, at which the signal arising from the component with the weakest lines can still be distinguished from the background noise. When this condition is violated one will not be able to observe the double resonance indicative of the compound whose pressure is exceeded.

Guided by this consideration in conjunction with the signal versus pressure curves obtained for the pure and diluted samples of the previous sections, the partial pressures of the three gases mixed together in the first experiment were selected as listed in the second column of Table V. At the resulting total pressure of ~ 50 μHg all three double resonances were obtained as can be seen from Fig. 35. An analogous experiment was later performed on a mixture of four compounds with partial pressures adjusted as given in Table VI. The results of this experiment are shown in Fig. 36.

The apparently artificial pressure selection is dictated by the limitation in sensitivity. But the point to be examined here is the selectivity and specificity of the double resonance technique. Examining the figures with this point in mind it is seen that each double resonance is free from any interference due to adjacent lines of the same or any of the other three compounds present in the mixture. This fact represents the most distinct and most important property of microwave double resonance spectroscopy. Even in the presence of several compounds producing numerous and possibly interfering lines (all of which would contribute to the signals observed on a Stark spectrometer) the double resonance signal will not be obscured or falsified and a single double resonance connection will unambiguously pinpoint the molecule from which the signal arises.

TABLE V. - EXPERIMENTAL DATA FOR DOUBLE RESONANCE EXPERIMENT ON MIXTURE OF THREE COMPOUNDS

Compound	Partial Pressure in μHg	Pump Frequency in MHz	Signal Frequency in MHz	Signal Strength Arbitrary Units	Fig. 35
CH_3CH_2COOH	10	17269.0 = $6_{15} \rightarrow 6_{24}$	30436.5 = $6_{24} \quad 6_{33}$	3	a
CH_3CH_2COH	5	13474.9 = $2_{11} \leftarrow 2_{02}$	33347.0 = $2_{11} \rightarrow 3_{12}$	4	b
$(CH_3)_2S$	35	17875.2 = $3_{03} \rightarrow 3_{12}$	29058.5 = $3_{12} \rightarrow 3_{21}$	14	c

TABLE VI. - EXPERIMENTAL DATA FOR DOUBLE RESONANCE EXPERIMENT ON MIXTURE OF FOUR COMPOUNDS

Compound	Partial Pressure in μHg	Pump Frequency in MHz	Signal Frequency in MHz	Signal Strength Arbitrary Units	Fig. 36
CH_3CH_2COOH	12	17269.0 = $6_{15} \rightarrow 6_{24}$	30436.5 = $6_{24} \rightarrow 6_{33}$	2	a
CH_3CH_2COH	7	13473.9 = $2_{02} - 2_{11}$	33347.0 = $2_{11} \rightarrow 3_{12}$	3.5	b
$(CH_3)_2S$	14	17875.2 = $3_{03} \rightarrow 3_{12}$	29058.5 = $3_{12} \rightarrow 3_{21}$	16	c
$CH_3CH_2CH_2Cl$	12	12775 = $5_{05} \rightarrow 5_{14}$	30508.0 = $4_{04} \rightarrow 5_{05}$	8	d

