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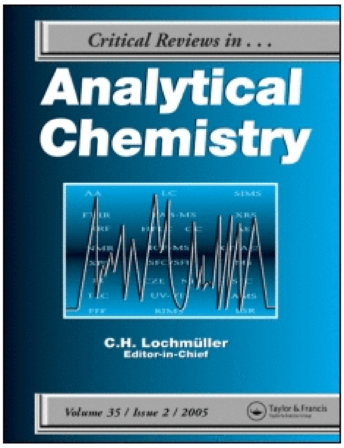

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Jones, Gordon E. , Cook, Robert L. and Lide Jr, David R.(1973) 'Chemical Analysis by Microwave Spectroscopy', Critical Reviews in Analytical Chemistry, 3: 4, 455 — 506

To link to this Article: DOI: 10.1080/10408347308542668

URL: http://dx.doi.org/10.1080/10408347308542668

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CHEMICAL ANALYSIS BY MICROWAVE SPECTROSCOPY

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I. INTRODUCTION

Microwave spectroscopy is concerned with the observation and analysis of transitions between molecular rotational energy levels. These transitions fall within the segment of the electromagnetic spectrum called the microwave region. This region lies between the conventional radio wave region and the infrared region and extends from frequencies around 1,000 MHz ($\lambda = 30$ cm) to around 1,000,000 MHz ($\lambda = 0.3$ mm). In this spectral region, it is common practice to express frequencies in megahertz (MHz) or gigahertz (GHz), where the Hertz (Hz) unit denotes cycles per second, 1 MHz = 10^6 Hz, and 1 GHz = 10^9 Hz. The region may be further divided into the centimeter-wave ($\lambda = 1$ to 30 cm), millimeter-wave ($\lambda = 1$ to 10 mm), and submillimeter-wave regions ($\lambda < 1$ mm). Whereas the infrared region is associated with the phenomena of molecular vibrations, the microwave region is associated with molecular rotations. Microwave spectroscopy usually implies gas-phase molecular rotational spectroscopy, though other areas of spectroscopy, such as EPR, operate in the microwave region. The term molecular rotational resonance (MRR) spectroscopy has also been applied.

In 1946, after the close of World War II, serious exploration of the microwave region became possible because of the developments of the various components for microwave radar during the war, such as klystrons and wave guide devices. Since that time, the field has grown rapidly, much information on molecular properties has been obtained, and much more can be expected with the continuing advances in instrumentation and theoretical methods. A recent survey of the molecular information obtainable from a microwave study and a description of the theoretical methods are given by Gordy and Cook.[1]

Even though microwave spectroscopy has been a powerful research tool for over 25 years, it has attracted substantial interest as a serious analytical tool only in the last few years with the advent of commercial spectrometers. Commercial spectrometers, which are reliable and particularly suitable for routine analysis, presently operate in the region from 8 to 40 GHz. The higher frequency region from 26 to 40 GHz, the so-called R-band region, offers the highest sensitivity. The instrumentation has now reached the stage where low-resolution spectra of a whole microwave band can be displayed on a desk size (or smaller) recording much like IR spectra. Chemical analysis by microwaves is a nondestructive technique limited essentially to compounds having a permanent electric dipole moment and a vapor pressure of approximately 10 mtorr. Weak magnetic dipole transitions are also possible; however, few stable molecules have a magnetic dipole. Only a very small sample, on the order of tenths of a milligram, is required for an analysis. In qualitative analysis, microwave spectroscopy identifies molecules by their characteristic absorption of microwave radiation. The measured quantity is the frequency of a rotational absorption line. Conventional spectrometers commonly measure frequencies with accuracies of one part in 10^6 or better and with resolutions on the order of 0.1 MHz. In fact, the distinguishing features that characterize microwave spectroscopy are this high precision and high resolution. Because of these characteristics, only a few measured lines, in principle, are required to uniquely identify the absorbing molecule. In quantitative analysis, the intensities of the absorption lines provide the basis for determining concentration. The most common method of evaluating molecular concentration relies on a comparison of the intensity of a given absorption line in an unknown mixture with the intensity of the same line in a mixture whose composition is known. As infrared spectra can be used for qualitative or quantitative analysis without a normal coordinate analysis, so microwave spectra can be employed without an interpretation or assignment of the spectral patterns. Hence, one does not have to be an expert in microwave spectroscopy to employ it as an analytical tool.

Microwave spectroscopy has, in fact, an early history of detecting atmospheric pollutants. An interesting incident, which occurred during World War II, has been reported by Gordy[2] and is as follows: "A group of scientists at the MIT Radiation Laboratory were testing the new K-band radar by observing signals from buildings in Back Bay across the Charles. Mysteriously, the signals blacked out temporarily each day at almost the same time. This puzzling phenomenon was solved when an alert technician correlated the blackout with the daily passing of a garbage boat up the river. From the boat came the unmistakable smell of ammonia." Although the authenticity of the incident is not guaranteed,[2] it surely illustrates the capabilities of microwave spectroscopy in spectrochemical analysis.

Although it was recognized quite early that microwave spectroscopy could be employed as an analytical technique, relatively few applications have been carried out to date. Part of the reason for this is that the researcher in microwave spectroscopy was usually interested in determining molecular properties rather than in chemical analysis per se. Furthermore, microwave spectrometers were constructed in research laboratories and, except in a few cases, were not particularly designed for intensity measurements and ease of operation – two important considerations in analytical applications. The latter problem has been overcome, as mentioned previously, with the introduction of commercial spectrometers. However, analytical applications still seem to be limited to only a few laboratories, and these are primarily laboratories with expertise in microwave spectroscopy. Specialists in analytical chemistry have not yet begun to use the technique on a widespread scale. With this in mind, we will not only try to provide a critical review but will also furnish the nonspecialist with some fundamentals of the technique and attempt to familiarize him with the important spectral and instrumental characteristics of rotational spectroscopy. In addition, the various possibilities and problems associated with analytical applications will be discussed.

Earlier reviews on the subject of spectrochemical analysis by microwave spectroscopy have been given by Hughes,[3] Dailey,[4] Gordy,[5] and Millen.[6] More recent reviews have been given by Lide,[7,8] Scharpen and Laurie,[9] Sheridian,[10] and Cook and Jones.[11] Recent reviews covering the general field, and other particular areas of microwave spectroscopy, are available by Flygare,[12] Morino and Hirota,[13] Rudolph,[14] Morino and Saito,[15] Boggs,[16] Dreizler,[17] and Laurie.[18] Reviews of the techniques and information obtainable in the shorter millimeter-wave region and submillimeter-wave region have been given by Gordy[19] and by Winnewisser, Winnewisser, and Winnewisser.[20] A number of books devoted to the subject of microwave spectroscopy are available, and the reader is directed to these for a more detailed discussion of the field and the theory of rotational spectra. Books are available by Gordy, Smith, and

Trambarulo,[21] Townes and Schawlow,[22] Sugden and Kenney,[23] Wollrab,[24] and Gordy and Cook.[1] Microwave spectroscopy bibliographies have been compiled by Starck[25,26] and by Guarnieri and Favero.[27] Of particular use for analytical applications are the tabulations of line frequencies for compounds reported in the literature. These are available from the National Bureau of Standards.[28]

II. BACKGROUND MATERIAL

In this section, we introduce the reader to some fundamentals of microwave spectroscopy and indicate the consideration of importance in analytical application.

A. Rotational Energy Levels and Spectra

To a good approximation, the electronic, vibrational, and rotational motions may be treated separately, and the energy of a molecule may be expressed as the sum of the energies of these three motions. In pure rotational spectra, transitions take place from the rotational sublevels of a particular vibrational state associated with a given electronic state to other rotational levels of the same vibrational and electronic state. The frequencies of electromagnetic radiation absorbed are given by the Bohr relation

$$\nu = (E_j - E_i)/h, \qquad (1)$$

where h is Planck's constant, and E_j and E_i are the upper and lower rotational energy states of the molecule. A basic problem of rotational spectroscopy is the evaluation of these quantized rotational energies by quantum mechanical techniques. Because gaseous molecules are constrained to have only discrete values of rotational energy and total angular momentum, they rotate at only certain rates. By absorption of a quantum of energy $h\nu$, the molecule is raised to a higher energy level and thus rotates at the next higher allowed rate. Such rotational transitions are induced through the interaction of the molecular electric dipole moment with the electric vector of the microwave radiation field. The type of transition which can occur between rotational energy levels is governed by the electric dipole moment matrix element,

$$\mu_{ij} = \int \psi_i^* \underline{\mu} \psi_j \, d\tau, \qquad (2)$$

usually called the transition moment. Here ψ_i^* and ψ_j are, respectively, the wave functions for the lower and upper rotational states, each characterized by the set of quantum numbers i and j. For a transition to be allowed, the above matrix element must be nonvanishing. The restrictions which are thereby placed on the quantum numbers i and j are called selection rules. The transition moment automatically vanishes if the molecule does not have a permanent electric dipole moment. Therefore, only polar molecules give rise to pure rotational spectra.

The gross features of the rotational spectrum of a molecule may be ascertained by treating the molecule as a rigid, nonvibrating rotor. The molecular geometry via the moments of inertia determines, primarily, the pattern of the rotational spectrum. This pattern is relatively simple for linear and symmetric-top molecules; however, for asymmetric rotors there is little regularity to the spectrum except in certain cases.

The three mutually perpendicular axes with origin at the center of mass, so oriented in the molecule that with respect to these axes the moment of inertia matrix is diagonal, are called the principal inertial axes. These axes are denoted by a, b, and c. The corresponding moments of inertia I_a, I_b, and I_c are called the principal moments of inertia and labeled so that $I_a < I_b < I_c$. These quantities depend on the mass and coordinates of the atoms in the principal axis system, i.e.,

$$I_a = \Sigma m_i(b_i^2 + c_i^2). \qquad (3)$$

Similar expressions for I_b and I_c are obtained by cyclic permutation of a, b, and c. The rotational energies for the various types of rotors depend on the rotational constants designated by A, B, and C, with A> B> C, and defined by

$$A = h/8\pi^2 I_a, \qquad (4)$$

etc. The relation between A in units of megahertz and I_a in atomic mass units-angstrom units squared is

$$A(\text{MHz}) = 505{,}376/I_a(\text{amu Å}^2). \qquad (5)$$

This conversion factor is based on the ^{12}C mass scale.

The various types of rotors may be grouped according to the values of the principal moments of inertia. When all three moments of inertia are equal ($I_a = I_b = I_c$), we have a spherical top. Molecules of this type are not of interest in microwave spectroscopy since they do not have a permanent dipole moment. In the case of a linear molecule, the moment of inertia about the internuclear axis vanishes ($I_a = 0$), and the moments of inertia perpendicular to the internuclear axis are equal ($I_b = I_c$). Molecules with a threefold or higher axis of symmetry are symmetric tops. The symmetry axis of the molecule is one of the principal axes, and the dipole moment lies along this axis. Also, any two perpendicular axes which are perpendicular to the symmetry axis are principal inertial axes, and the corresponding moments of inertia are equal. The molecule is designated a prolate or oblate symmetric top, depending on which inertial axis corresponds to the molecular symmetry axis. The two cases may be summarized as follows:

Prolate top $I_a < I_b = I_c$	Axis of least moment of inertia, a, along the symmetry axis.
Oblate top $I_a = I_b < I_c$	Axis of largest moment of inertia, c, along the symmetry axis.

In the case of an asymmetric top, all three principal moments of inertia are different: $I_a \neq I_b \neq I_c$; $A > B > C$. This particular case is most often met since most molecules (to the extent that they can be considered rigid bodies) are asymmetric tops. If the molecule has some symmetry, one or more principal axes may be selected by inspection. If a molecule has a twofold axis of symmetry, this axis must be a principal axis. If a symmetry plane is present, then two principal axes lie in this plane and the third must be perpendicular to this plane.

The energy for a rigid rotor may be written in the general form

$$E_{J,\tau} = \tfrac{1}{2}(B+C)J(J+1)+[A-\tfrac{1}{2}(B+C)]\,W_{J_\tau}(b_p), \tag{6}$$

where J is the total rotational angular momentum quantum number, which can have the integral values 0, 1, 2, 3, ... The W_{J_τ} is called a reduced energy. The simplest rotor is a linear molecule where $B = C$, $W = 0$, and the energy expression, Equation 6, takes the form

$$E_J = BJ\,(J+1). \tag{7}$$

For linear molecules, the rotational energy levels are characterized by two quantum numbers, J and M. The quantum number M (= 0, ± 1, ± 2, . . . , ± J) specifies the possible components of the total angular momentum along an axis fixed in space. In the absence of external fields, the rotational energies do not depend on M, as Equation 7 implies, and all levels are $(2J + 1)$-fold degenerate. However, when an external field is applied, this degeneracy is lifted, and the energy depends on the space orientation quantum number M. A similar condition holds for symmetric and asymmetric tops. For rotational absorption of radiation, the selection rule

$$J \rightarrow J + 1$$

applies, and the rotational frequencies of a linear molecule are given by

$$\nu = E_{J+1} - E_J = 2B\,(J+1). \tag{8}$$

A series of lines at 2B, 4B, 6B, . . . is thus expected for a rigid rotor. The spectrum of Figure 2 is like that of a linear rotor. The molecule OCS, which is commonly used as a standard for various purposes by microwave spectroscopists, has lines which occur at 12,162.97, 24,325.92, 36,488.80, 48,651.40 MHz, . . . for the most common isotope. At high J, i.e., higher rotational energies, the molecular bond lengths will increase slightly due to the centrifugal force arising from the rotation. The moments of inertia thus increase slightly, and the energy decreases. This distortion effect is very small and primarily important only for high J values. The effect of this on the rotational spectrum is to decrease slightly the separation between consecutive lines, altering somewhat the regular separation of 2B between the absorption lines for a rigid rotor.

For a prolate symmetric top $B = C$, $W = K^2$ and the energy levels are

$$E_{J,K} = BJ(J+1) + (A-B)K^2. \tag{9}$$

The energy levels are now characterized by the quantum numbers J, K, and M. The quantum number K(= 0, ± 1, ± 2, . . . , ± J) specifies the possible components of the total angular momentum along the molecular symmetry axis. By replacement of A by C, the energy expression for an oblate top may be obtained from Equation 9.

Note there are (J + 1) different rotational levels for each J value since the energy does not depend on the sign of K. For absorption of radiation, the important selection rules are

$$J \rightarrow J+1,\ K \rightarrow K.$$

The rotational line frequencies are therefore again given by Equation 8, and the rotational spectrum, in this rigid rotor approximation, is like that of a linear molecule. When centrifugal distortion effects are considered, the absorption frequencies are no longer independent of the quantum number K, and this gives rise to a splitting of a given $J \rightarrow J+1$ transition into (J+1) closely spaced lines. This distinguishes the rotational spectrum of a symmetric top from that of a linear molecule.

For an asymmetric-top molecule, the rotational energy levels are given by Equation 6, and the quantity $W_{J_\tau}(b_p)$ is a function of Wang's asymmetry parameter

$$b_p = \frac{(C-B)}{[2A-(B+C)]}, \tag{10}$$

which is appropriate for a near prolate top, where $B \simeq C$ and $b_p \simeq 0$. For a near oblate top, A and C are interchanged in Equations 6 and 10. An alternate measure of the asymmetry is Ray's parameter

$$\kappa = \frac{2B-A-C}{A-C}. \tag{11}$$

For a prolate symmetric top $\kappa = -1$, and for a oblate top $\kappa = +1$. If $B \simeq C$, $\kappa \simeq -1$, the asymmetric top may be classified as a near prolate rotor. If $A \simeq B$, $\kappa \simeq +1$, we have a near oblate asymmetric rotor. The case $\kappa = 0$ corresponds to the most asymmetric top possible. The effect of the asymmetry is to remove the twofold degeneracy of the K levels ($K \neq 0$) for a symmetric top. This "K-splitting" of the levels increases as the asymmetry increases. There are thus (2J+1) different rotational levels or values of $W(b_p)$ for each value of J. The evaluation of the quantities $W(b_p)$ requires numerical diagonalization techniques and is discussed elsewhere.[1] In the case of near prolate or oblate asymmetric rotors, the $W(b_p)$ differ only slightly from K^2 and may be conveniently expressed as an expansion in terms of Wang's asymmetry parameter.[1] To distinguish the sublevels for a given J, the notation J_τ is employed where τ takes on (2J+1) integer values ranging from −J to +J. These are assigned to the energy levels such that $\tau = -J$ corresponds to the lowest energy, $\tau = -J+1$ to the next lowest energy level, and finally $\tau = J$ to the highest level. The energy levels for an asymmetric rotor are thus characterized by the quantum numbers J and M and by the pseudoquantum number τ. An alternate notation is more frequently employed where two subscripts are added to J, i.e., J_{K_{-1},K_1}. A particular asymmetric-top level will converge to a particular prolate symmetric-top level (corresponding to a particular value of |K|) as κ approaches −1 and to a particular oblate symmetric-top level as κ approaches +1. The subscript K_{-1} is therefore the |K| value of the prolate rotor limit, $\kappa = -1$, and K_1 is the |K| value of the oblate rotor limit, $\kappa = 1$. The relation between the two notations is

$$\tau = K_{-1} - K_1. \tag{12}$$

The possible energy levels for J = 1 may hence be denoted as 1_{-1}, 1_0, 1_1 or more commonly as $1_{0,1}$, $1_{1,1}$, $1_{1,0}$.

For dipole absorption of radiation, the selection rules for J are given below along with their general designations:

$J \rightarrow J+1$, R-branch transition
$J \rightarrow J$, Q-branch transition
$J \rightarrow J-1$, P-branch transition.

The transitions $\Delta J = 0$, $\Delta J = -1$ can give rise to absorption lines for an asymmetric rotor, though not for a rigid linear or symmetric rotor. The $\Delta J = -1$ transitions arise because all levels are not always ordered by their J values. The selection rules for K_{-1} and K_1 depend on the possible components of the molecular dipole along the principal inertial axes. In general, an asymmetric top can have a dipole moment component along all three principal axes. The dipole component along the axis associated with the least, the intermediate, and the greatest moment of inertia are denoted μ_a, μ_b and μ_c, respectively. Transitions that arise from the μ_a component are designated as "a"-type transitions. Similarly, those due to μ_b or μ_c are designated as "b"-type or "c"-type transitions. If, for example, $\mu_a = 0$, then no "a"-type transitions are allowed. The selection rules for the subscripts K_{-1} and K_1 can be expressed in terms of the allowed changes of K_{-1} and K_1 or in terms of the evenness or oddness of the subscripts. If K_{-1} is an even (odd) integer, it is designated e(o); similarly for K_1. The resulting selection rules are summarized as follows:

Direction of dipole component	Permitted transitions				
	ΔK_{-1}	ΔK_1	$K_{-1}K_1$	↔	$K'_{-1}K'_1$
μ_a	0,±2,–	±1,±3,–	ee	↔	eo
			oe	↔	oo
μ_b	±1,±3,–	±1,±3,–	ee	↔	oo
			oe	↔	eo
μ_c	±1,±3,–	0,±2,–	ee	↔	oe
			eo	↔	oo

A transition such as $1_{0,1} \rightarrow 2_{0,2}$ is hence an R-branch, "a"-type transition, while the transition $2_{1,1} \rightarrow 2_{2,0}$ is a Q-branch, "b"-type transition.

As an approximate rule, the most intense lines will be those for which $\Delta K_{-1} = 0, \pm 1$ for $\kappa \simeq -1$, and $\Delta K_1 = 0, \pm 1$ for $\kappa \simeq +1$. Intensities of rotational lines will be considered further in Section II.C. Unlike linear and symmetric-top molecules, transitions between high J levels can fall at low frequencies for an asymmetric top. Because of the greater number of possible transitions and the lack, in many cases, of any regular spectral pattern, the rotational spectum of an asymmetric rotor is more complicated and more difficult to assign. Various effects, like the Stark effect, have been found to be useful aids in the assignment of such spectra. A rotational spectrum of an asymmetric rotor is given in Figure 1. The spectrum is a moderately rich spectrum, and the lack of any obvious pattern is apparent. In some situations, spectra with a rather regular pattern are obtained. For "a"-type transitions ($\Delta J = 1$, $\Delta K_{-1} = 0$) of a very near prolate rotor ($\kappa \simeq -1$), a spectral pattern which closely resembles that of a symmetric top is obtained. For small asymmetry $W(b_p) \simeq K^2$, and Equation 6 gives for the absorption frequencies

$$\nu \simeq (B+C)(J+1). \qquad (13)$$

What will be observed is a group, or cluster, of lines centered approximately at the above frequency. Each group of lines will be separated from the next group by approximately (B+C). Such a spectrum is shown in Figure 2. Note the regular separation between the absorption bands. A similar situation occurs for the "c"-type transitions of a very near oblate rotor ($\kappa \simeq 1$); the separation is now approximately (A+B). These bandlike spectra are particularly useful for qualitative analysis, as is discussed further in Section IV.B.

B. Interaction Effects in Rotational Spectra

The salient characteristics of the rotational spectra for the various types of rotors have been discussed. These gross characteristics will be modified somewhat when the effects of vibration, nuclear coupling, etc. are taken into account. These effects and their implications for chemical analysis will be discussed briefly. Lest the reader feel that the various interactions, which are outlined below, would make chemical analysis by microwave spectroscopy prohibitively complicated, it should perhaps be repeated that a complete or even partial analysis of the spectrum is not necessary to carry out either a qualitative or *quantitative chemical analysis. This will become* apparent in later sections. Nonetheless, some idea of these effects will be useful even to one concerned only with chemical analysis.