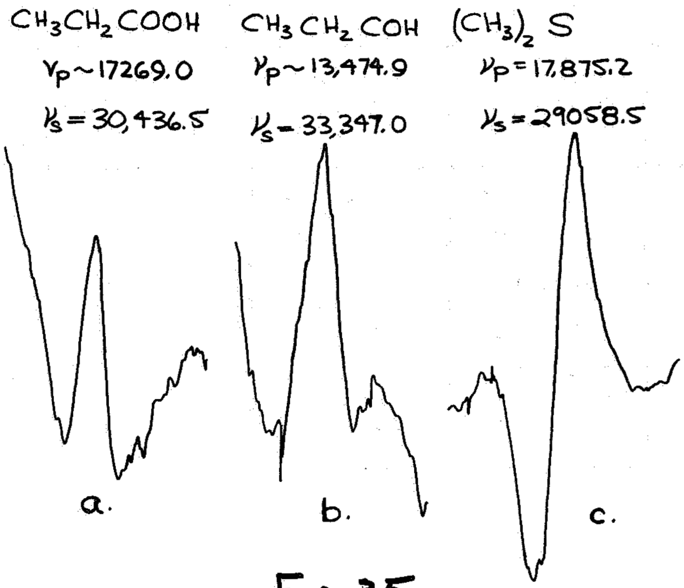


Fig 35

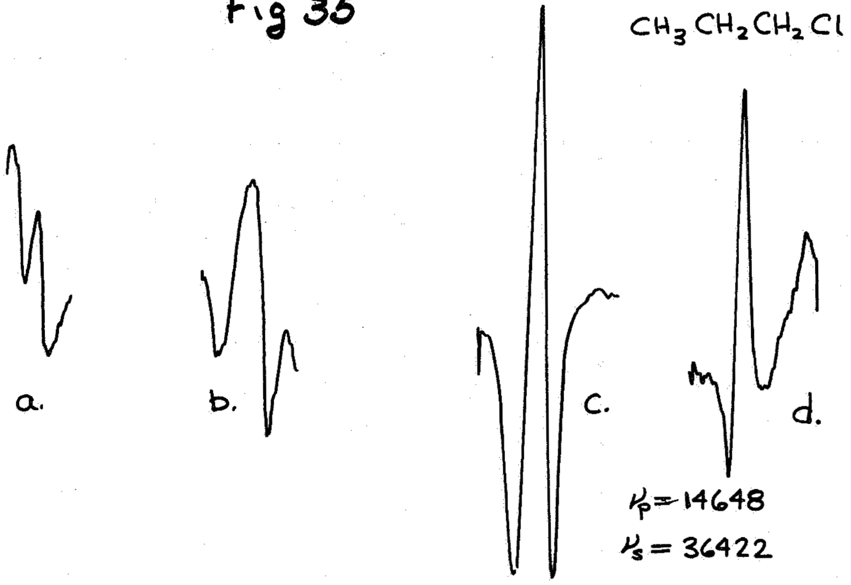


Fig. 36

Double resonance signals obtained in a mixture of four gases.

Instrumental parameters. - Very little has been said so far about the performance of the spectrometer or possible repercussions of instrumental limitations on the results of the previous sections. The main questions arising here are: What is the ultimate sensitivity of the double resonance spectrometer, could it be improved, and how does it compare with conventional Stark modulated spectrometers?

The experiments and calculations to be reported in the following paragraphs will throw some light onto these questions.

Signal amplitude as a function of pump power: The amplitude of a double resonance signal depends on the change in the relative populations of rotational energy levels, which is produced by the "pump" radiation. The magnitude of this change (deviation from the Boltzmann distribution) is proportional to the square of the electric field strength, E_p^2, i.e. the power density, P, of the pump radiation in the absorption cell.(13)

Let us, therefore, estimate the power density at the frequency of a typical pump transition, say at the $2_{02} \rightarrow 2_{11}$ transition of propionaldehyde at $\nu_p \sim .53 \times 10^{-2}$ e.s.u. With this value one obtains as the smallest possible difference between the populations of the 2_{02} - and 2_{11} - level of propionaldehyde with $\left|\mu_{2_{02}} \rightarrow 2_{11}\right|^2 \sim 40 \times 10^{-36}$ e.s.u., $\tau \sim 10^{-7}$ sec.

$$\left(n_{2_{02}} - n_{2_{11}}\right) P \geq \frac{1}{10}\left(n_{2_{02}} - n_{2_{11}}\right)$$

where

$\left(n_{2_{02}} - n_{2_{11}}\right) P$ = difference in populations when pump radiation is applied

$\left(n_{2_{02}} - n_{2_{11}}\right) B$ = difference in populations according to Boltzmann distribution

This result means that even with the very optimistic assumption contained in the above calculation, we are not able to appreciably saturate the pump transition. The double resonance signals observed on our spectrometer may, therefore, be several times weaker than the signals which could be obtained if sufficient pump power were available.

The validity of this statement is supported by an experiment in which the signal amplitude of the propionaldehyde double resonance was measured as a function of the pump power. The latter was varied with an attenuator inserted between the isolator and the directional coupler in the P-band arm in front of the cell. The crystal current on the P-band detector behind the cell was taken as a measure for the amount of pump power within the absorption cell (Fig. 37).