Effects of centrifugal distortion have already been considered. These give rise to a shift in the absorption frequency from the rigid rotor frequency. Other nonrigidity effects will also affect the spectra. Since a molecule is vibrating, as well as rotating, even in the ground vibrational state, the moments of inertia are averaged in a complicated way over the molecular vibrations. The rotational constants must hence be regarded as effective constants, A_v, B_v, and C_v. The effective rotational constants will be different for each vibrational state, and a separate rotational spectrum is hence obtained for each vibrational state. These excited-state lines may be shifted many hundreds of megahertz away from the ground state line, or, in some cases, they may be shifted only a few magahertz. Only low-lying vibrational levels will give rise to lines that have sufficient intensity to be observed. If a number of low-lying vibrational

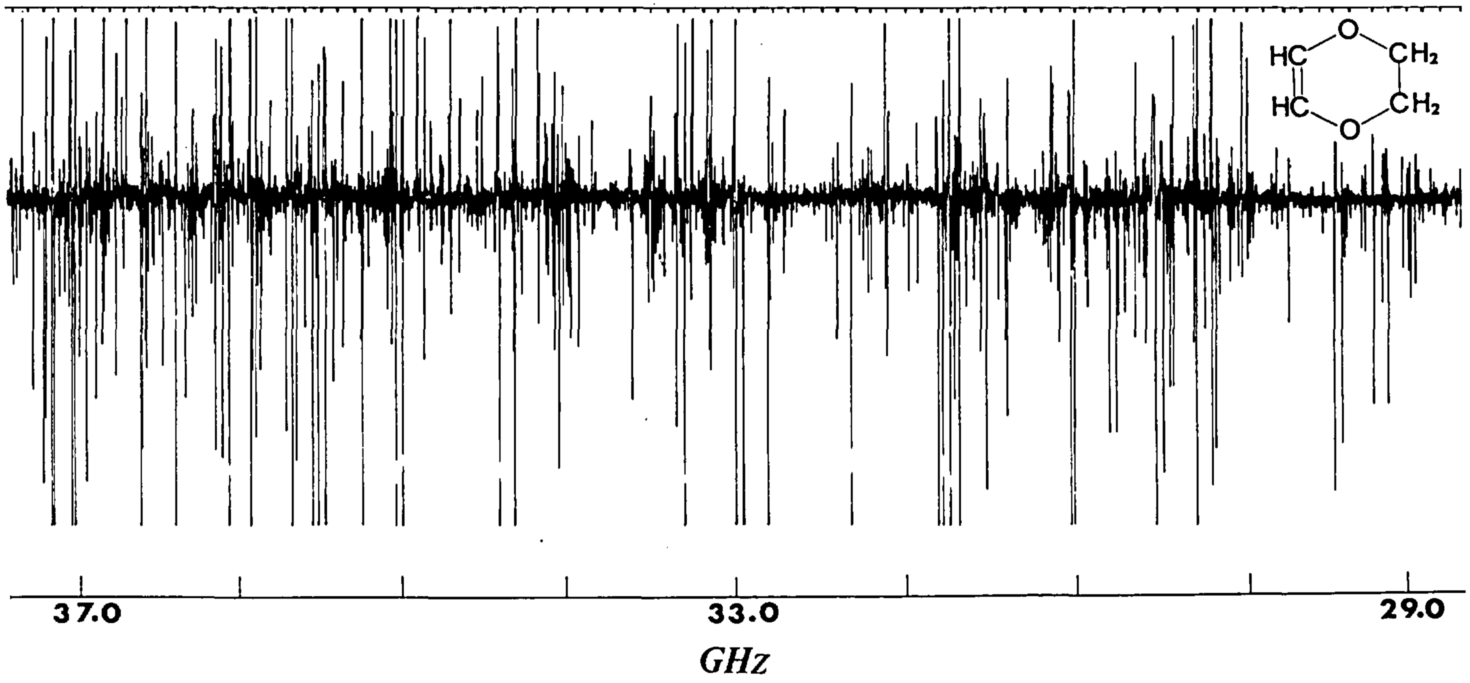

FIGURE 1. Low-resolution microwave spectrum of 2,3-dihydro-*p*-dioxin (Dioxene). This molecule is an oblate asymmetric top (κ = 0.485) with b-type transitions. The spectrum was recorded at room temperature with a scan rate of 3 MHz/sec, a pressure of about 80 mtorr, a detector time constant of 1 sec, and a Stark-modulation voltage of 1,500 V. (From Wells, J. A. and Malloy, T. B., Jr., presented at the 28th Annual Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June 1973 [Paper P10].

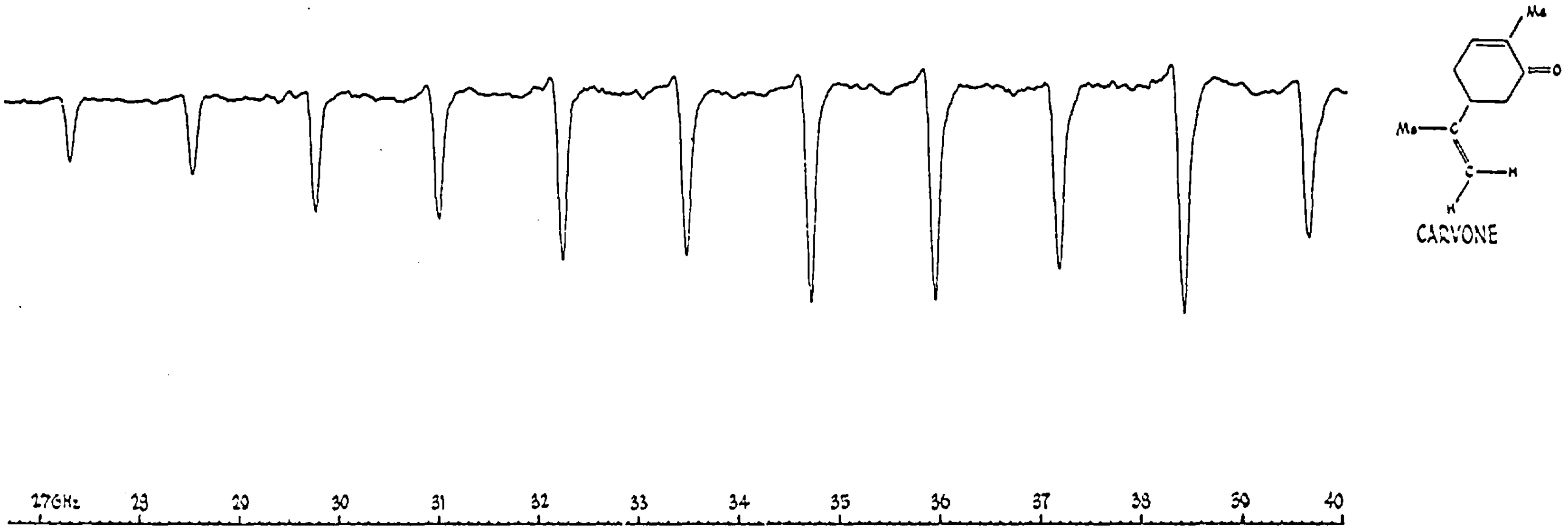

FIGURE 2. Low-resolution spectrum (band spectrum) of carvone. Scan rate 10 MHz/sec, pressure about 100 mtorr, 1,000-V Stark modulation. Each band consists of a number of closely spaced lines which appear as a single unresolved line. Taken on a HP 8460A spectrometer. (With permission of the Hewlett-Packard Company.)

modes are present, this would have the effect of weakening the lines of the spectrum, as the intensity of a given rotational line is then effectively spread among the various vibrational states. If the molecular dipole moment is small to begin with, this effect could cause difficulty in detecting absorption lines and would present a serious problem from the standpoint of chemical analysis.

For molecules which can undergo internal rotation, i.e., the rotation of one part of a molecule with respect to the other about a single bond, a more complex spectrum can be obtained. This results from the interaction of internal rotation and overall molecular rotation. The appearance of the spectrum depends on the type of internal rotor and on the barrier height hindering internal rotation. Rotation of a methyl group can, for example, lead to a splitting of the spectral lines into doublets. In other cases, internal rotation can give rise to distinct rotational isomers, which are stable enough to give separate rotational spectra even when they cannot be chemically separated. The rotational isomers can be readily distinguished because of the very high sensitivity of the moments of inertia to the molecular geometry.

Effects of nuclear coupling can give rise to hyperfine structure in the rotational spectrum. The most important type of nuclear interaction occurs when a nucleus with a nonzero nuclear quadrupole moment ($I > \frac{1}{2}$) is present in the molecule. In such cases, the nuclear spin $\underset{\sim}{I}$ is coupled to the overall rotation J, and a nuclear quadrupole hyperfine structure results. A new quantum number F is now required to characterize the energy levels. A given rotational transition can be split into a number of components, and a group of closely spaced lines is observed. This splitting would, in general, increase for some of the more common nuclei in the order: $N < CL < Br < I$. These splittings decrease with increasing J, often becoming unresolvable at sufficiently high J. Recognition of nuclear quadrupole hyperfine structure in the rotational spectrum could be useful in chemical analysis since it indicates the presence of a quadrupolar nucleus, such as Cl.

Applied electric or magnetic fields will affect the rotational spectrum. The most important of these is the effect of electric fields, commonly called the Stark effect. The electric field interacts with the molecular dipole moment, and the rotational energy levels will split into a number of sublevels, the degeneracy of the levels in the space orientation quantum number, M, being lifted by the interaction. A rotational line will, therefore, split into a number of components. Usually, the electric field is applied parallel to the electric vector of the radiation, and the selection rule $\Delta M = 0$ applies. The Stark-effect pattern can provide a valuable aid to the assignment of rotational spectra, particularly for asymmetric rotors. To aid in the detection of rotational spectra, the Stark effect is usually used to modulate rotational lines. This forms the basis of the Stark-modulation spectrometers, which will be discussed in Section III.A. With such spectrometers, both the Stark lines and the zero-field transitions are displayed. Since sensitivity is particularly important in the detection of small concentrations of a gas, a Stark-effect spectrometer is useful for chemical analysis in the centimeter-wave region.

C. Line Intensities and Shapes

A sample of gas in a cell of length L, subject to microwave radiation corresponding in frequency to a particular rotational transition, will absorb a small amount of power given by

$$\Delta P = \alpha_\nu \ell P_o, \tag{14}$$

where α_ν is the absorption coefficient or intensity coefficient (normally, $\alpha_\nu \ll 1$) of the gas at the microwave frequency ν, P_o is the power at the radiation detector with no gas in the cell. If there are no reflections in the absorption cell, the effective cell length ℓ is given by $\ell = (\lambda_g/\lambda)L$. Here λ is the free-space wavelength of the microwave radiation, and λ_g is the wavelength in the wave guide. Only a very small fraction of the incident power is absorbed (on the order of microwatts) in a normal laboratory path length. The power absorbed will be maximum where α_ν is maximum, i.e., at the resonant frequency, $\nu = \nu_o$, and for low pressures will be spread over a small frequency range. The absorption line will hence not be perfectly sharp but will usually be symmetrically shaped about the resonant frequency. The absorption line may be characterized by its resonant frequency, by its shape or profile, and by its line width, $2(\Delta\nu)$. The line width is the width in frequency units measured between the half-intensity points of the line. The symbol $\Delta\nu$ is commonly used to denote the half-width. The magnitude of the half-width sets an upper limit on the resolution obtainable.

Various factors contribute to the line width and the overall line shape. At very low pressures, less than 10 mtorr (1 mtorr = 10^{-3} torr; 1 mtorr = 1 μm = 10^{-3} mm of Hg = 0.133 Pa in SI units), the line width arises primarily from Doppler broadening, wall-collision broadening, and modulation broadening. These effects give line widths which are independent of sample pressure. Usually the major one of these is Doppler broadening, which in the centimeter-wave region gives line widths less than 100 kHz. Because of the random motion of the molecules, the velocities of which obey a Maxwell-Boltzmann distribution, the absorption frequency is effectively Doppler-shifted by various amounts, and the absorption is spread over a small frequency range. The line shape is found to be Gaussian in nature. The line width is independent of pressure and decreases with frequency, temperature, and increased molecular mass. As the pressure is raised in this region, the peak line intensity increases, while the line width remains constant. Contributions of cell-wall broadening and modulation broadening further increase the line width. These effects are relatively small, however, contributing less than 25 kHz and 100 kHz, respectively, to the line width. Without special instrumental design, the various effects listed above lead to a minimum half-width of about 0.1 MHz.

As the pressure is increased, collision broadening becomes important, and both Doppler and collision broadening effects contribute to the line shape and width. At pressures greater than approximately 10 mtorr, broadening due to molecular collision becomes dominant. In the pressure broadening region, the line shape is Lorentzian, and the half-width is given by

$$\Delta \nu = 1/2\pi\tau, \tag{15}$$

where τ is the mean time between molecular collisions. While the peak intensity is independent of pressure, the half-width is found to be directly proportional to the pressure; that is,

$$\Delta \nu = \mathrm{k\,p}, \tag{16}$$

where k is temperature dependent. Furthermore, k and hence $\Delta\nu$ depend on the sample composition. This fact is important in chemical analysis (see Section V.A). At pressures of 100 mtorr, a typical half-width would be 1 MHz. The half-width, however, can differ considerably from molecule to molecule, and molecules with large dipole moments have large $\Delta\nu$. The effects of increasing the pressure of a sample are illustrated schematically in Figure 3. Where the peak intensity is independent of pressure, the line shape is Lorentzian. An actual recording of a transition of CH_3OH at different pressures is shown in Figure 4.

Other factors, such as unresolved nuclear quadrupole hyperfine structure, interference from neighboring lines, incomplete Stark modulation, and power saturation can also affect the line shape and half-width.

Obviously, from the above discussion, maximum resolution is obtained by reducing the pressure to the point where Doppler broadening becomes dominant. On the other hand, when maximum sensitivity is desired, as is usually the case for chemical analysis, somewhat less resolution would be accepted for the sake of the accompanying gain in sensitivity. The pressure should hence be increased to the point where pressure broadening dominates and the maximum peak absorption is attained. At this point, a further increase in pressure will not usually be beneficial but leads only to increased $\Delta\nu$ and thus reduced resolution.

In considering either relative or absolute intensity measurements, which can be applied to determine such things as concentration or the relative populations of two quantum states, one must have a clear understanding of the quantities which go into the definition of the absorption coefficient.

1. The α-Coefficient

At pressures of about 10 mtorr to 1 torr, broadening due to collisions between molecules is dominant, and the absorption coefficient for the transition $\mathrm{J},\tau \rightarrow \mathrm{J}',\tau'$ is given by

$$\alpha_\nu = \frac{8\pi^2 \mathrm{N}\, \mathrm{F}_{\mathrm{J},\tau} \nu^2 \mu_\mathrm{g}{}^2 \lambda_\mathrm{g}(\mathrm{J},\tau;\mathrm{J}',\tau')}{3\,\mathrm{c\,k\,T}\,(2\mathrm{J}+1)} \left[\frac{\Delta\nu}{(\nu_\mathrm{o}-\nu)^2 + \Delta\nu^2},\right] \tag{17}$$

where the factor in brackets is the Lorentzian line shape function. In addition,

N = number of molecules per unit volume;

ν = frequency of the microwave radiation;

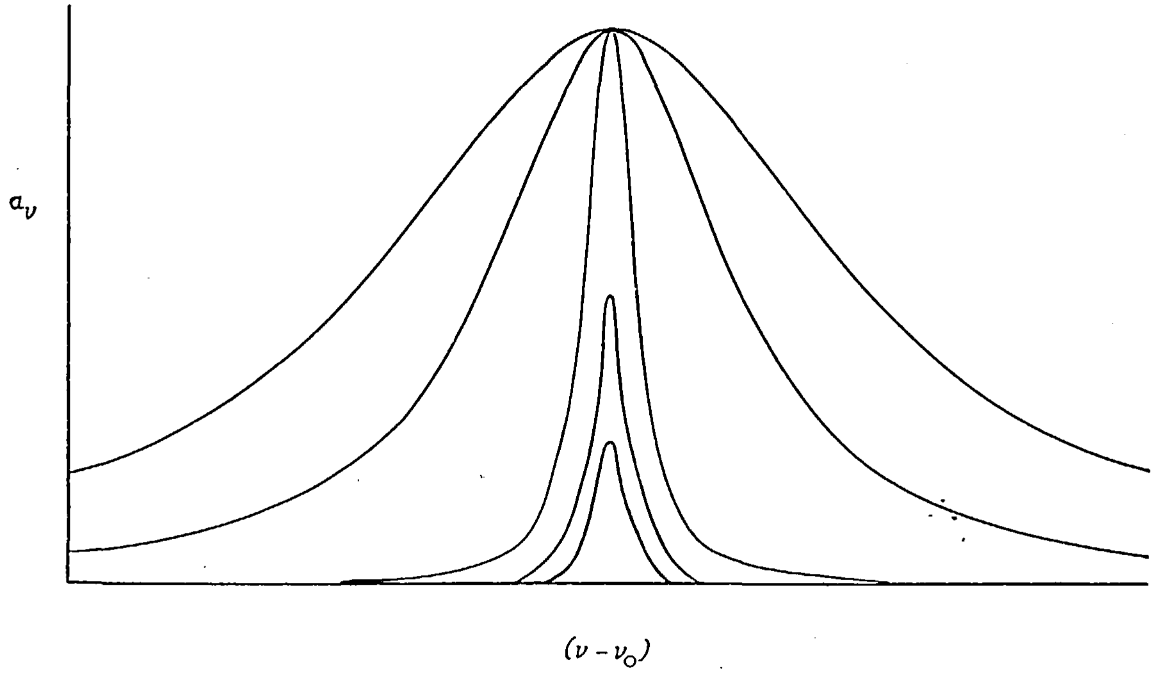

FIGURE 3. Illustration of the effects of pressure on a microwave absorption line. At low pressures, the peak absorption increases while the line width remains constant. At higher pressures, the peak absorption remains constant and the line width increases linearly with pressure.

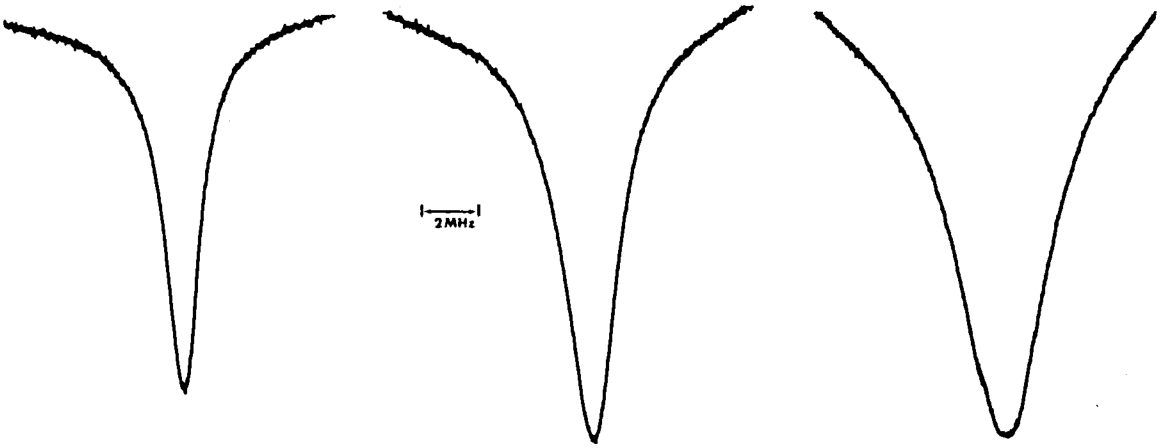

FIGURE 4. A transition of CH_3OH recorded at increasing pressure from left to right.

ν_0 = resonant frequency, the frequency for which the absorption is a maximum;
$\Delta\nu$ = half-width of the line;
μ_g = electric dipole moment component giving rise to the particular transition under observation. The subscript g refers to one of the principal inertial axes

c = speed of light;
k = Boltzman constant;
T = absolute temperature of the gas.

The value of α_ν at the resonant frequency ν_0 is called the peak absorption coefficient and is designated by α_0. At the frequencies given by $\nu = \nu_0 \pm \Delta\nu$, i.e., the half-intensity points, the absorption coefficient is $\alpha_\nu = \alpha_0/2$. The $\lambda_g(J,\tau;J',\tau')$ is the line strength of the transition, which is related to the transition moment by

$$|\mu_{ij}|^2 = \mu_g^2 \lambda_g(i;j)/(2J+1). \tag{18}$$

The line strengths for the transitions of various classes of molecules are available.[29] The fraction of molecules in the lower rotational state J,τ of the transition in the vibrational state v is given by

$$F_{J,\tau} = \frac{F_v\, g(2J+1)e^{-E_{J,\tau}/kT}}{Q_r} \tag{19}$$

where g is a statistical weight factor and $E_{J,\tau}$ the lower state rotational energy. The important dependences of the rotational partition function on the temperature and the rotational constants for various types of molecule are as follows:

$$\begin{array}{ll} Q_r \sim T/B & \text{(linear molecule)} \\ Q_r \sim (T^3/AB^2)^{1/2} & \text{(symmetric top)} \\ Q_r \sim (T^3/ABC)^{1/2} & \text{(asymmetric top)} \end{array} \tag{20}$$

The fraction of molecules in the vibrational state $v \equiv v_1, v_2, v_3, \ldots$ being observed is related to the vibrational energy of the state as follows:

$$F_v = \frac{e^{-h\Sigma v_i \omega_i/kT}}{Q_v}, \tag{21}$$

where Q_v is the vibrational partition function, and ω_i are the normal vibrational frequencies. Direct evaluation of α_ν from molecular parameters is not required for chemical analysis.

A major concern in applying microwave spectroscopy to analytical problems will be whether the absorption spectrum of a particular molecule can be detected. This depends on the absorption coefficient. Molecules with large absorption coefficients have strong lines, and small concentrations of such molecules can be more easily detected. The various factors in α_ν which lead to increased absorption have, therefore, important implications for analytical applications. Because of the ν^2 dependence of α_ν, the stronger lines, in general, are at higher frequencies. The presently available commercial spectrometers cover the 8 to 40 GHz region in four separate bands. The R-band region (26 to 40 GHz) is hence particularly useful for analytical applications. Lines of greater intensity are also expected for highly polar substances. Nonetheless, the spectra of molecules with very small dipole moments, such as 0.01D, have been observed. The $F_{J,\tau}/T$ factor in α_ν is increased by decreasing the temperature. This follows from the inverse temperature dependence coming from the factor 1/T and from the partition function Q_r. Also, lowering the temperature increases F_v for the ground-vibrational state, leading to an increase in the ground-state line intensities. It is hence common practice to pack the outside of the wave guide absorption cell with dry ice to obtain greater line intensities. This, of course, is not possible if the vapor pressure at such temperatures is too low. Weaker absorptions are expected for large molecules because they have large moments of inertia and hence large partition functions Q_r, which decrease α_ν. Furthermore, a greater number of low frequency vibrations are possible with large molecules, and this further distributes the intensity among more vibrational states. The line strength factor λ depends on the rotational quantum numbers of the transition and increases with J for linear and symmetric-top molecules and for certain asymmetric-top transitions. The general behavior of λ for the latter is, however, more complicated.

A useful measure of the intensity of a rotational transition is given by the peak absorption coefficient, α_0. For quantitative analysis, both the peak intensity and the integrated line intensity find application. The peak absorption coefficient from Equation 17 is

$$\alpha_0 = C\nu_0^2\, x/(\Delta\nu/p), \tag{22}$$

where we have used $N = xp/kT$, with x the mole fraction of the absorbing molecular species and p the total pressure in the absorption cell. The constant C depends on the temperature and various molecular quantities but at a given temperature is a constant for a given transition in a particular vibrational state. It is expressed by

$$C = \frac{8\pi^2 F_{J,\tau}\mu_g^2\, \lambda_g(J,\tau;J',\tau')}{3\,c\,k^2T^2(2J+1)}, \tag{23}$$

Since $\Delta\nu$ is proportional to p, α_0 is independent of total pressure. However, α_0 does not usually vary linearly with the mole fraction x. Because $\Delta\nu$ is a more complicated function of the sample composition, so too is α_0. This is discussed further in Section V.A. The integrated line intensity is defined by

$$\alpha_{int} = \int_0^\infty \alpha_\nu\, d\nu = \pi\,\alpha_0\,\Delta\nu. \tag{24}$$

Either the measurement of the area under the absorption curve or the measurement of α_0 and $\Delta\nu$ will give α_{int}. Examination of Equation 22 reveals that α_{int} is independent of the line width $\Delta\nu$ and is linearly dependent on the partial pressure of the absorbing species.