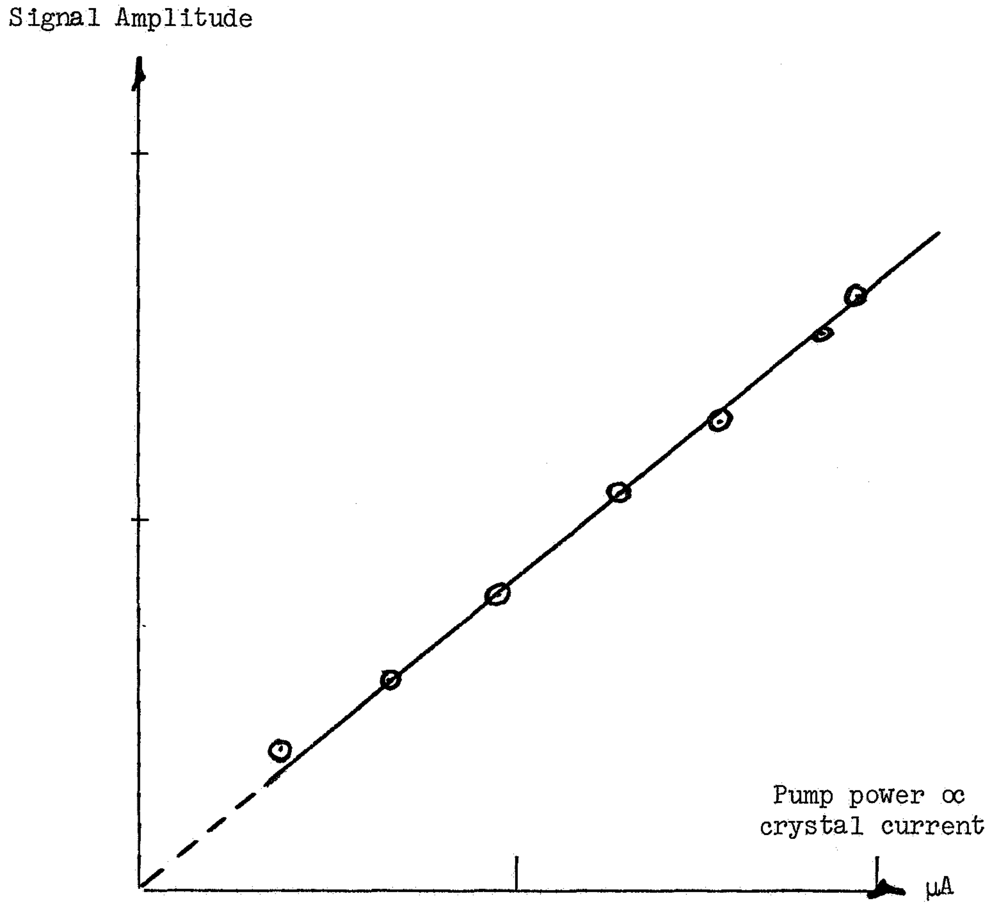


Fig. 37

Double resonance signal amplitude as a function of pump power.

The result of this experiment is represented in Table VII and shown graphically in Fig. 38.