To measure α_0 or α_{int}, sufficiently low radiation power levels must be employed to avoid power saturation. With too much power, the relaxation processes, which tend to maintain thermal equilibrium by returning the molecules to the lower state, cannot keep up with the excitation to the upper state by absorption. The population difference of the upper and lower levels thus becomes less than at thermal equilibrium, and radiation saturation occurs. This leads to a decrease in α_0, or the power absorbed, and under such circumstances the peak absorption coefficient is given by[22]

$$\alpha = \frac{\alpha_0}{(1 + KP_0)}, \tag{25}$$

where α_0 is the unsaturated coefficient. The power saturation coefficient is given in cgs units by[30]

$$K = (\lambda_g/\lambda)\frac{64\pi^3|\mu_{ij}|^2 t\tau}{3h^2 c A}, \tag{26}$$

where λ_g/λ is the ratio of the wave guide to free-space wavelength, $|\mu_{ij}|$ is the dipole transition moment, and A is the cross-sectional area of the cell. The mean time τ between collisions, which broaden the line, is related to $\Delta\nu$ by $\tau = 1/2\pi\Delta\nu$, and t is the mean time between collisions restoring equilibrium. The saturation coefficient depends on the particular molecule, the transition studied, and sample pressure and composition. Also, the more effective the relaxation (small t), the smaller K and the less easily power saturation occurs.

2. *The* Γ-*Coefficient*

A new intensity coefficient has been proposed by Harrington[30,31] which is particularly useful for quantitative analysis. This coefficient takes advantage of the phenomenon of power saturation and is defined as

$$\Gamma = \frac{\Delta P}{\ell P_0^{1/2}}. \tag{27}$$

For a constant power distribution in the cell, the absorption coefficient at the resonant frequency can be written, making use of Equations 25 and 27, as

$$\Gamma = \eta\phi, \tag{28}$$

where

$$\eta = \alpha_0/K^{1/2} \tag{29}$$

and

$$\phi = \frac{(KP_0)^{1/2}}{(1 + KP_0)}. \tag{30}$$

The dimensionless power density function ϕ is a function of the dimensionless product KP_0. For a Stark cell, the power distribution in the absorption cell is not constant; however, Equation 28 still applies with ϕ defined as

$$\phi = (KP_0)^{-1/2}\,[1-(1 + KP_0)^{-1/2}]. \tag{31}$$

These expressions for ϕ have similar properties; they show that, as P_0 increases, ϕ increases rather rapidly to a broad maximum and then decreases as the power is further increased. This general behavior of ϕ is illustrated in Figure 5.

The Γ-coefficient offers two significant advantages: (1) It effects the separation of the line-width factor ($\sim 1/\tau$) and the molecular concentration, and (2) it allows one to work with the optimum spectrometer signal. This becomes apparent from the following considerations. The power saturation coefficient K depends on the sample composition and total pressure via τ. The function ϕ depends on KP_0, and any particular point on the ϕ versus P_0 curve corresponding to a fixed value of KP_0 can be reached by adjusting P_0 appropriately. Clearly, as K changes, P_0 may be adjusted to return to a specific value of KP_0. This allows ϕ to be maintained constant in experiments where η or, as we see below, sample composition is varied in a series of measurements. An easily identifiable point on the ϕ-curve is that at which ϕ has its maximum value. Since η is independent of P_0, maximizing ϕ by adjusting P_0 gives the maximum value of Γ. Harrington[30] has shown that, for a Stark-modulated spectrometer, Γ is proportional to the signal amplitude (signal voltage), provided the rectified crystal detector current is kept constant. Therefore, the choice of power level for which $\phi = \phi_{max}$ corresponds to the maximum signal amplitude, S. The general behavior of Γ versus power is shown in Figure 5. Furthermore, according to Equation 29, $\eta \sim (\tau/t)^{1/2} xp$ for a given transition. Hence, as long as the ratio (τ/t) is constant, η is proportional to the partial pressure of the absorbing species.

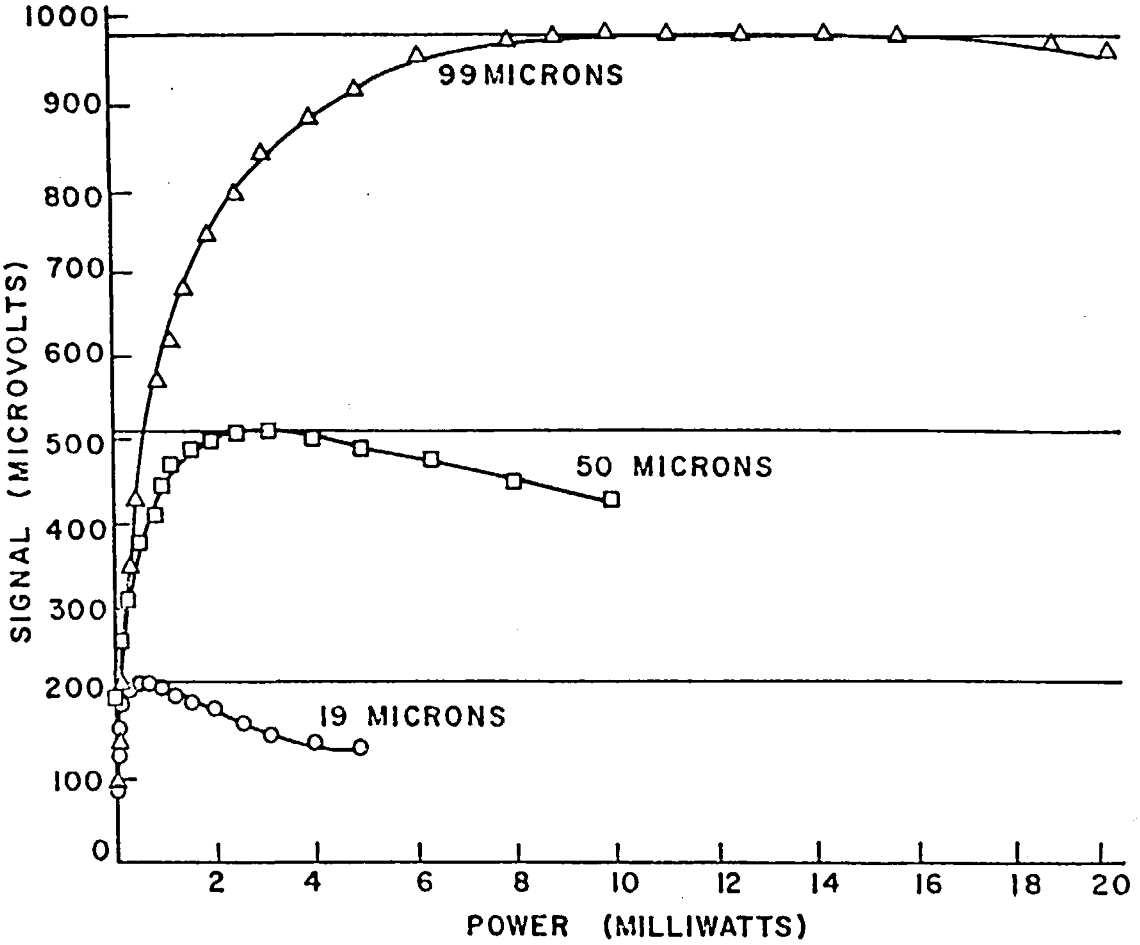

FIGURE 5. Spectrometer signal for the $1_{0,1} \rightarrow 1_{1,0}$ transition in ethylene oxide as a function of the radiation power P_0. In each case the signal ($\sim\Gamma$) increases with increased power, finally reaching a broad maximum. The power required to reach the maximum signal is different for different pressures of pure sample. (From Harrington, H. W., *J. Chem. Phys.*, 46, 3698 (1967). With permission.)

Preliminary evidence indicates that this is indeed the case, and the reasonable assumption that each collision is effective in restoring an equilibrium distribution ($t = \tau$) is usually made. Thus η is dependent on xp but is independent of $\Delta\nu$ and thus the sample composition. This is in contrast to the behavior of α_0. In summary, molecular concentration data contained in η can be obtained under conditions of maximum signal and in a way which is independent of the line width:

$$S \sim \Gamma_{max} = \eta\, \phi_{max} \sim xp. \qquad (32)$$

Crable and Wahr[74] have used an instrumental approach to confirm that S depends only on the partial pressure of the absorbing gas, provided that the detector output is proportional to the square root of the intensity (or power).

III. INSTRUMENTATION

A detailed treatment of the instruments and hardware used in microwave spectroscopy is complicated by the fact that the wavelengths of microwaves are of the same order of magnitude as the dimensions of the instrumental components; thus, many aspects of the behavior of microwaves are not conveniently handled by ordinary alternating-current circuit theory. There are some exceptions to this statement, namely, certain features of microwave tuning and transmission. Low-frequency microwaves can be efficiently transmitted by coaxial cables, for example. Geometrical optics, on the other hand, does not provide an entirely satisfactory description either, as the wavelengths of microwaves are not short enough. There are exceptions to this statement also, as microwaves can be transmitted using lenses and mirrors, and this is occasionally the most convenient way of handling them. Generally, however, microwaves are most efficiently transmitted through wave guides, and these, as well as many other microwave instruments, are best described in terms of electromagnetic theory.

We shall give only a survey of the aspects of microwave instrumentation relevant to chemical analysis, referring the reader elsewhere for details.[21-24]

A. The Conventional Microwave Spectrometer

1. Basic Components

Many of the characteristics of microwave instruments derive from the nature of the electronic energy sources, which generate highly monochromatic beams of radiation. The heat sources used in the infrared region produce very little usable energy at wavelengths above 0.5 mm. Microwave sources, on the other hand, provide several milliwatts of power in a frequency band sometimes much less than 1 MHz. The temperature required of a hot body to produce a similar radiation is approximately 10^{14}°C.[22] Electronic microwave sources offer the added advantage of being frequency tunable, either electronically or manually. A microwave spectrum is therefore scanned by varying the frequency of the source rather than by the use of dispersing elements such as gratings and prisms.

Until the last few years, the microwave source used in practically all spectrometers has been the reflex klystron, which is available for all frequencies from 3 GHz to above 100 GHz. Klystrons, being very stable, produce relatively little noise. For very careful work, they can be further stabilized by electronic means. The frequency of reflex klystrons can be changed electronically over a range of several hundred MHz, or manually over as much as 5 or 6 GHz. This means that several klystrons may be required to cover a frequency range of interest. More troublesome than the bandwidth limitation is the manual optimizing of the controls due to significant power variations over the range. These unattractive features do not appear in the more recently developed backward wave oscillator tube, or BWO. A BWO is capable of being electronically tuned over 15 GHz or more. Microwave power variations can be minimized by automatic electronic methods. Because of these advantages, backward wave oscillators are used in commercial spectrometers.

Solid state diodes that can generate microwave energy when energized by a DC power supply have recently become available. One of these, the "Gunn-diode," when supplied by a 4-V, 1.5-A battery, can produce more than 20 mW of microwave power at frequencies up to 60 GHz. These diodes do not yet have the electronic tuning capabilities and wide bandwidths of backward wave oscillators or the relatively high power and frequencies of klystrons. The output frequency can be tuned over a few GHz, however, by locking the diode frequency to a resonant cavity and mechanically tuning the cavity. These diodes show promise for chemical analysis, as the need for simple, portable methods of detecting gaseous pollutants is evident.

The simplest absorption cell, and the one most commonly used, is a section of wave guide sealed at each end by thin mica windows. The optimum length for these cells depends on certain features of the detection system and on power losses in the wave guide. Research spectrometers have typically used cells from 2 to 5 m in length. Commercial spectrometers use cells approximately 2 m long. An oversized wave guide is usually used to minimize cell-wall broadening and so that more molecules can be contained and power saturation thereby avoided. Tapered transitions must then be used to match the cell to the smaller wave guide at the source and the detector. Otherwise, troublesome reflections of microwave radiation occur. Several round holes, used for evacuation of the cell and introduction of the sample, can be drilled in the wide face of the wave guide without appreciably altering its electrical properties. The interior of absorption cells is sometimes gold-plated to resist corrosive gases and to reduce chemical decomposition.

The last basic component of a conventional microwave spectrometer is a detector of microwave radiation. Although some thermal detectors have been used, crystal detectors are by far the most common. A crystal detector consists of a small chip of semiconductor, sometimes germanium but usually silicon, in contact with a very fine tungsten wire. The wire and crystal are encapsulated in a metal casing. Because the contact area is very small, the capacitance is small, allowing detection of microwave frequencies. The contact resistance is greater in one direction than the other, and the voltage-current characteristics are very nonlinear for low voltages, so the alternating current induced by the microwave field is rectified. The rectified current or the corresponding voltage can be measured by a meter, which is considered part of the detection system in Figure 6. Because this output signal is small, it usually must be greatly amplified. The development of wide-banded detectors along with BWO tubes now enables one to conveniently record spectra over wide frequency ranges.

A block diagram of a simple microwave spectrometer, consisting of the source, absorption cell, and detector, is shown in Figure 6.

2. Modulation

Using only the basic components described above, one would observe an absorption line as a decrease in the meter reading as the frequency of the source is varied through the resonant frequency. This arrangement is neither sensitive nor convenient. A much more convenient spectrometer, called a "video" spectrometer, is modulated by sweeping the source through 40 or 50 MHz approximately 60 times a second with a sawtooth voltage applied to the appropriate electrode. The same sawtooth voltage can be applied to the horizontal sweep of an oscilloscope, while the amplified detector output is applied to the vertical plates. If the center frequency of the source is at the resonant frequency of an absorption line, the line appears 60 times a second as a narrow dip in the oscilloscope trace.

The video spectrometer, though very convenient in searching for absorption lines, is not very sensitive due to relatively high crystal noise at this relatively low modulation frequency. The power absorbed by the sample may be only 10^{-6} of the power through the cell. To observe such small changes in microwave power, a more complicated detection scheme must be used. The method most satisfactory for chemical analysis makes use of Stark modulation.

As we saw in Section II.B, the application of an electric field to polar molecules produces shifts and splittings of the rotational energy levels with consequent changes in the microwave spectrum. Known as the Stark effect, this phenomenon can be used to modulate the microwave power absorbed by the molecules.[32] A thin metal septum is usually mounted with insulating material, commonly Teflon®, in the absorption cell parallel to the broad face of the wave guide. An alternating voltage, usually a zero-based square wave, is applied to the septum. If the frequency of the source is tuned to the resonant frequency of an absorption line, the Stark voltage causes a variation in power detected by the crystal by periodically shifting the absorption frequency away from the frequency of the source. The absorption line is thus modulated at the frequency of the voltage modulator. Both the "field-off" absorption line and the "field-on" absorption lines may be observed. The great increase in sensitivity of Stark modulation over that described in the preceding paragraph occurs because of the high modulation frequency (5 kHz to 100 kHz) that is possible and the use of tuned amplifiers. Much less thermal noise is generated in the detector crystals by high frequency modulation. Further sensitivity is achieved by the use of phase-sensitive detection. The output voltage of the crystal is fed into an amplifier referenced to the modulation frequency in such a way that only the noise that has the same frequency and phase as the modulation signal is amplified. In addition to the high sensitivity, this modulation technique has the significant advantage of being almost completely insensitive to spurious variations in the source power, such as those caused by reflections of microwave radiation. With phase-sensitive detection, the "field-on" absorption lines, called Stark components or lobes, are displayed in opposite phase to the "field-off" line. Furthermore, the pattern of lines produced when the electric field is on is useful for assigning quantum numbers to the transitions. Figure 7

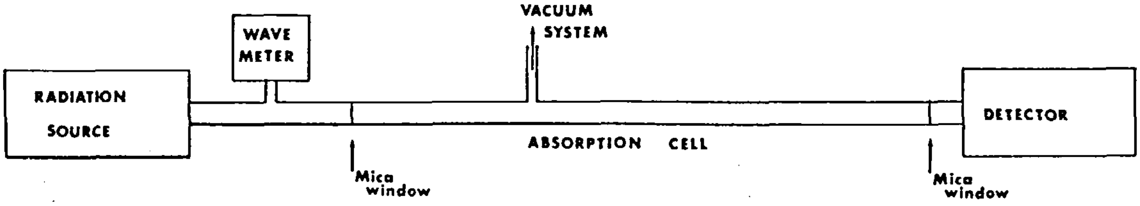

FIGURE 6. A simple microwave spectrometer.

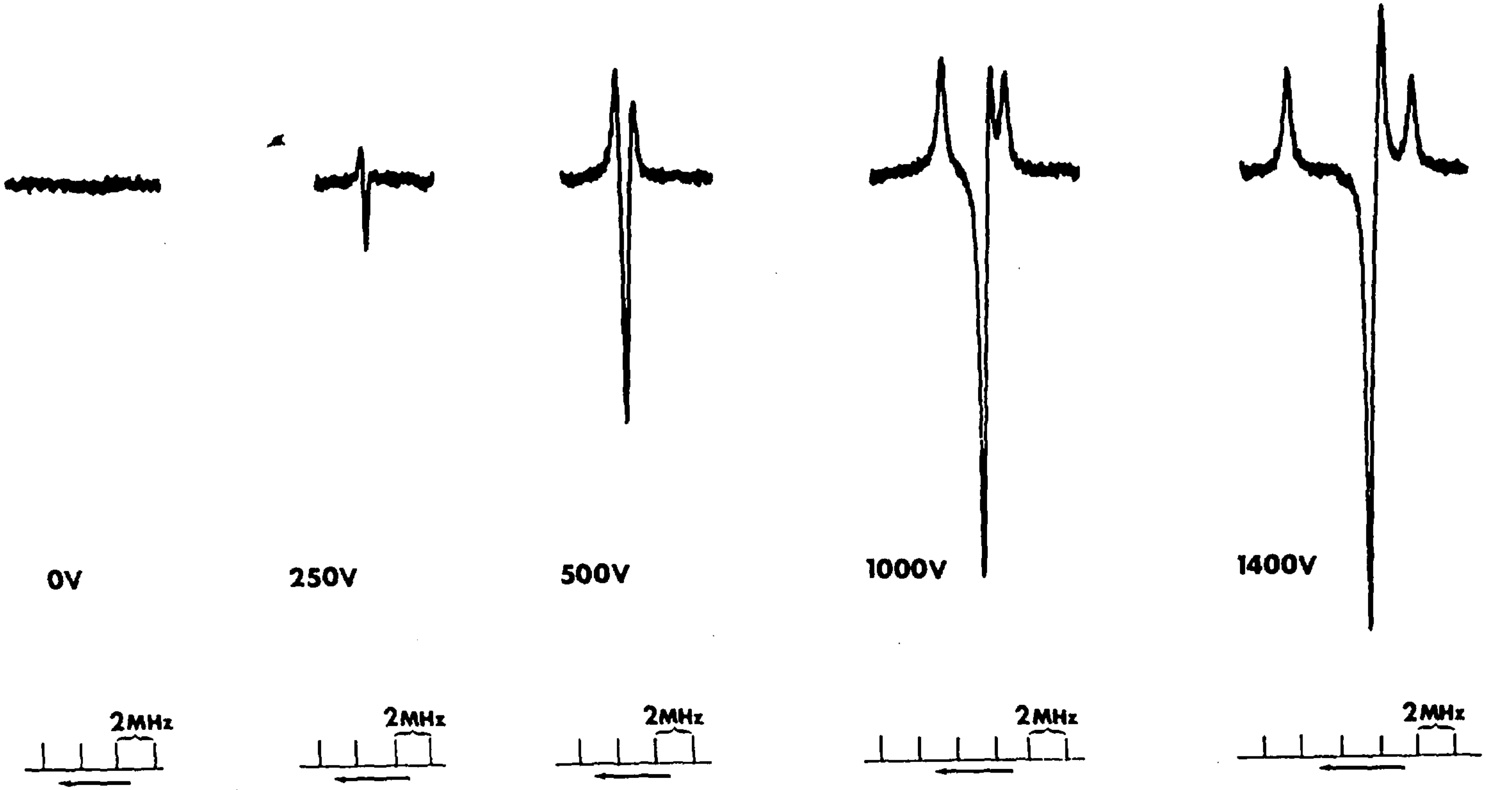

FIGURE 7. The effect of the square-wave Stark-modulation voltage on the appearance of the J = 2→3 transition of OCS. Note that as the Stark lobes are displaced from the field-off line the intensity of the line increases.

illustrates the appearance of a rotational transition obtained using Stark modulation for different values of the modulation voltage. Note how the line shape and intensity depend on the Stark voltage. Observation of true line shape requires that the Stark lobes be removed from the line. The voltage necessary to completely resolve the Stark components depends on the dimensions of the wave guide and on the characteristics of the molecule. Voltages from 50 to 2,000 V are typically applied.

To reduce the interference from Stark lobes of nearby lines, the Stark modulator is sometimes provided with the ability to apply a decaying square wave. This produces an inhomogeneous electric field and thereby smears out the Stark lobes, resulting in less interference.

3. Frequency Measurements

The frequency of the microwave source can be measured very quickly and conveniently using a cavity wavemeter. Some of the radiation is absorbed when its frequency is equal to the resonant frequency of the cavity. The best cavity wavemeters will measure frequencies to approximately 10 MHz, which is better than 1 part in 10^3. The centers of many absorption lines can be located, however, with precisions of 20 kHz, and relatively complicated radio techniques have been used to take advantage of this resolution. Typically, the output of a secondary frequency standard is multiplied until it is within a few MHz of the source frequency. The difference in the source frequency and the appropriate harmonic of the frequency standard appears as a beat frequency, which can be measured directly by a conventional radio receiver. Using proper care on sufficiently narrow lines, one can use this technique to produce precisions of 1 part in 10^7 in frequency measurements. A more convenient variation of this technique makes use of electronic counters.

B. Commercial Spectrometers

Hewlett-Packard® introduced a complete microwave spectrometer in 1965. A block diagram is shown in Figure 8. The original spectrometer has evolved into the current Model 8460A, pictured in Figure 9. The source is a backward wave oscillator, which is phase stabilized to give good frequency stability. A square wave generator at 33.3 kHz is used to Stark-modulate the gas in a 2-m sample cell. The cell is sufficiently well designed that reflections are not usually a serious problem. Some of the radiation from the BWO is compared to a harmonic of a signal from a very stable, crystal-controlled oscillator. The difference frequency is used as the input of a digital electronic counter, which displays the frequency of the BWO. Both the absorption line and frequency markers are printed out by a chart recorder. The Model 8460A operates on four frequency bands between 8.0 and 40.0 GHz. The four wave guide bands are: X-band (8 to 12.4 GHz), P-band (12.4 to 18 GHz), K-band (18 to 26.5 GHz), and R-band (26.5 to 40 GHz). The bands are changed by switching plug-in units. The broadbanded characteristics and feedback power leveling eliminate the need for frequent manual adjustments.