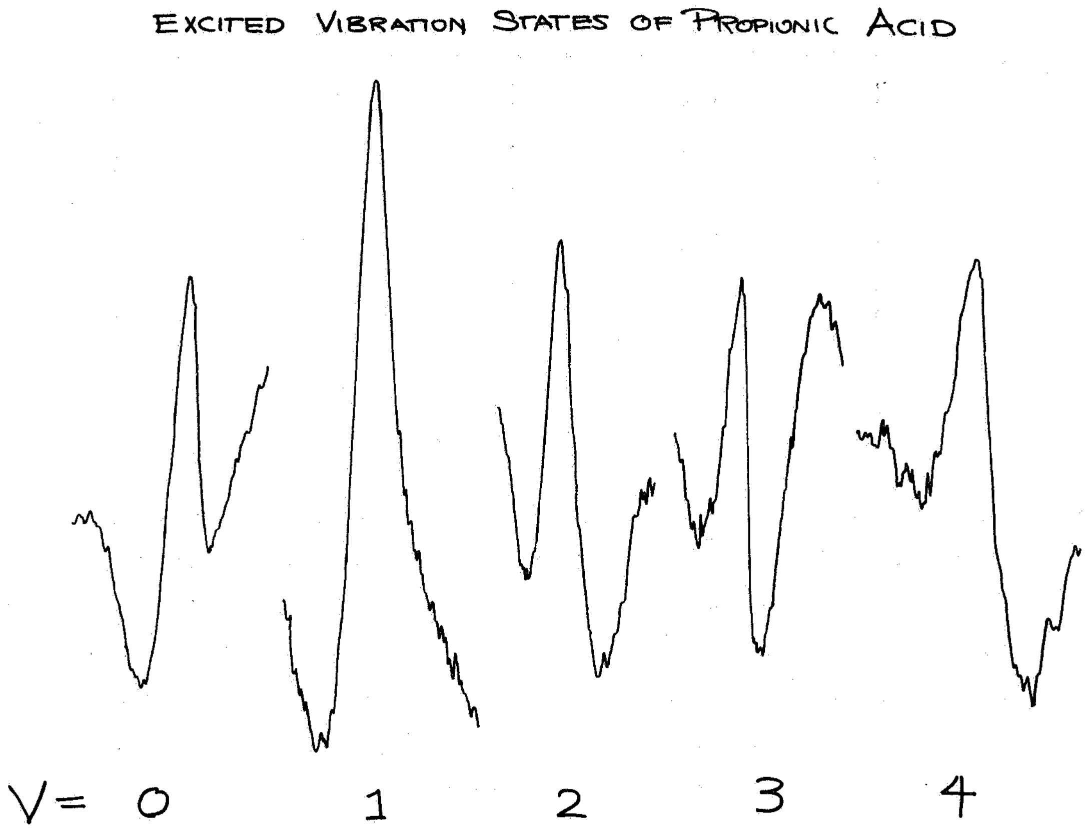


Fig. 38

Double resonances of excited states
of propionic acid.

TABLE VII. - DOUBLE RESONANCE SIGNAL AMPLITUDE AS FUNCTION OF PUMP POWER

X-tal Current in μA ($\propto$ Pump Power)	Signal Amplitude in Arbitrary Units
200	8.3
190	7.9
160	6.6
135	5.6
100	4.2
70	2.9
40	2.0

The linear increase in signal amplitude with increase in pump power is conclusive evidence that even at the highest available pump power we are still far away from saturation and, therefore, from the optimal signal amplitude.

Estimate of the ultimate sensitivity: The ultimate sensitivity of the spectrometer can be estimated by comparing the observed signal/noise ratio of a line with the calculated absolute intensity of this transition. We selected the $2_{11} \rightarrow 3_{12}$ transition of propionaldehyde for this purpose.

Calculation of the absolute line intensity

$$\gamma_{max} = \frac{8\pi^2 Nf}{3\ crT} \left| \mu_{ij} \right|^2 \frac{\nu^2}{\Delta\nu}$$

where

N = number of molecules per cc in cell
f = fraction of molecules in lower rotational level
μ_{ij} = dipole moment matrix element
ν = transition frequency
$\Delta\nu$ = half width of line
k = Boltzmann constant
c = velocity of light
T = temperature

Assuming $\Delta\nu = 25$ MHz/mm

and taking $N = 3.2 \times 10^{-16}$ molecules/cm^3 at 1 mm Hg

$T = 300° K$

$\nu = 3.3347 \times 10^{10}$ sec^{-1}

$|\mu_{2_{11} \rightarrow 3_{12}}|^2 \sim 20$

we obtain as intermediate result

$$\gamma_{max} \sim 5 \times 10^{-2} \times f \, [\mathrm{cm}^{-1}]$$

Calculating the fraction of molecules in the 2_{11} state, we have to take into account the existence of two isomers, the presence of two low lying vibrations and the nuclear statistical weight arising from the 2 sets of 2 equivalent hydrogen atoms, and obtain

$$f \sim 10^{-5} \; .$$

Therefore

$$\gamma_{max} \sim 5 \times 10^{-7} \; \mathrm{cm}^{-1}$$

By comparing this number with the signal/noise ratio of the propionaldehyde traces obtained on the pure sample (Fig. 11) or with the double resonances obtained on the 1:300 diluted sample (Fig. 34) it is judged that the ultimate sensitivity of the spectrometer is of the order of 10^{-9} cm^{-1}.

Comparison with Stark spectra: In order to make a valid comparison between the ultimate sensitivity provided by the double resonance method on one side and the Stark modulation technique on the other side, it would be necessary first to use a spectrometer capable of both methods in order to eliminate all differences which might otherwise arise from the use of different absorption cells or different electronic equipment and, secondly, to make sure that the microwave transitions chosen can be fully modulated in both cases (power requirement in double resonance, electric field requirement in Stark spectroscopy.) If such an ideal experiment could be made it would turn out that both methods are essentially* equivalent as far as the ultimate sensitivity is concerned.

After this has been clarified it will be obvious that the difference encountered in the experiments to follow is mainly due to the difference in electronic equipment and cell length between the double resonance spectrometer, [built by RSI for NASA, Langley] and the Stark spectrometers with which the former is to be compared.

Excited states of propionic acid: The excited states of the torsional vibration in propionic acid, which have previously been observed and assigned on a Stark spectrometer, offer an excellent opportunity for a sensitivity comparison between the double resonance and Stark spectrometer. An attempt was made, therefore, to obtain double resonances for all the excited states for which the signal line had been observed on the Stark-modulated instrument.

The double resonance connection used here was

$$\nu_p = 6_{15} \rightarrow 6_{24}; \; \nu_s = 6_{24} \rightarrow 6_{33}$$

and the respective frequencies of these transitions are listed in Table VIII. The double resonances observed are shown in Fig. 38.

---

*Noticeable differences have to be expected for a certain type of low-J, R-branch transitions.

TABLE VIII. - DOUBLE RESONANCE CONNECTIONS FOR EXCITED STATES OF PROPIONIC ACID

Vibrational State	Pump Freq. MHz $6_{15} \rightarrow 6_{24}$	Signal Freq. MHz $6_{24} \rightarrow 6_{33}$
Ground state	17,269	30,436.5
$V_T = 1$	17,093	30,140.0
$V_T = 2$	16,910	29,829.6
$V_T = 3$	16,715	29,500.2
$V_T = 4$	16,506	29,145.7

With an average energy separation of ~ 65 cm^{-1} between successive states of the C-C-C-torsional vibration (T), the intensity of the vibrational satellite decreases by a factor of ~ .7 per excited state. The intensity of the V = 4 transition is therefore $\approx \frac{1}{4}$ of the ground state line.

Inspection of the traces shows that the $V_T = 1$ double resonance was obtained with a better signal/noise ratio than the ground state double resonance. This can be explained only by assuming that there is greater pump power available at the pump frequency of $V_T = 1$ than there is at $V_T = 0$. Subsequent examination of the power output of the P-band sweeper has proven that this is the correct explanation for the observed anomaly. Unfortunately no Stark traces are available that could be reproduced here for comparison. However, the simple fact that the signals from the excited state lines could indeed be observed represents enough evidence that the double resonance spectrometer preserves the sensitivity of a Stark spectrometer.

Spectra of propionic acid and diluted propionaldehyde: A second possibility to obtain a sensitivity relation between the double resonance and Stark spectrometer is to compare the spectra of diluted samples or other samples known to have weak absorption lines. The $2_{11} \rightarrow 3_{12}$ transition of 1:100 diluted propionaldehyde and the $5_{24} \rightarrow 6_{15}$ transition of propionic acid were considered good test-cases and their Stark signals were, therefore, recorded. In Fig. 39 the Stark traces obtained can be compared with the corresponding double resonance signals. From this figure it is easily seen that the signal/