Aside from its convenience, stability, and reliability, the H-P Model 8460A has two features that make it particularly suitable for quantitative analysis. First, this spectrometer is a bridge type. The microwave power is split into two parts which travel through two wave guide arms. One arm contains the absorption cell, while the other contains a balance cell almost identical to the absorption cell. The radiation through the two arms is recombined to give a signal which is equal to the difference of the signals from the two arms. When the absorption cell is empty, this difference is zero, and the bridge is balanced. With an absorbing gas in the sample cell, the bridge is unbalanced, causing an output signal at the detector. The advantage of the bridge is that it allows the operator to use a high power in the cell and yet have low power at the detector crystal, both conditions being necessary for optimum sensitivity. This has direct application in quantitative analyses by procedures based on the Γ-coefficient, which is discussed in Section V. In these procedures, the bridge is used to hold the power or crystal current at the detector constant while the microwave power in the sample is varied to obtain maximum signal. With conventional, or "in-line," spectrometers, the crystal current is dictated by the power level at which Γ_{max} or, equivalently, maximum signal, occurs.

The second feature of the Hewlett-Packard Model 8460A that is useful in quantitative analyses is a calibration arm. This arm consists of a phase shifter, calibrated attenuators, and a PIN diode modulator. The PIN diodes are recently developed devices that can be biased to attenuate microwaves. Power from the source is passed

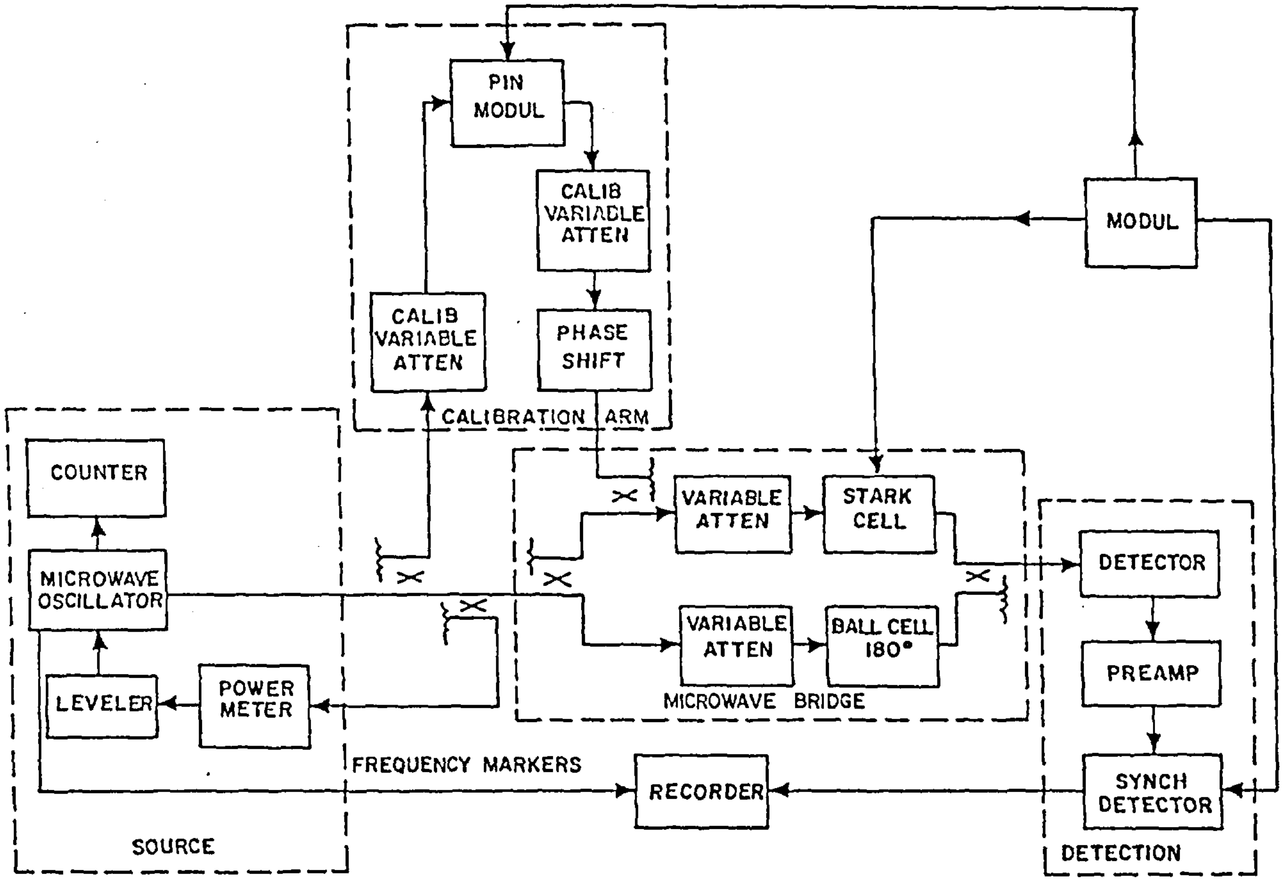

FIGURE 8. Diagram of a microwave spectrometer employing a microwave bridge, phase-sensitive detection, Stark modulation, and automatic recording. Intensity measurements are made with the calibration arm. (With permission of the Hewlett-Packard Company.)

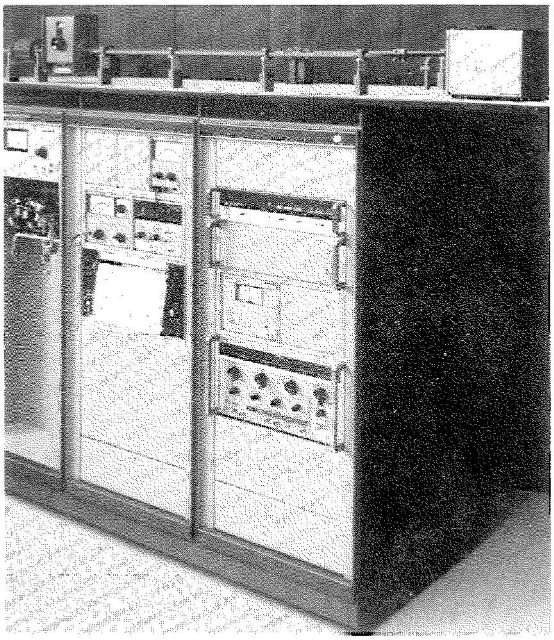

FIGURE 9. The Hewlett-Packard Model 8460A spectrometer. The spectrometer is set up for P-band. By exchanging the wave guide components on the tabletop and the source plug-in unit, the other frequency bands may be covered. The X-band sample cell at the back of the tabletop is used for all bands. The rectangular unit on the right-hand side is the preamplifier, and the detector can be seen to the right of this unit. To the far left a microwave power attenuator is found. The left-hand instrument unit below the tabletop houses the vacuum system and the system for sample admission. The center unit houses the Stark modulator, phase-sensitive detector, and a recorder for displaying the absorption line and frequency markers. The right-hand unit contains the microwave source, stabilization system, and controls, e.g., to set the source frequency, sweep range, and sweep rate. (With permission of the Hewlett-Packard Company.)

through a PIN modulator biased by the generator which modulates the Stark cell. The signal through the calibration arm is modulated, phase shifted, and attenuated in such a manner that it is equal in intensity to an absorption line produced by the sample. The readings in decibels of the calibrated attenuators allow a determination of concentration. The artificial signal can be compared directly with the true signal, or, for greater precision, it can be combined in opposite phase with the true absorption to give a null signal. An example of the application of the calibration arm is given in Section V.B.

Cambridge Scientific Instruments Limited[33] has recently developed a microwave spectrometer, which it refers to as Camspek®. This spectrometer is designed specifically for analytical application. It operates in the R-band region with a BWO source and employs Stark modulation with phase-sensitive detection. Camspek is especially well suited to measuring integrated absorption coefficients. This is accomplished by means of an electronic digital line-area integrator.

C. Cavity Spectrometers

As follows from Equation 14, another way of increasing sensitivity is to increase the path length ℓ. A spectrometer with very high sensitivity can be constructed by using as an absorption cell a microwave cavity instead of a long section of wave guide. A cavity is resonant, meaning that it transmits only a narrow band of frequencies. The center of the band, or resonant frequency, of the cavity is determined by its size and shape. Radiation at the resonant frequency is reflected from the walls of the cavity and passes through the sample many times before being detected. If the sample fills the cavity, the effective radiation path length is related to the product of the number of reflections and the appropriate cavity dimension. Therefore, a cavity only a few centimeters long can offer an effective path length of several meters. Cavity spectrometers are also easily stabilized. Although these can be great conveniences, the cavity spectrometer does not have the general usefulness of a conventional spectrometer due to its very narrow bandwidth, which is not conveniently scanned. The bandwidth of the cavity is of the same order of magnitude as the width of a spectral line. Narrow bandwidth would not be an inconvenience, however, in a spectrometer constructed to monitor a single transition of a particular gas. In addition, cavity spectrometers are particularly suitable for applications in pollution detection because conventional spectrometers cannot generally match gas chromatography and mass spectroscopy in sensitivity in detecting trace gases. Hrubesh[34] has recently reported on a cavity spectrometer designed to monitor trace gases. Power saturation is usually a consideration in cavity spectrometers due to the high power densities present. This makes quantitative procedures using the Γ-coefficient (Section

V.B.) particularly advantageous in cavity spectrometers. Although Stark modulation is not as convenient as source modulation for cavity spectrometers, Dymanus et al.[35] used a Stark cavity spectrometer to measure microwave integrated line intensities. More recently, Srinivasan[36] has used a Stark cavity microwave spectrometer to test the possibility of measuring the concentration of ammonia in blood serum.

Various other cavity spectrometers have been described.[37-41]

D. *Millimeter-wave Spectrometers*

Millimeter-wave spectrometers are usually video spectrometers operating in the shorter millimeter- and submillimeter-wave region. The source is commonly a reflex klystron whose microwave energy is coupled to a frequency multiplier, which generates higher harmonics of the fundamental source frequency. Such multipliers use a point contact crystal rectifier for harmonic generation. A similar configuration is employed as a detector. The shorter millimeter-wave and submillimeter-wave regions offer to analytical microwave spectroscopy the advantage of increased line intensity; however, at this time, the instrumentation is not suitable for routine analysis. Significant advances have been made recently,[42] however.

E. Automated Spectrometers

The use of computers in conjunction with microwave spectrometers has been discussed by Gwinn et al.[43] and by Winnewisser.[44] Use of computers for signal averaging can provide a considerable improvement in the spectrometer sensitivity. Also, preliminary data reduction can prove very convenient. Obviously, computer-controlled spectrometers can be of great usefulness in chemical analysis. This has been discussed by White,[45] who employed a Hewlett-Packard Model 8460A spectrometer and a Model 2116B computer. Scharpen et al.[45] applied a similar system to the quantitative analysis of mixtures of the five species of propene-d_1 obtained by an exchange reaction (Section V.A.4).

Clearly, systematic procedures could be devised for qualitative and quantitative analysis with a computer-controlled spectrometer. This would incorporate data-reduction capabilities and computer access to a microwave spectral atlas for identification purposes. The only drawback to such a system would be its cost.

F. Accessories

The only ancillary instruments necessary are those required for sample handling. A modest vacuum system is required to evacuate the absorption cell. A small mechanical pump and a proportional oil diffusion pump normally suffice. An ordinary assortment of glass or stainless steel tubes and valves is needed to contain and transfer the sample. Although the equipment necessary is standard, this does not mean that there are no problems associated with sample handling. There are problems that can be quite severe. For example, the concentration of a sample can be changed as it passes through the orifice of a valve. Other problems are mentioned in the sections on qualitative and quantitative analysis.

Recent advances in the measurement of pressure have been very timely for chemical analysis by microwaves. A capacitance manometer, the Baratron®, has been developed by MKS Instruments, Inc. (Burlington, Mass.). This manometer consists of a metal membrane stretched flat under radial tension. Any pressure differential between the two sides of the membrane deflects it and varies its electrical capacitance. Displacements as small as 10^{-9} in. are sensed by bridge circuitry and converted into pressure readings that, unlike those from other devices, are independent of gas composition. These gauges are applicable for most gases, are convenient even at high precisions, are bakeable, and, most important, are accurate to approximately 0.1% of readings.

IV. QUALITATIVE ANALYSIS

Qualitative or quantitative analysis by microwave spectroscopy, as by other more conventional spectroscopic methods, is based on observation of a characteristic spectrum – the rotational spectrum. The rotational absorption spectrum depends on the principal moments of inertia and, hence, is characteristic of the whole molecule and very sensitive to the molecular structure and the isotopic composition. The sensitivity of the transition frequency to isotopic composition is shown in Figure 10. Note the wide separation between the same transition for different isotopes. This sensitivity to small structural characteristics, coupled with the high resolution and accurate frequency-measuring techniques, makes it highly improbable that different substances will have a

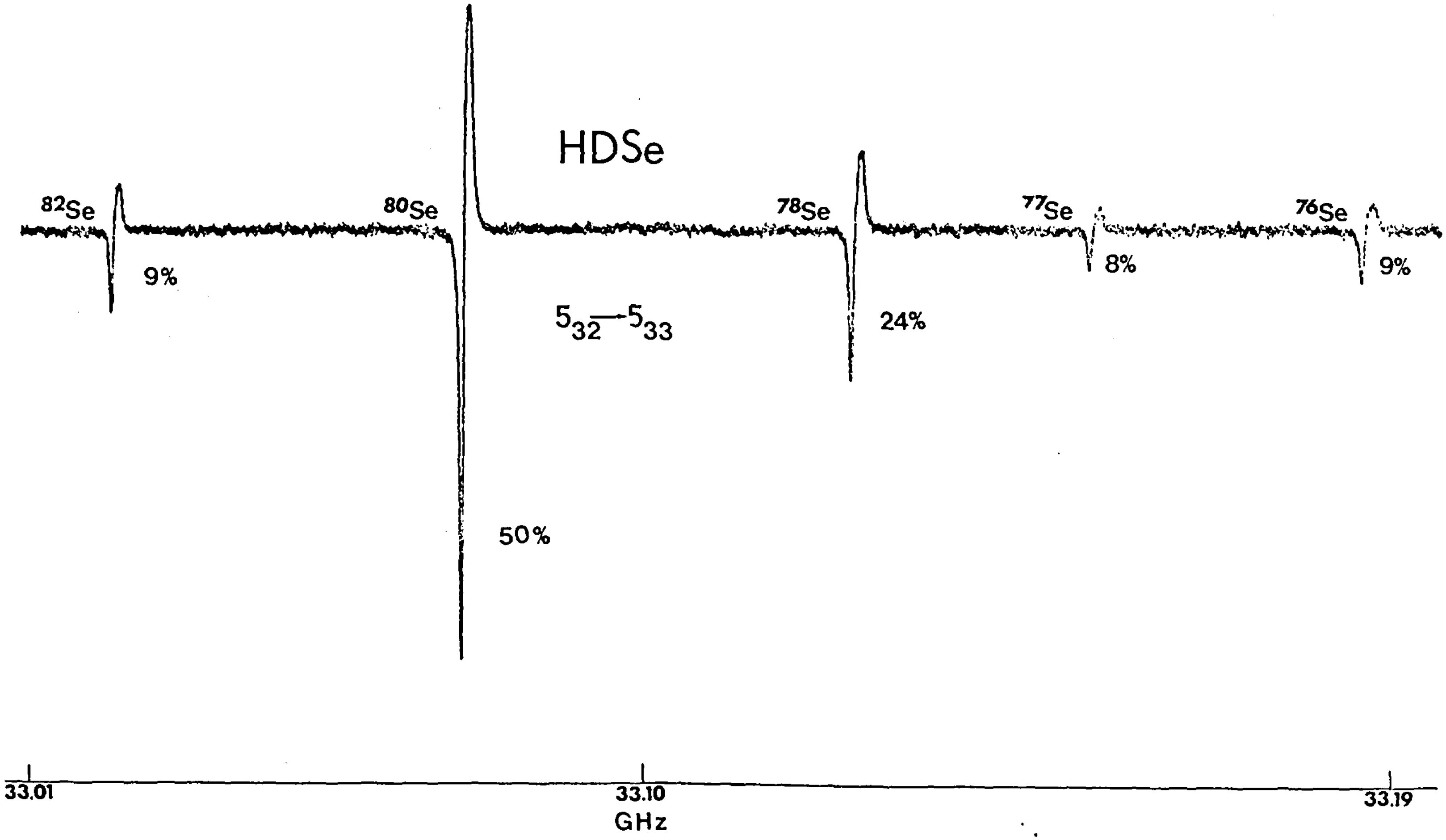

FIGURE 10. A transition of the asymmetric rotor HDSe. Spectral trace recorded from left to right and extends approximately 170 MHz. The *five major isotopic species* of Se are clearly evident. The spectrum was taken at the temperature of dry ice; nevertheless, HDSe decomposes in the Stark cell. This is evident from the decrease in line intensity of ^{76}Se compared with that of ^{82}Se.

number of identical line frequencies. The rotational line frequencies, which are specific to each kind of molecule, thus provide a positive method of identification. Qualitative identification can be made by comparing the measured lines of the unknown substance with compilations of the line frequencies of known compounds. As we shall see, qualitative identification can also be made from spectral characteristics other than line frequencies.

The catalog, or microwave atlas, of spectra is simply a table of numbers corresponding to the line frequencies of various pure substances. Tables are presently available from the National Bureau of Standards that give the line frequencies for substances which have been reported in the literature.[28] The tabulated lines are, however, generally not the strongest, and more work needs to be done in this area with analytical applications specifically in mind. An abbreviated atlas containing perhaps ten of the strongest lines of each molecule spread over the R-band region would be particularly useful. The most intense lines are naturally the ones most useful for analytical analysis. To analyze a gas mixture, for example, one could run a preliminary fast scan of the region to locate the strongest lines. These in turn would be measured under high resolution and compared with the microwave atlas. One may then proceed to the next strongest lines if necessary.

Microwave spectroscopy can be applied to a number of problems without a comprehensive catalog. Many important molecules have well-known lines, and for single-component samples or relatively simple gas mixtures, present tabulations will be satisfactory. Also, measurements on pure samples can be used instead of a catalog for identification, particularly when the possible components of the gas mixture are known. In addition to the analysis of gas mixtures, the method is particularly well suited to the analysis of isotopic mixtures or the various structural isomers of a molecule.

A. Sensitivity

One of the principal problems facing microwave spectroscopy as an analytical tool will be the detection of molecules present in small concentrations. Molecules with large absorption coefficients are more easily detected. Various factors affect the absorption coefficient, and these have been discussed in Section II.C. In general, small molecules with large dipole moments will have strong microwave spectra. Linear and symmetric-top molecules will usually have more intense spectra than asymmetric tops. The ease of detectability of a given molecule can be determined if sufficient information is known to evaluate α_o.

A good Stark-modulated microwave spectrometer can detect a weak line with a peak absorption coefficient as small as 10^{-9} cm^{-1}. This sensitivity is illustrated in Figure 11 for a line with $\alpha_o \cong 3 \times 10^{-9}$ cm^{-1}. The line has a signal-to-noise ratio of better than 3:1. Such a coefficient results in a very small amount of power being absorbed by the molecules at the peak frequency. For a cell of length 1 m and $\alpha_o = 10^{-4}$ cm^{-1}, the fractional power absorbed is, from Equation 14, $\Delta P/P_o$ = 0.01, or only 1% of the incident power is absorbed. Such weak absorptions require a highly sensitive spectrometer, as discussed previously. In the centimeter-wave region, absorption coefficients are usually in the range of 10^{-5} to 10^{-7} cm^{-1} or smaller, although strong absorbers with coefficients greater than 10^{-5} cm^{-1} have been observed.

The minimum concentration of a substance which can be detected in a gas mixture may be estimated from the absorption coefficient. For a strong line, $\alpha_o = 10^{-3}$ cm^{-1}; if 10^{-9} cm^{-1} is an upper limit of detectability, a mole fraction of as little as 10^{-6} (1 ppm) could be observed. For a typical weak line with $\alpha_o = 10^{-7}$ cm^{-1}, a concentration of about 10,000 ppm (1%) would be required for observation.

Any technique which will provide sample enrichment will be useful for weak absorbers to obtain sufficient concentration for detection. A gas chromatograph would be particularly useful in conjunction with a microwave spectrometer. Enrichment techniques using gas-permeable membranes are promising and are being studied in regard to air pollution monitoring.[34] Minimum detectable limits of 5 ppb for SO_2 and 0.2 ppb for H_2CO have been obtained using liquid nitrogen to concentrate condensables.[47]

B. Selectivity

Various considerations bear on the selectivity of a microwave chemical analysis. The number of spectral spaces available, for example, depends on the frequency range and the resolution. Resolutions of 100 kHz can often be obtained as shown in Figure 12. If one considers the R-band region

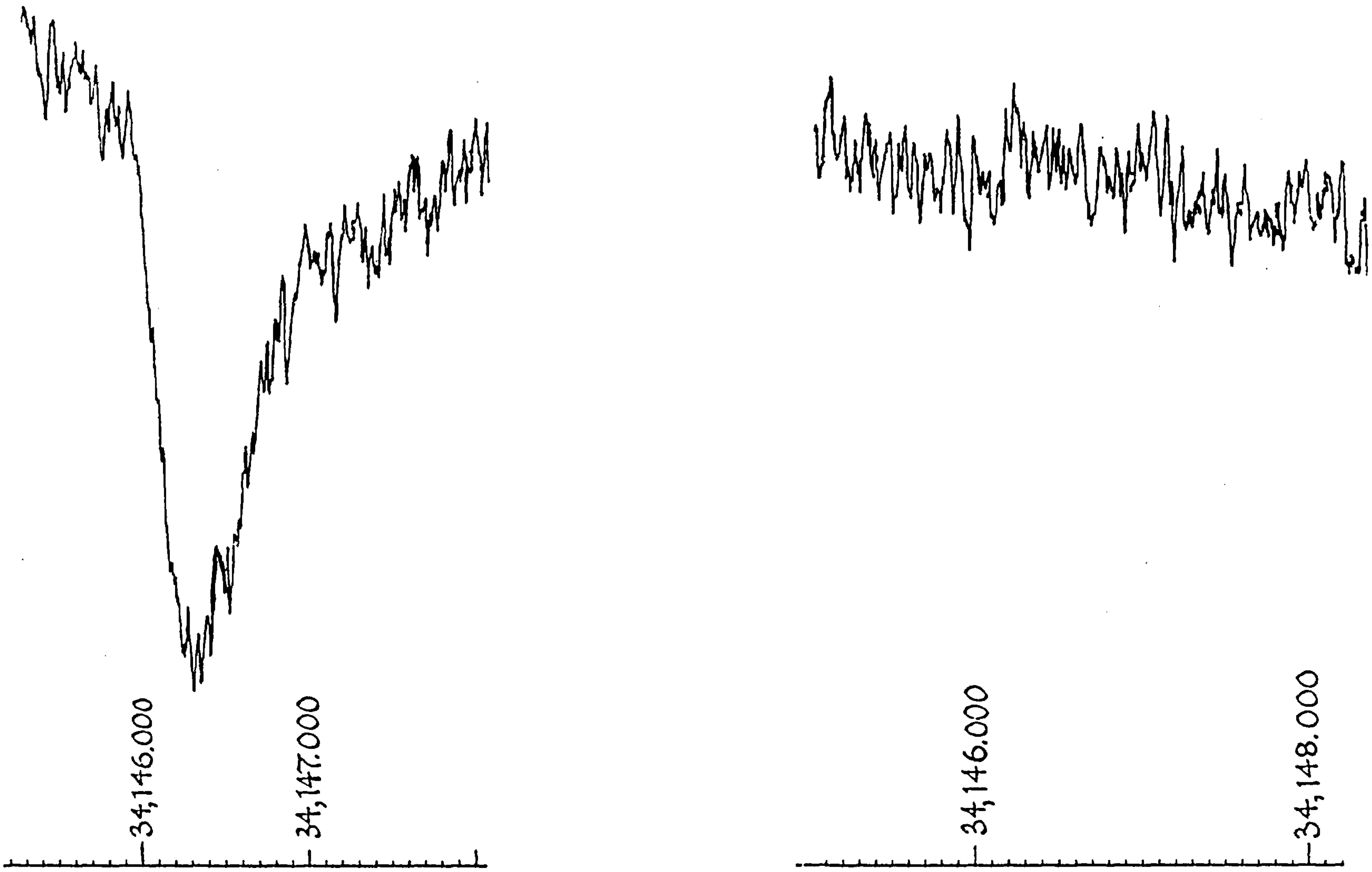

FIGURE 11. Illustration of the sensitivity attainable with a Stark-modulated microwave spectrometer. The trace on the right is taken with no sample in the Stark cell. The trace on the left is that of $^{18}O^{13}C^{32}S$, $\alpha_0 \approx 3 \times 10^{-9}$ cm^{-1}. Spectrum recorded at room temperature with a Stark voltage of 1,000 V. Taken on a HP 8460A spectrometer. (With permission of the Hewlett-Packard Company.)