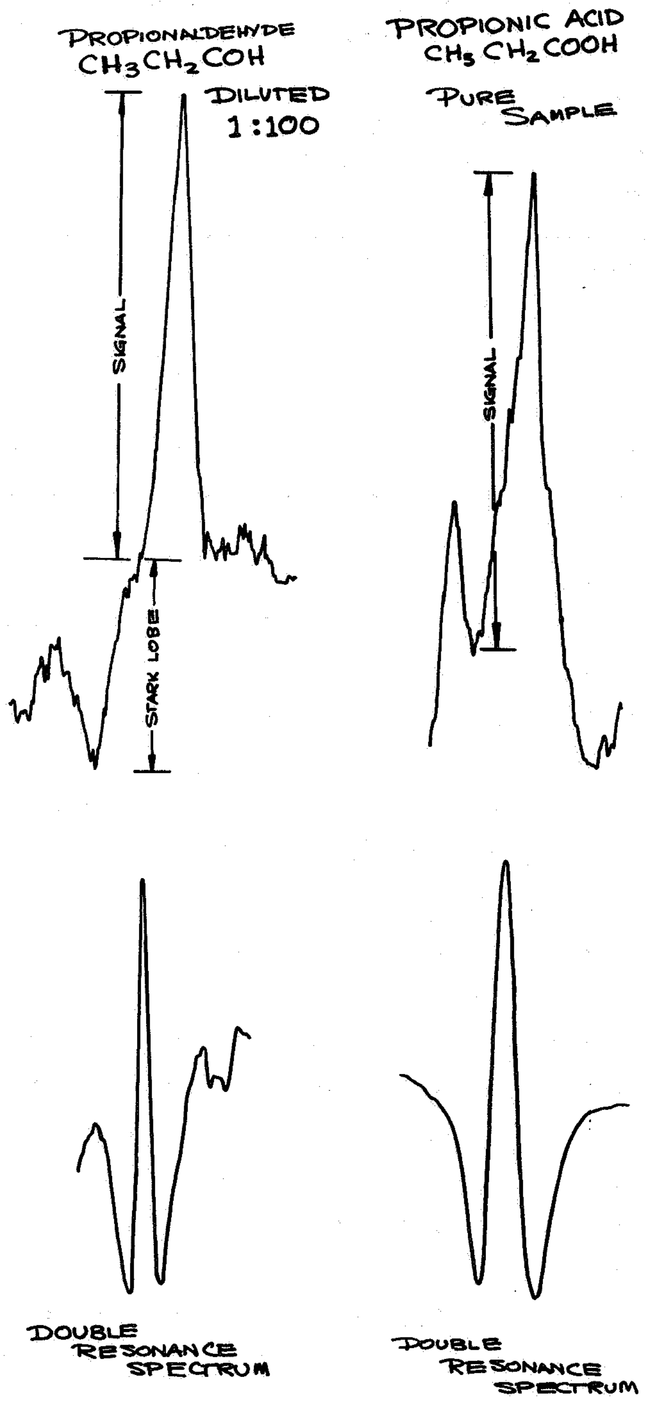


Fig. 39

Comparison between double resonance signals and signals obtained on a Stark spectrometer.

noise ratio is considerably better for the double resonance signals.

Summary. - The experiments and calculations presented in this section can be summarized as follows:

1. The pump power available on the double resonance spectrometer is not sufficient to obtain the optimum signal amplitude. With more pump power a considerable improvement in sensitivity could be obtained.
2. The ultimate sensitivity of the double resonance spectrometer is estimated to be of the order of 10^{-9} cm^{-1}.
3. There is no intrinsic difference in sensitivity between the double resonance and Stark modulation technique. However, the use of longer absorption cells is facilitated in double resonance spectroscopy and hence a higher sensitivity can be obtained with greater ease than on a Stark spectrometer.
4. A comparison of weak absorption signals, obtained on both a Stark system and the double resonance spectrometer, indicates that the double resonance spectrometer is approximately five times better in signal/noise ratio than the Stark system tested.

CONCLUSION

The investigations of this report show that microwave double resonance spectroscopy does not differ appreciably from conventional Stark spectroscopy when sensitivity and resolution are considered. An important and very distinct advantage over the latter is brought about, however, by the great simplification of complex spectra and unique selectivity. These two assets at double resonance spectroscopy allow a much faster and still unambiguous identification of polar gases than could be achieved by the Stark modulation technique.

The pressure range in which the double resonance technique can be employed extends from $\sim$ μHg to $\sim$ 100 μHg. This identifies a double resonance spectrometer as a low pressure device and curtails its major drawback. In order to make it applicable for the detection of trace contaminants in an atmosphere of 760 mm Hg, the sample pressure [i.e. the amount of gas to be detected] has to be reduced by a factor of $\sim 10^4$, resulting in a corresponding loss of sensitivity.

It is felt that research into preconcentration techniques is now needed in order to eliminate this drawback. Once this is accomplished, microwave double resonance spectroscopy could become an extremely powerful tool for gas contaminant identification.

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APPENDIX

Stark Modulated Microwave Spectrometer

Let us assume that we have a gas of molecules which has only two quantum states 1 and 2 separated in energy by $(En)_{12} = h\nu_{12}$. Further, we assume that the average lifetime of a molecule in either of these two states is the same and equal to τ, where τ is the mean time between collisions of the molecules. It is crucial to note at this point that τ is a function of pressure. In fact, for an ideal gas, if we <u>double</u> the pressure τ is <u>decreased</u> by a factor of two. Thus τ and p (the pressure) are related by the equation

$$\tau = c/p$$

where c is some constant whose value turns out not to be important to us. Suppose now we allow a monochromatic source of radiation at frequency ω to impinge upon this gas of molecules, and we ask how much power is absorbed at frequency ω by the gas from the radiation field. The radiation field may be represented by