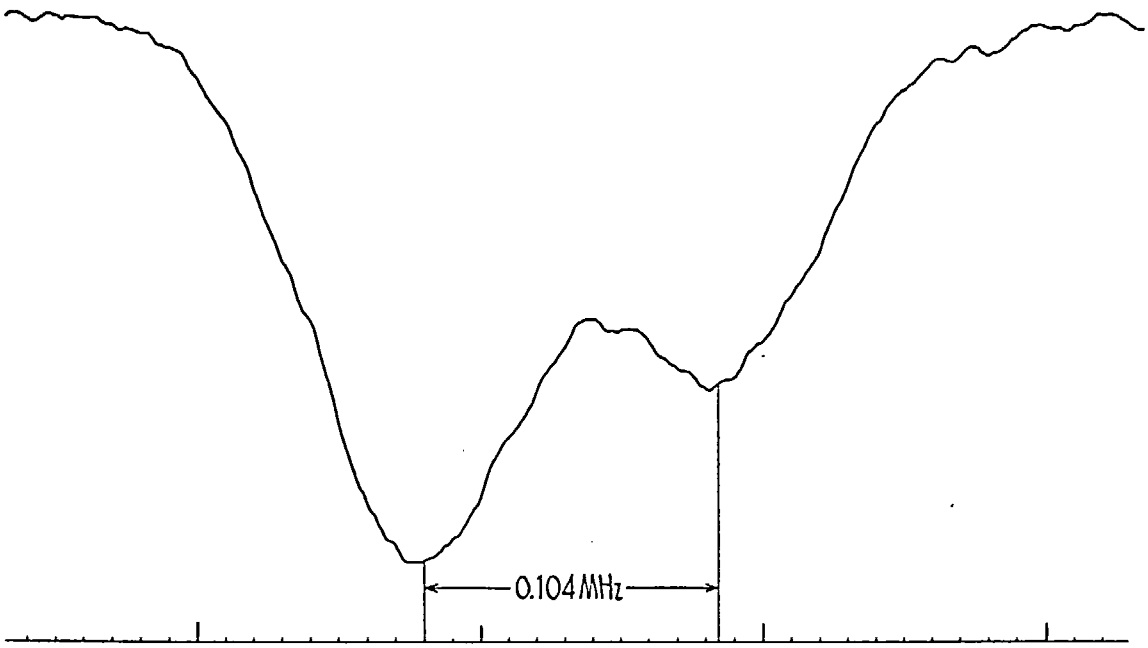

FIGURE 12. Illustration of the resolution possible with a Stark-modulated microwave spectrometer. Taken on a HP 8460A spectrometer. (With permission of the Hewlett-Packard Company.)

(26 to 40 GHz) and assumes that lines 100 kHz apart can be resolved, it follows that there are 140,000 spectral positions available. This is enough room to accommodate a large number of lines without serious overlap. In addition, line frequencies can be measured easily to an accuracy of 50 to 100 kHz. Identification of a substance will usually be made by frequency measurements. With simple mixtures, a single frequency measurement would suffice to uniquely identify the substance. When complex mixtures are to be studied, an unambiguous identification will require more than one frequency measurement.

1. Number of Frequency Measurements for Identification

Problems of identification become greater as (1) the number of components of a gas sample increases, (2) the number of substances considered as possible components of the sample becomes greater, and (3) the density of the spectra from the molecules which make up the sample increases. Under such conditions, the possibility of overlapping lines becomes much greater. A study of the problem has been made by Jones and Beers.[48] A set of 33 molecules, which had a total of 10,000 measured absorption lines, was considered. The average percentage of cases that a line with a given measurement accuracy would be overlapped by a line from the other 32 molecules is shown in Figure 13. The results of Figure 13 can be interpreted as follows: If a single line of an unknown is measured to a high precision of ±0.01 MHz, and if a microwave atlas indicates that a substance has a line catalogued at this frequency, one can be 96% confident that the unknown is that substance (curve A). A measurement with the low precision of ±0.2 MHz, however, would yield a confidence factor of only 55%. On the other hand, if two lines were measured with this precision, only a 2% chance of overlap is obtained, and, hence, the confidence factor is now increased to 98%. The more knowledge one has about the unknown sample, so as to limit the possibilities which have to be considered, the less likely are overlaps to occur. The results of Figure 13 can be used as a rough guide in selecting the number of lines to be measured to obtain the degree of confidence desired.

With comprehensive catalogs listing all transitions of a substance, the probability of overlap considered above can be expected to increase significantly. An analysis similar to that described would undoubtedly require measurement of many

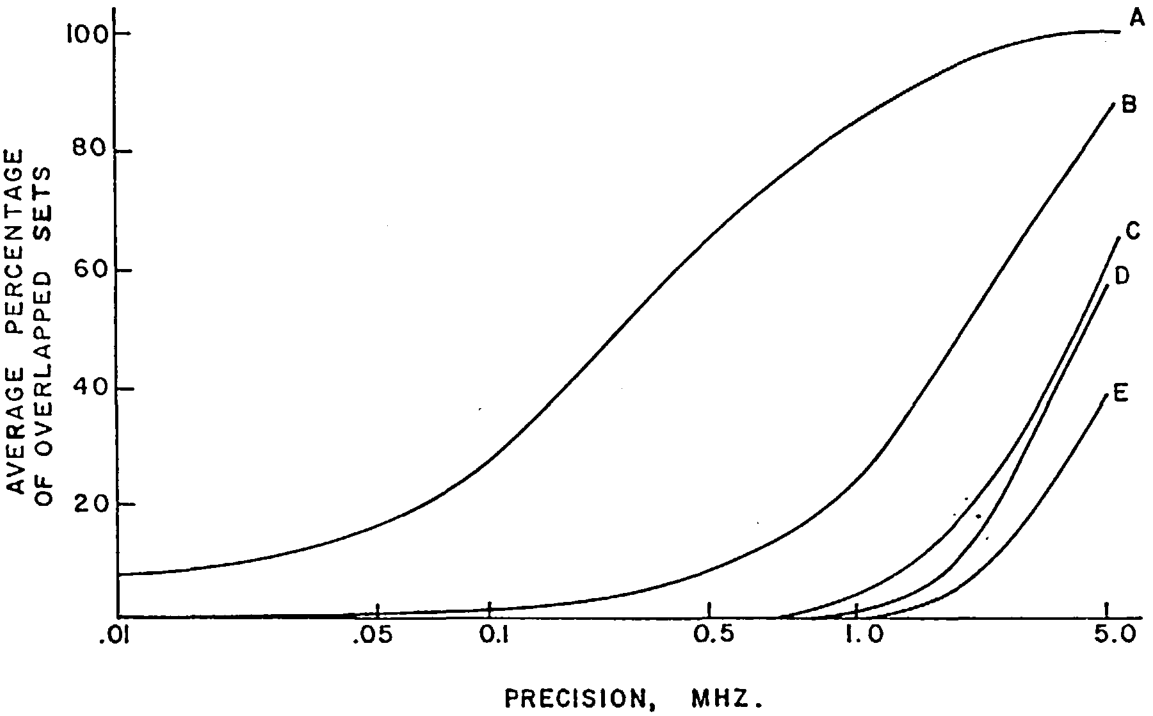

FIGURE 13. Average percentage of overlapped sets of lines versus precision of measurement for a sample of 33 gases, plotted on a semilogarithmic scale. Each point on the curves represents an average of the percentage of overlap for ten molecules. Curve A: set of 1 line; B: set of 2 lines; C: set of 3 lines; D: set of 4 lines; E: set of 5 lines. (From Jones, G. E. and Beers, E. T., *Anal. Chem.*, 43, 656 (1971). With permission.)

more lines for a unique identification. On the other hand, many of the lines tabulated would be too weak to observe in a mixture, especially if the molecule were present in small concentration. Perhaps a suitable compromise would be an abbreviated atlas, as mentioned previously.

2. *Identification by Low-resolution Spectra*

In addition to using line frequencies, obtained under high-resolution conditions, to identify the absorbing molecules, one can also use low-resolution spectra to distinguish various substances. Under fast sweep conditions, spectra of considerably reduced resolution are obtained. Nonetheless, considerable sensitivity to molecular composition still remains. A low-resolution spectrum without any particular pattern is given in Figure 14. This may be compared with Figure 1, which is a recording of the same molecule at, however, a different modulation voltage. The appearances of such spectra obviously can depend on the Stark voltage as well as the sample pressure and scan rate. With scan rates of 10 MHz/sec, a whole R-band region may be covered in approximately 20 min.

These low-resolution spectra are particularly useful for molecules which give rise to band spectra, e.g., near prolate asymmetric tops with "a"-type transitions or near oblate tops with "c"-type transitions. The band spectrum of bromonitrofenchane is shown in Figure 15. Each band consists of a number of unresolved lines. The doublet structure is due to the ^{81}Br and ^{79}Br isotopes of the substance. The sensitivity to isotopic composition even from spectra of low resolution is still very high.

The rotational isomers of crotonic acid are clearly evident in the low-resolution spectrum of Figure 16, where two sets of band spectra are found. The spacing between the bands of a given series, as we have seen in Section II.A, is related to the moments of inertia. Thus, a given isomer may be assigned to a particular series by comparison of the observed and calculated moments of inertia obtained by assuming the structural parameters and conformation.

Under slightly slower scan rates, say 3 MHz/sec, increased resolution is obtained, and individual lines are observed within each absorption band. This is illustrated in Figure 17. Nevertheless, the

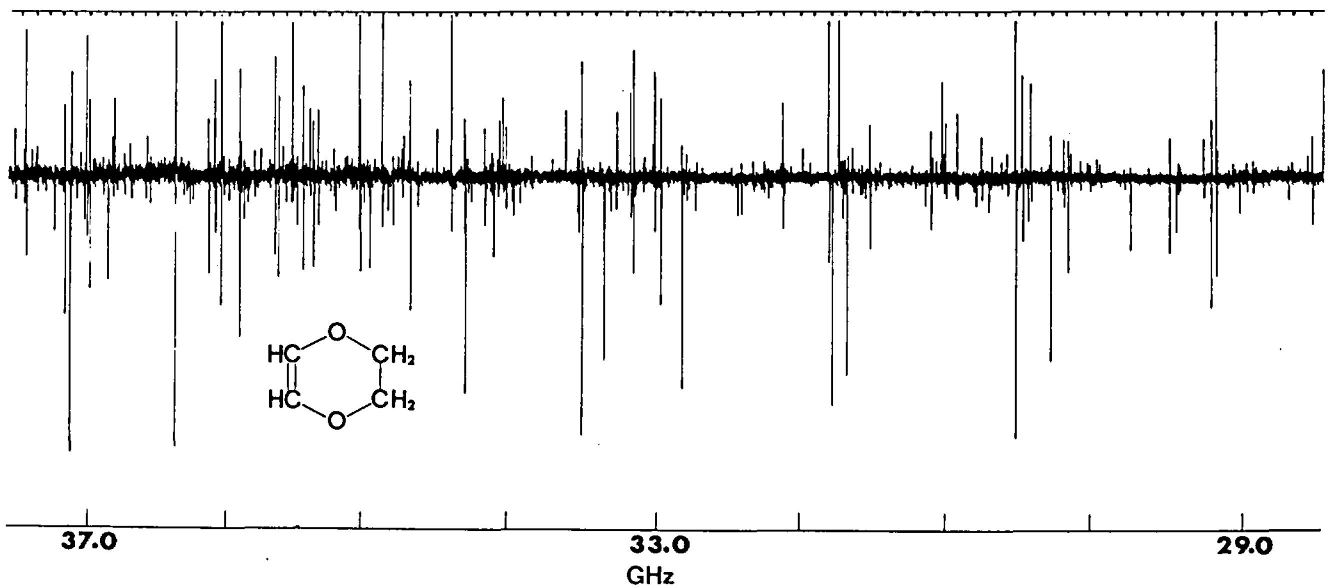

FIGURE 14. Low-resolution microwave spectrum of 2,3-dihydro-*p*-dioxin (Dioxene). The spectrum was recorded at room temperature with a scan rate of 3 MHz/sec, a pressure of about 80 mtorr, a detector time constant of 1 sec, and a Stark-modulation voltage of 375 V. Compare this with Figure 1, which was run at a higher Stark voltage. (From Wells, J. A. and Malloy, T. B., Jr., presented at the 28th Annual Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June 1973 [Paper P10].

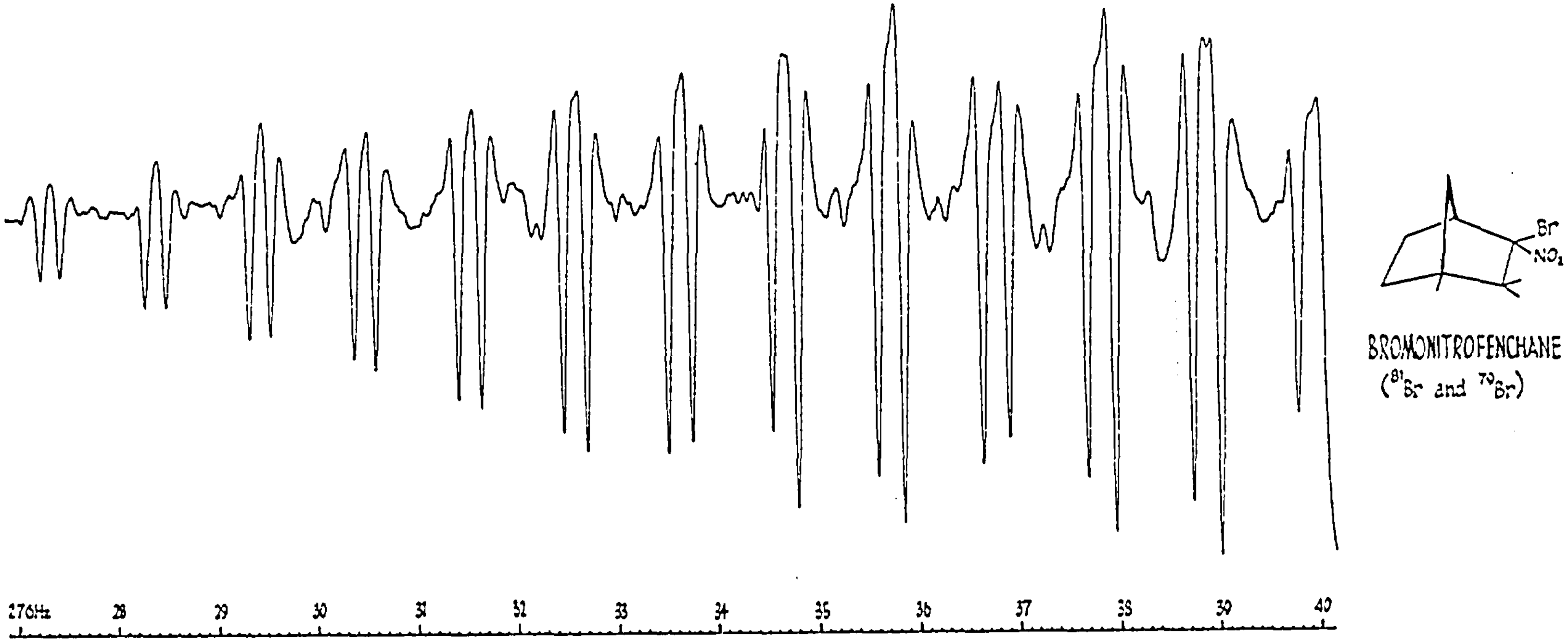

FIGURE 15. Low-resolution microwave spectrum of bromonitrofenchane. Scan rate 10 MHz/sec, pressure about 100 mtorr, 1,000-V Stark modulation. The doublet structure is due to ^{81}Br- and ^{79}Br-containing molecules, each present to the extent of approximately 50%. Taken on a HP 8460A spectrometer. (With permission of the Hewlett-Packard Company.)

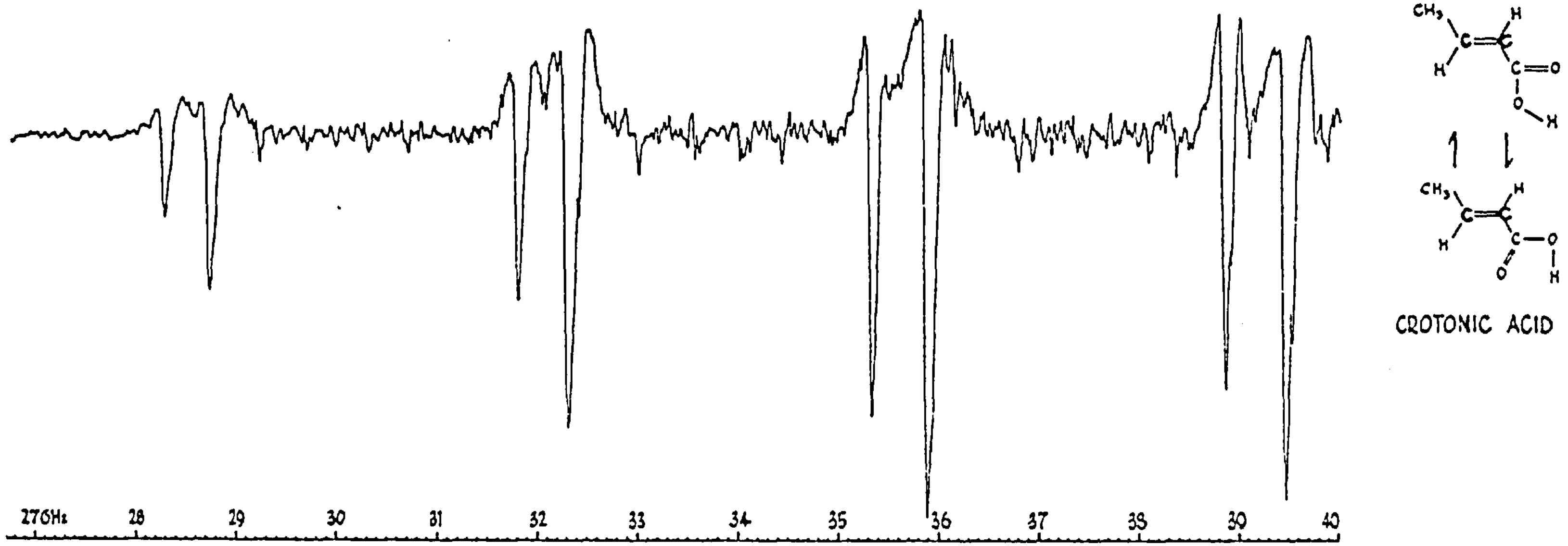

FIGURE 16. Low-resolution microwave spectrum of crotonic acid. Scan rate 10 MHz/sec, pressure about 15 mtorr, 1,000-V Stark modulation. Spectra of two rotational isomers (s-*trans* and s-*cis*) are evident. Strongest bands are due to s-*trans*. Taken on a HP 8460A spectrometer. (With permission of the Hewlett-Packard Company.)

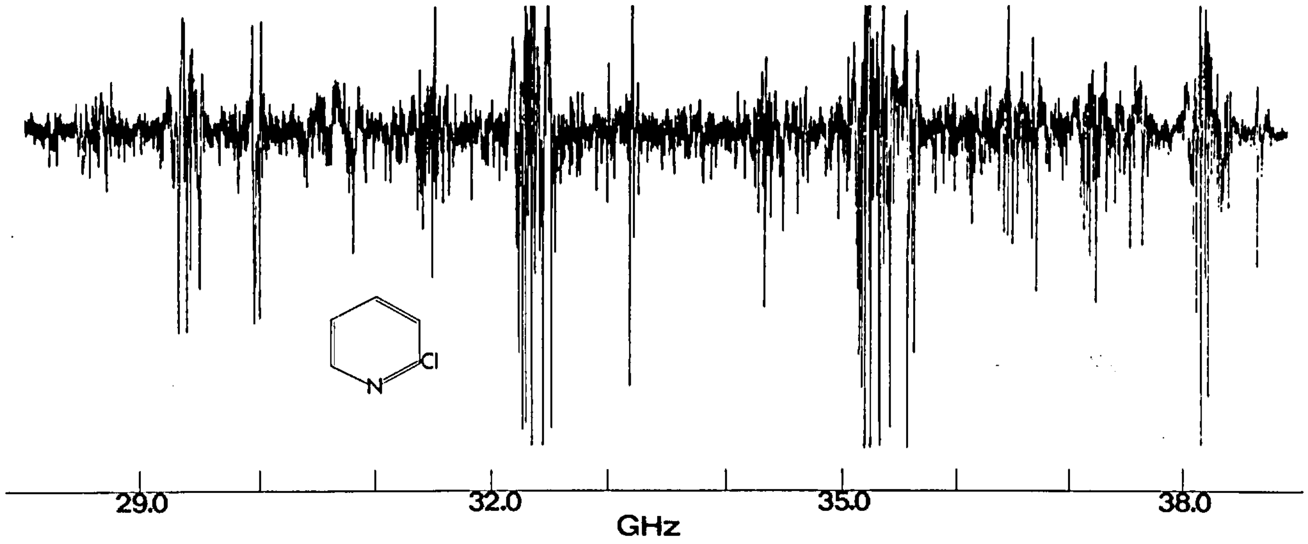

FIGURE 17. Low-resolution R-band spectrum of 2-chloropyridine. Scan rate about 3 MHz/sec, time constant 0.4 sec, 130-V Stark modulation. The ^{37}Cl species give a cluster of lines at frequencies lower than those of the strong ^{35}Cl lines. (See Walden, R. T., Ph.D. dissertation, Mississippi State University, 1973.)

bunching of lines into groups is clearly evident. Comparison of Figures 17 and 18 shows that these chemical isomers give distinct spectra and are therefore easily distinguished.

C. Applications

Qualitative analytical applications of microwave spectroscopy are growing in number. The qualitative identification of SO_2 and the other sulfides in a mixture is illustrated in Figure 19. The assignment of the absorption lines to the various compounds was made by employment of the spectra obtained from pure compounds (Figure 20). The strongest lines of each of the components of the gas mixture are used for the analysis.

Preliminary applications of microwave spectroscopy to the identification of the polar constituents of cigarette smoke and car exhaust have been carried out by Harris and Jones.[49] Similar work by Harrington has recently been reported in an article by Karasek.[50] One interesting aspect of these studies is the detection of HCN in cigarette smoke.

Saito[51] used a Stark wave guide absorption cell and a 110-kHz sinusoidal Stark modulation to confirm the existence of the free radical SO in a pyrolyzed sample of ethylene episulfoxide. The cell was coated with "Corning® K" coat to prevent the decomposition and reaction of radicals. A continuous flow process was also employed.

Crable[52] has recently reported to the Environmental Protection Agency on the results and evaluation of his experiments on the effectiveness of microwave spectroscopy as an analytical tool for air contamination studies. The conclusions of Crable emphasize that microwave spectroscopy is not expected to become better in every way than all other existing methods. He found that the sensitivity of a conventional Stark spectrometer to important air pollutants is definitely below that of gas chromatographs and mass spectrometers. Sample-enrichment techniques can be used to extend detectable concentrations of impurities such as NO_2 down to a few parts per million and less. On the other hand, simple enrichment methods are also available to gas-chromatography. These results suggest that, if sensitivity is a primary concern, one must go to cavity spectrometers to obtain sensitivities equal to those of established techniques. Further aspects of Crable's report are discussed in Sections V.A.4. and V.B.2.

Whereas the work of Crable indicates that a conventional microwave spectrometer is not the best analytical tool for air pollution studies, a report by Hrubesh[34] suggests that microwave cavity spectrometers can compete more successfully. Microwave spectroscopy, despite its attractive features, has not received much interest as a pollution detector. Hrubesh gives several reasons for this: (1) Conventional spectrometers are large, expensive, complex, and sophisticated; (2) elec-

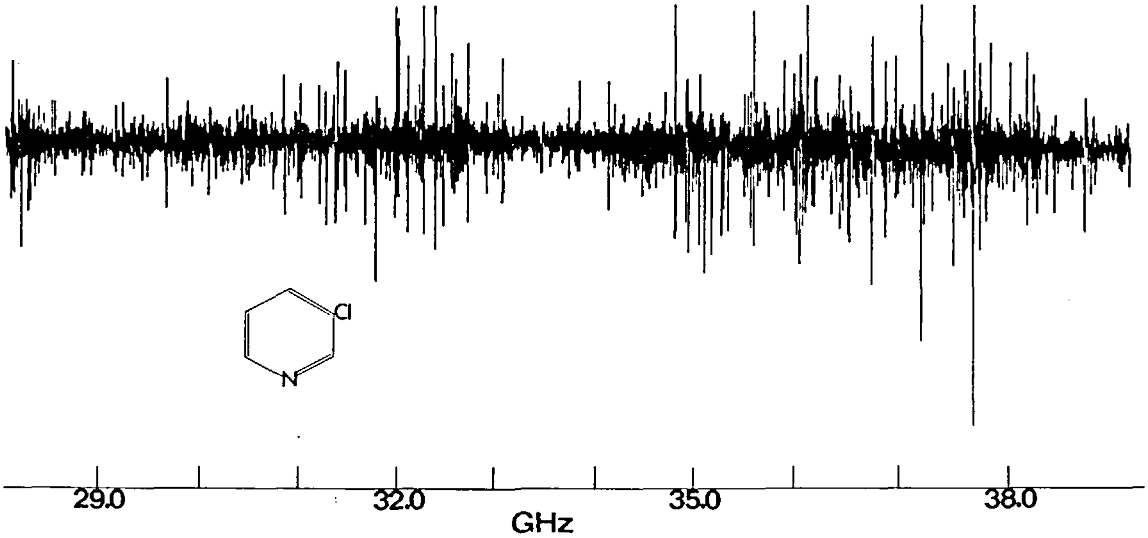

FIGURE 18. Low-resolution R-band spectrum of 3-chloropyridine. Scan rate about 3 MHz/sec, time constant 0.4 sec, 130-V Stark modulation. Sample obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis., and used without further purification.

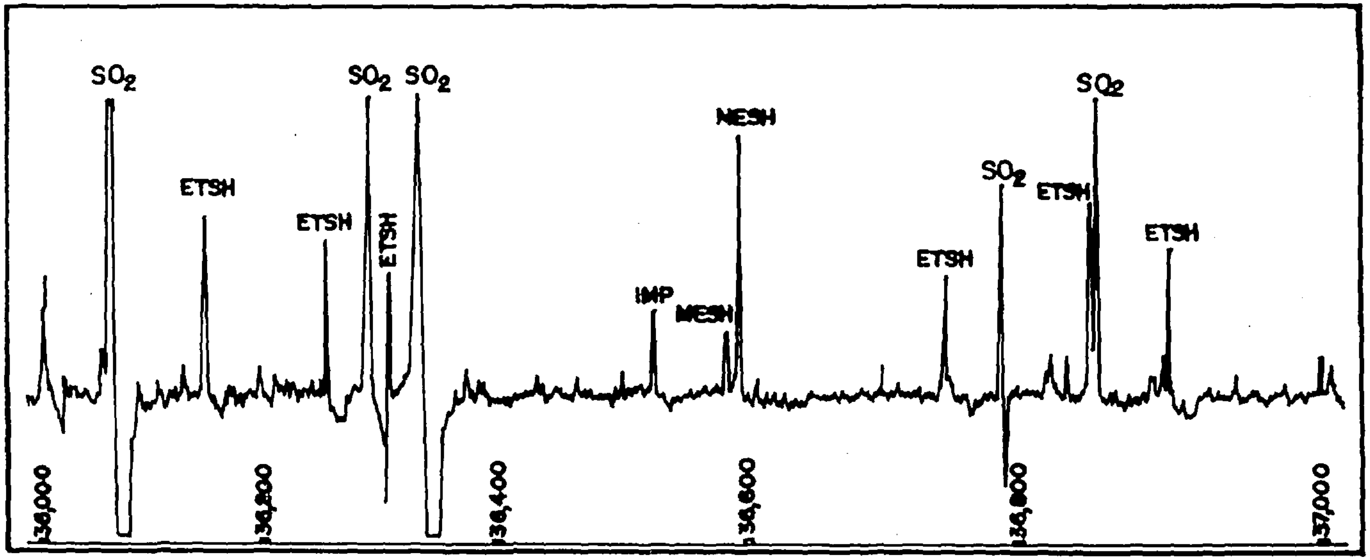

FIGURE 19. Rotational spectrum of a gas mixture made up of 45% CH_3SH (MeSH), 45% CH_3CH_2SH (EtSH), and 10% SO_2. The absorption lines are up, while the Stark lobes are shown downward. The presence of SO_2 is clearly indicated. The spectrum was run with a total gas pressure of 50 mtorr, a volume of 500 cm^3, a time constant of 0.3 sec, and a scan time of 1,000 sec. (With permission of Hewlett-Packard.)

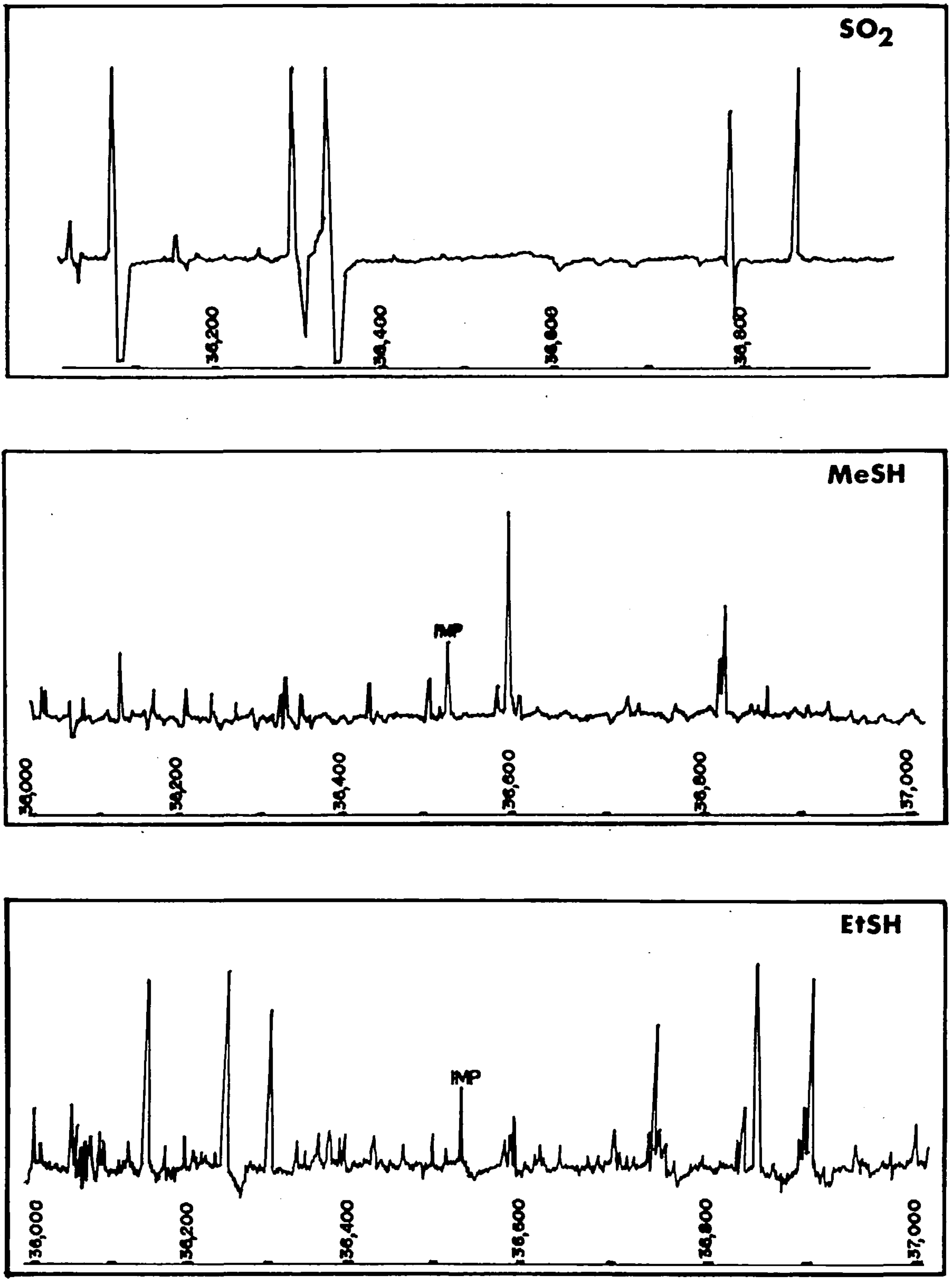

FIGURE 20. 1,000-MHz portions of the microwave spectra of sulfur dioxide, methyl mercaptan, and ethyl mercaptan. SO$_2$ and MeSH samples were 99% pure, EtSH was practical grade. (With permission of Hewlett-Packard.)

trical power requirements of conventional spectrometers are significant and thus of limited use for remote monitors; (3) requirements for low operating pressures make accurate gas-sampling difficult; and (4) no feasibility studies have indicated the utility of microwaves as a monitoring technique. The investigation by Hrubesh gives very significant answers to these criticisms. Furthermore, he has demonstrated the feasibility of replacing a sophisticated multipurpose conventional microwave spectrometer with a relatively simple single-purpose instrument.

He constructed a spectrometer using a "Gunn-diode" as a source and a cavity as an absorption cell. The source, powered by a 6-V battery, provided 40 mW of power over a frequency range of 23 to 26 GHz and was stabilized by the sample cavity. In addition to Stark modulation, Zeeman modulation[21,22] was employed. This latter technique made use of the magnetic dipole moment of some important air pollutants, notably NO_2. Preliminary measurements gave signal-to-noise ratios of 2 to 1 for concentrations of NO_2 and SO_2 of 11 ppm and 3 ppm, respectively. It was felt that this sensitivity could be further improved.

Hrubesh gave considerable attention to sampling techniques. To determine the applicability of his spectrometer to atmospheric monitoring, he considered gas-permeable membrane separators and dilution with an inert carrier gas. Membranes can be used to enrich samples, as well. The use of the carrier gas had the advantage that sampling could be easily calibrated. The usefulness of a microwave cavity spectrometer used as a specific detector in conjunction with gas chromatography was demonstrated.

D. General Considerations

1. Sample Considerations

For an analysis by microwave spectroscopy, the substance must have a nonzero electric dipole moment and a minimum vapor pressure of approximately 1 mtorr. The range of molecules studied can be greatly increased by heating the absorption cell in order to obtain the required vapor pressure. Ordinary Stark cells can be heated to about 100°C without damaging the cell. Only about 10^{-6} mol of gas is required to fill a sample cell, and most of this can be recovered since the microwave radiation is nondestructive. Unfortunately, since metal cells are usually employed, both adsorption and chemical decomposition in the cell can be a serious problem for certain molecules. Usually, some arrangement for heating the cell is necessary to facilitate outgassing the cell between introduction of new samples. Chemical decomposition and reaction of unstable molecules can be handled, in many cases, by cooling or by "conditioning" the cell. This latter technique involves filling the cell with successive samples at high pressure over a period of time. Another technique useful for very reactive species involves flowing the sample continuously through the absorption cell. The flow rate is adjusted to obtain the desired pressure and renewal rate. Another procedure which has proven useful is to coat the inner surface of the sample cells with an appropriate coating, thereby increasing the lifetime of the reactive species in the cell.[53,54]

2. Time Required

Only rough estimates of the analysis time can be made. Obviously, for a complex mixture in which little is known, a considerable time will have to be spent in the analysis. On the other hand, if some idea of the potential components is available, then checks can be made at particular frequencies where absorption lines are expected. For reasonably strong lines, three or four frequencies can be measured in approximately 10 min. Alternatively, a fast scan over all or part of the frequency region can be made to locate the strongest lines of the spectrum. The whole R-band region can be scanned in approximately 20 min at a scan rate of 10 MHz/sec. The strong lines can then be measured more accurately at slow scan rates and higher resolution to confirm an identification. The search for components with weak lines or for strong absorbers in small concentration will be more time-consuming. To obtain maximum sensitivity, slow scan rates and large time constants are required. At a scan rate of 0.1 MHz/sec, approximately 3 hr would be required to search over a range of 1,000 MHz.

V. QUANTITATIVE ANALYSIS

A. Nonsaturation Techniques

1. Dependence of α_0 on Concentration

From Equation 14 it follows that the intensity coefficient α may be written:

$$\alpha = \frac{\Delta P}{\ell P_0}. \tag{33}$$

The coefficient α can be obtained experimentally at any given frequency at which the molecule absorbs radiation by measuring the quantities on the right side of Equation 33 when the spectrometer is tuned to that frequency. Especially convenient is the peak absorption coefficient α_o.

At the resonant frequency, Equation 22 can be written

$$\alpha_o \, \Delta\nu = C \, \nu_o^2 \, xp. \tag{34}$$

In principle, the most straightforward method of determining abundances consists of using this equation together with measured values of ν_o, α_o, and $\Delta\nu$ and a knowledge of molecular constants to calculate the constant C. One then solves for the partial pressure xp and uses a measurement of total pressure to obtain the mole-fraction x. However, this procedure would prove useful in only a small minority of practical cases due to limited knowledge of the molecular constants.

Even methods of determining the mole-fraction x that do not require a knowledge of the constant C are complicated by the fact that the half-width $\Delta\nu$ depends on sample composition. This dependence is expressed by the equation[3,5]

$$(\Delta\nu)_A = (k_{AA}x_A + k_{AB}x_B + k_{AC}x_C + \cdots)\, p, \tag{35}$$

where $(\Delta\nu)_A$ is the half-width for the measured transition of constituent A; x_A, x_B, x_C, etc. are the mole-fractions of the various constituents; k_{AA}, k_{AB}, k_{AC}, etc. are the collision-broadening factors of A due to constituents A, B, C, . . . , respectively. This equation assumes that the broadening effects of the various gases are additive. A similar equation exists for the half-width of each gas in the mixture. Consequently, if the pressure and collision-broadening factors are known, measurements of the half-widths make it possible to calculate all the mole-fractions. Equation 35 can be used to express Equation 34 in the following form:

$$(\alpha_o)_A = (C_A x_A)/(k_{AA}x_A + k_{AB}x_B + k_{AC}x_C + \cdots). \tag{36}$$

Here C_A contains the frequency dependence explicit in Equation 34. Equations 34 and 35 have been of little practical use in determining concentrations, as not many of the k's are known. These equations are useful, however, in an examination of the behavior of α_o. It is clear from Equation 36 that, because of the linear dependence of the half-width on pressure, the coefficient α_o is pressure independent. Furthermore, both the half-width and the peak absorption coefficient are affected by the mole-fraction and the collision diameters of every constituent of the mixture. In a pure sample of gas A, $x_A = 1$, k_{AA} is nonzero, and all other x's and k's vanish from Equation 36. Increasing the pressure of gas A, therefore, has no effect upon α_o but increases $\Delta\nu$. Diluting gas A with a second gas B, however, necessarily reduces α_o and increases $\Delta\nu$. If the sample pressure is then reduced to the original pressure of gas A, the half-width can show either a decrease or increase over that of the pure gas. The magnitude of the decrease in α_o and the effect on $\Delta\nu$ are determined by the magnitude of the collision-broadening factor of gas B. The peak absorption coefficient decreases and $\Delta\nu$ increases much more if the molecules of gas B are very polar than if they are nonpolar. Notice from Equation 35 that if $k_{AA} = k_{AB} = k_{AC} = \ldots$, then $\Delta\nu/p$ is independent of *the composition of the mixture*. This has found application in isotopic analysis; examples are given in Section V.A.4. The effect of dilution on a transition of CH_3OH by adding air is shown in Figure 21.

In addition to direct substitution into Equation 34, there are other methods of determining abundances using absolute measurements of α_o that do not require accurate molecular information. ("Absolute" implies that α_o is determined directly by measurements only on one absorption line.) Because of difficulties in obtaining accurate measurements of peak absorption coefficients, half-widths, and pressure, these methods have become generally feasible only with the advent of reliable commercial spectrometers and reliable pressure gauges of the appropriate range. We will consider intensity measurements made with these spectrometers after a discussion of methods used prior to their introduction. These methods make use of relative intensity measurements to determine the ratios of values of α_o for pairs of absorption lines.

2. *Relative Intensity Measurements*

The simplest (and historically the first) approach to quantitative analysis by microwave spectroscopy makes use of comparisons of absorption coefficients in the sample with those in a reference mixture. If certain restrictions are observed, such comparisons can be replaced by a

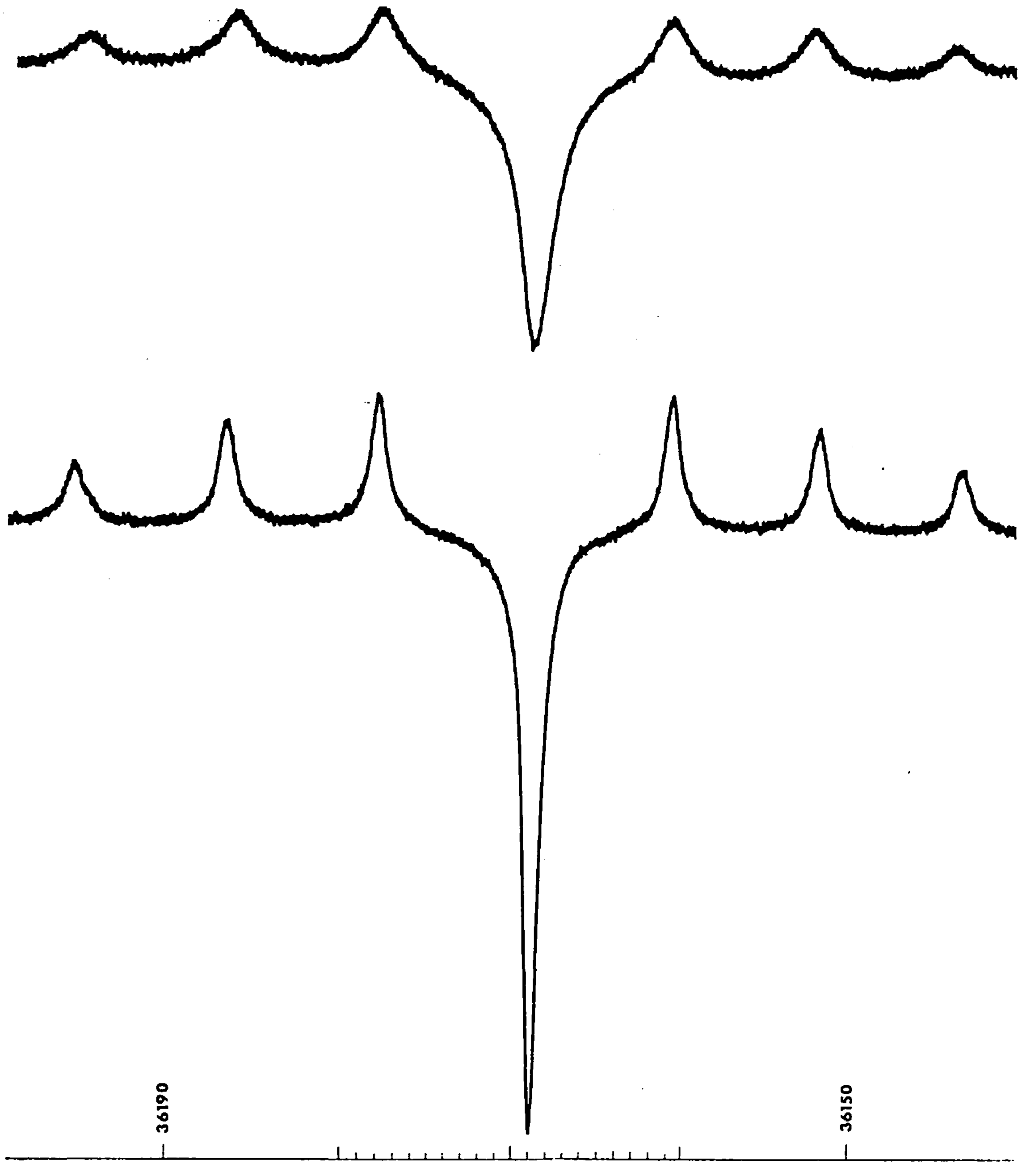

FIGURE 21. A methanol transition recorded with 175-V Stark modulation. The lower trace is from a pure sample of CH_3OH. The upper trace was obtained after adding air so that final pressure was about three times the initial pressure.

comparison of peak heights. Measurements of peak heights are both simple and accurate. If the effective radiation path lengths and the microwave power levels are equal during the measurements of a given transition in two different samples, then the ratio of the output signals from a Stark spectrometer is equal to the ratio of the absorption coefficients.[55] The microwave power is proportional to the rectified current in the detecting crystal for crystal currents below a few hundred microamperes. The power level can, therefore, be held constant for the two measurements by monitoring the crystal current. According to Equation 34, α_0 for a given absorption line is proportional to the corresponding concentration x provided the factors $\Delta\nu/p$ and C can be considered constant. Then, for lines at the same frequency, the ratio of the peak heights is equal to the ratio of the concentrations. Concentrations are then determined by simply comparing the signal of an absorption line in a reference sample of known concentration with the signal produced by the same absorption line in the sample under investigation.