$$E = E_0 \cos \omega t$$

where E_0 is a constant independent of the time t and is generally called the amplitude of the radiation field. In this case the power absorbed by the gas at frequency ω can be shown to be (reference 1, chapter 13, reference 2)

$$P_\omega \text{ (absorbed)} = (n_1 - n_2) \frac{2\tau \left| \frac{\mu_{12} E_0}{2\hbar} \right|^2 h\nu_{12}}{1 + (\omega - \omega_0)^2 \tau^2 + 4 \left| \frac{\mu_{12} E_0}{2\hbar} \right|^2 \tau^2}$$

where

n_1 = number of molecules per cm^3 in state 1 for the gas at thermal equilibrium

n_2 = number of molecules per cm^3 in state 2 for the gas at thermal equilibrium

$\omega_o = 2\pi\ \nu_{12}$

μ_{12} = dipole moment of the molecular system for the transition from state 1 to 2.

h is Planck's constant

$\hbar = h/2\pi$

The parameter $|\mu_{12}\ E_o/2\hbar|^2$ occurs frequently in the following discussion and so we define

$$|y| = \mu_{12}\ E_o/2\hbar|$$

and the absorbed power becomes

$$P_\omega\ (\text{absorbed}) = (n_1\ - n_2)\ \frac{2\tau|y|^2\ h\nu_{12}}{1 + (\omega-\omega_o)^2\ \tau^2 + 4|y|^2\ \tau^2}$$

Note that 7 depends upon the molecular system through μ_{12} and on the amplitude of the radiation field through E_o. However, y is <u>independent</u> of pressure.

<u>Dependence of signal strength on power absorbed</u>. - In general for Stark modulated spectrometers the signal S observed depends linearly on the power absorbed so that we may say

$$S_\omega = g\ P_\omega\ (\text{absorbed})$$

where g is a constant depending upon the length of the waveguide, the gain of the amplifiers and many other parameters. It turns out that the exact form of g is completely unimportant to us. What is important to realize is that the signal seen on the Stark modulated spectrometer is some constant multiple of P_ω (absorbed). Incidently, this result is not obvious and in fact in some cases is not even true. These cases will not concern us here. Thus we always take

$$S_\omega \sim (n_1\ - n_2)\ \frac{2\tau|y|^2\ h\nu_{12}}{1 + (\omega-\omega_o)^2\ \tau^2 + 4|y|^2\ \tau^2}$$

For low amplitude radiation fields it is usually the case that

$$4|y|^2 \tau^2 \ll 1 \quad .$$

With this approximation we may take

$$S_\omega \sim (n_1 - n_2) \frac{2\tau |y|^2 h\nu_{12}}{1 + (\omega - \omega_o)^2 \tau^2} \quad .$$

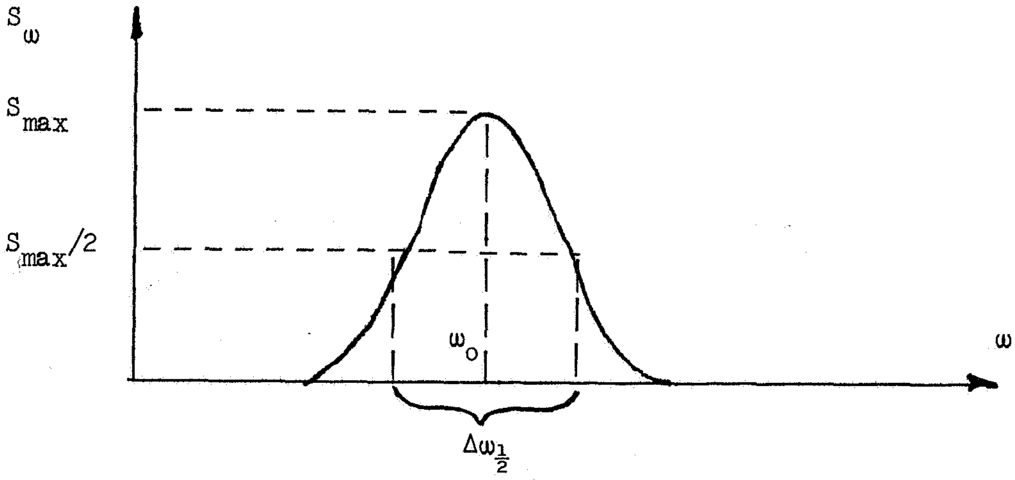
Let us rewrite this without using the y shorthand as

$$S_\omega \sim (n_1 - n_2) \frac{2\tau \left| \frac{\mu_{12} E_o}{2\hbar} \right|^2 h\nu_{12}}{1 + (\omega - \omega_o)^2 \tau^2} \quad .$$

We would like to plot S_ω as a function of ω for a gas at constant temperature and pressure. Holding temperature and pressure constant simply insures that n_1, n_2, τ are constants. Furthermore, we also hold the amplitude E_o of the radiation field

$$E = E_o \cos \omega t$$

constant and vary only its frequency ω. Under these conditions the only variable in S_ω is ω.



There are several important points to note about the shape and character of S_ω.

1. $S_{max} = S_{\omega_o} \sim (n_1 - n_2)\ 2\tau \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 h\nu_{12}$

2. $S_{max}/2$ occurs at $\omega = \omega_o \pm 1/\tau$. This follows by setting

$$(n_1 - n_2)\ \frac{2\tau \left|\frac{\mu_{12} E_o}{2\hbar}\right|^2 h\nu_{12}}{1 + (\omega-\omega_o)^2\ \tau^2} = \tfrac{1}{2} S_{max}$$

   and solving for ω.

3. From (2) it follows that $\Delta\omega_{\frac{1}{2}} = 2/\tau$. $\Delta\omega_{\frac{1}{2}}$ is the full width at half height of the absorption signal.

We may now consider the behavior of S_ω as a function of power and as a function of the pressure in the applied radiation field.

1. S_ω as a Function of Power in the Field:

   The power in a radiation field of the form

$$E = E_o \cos \omega t$$

is proportional to E_o^2 . That is

$$\text{Power (Field)} \sim E_o^2 \quad .$$

Note also that $S_\omega \sim E_o^2$ so that we have

$$S_\omega \sim \text{Power} \quad .$$

The signal height is directly proportional to the power of the applied field. It is important to remember that this result has been derived with the approximation

$$4|y|^2\ \tau^2 \ll 1 \qquad \text{or}$$

$$|\mu_{12}\ E_o/h|^2\ \tau^2 \ll 1$$

Thus if E_o^2 becomes so large that the above in-equality no longer holds S_ω is no longer linearly related to Power (Field). In the case where $|\mu_{12}\, E_o/\hbar|^2\, \tau^2 \geq 1$ the signal is said to be saturated or saturation broadened or power broadened. Physically this corresponds to a situation where the radiation field is so intense that the rate at which molecules are excited from state 1 to state 2 by the field is much greater than the rate at which they relax from state 2 to state 1 by collision processes.

2. S_ω as a Function of Gas Pressure:

a. We have

$$S_{max} \sim (n_1 - n_2)\, \tau \left\{2\left|\frac{\mu_{12}\, E_o}{2\hbar}\right|^2 h\nu_{12}\right\}$$

See the quantities in the curly bracket are independent of pressure. Thus the only pressure dependence of S_{max} is in $(n_1 - n_2)\,\tau$. Previously we noted $\tau \sim 1/p$. To a sufficient degree of accuracy n_1, n_2 (the number of molecules per cm^3 in states 1, 2) are linearly related to pressure. Thus $(n_1 - n_2) \sim p$ so that we have the important result:

S_{max} is independent of pressure .

[The maximum height of the absorption signal is independent of pressure.]

b. We have

$$\Delta\omega_{\frac{1}{2}} = 2/\tau \ .$$

However, we also know $\tau \sim 1/p$. Thus

$$\underline{\Delta\omega_{\frac{1}{2}} \sim p} \ .$$

The line width of the absorption is directly proportional to pressure.

Conclusion (Part I). - The above considerations may seem tedious to those well acquainted with pressure broadening concepts in microwave spectrocopy or too brief for those with no contact at all. This presentation has been given to serve as a basis for understanding the double resonance line shape characteristics. Further details on the preceding can be found in references 1 and 2.

Results for ordinary Stark modulation:

1. Linewidth doubles if pressure is increased by a factor of two (directly proportional).
2. Signal height at peak ($\omega = \omega_0$) is independent of pressure. This is because $(n_1 - n_2)$ is directly proportional to pressure but τ is inversely proportional. Thus $(n_1 - n_2)$ is independent of pressure.

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