Although C is the same for the same transition in two different samples, $\Delta\nu/p$ is not in general constant but depends on sample composition, as we have seen. Serious errors can result if this is ignored. The mole fraction is actually proportional to. $\alpha_o \frac{\Delta\nu}{p}$ rather than to α_o. There are several procedures available for including the effects of sample composition. If one has sufficient knowledge of the unknown sample, a standard sample of known concentration with approximately the same composition as the unknown can be prepared. This is the simplest technique and is especially practicable when a large number of determinations is to be made. Furthermore, it offers accuracies of a few percent if the signals are reasonably strong. Another approach is to dilute the unknown sample with a nonpolar gas, such as nitrogen or helium, for which line-width information has been previously obtained, and apply Equation 35, making the approximation of large diluent concentration in Equation 37. This is feasible only if the line is relatively strong. The line-width information on the diluent is unnecessary if the standard sample is also diluted with the same diluent, as $\Delta\nu/p$ will then be very nearly the same for both samples. Finally, one can measure $\Delta\nu/p$ for the same transition in both the standard and the sample and use the exact equation

$$\frac{x_1}{x_2} = \frac{(\alpha_o)_1}{(\alpha_o)_2} \cdot \frac{(\Delta\nu/p)_1}{(\Delta\nu/p)_2} = \frac{(\alpha_{int}/p)_1}{(\alpha_{int}/p)_2}, \tag{37}$$

where $\frac{(\alpha_o)_1}{(\alpha_o)_2}$ is given by the ratio of the peak heights.

The greatest use of microwave methods in quantitative analysis has been in the determinations of isotopic abundances. In these studies, the above procedure for relative intensity measurements has often been applied to two absorption lines at different frequencies. Provided the direct crystal current is held constant, the ratio of the signals produced by two different absorption lines is equal to the ratio of the corresponding values of $\alpha_o \ell$, where ℓ is the effective radiation path length. The change in the effective path length with frequency may be calculated directly from the geometric length, L, and cutoff frequency, ν_c, of the wave guide from the equation $\ell = L/(1-\nu_c^2/\nu^2)^{1/2}$. This variation, however, is not usually important at frequencies sufficiently above the cutoff frequency of the wave guide. On the other hand, multiple reflections will alter the radiation path length in a manner that can depend strongly on frequency. Even with frequencies only 10 MHz apart the effective path length can be significantly different. Such reflections should, however, be small in commercial spectrometers[31] with high quality wave guide components and ferrite isolators. If the change in ℓ with frequency is negligible, then the ratio of the signal heights at two different frequencies again reduces to the ratio of the values of α_o. Examining Equation 34 for the same transition from two different isotopes, we expect the constant C, which includes the dipole moment and the line strength factor, to be essentially the same for different isotopic species. The effect of different absorption frequencies (the ν_o^2 factor) could be corrected for explicitly, but this will be negligible for most pairs of lines. Finally, if the relative abundance of two isotopes in a given sample is to be determined by comparing peak heights, then $\Delta\nu/p$ is the same for each isotope and independent of sample composition. Therefore, the concentration ratio x_1/x_2 will be given simply by the ratio $(\alpha_o)_1/(\alpha_o)_2$ or, equivalently, by the ratio of their peak signal heights.

3. *Absolute Intensity Measurements and the Integrated Coefficient*

Absolute measurements of the peak absorption coefficient α_o and the half-width $\Delta\nu$ of a line are essentially determinations of the integrated intensity of the line, as seen by Equation 24. Unlike the peak absorption α_o, the integrated intensity does not depend on the line broadening parameter. Rather, α_{int} depends directly on the partial pressure of the absorber. Determinations of α_{int} and the total pressure p for a standard mixture and the sample being studied provide the mole-fraction x by Equation 37. The integrated intensity can be found either by separate measurements of α_o and $\Delta\nu$ or by measuring the area under the absorption line.

One of the difficulties of the first method is that completely different techniques are usually needed for the measurements of α_0 and $\Delta\nu$. The primary problem in the determination of α_0 is the measurement of very small changes in microwave power at the detector produced by the absorbing molecules. Since the power at the detector is proportional to the rectified crystal current for low power levels, α_0 can be obtained from Equation 33 if small changes in power or crystal current are measured. For conventional spectrometers, this, in turn, requires accurate detector characteristics, which relate the output voltage at the detector to the crystal current. At low power levels, these characteristics obey a square-law; at higher powers the characteristics are generally more complicated. These higher powers may be required for good sensitivity and measurement of $\Delta\nu$. In addition to the difficulties associated with measuring α_0, ordinary techniques for measuring $\Delta\nu$ can be difficult to apply to lines that are sharp and narrow. The precision with which frequency markers can be placed at the correct points on the absorption line limits the accuracy of $\Delta\nu$ to a few percent. In short, most conventional microwave spectrometers built before 1965 in research laboratories for studies of molecular structure were unsuited to measurements of α_0 and $\Delta\nu$. There were a few exceptions, notably the instruments designed especially for the measurements of absorption coefficients (Bird,[56] Mattuck and Strandberg,[57] Dymanus et al.[35]).

Commercial spectrometers now available make possible accurate measurement of absolute values of α_0 and α_{int}. Detailed procedures for measurement of α_0 using the Hewlett-Packard Model 8460A are given in the operating manual. In principle, α_0 is determined by a measurement of the ratio of the power absorbed by the gas to the total power entering the absorption cell. Curl[73] discusses absolute intensity measurements and has suggested a modification in the location of the calibration arm to make measurements of α_0 more convenient. Concentrations are determined by measuring α_0, $\Delta\nu$, and p for a given transition in a standard sample. These quantities are then measured in the unknown sample and the concentration calculated from Equation 37. A survey of the literature indicates that few measurements of concentration by this method have so far been made with commercial spectrometers.

Perhaps the most straightforward way to measure the integrated intensity α_{int} is to measure the area under the absorption curve. If accuracy considerations permit and if the line is reasonably strong, this can be done simply and directly by counting squares on chart paper or by using a planimeter. A measurement of pressure then allows an immediate determination of the concentration (see Equation 37) by comparison with similar measurements on a standard mixture. Very accurate and convenient measurements of areas are now possible with commercial electronic digital integrators. The output signal of the spectrometer can be sent directly into the integrator, which integrates the line intensity as the line is scanned. Precisions of 1% and better in area measurements are claimed for some of these integrators. In principle, the integration of the absorption line must extend to infinity on each side of the resonant frequency, but in practice one measures the area only to points at which the curve closely approaches the base line. As suggested by Hughes,[3] one can measure the area under the curve out to convenient points, such as those marking the half-width, and multiply by an appropriate factor based on a Lorentzian line shape. This procedure can conveniently be used with a digital integrator and can find application in detecting the presence of unresolved Stark components, overlapping spectral lines, or power saturation. To do this, one integrates from a set of convenient points on the line and multiplies by the appropriate factor to determine the area. This procedure is repeated, integrating to the second, then to the third predetermined points on the line. If the same area is obtained each time, then the line is truly Lorentzian and free from interference. Inconsistent areas indicate the presence of some undesirable condition, such as an interfering Stark lobe, which must be removed. The Camspek spectrometer makes use of such an automatic electronic integration system for measuring α_{int}, with provisions for detecting and correcting for line shape distortions. The concentration would be evaluated from Equation 37 with a pressure measurement.

4. Applications Using the α-Coefficient

The greatest number of applications of microwave spectroscopy to quantitative analysis has been in the determinations of isotopic abundances. This type of analysis is especially convenient with microwaves because the collision diameters of isotopes are expected to be equal (see Section

V.A.1). This means that the factor $\Delta\nu/p$ is the same, so the ratio of absorption coefficients, which may be taken as equal to the ratio of the peak heights, is equal to the ratio of the concentrations as indicated by Equation 37. One of the earliest applications was the determination of the natural abundance of chlorine-37. Townes et al.[58] used relative intensity measurements of absorption lines of $Cl^{35}CN$ and $Cl^{37}CN$ and found the ratio of chlorine-37 to chlorine-35 to be 0.3. The natural abundance of the radioactive isotope chlorine-36 was measured by Wu et al.[59]

Southern et al.[60] used relative intensity measurements to determine the concentrations of nitrogen-15 in ammonia and carbon-13 in cyanogen chloride. In order to eliminate uncertainties in the position of the base line, peak heights were measured from the peak of the main line to the peak of the partially resolved Stark component. Nonlinearities in the spectrometer system necessitated the use of calibration curves. Great care was taken to avoid errors resulting from variations of peak height ratios due to changes in spectrometer characteristics. Instead of plotting ratios of peak heights of $N^{15}H_3$ to $N^{14}H_3$ versus concentration of $N^{15}H_3$, the investigators measured ratio of peak heights of $N^{15}H_3$ to $N^{14}H_3$ for various prepared concentrations of ammonia and divided these by the ratio of peak heights of $N^{15}H_3$ to $N^{14}H_3$ in normal ammonia. Calibration curves were made by plotting this against concentrations of $N^{15}H_3$. Errors due to changes in spectrometer characteristics were thereby minimized, as variations caused the enriched and normal ratios to change proportionately. Ratios of N^{15}/N^{14} and C^{13}/C^{12} in the sample were measured and concentrations read from the calibration curves. The results obtained were quite good, considering the quality of instrumentation that was available. The accuracy of the nitrogen-15 determination was within 3% of its concentration, which varied from 0.38% to 4.5%. For carbon-13, occurring in the range of 1.1% to 10%, the average error was less than 2% of its concentration. A typical analysis required only 0.00015 mol of gas, and most of this could be recovered. Adsorption of ammonia on the cell walls caused problems. The cell was "conditioned" by using pressures as high as 100 mtorr, and measurements were begun only after the pressure became constant. Adsorbed gases were removed by continual heating and pumping.

Another early application of microwaves to quantitative analysis was a determination of concentrations of NH_3 in mixtures of deuterated ammonias by Weber and Laidler.[61] They also studied the kinetics of the catalyzed NH_3-D_2 isotopic exchange reaction. Their spectrometer was unmodulated, and concentrations were determined simply by measuring the output signals with and without a sample in the cell. This method offers very poor sensitivity and is useful only for very strong absorbers such as ammonia. Accuracies for the concentrations of ammonia were reported to be within 0.5%.

More recently, Esbitt and Wilson[62] made a careful study of relative intensity measurements. The investigators used a Stark-spectrometer and gave close attention to several sources of error. Commercial tapered transitions from the cell to the waveguide, tapered ends on the Stark septum, and ferrite isolators were used to minimize reflections of microwave radiation in the cell. The effects of crystal tuning on peak heights were considered. The Stark modulation was carefully zero-based to avoid a systematic error that can be large if the lines measured have a first-order Stark effect. Errors due to nonlinear response of the detection system were circumvented by using a calibrated attenuator to reduce the height of the larger of a pair of lines by a known amount until it approximately equaled the height of the smaller line. "Pickup" of extraneous electrical signals was minimized. Errors in relative intensity ratios of a few percent were obtained. The ratio of the abundance of C^{12} to C^{13} in enriched methyl formate was determined to be 0.635 with a 2.8% standard deviation. These authors also discussed errors which can arise when one is interested in measuring intensity ratios to obtain the relative populations of two vibrational states rather then concentrations.

Dymanus et al.[35] used a very sophisticated Stark cavity spectrometer to obtain both the peak intensity α_0 and the half-width $\Delta\nu$ of the line from a single set of measurements. The spectrometer used a calibrated "antimodulator" in series with a Stark cell to modulate the microwave power in opposite phase to the Stark modulation imposed on the molecules. The calibrated antimodulator was adjusted to just cancel the absorption line. Any errors introduced by uncertainty in the detector characteristics were minimal since it was a null measurement. Measurements on the $J = 1 \rightarrow 2$

rotational transitions of OCS yielded accuracies of approximately 3% for line widths, 4% for integrated intensities, and 2 to 3% for α_0.

The uniqueness of microwave spectroscopy and its utility as an analytical tool are apparent in a series of investigations by Hirota and co-workers[63-65] on the use of microwaves to study catalytic activities of nickel and palladium in the isotopic hydrogen exchange of propene with deuterium oxide. Propene contains three kinds of hydrogen-carbon bonding: CH, CH_2, and CH_3. Infrared spectroscopy and nuclear magnetic resonance methods were found unable to specify the position of the deuterium substitution. Relative intensities of microwave absorption lines were therefore used to obtain the relative amounts of the products of the reaction.

Kim and Gwinn[66] have used the sensitivity of microwave spectra to isotopic substitution to study the rearrangement of methylene groups during the reaction between cyclobutanol and PCl_5. The relative abundance of the chlorine-35 and chlorine-37 isotopes of cyclobutyl chloride obtained from the spectrum were also measured by the authors.

Sakurai et al.[67] combined microwave spectroscopy with gas chromatography and mass spectroscopy to study the hydrogen transfer mechanism involved in isomerization. Relative intensities were used to determine the abundances of various possible species resulting from replacing hydrogen by deuterium during the isomerization of *cis*-2-butene and 1-butene.

Scharpen et al.[46] used an isotopic analysis to test the reliability and accuracy of the Hewlett-Packard Model 8460A spectrometer. Quantitative analyses of mixtures of five subspecies of propene-d_1, differing in the location of the deuterium atom, were performed; these mixtures were obtained as products of the hydrogen-deuterium exchange between CH_3OD and propene-d_0 in the presence of homogeneous catalysts of Pt, Rh, and Ni. Careful attention was given to possible sources of systematic error, including those identified by Esbitt and Wilson.[62] Assuming the power saturation coefficient to be the same for each isotopic species, the investigators corrected for the fact that changes in microwave power were required to maintain the crystal current constant over the series of measurements. Variations in the base-line signal voltage due to "pickup" were measured but were found to be insignificant. A procedure was used to correct for possible changes in sample composition and total pressure that might occur during the experiment due to absorption and desorption of gases at the cell walls. The concentrations of the subspecies ranged from 1.5% to 17% of the total sample. A thorough error analysis gave an error of approximately 2% of the concentrations values.

A comparison by the authors of their results with the work described previously by Hirota and co-workers[63-65] showed the Hewlett-Packard Model 8460A spectrometer to be superior in accuracy and sensitivity to the spectrometer used in the former investigation. Another interesting aspect of the investigation by Scharpen et al. was the use of a computer to control the spectrometer frequency and modulation voltage and to perform digital averaging of the output signals as well as data reduction.

Aleksandrov and Tysovskii[68] constructed a broadband microwave spectrometer using a traveling wave tube as an energy source. Relative intensities were used to determine the concentrations of ethanol and isopropanol in gasoline. This particular problem provides a useful and practical assessment of microwaves as an analytical tool, as analysis of this mixture by other methods, including infrared spectroscopy and chromatography, is difficult. Using a variation of the procedures that we have discussed, the authors added methanol in equal concentrations to the gasoline sample and prepared standard mixtures of ethanol and isopropanol. It was shown that the concentration of a test component, ethanol, for example, is proportional to the ratio of the intensity of an ethanol transition to a transition of the internal standard methanol. The constant of proportionality was obtained from the corresponding ratio in a standard sample. The investigators gave considerable care to experimental procedures, using, e.g., a thermostat to keep the temperature of the Stark cell constant. To eliminate differences between the concentration of a sample in its liquid and gas phases, the liquid was completely converted to the gas state before it was admitted to the cell. Samples were flowed continuously through the cell to minimize selective adsorption onto the cell walls. An average experimental error in concentration of approximately 10% was obtained.

Crable[52] found relative intensity measurements useful in determining small concentrations of impurities in large amounts of air. In these situations, the collision cross section does not change appreciably with small variations in concentration, and the factor ($\Delta\nu/p$) can be considered constant. Second to relative intensity measurements in convenience and accuracy was found to be the use of line areas to determine concentration. Crable was able to obtain accuracies of a few percent using a planimeter. To obtain areas of lines partially overlapped by other lines, Crable measured area only on the side opposite the interfering line and multiplied by 2.

Chemical analysis by microwaves has found an industrial application in the production of toilet soap. Zeman and Zemanova[69] have recently used a continuous microwave analyzer for the determination of moisture content. The moisture content was converted using an empirical relationship into soap fatty acid content. Water concentrations as low as 0.15% were measurable.

B. Saturation Techniques

1. Development of the Method

It must be remembered that all of the previous considerations regarding the α-coefficient assume that the total pressure in the absorption cell is sufficiently high that pressure broadening is the major contribution to the line width. A second condition that must be satisfied if our considerations of the Beer's law coefficient α are to be valid is that the microwave power level must be sufficiently low that saturation effects are negligible. Otherwise, Equation 34 does not give the correct relationship between α_o and the concentration. This second condition points to an intrinsic weakness in the use of the α-coefficient, one that manifests itself when absorption lines are weak. This can be seen by combining Equations 27 and 33 to give

$$\Gamma = \alpha_o P_o^{1/2}, \tag{38}$$

which is valid in the unsaturated region (where $KP_o \ll 1$). Since Γ is proportional to the spectrometer signal, it follows that the signal is proportional to $P_o^{1/2}$. Then low power levels, which are necessary to avoid saturation, result in weak signals and, therefore, low accuracies. This limitation is circumvented by a recently developed approach to quantitative analysis that is entirely different from that based on the α-coefficient. Based on Harrington's intensity coefficient Γ, this approach, as mentioned previously, actually takes advantage of the phenomenon of power saturation.

It was seen in Section II.C that by adjusting the value of power such that the signal assumes its maximum value S, Γ becomes maximum. Then the signal is proportional to the partial pressure of the absorbing gas. That is,

$$\Gamma_{max} \sim S \sim xp. \tag{39}$$

The coefficient Γ differs from α_o in that it is proportional to concentration but is independent of line width. Equation 39 predicts that a plot of S versus xp is a straight line through the origin. Figure 22 confirms this linearity for a pure sample ($x = 1$) of ethylene oxide. The effect of introducing an impurity while holding the partial pressure of ethylene oxide fixed is also illustrated. As predicted by Equation 39, the maximum signal S is seen not to change as the impurity gas is added.

A procedure for obtaining the concentrations that readily suggests itself is to make a calibration curve by using a sample of pure gas to plot S versus p. The maximum signal S is then measured for the same transition in the sample of unknown concentration and the partial pressure read from the calibration curve. The mole-fraction x then follows immediately from a measurement of the total pressure.

If Equation 39 is exactly correct, a calibration curve is not necessary. If the plot of S versus p goes through the origin, then we can obtain the mole-fraction from the analytical expression

$$x = \left(\frac{S_m}{S_p}\right)\left(\frac{p_p}{p_m}\right), \tag{40}$$

where S_m is the maximum signal for a transition in the mixture, S_p is the maximum signal for the same transition in the pure sample, and p_p and p_m are the total pressures of the pure gas and the mixture, respectively. If a spectrometer with a calibration arm is used (see Section III.B) and a null method employed, the maximum signals are read directly in decibels from precision attenuators. In terms of attenuator readings in decibels, then Equation 40 can be rewritten

$$x = \left(\frac{p_p}{p_m}\right) \text{antilog} \left(\frac{D_m - D_p}{20}\right), \tag{41}$$

where D_m and D_p are the decibel readings of the maximum signal intensities S_m and S_p, produced

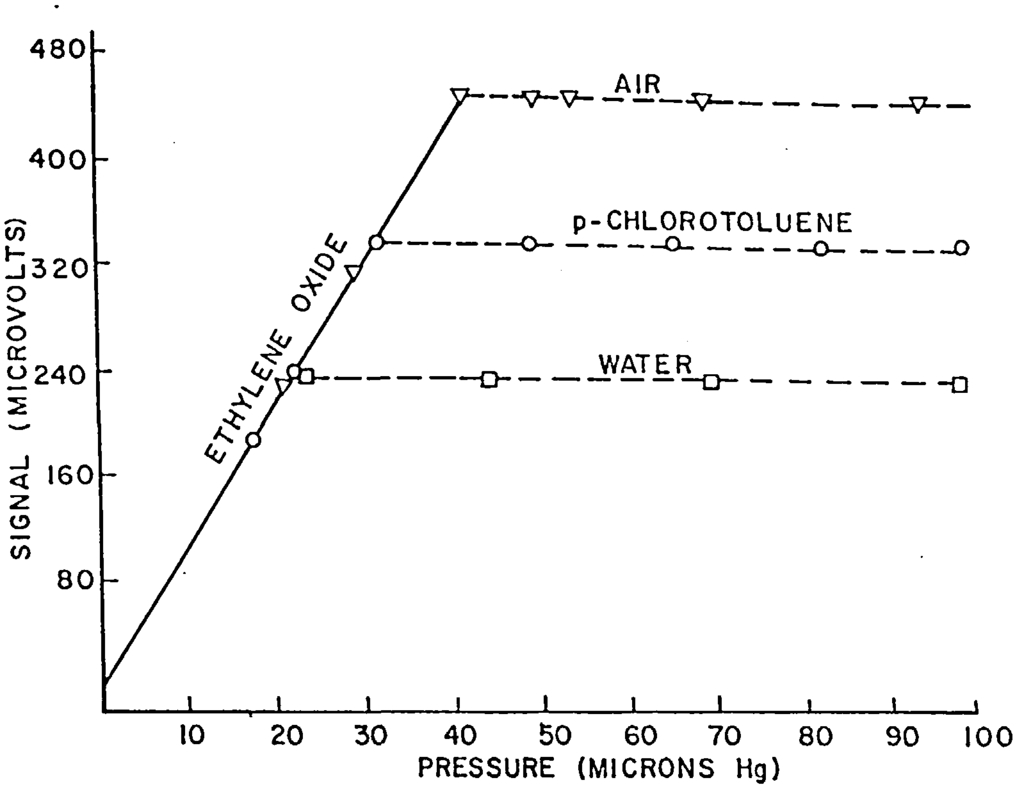

FIGURE 22. The linear dependence of Γ_{max} on the concentration of the absorbing species (ethylene oxide) and its independence of τ. The figure shows the results of three different runs using a different amount of ethylene oxide and a different impurity gas each time. The maximum signal is seen to increase linearly with increased pressure of the pure sample and does not change as an impurity gas is added while keeping the partial pressure of ethylene oxide constant. (From Harrington, H. W., *J. Chem. Phys.*, 46, 3698 (1967). With permission.)

by the calibration arm, that are required to nullify the absorption line.

As an example of the use of Equation 41, consider Table 1. The maximum signals from a pure sample of SO_2 at 22.5 mtorr of pressure and from a sample of SO_2 diluted with air were measured. The values from the table, substituted into Equation 41, give the concentration of SO_2 as 10.7%.

From the above considerations and the preliminary work mentioned which tends to confirm them, the Γ-coefficient appears to offer an accurate and convenient method of analysis. It must be remembered, however, that the validity of the above approach depends on Equation 39, which predicts that a plot of Γ_{max} versus xp is a straight line through the origin. This prediction was tested by Rinehart[70] shortly after the Γ-theory was proposed. Figure 23 is a graph obtained by plotting the maximum signal produced by a transition in methanol against the partial pressure of methanol. Clearly this is not a straight line through the origin, the departure at low pressure being pronounced (see, however, Section V.B.2). The curve is a straight line through the origin for pressures up to 1 mtorr. It becomes a straight line with a steeper slope for pressures above 3.5 mtorr. The break in the curve below 3.5 mtorr has not been completely explained but is probably due to contributions to the line width other than colli-

TABLE 1

Determination of SO_2[a]

Pressure mtorr	Maximum signal db	% SO_2
22.5	89.3	100%
23.0	108.5	10.7%

[a] After Hewlett-Packard Spectroscopy Instrumentation Note 841-1, 1967.

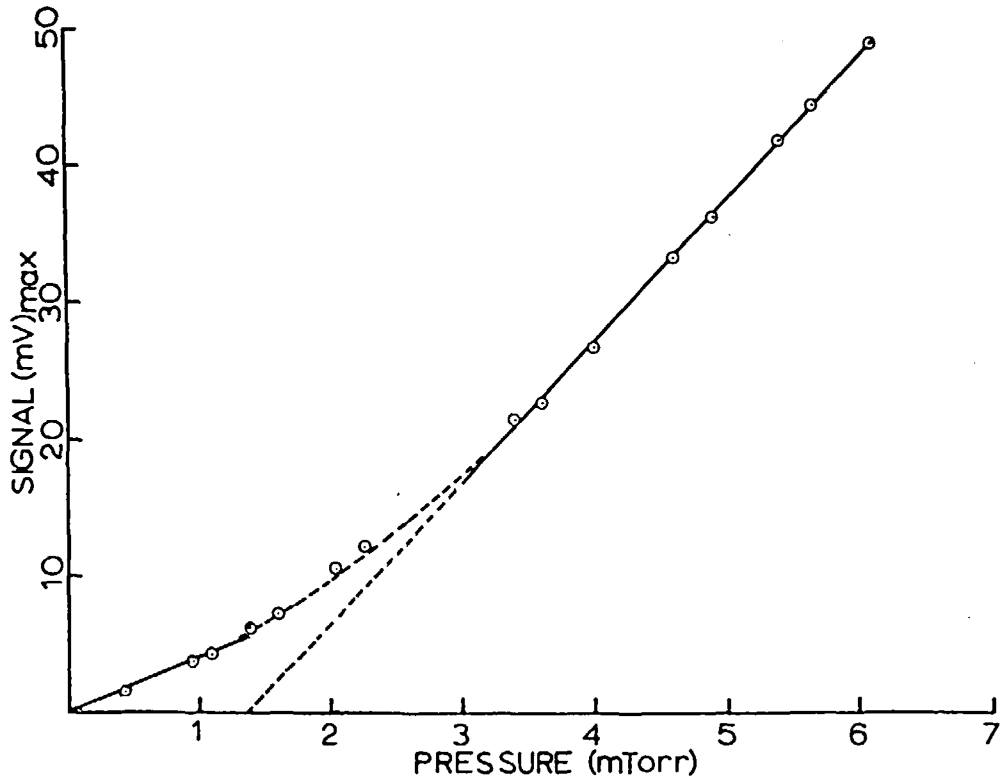

FIGURE 23. The dependence of maximum signal on pressure for a transition of methanol at 37,703.72 MHz. (After Rinehart.[70])

sion-broadening. The portion of the curve above 3.5 mtorr, though linear, does not pass through the origin. This would indicate an inherent deficiency in Equations 39 and 41. The magnitude of this error and its possible dependence on pressure has not been satisfactorily explored. Although the work by Rinehart seems to cast doubt on the validity of Equation 41, the curve in Figure 23 in any event serves as a calibration curve. The necessity for plotting calibration curves implies that methods based on the Γ-coefficient are less convenient than first appearances indicated, but accurate analyses can still be performed. The pressure region below 3 or 4 mtorr should be avoided, however, as the assumed dominance of pressure broadening is not realized here.

Working with an in-line spectrometer (see Section III), Rinehart[70] avoided the effects of changes of crystal current by comparing the absorption signal of a gas with a reference signal produced by the calibration arm. This provided a stable calibration curve that did not depend strongly on the idiosyncracies of a particular spectrometer. For this reason, curves of this type could perhaps be transferred between similar spectrometers. The calibration curve obtained, although it did not pass through the origin, was very nearly a straight line in the pressure region above 3.5 mtorr.

Rinehart[70] obtained his most accurate results by still another procedure, also based on the Γ-coefficient. A relative intensity S_{rel} was again defined as the ratio of the maximum intensity of an observed line to that of a standard reference line produced by the calibration arm. The relative intensity was plotted, not against the partial pressure of the absorber, but against the total pressure of the mixture. Since S_{rel} is proportional to xp, this is equivalent to plotting Rxp versus p, where R is the constant of proportionality relating S_{rel} to xp. A plot of Rxp versus p would yield a straight line with a slope, given by

$$\text{slope} = \frac{Rxp_2 - Rxp_1}{p_2 - p_1}$$

or

$$\text{slope} = Rx.$$

Similarly, a plot of S_{rel} versus p for a reference sample in which the concentration of the absorber is a known value, x_s, has a slope Rx_s. The ratio of the two slopes is therefore $Rx/Rx_s = x/x_s$, and, if $x_s = 1$, the ratio of the slopes gives the unknown mole-fraction x. Results obtained by Rinehart using this method are discussed in the next section.

In the above procedures based on the Γ-coefficient, the microwave power level must be high enough to reach maximum signal. For sample pressures of 50 to 100 mtorr, this may require more power than many microwave sources can provide. For example, backward wave oscillators found in spectrometers typically have maximum power outputs of 10 mW. To achieve saturation, that is, maximum signal, pressures may have to be lowered to 5 or 10 mtorr. This could prove inconvenient in some cases, as signals are smaller and pressure measurements are more difficult at these pressures. By using cells with smaller cross-sectional area, one could obtain saturation more easily. In addition, saturation is usually achieved easily in cavity spectrometers and, in fact, may be difficult to avoid. The Γ-method will probably find particular application in cavity spectrometers.

An investigation by Funkhouser et al.[71] offers hope that the requirement that the signal be maximum is not as stringent as the theory indicates. The study suggests that accurate determinations of concentrations can be made if the source power is such that the signal is merely near maximum. Figure 24 is a plot of output signal versus total sample pressure for various mixtures of acetone in nitrogen. A constant source power of 0.5 mW was used. Above a pressure of approximately 20 mtorr there was not sufficient power to reach maximum signal in the case of the 5.4% and 1.2% mixtures. The graphs show corresponding departures from linearity. Despite this, it appears that the curves can be used as accurate calibration curves. To see that this is so, let the 10.1% mixture momentarily represent a mixture of unknown concentration. Suppose further that the output signal of the acetone transition in the "unknown" is measured to be 400 μV. Using the curve corresponding to the 5.4% mixture as a calibration curve, notice that a 400 μV signal corresponds to a partial pressure of acetone equal to 5.4% x 30 μ = 1.6 μm of Hg. This concentration predicted by the 5.4% curve is consistent with the knowledge that the percentage of acetone in the "unknown" is 10.1% since the curve representing this mixture indicates that a 400-μV signal does indeed correspond to a pressure of approximately 10.1% x 16 μ = 1.6 μ. Therefore, even though the curves were not plotted using maximum signal, they appear to be valid calibration curves. Obviously, more study is needed here, as it is not at all clear just how near maximum the signal must be, nor is it apparent that the above curves will yield accurate concentrations of acetone in more complex mixtures.

It has been pointed out by Harrington[31] that determinations of concentrations by any of the procedures based on the Γ-coefficient offer an added advantage. This theory offers a technique, one that will not be discussed here, for detecting possible systematic errors that can arise due to sample changes during measurements, overlapping absorption lines, or overlapping Stark lobes.

2. *Applications Using the* Γ*-Coefficient*

There has been very little application of the Γ-coefficient to quantitative analysis having as its primary purpose the determination of concentrations. Rather, the work done has been for the purpose of testing the theory and developing the techniques. Consequently, most of the work published on this approach was mentioned in the preceding section. We elaborate here on some of the results obtained.

Rinehart[70] used the method of slopes (described in Section V.B.1) to determine concentrations of methanol in benzene with accuracies of approximately 0.1%. Great care was taken, and a least-squares fit was used to determine the slopes of the curves. The accuracy achieved by Rinehart was certainly sufficient to allow the method to qualify as a useful analytical tool. This is partially offset, however, by the fact that several hours may be required for an analysis if the precision required dictates that the calibration curves have to be plotted with care or a least-squares analysis used to determine the slopes of the straight lines. If low precision is acceptable, one can draw the calibration plot by measuring only a few data points, thereby speeding the process considerably. Similarly, considerable time will be saved in cases where calibration curves, once determined, can be used repeatedly. The use of Equation 41 provides concentrations in a matter of minutes, but one would first have to ascertain that the error inherent in this approach is acceptable.

Funkhouser et al.[71] used a Hewlett-Packard Model R-8400C microwave spectrometer to deter-

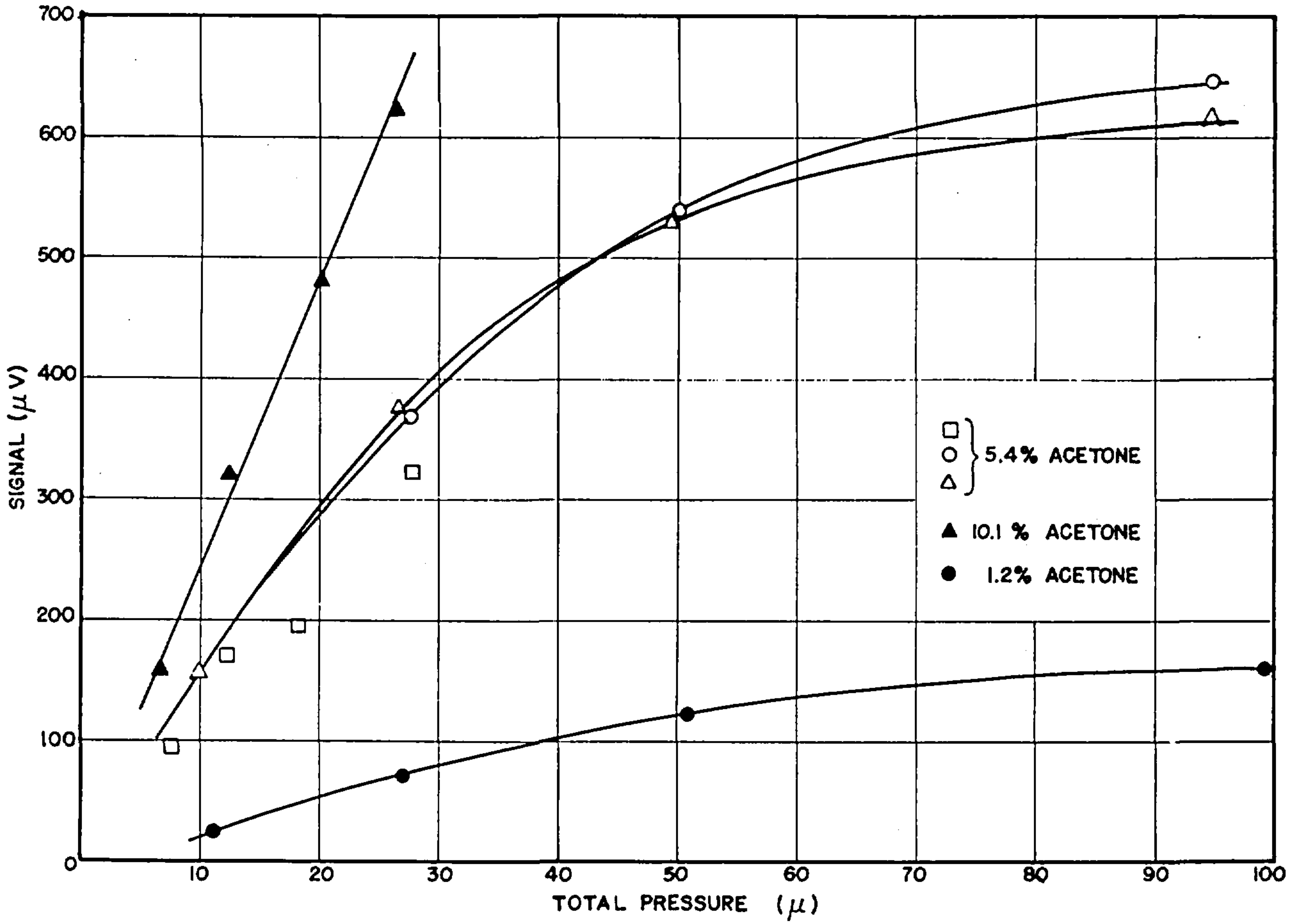

FIGURE 24. Calibration data of acetone. Source power at 0.5 mW. (After Funkhouser et al., *Anal. Chem.*, 40, 22A (1968). With permission.)

mine low concentrations of acetone and freon in nitrogen. Although the accuracy of the method was not investigated thoroughly, measured concentrations of acetone and freon were in good agreement with values obtained by mass spectrometry. It is not clear whether these results were obtained using sufficient source power to obtain maximum signal. Indications were that this restriction is not necessary as long as sufficient power is available to appreciably saturate the line. After the calibration curves had been plotted, the remainder of the measurement procedure required less than 10 min.

In his study of the applicability of microwave spectroscopy to measurements of air pollutants, Crable[52] found the Γ-method inapplicable because of the relatively large amounts of power required to saturate the absorption lines. Only lines that were narrow or that belonged to very strong absorbers were conveniently saturated.

The possibility of a novel application of a microwave spectrometer was reported very recently by Srinivasan,[72] who investigated the applicability of microwaves to a determination of concentration of ammonia in blood serum. A Stark-modulated, cavity, bridge-type spectrometer was used, the modulation being applied between two sections of the cavity that were insulated from each other. The cavity was tuned to 23.870 GHz, the frequency of the 3→3 transition of ammonia. The procedure was based on the saturation method. No difficulty was encountered in saturating the line, partly due to the relatively high power densities normally associated with cavities. A 12% solution of ammonia and water showed maximum signal at less than 0.25 mW of power. A 24% solution gave maximum signal at approximately 0.4 mW. Standard solutions of ammonia in water and methanol were prepared. Concentrations of ammonia in the standards ranged from 24% to 0.1% in water and from 2% to 0.1% in methanol. As predicted by theory, graphs of maximum spectrometer signals versus partial pressure of ammonia for partial pressures of 10 to 70 mtorr were linear. Significantly, the extrapolated lines pass very near the origin. Srinivasan determined ammonia concentrations in MeOH with an accuracy of 10%. The spectrometer was able to achieve a sensitivity of only 100 ppm, which is surprisingly poor considering the strength of the absorber and the advantage in sensitivity inherent in cavities. As Srinivasan pointed out, sensitivity could probably be significantly improved with slight instrumental modifications. For instance, the cavity operated in the TE_{024} mode, whereas it has been shown[39] that a cavity operated in the TE_{0m1} mode is more appropriate for Stark modulation due to increased field uniformity. It is significant that the method performed adequately on this problem, which was known to be a difficult one. Gas chromatography had not proved satisfactory. With instrumental improvements, the spectrograph used would probably reach a sensitivity near 1 ppm, which rivals that of enzymological methods. Remembering the failure of Rinehart's[70] curves to pass through the origin, one finds it interesting that, although Srinivasan's curves run on his cavity spectrometer do appear to pass through the origin, similar measurements by Srinivasan using a wave guide Stark cell produce straight lines that do not go through the origin. Srinivasan attributed this behavior to problems with sample handling.

C. General Considerations

1. *Sample Considerations*

Quantitative analysis by microwave spectroscopy must be preceded by a qualitative analysis unless the constituents of the sample are otherwise known. Furthermore, an absorption line must be known to belong to a particular molecule before it can be used to determine the concentration of the species. The sample considerations related to quantitative analyses are, therefore, identical to those previously discussed in regard to qualitative analysis. For example, the restriction of the use of microwaves to polar molecules as well as the previous considerations of sample size and selectivity apply in quantitative analysis. Quantitative analysis by microwave spectroscopy is nondestructive, as was qualitative analysis.

2. *Sensitivity, Accuracy, and Precision*

The considerations of sensitivity made in Section IV.A apply to quantitative as well as qualitative analysis by microwaves. In principle, more sensitivity is needed for quantitative analysis with microwaves than for qualitative analysis. This is because lines having signal-to-noise ratios of just over 1:1 can be used to identify a gas, whereas signal-to-noise ratios better than this are required for quantitative determinations of reasonable accuracy. The better the signal-to-noise ratio is, the higher, in general, will be the precision with which concentration can be determined.

With any of the procedures described, the weakness of the absorption line can impose the major limitation of the precision of the quantitative analysis. Reliable estimates for precisions obtainable for various signal-to-noise ratios of absorption lines are not yet available, however. Our discussion of precision will be confined to applications found in the literature, and these analyses have been performed on lines that are fairly intense, that is, having signal-to-noise ratios of 20:1 and greater.

The most precise determinations have been made in cases where measurements of neither the peak absorption coefficient α_0 nor the half-width $\Delta\nu$ were required. In the case of samples for which $\Delta\nu/p$ can be assumed to be the same for the standard and the unknown, the ratio of the peak heights provides the concentration. In such measurements, precisions of approximately 1% are possible due to the relative ease and precision associated with peak-height measurements. The method of relative intensities generally requires a measurement of $\Delta\nu/p$, and this usually limits precision to approximately 5%. Under the best of circumstances, involving lines that are not too narrow, measurements of $\Delta\nu$ and concentration can be determined to perhaps 1%.

The most precise absolute measurements of the peak absorption coefficient α_0 made before the appearance of commercial spectrometers are those of Dymanus et al.[35] Precisions of 2 to 3% are quoted for α_0, and half-widths were measured with precisions of 3%. Integrated intensities were obtained with precisions of 4%. It has been estimated that the Hewlett-Packard Model 8460 will provide precisions of approximately 2% in α_0 and 1 to 5% in $\Delta\nu$. Definitive figures have not yet appeared in the literature, however.

The Hewlett-Packard spectrometer was actually designed with the Γ-theory in mind, and, though they are scant, there are some literature reports of quantitative analysis based on this method. No general estimates of accuracy are available for the procedure in which a calibration curve is formed by plotting the maximum signal of the absorbing species versus partial pressure. However, Rinehart,[70] using the slopes of the straight line plots of maximum signal versus total sample pressure, obtained mole-fractions with precisions of 0.1% or better. This figure can perhaps not be quoted as typical, but it is indicative. Naturally the precision obtainable depends on the care used in obtaining the slopes. This can be done, as Rinehart did, with many data points and a least-squares fit, or it can be done quickly and roughly with only two measurements.

No data are available, but measurements of α_{int} by integrating the area under the absorption line using a digital integrator promise precisions comparable to those already discussed.

Attention has been given to the difficulty in measuring $\Delta\nu$ and α_0 as well as to the error in concentration due to lack of precision in these measurements. Since a measurement of total pressure is required to obtain the mole-fraction x from the partial pressure xp, the pressure measurement introduces additional uncertainty in the concentration. Until recently, errors in pressure measurements in the region 1 to 50 mtorr were probably much larger than uncertainties in α_0 and $\Delta\nu$. The MKS Baratron now seems to operate satisfactorily in this region, claiming an accuracy of 0.1% of the gauge readings.

3. *Time Required*

The time required for a quantitative analysis by microwave spectroscopy is probably one of its strong points except in cases requiring maximum precision. One of the most rapid techniques, though not always applicable, is the use of relative intensities assuming $\Delta\nu/p$ to be constant. The time required for an analysis is that required to sweep through two lines plus the time required to change samples in the absorption cell. The total time required can be less than 10 min. The nitrogen-15 analysis by Southern et al.,[60] involving 10 to 15 measurements of relative peak heights, required less than 30 min. The time required to obtain the calibration curves is not included in the above estimate. Use of the Γ-coefficient requires plotting calibration curves, but once this is done, Funkhouser et al.[71] demonstrated that a measurement required less than 10 min. This included time required to admit the sample into the cell, measure the pressure, and scan the line. Since no calibration curve is required, rather only a single scan and a pressure measurement, it would seem that the fastest method might be one in which the area under the absorption curve (that is, α_{int}) is measured electronically by a digital integrator.

4. General Problems and Precautions

It may be useful to summarize certain conditions and problems that must be considered if systematic errors are to be avoided. In methods based on the Γ-coefficient and in relative measurements of α_0, the crystal current must remain constant throughout all measurements. Power saturation must be avoided in methods based on the α-coefficient. Incomplete Stark modulation or line-broadening due to a nonzero voltage on the Stark septum during the "field-off" portion of the modulation cycle can lead to errors no matter which absorption coefficient is considered. Accurate measurements demand that sufficient Stark voltage must be applied to completely separate the Stark components from the main line, though this is not always possible. Use of the same pressure and Stark voltage for the mixture and the standard sample minimizes errors resulting from incomplete modulation. Concentrations must be determined using lines that are not overlapped by neighboring lines (see Esbitt and Wilson[62]). Reflections of microwave radiation in the wave guide must be avoided. Multiple passage of energy through the sample alters the radiation path length and leads to errors. Errors due to reflections were once considered very serious but are of secondary importance in well-designed cells (see Harrington[31]).

Probably the most serious problem in quantitative analysis by microwaves is that of selective adsorption of the sample on the metal walls of the cell. This effect is particularly troublesome in Stark spectrometers because of the additional area offered by the Stark septum and by the material used to insulate the septum from the cell. The problems caused by this effect are much more serious for some mixtures than others due to the greater tendency for some molecules to adhere to exposed surfaces. Although the problem cannot be avoided in Stark spectrometers, it can be minimized by "conditioning" the cell as discussed before. For quantitative analysis this technique will hopefully lead to a state where the concentration is observed not to vary in time. One must be very careful that the effects of selective adsorption do not overshadow all considerations of precision discussed previously.

VI. SUMMARY

Interest in microwave spectroscopy as a tool for chemical analysis has begun to grow only recently, despite the fact that its potential was recognized over 20 years ago. Until the appearance of commercial spectrometers, the advantages of microwaves were outweighed by formidable instrumental considerations. The only existing spectrometers were research instruments built by microwave spectroscopists. Reliability was poor, and operation was made inconvenient by the necessity for numerous manual adjustments. Reliable, sensitive, broadbanded, commercial spectrometers have removed the major obstacle to the development of microwave spectroscopy as a viable analytical technique.

Some of the limitations of this technique are inherent, however, and must be recognized when its applicability is being considered. Microwaves will be of no use, for example, in determinations of nonpolar molecules. Solids and liquids with very low vapor pressures are not susceptible to this technique. Large molecules capable of complex internal motions are best handled by some other method. Microwave spectroscopy, then, is not expected to become a tool to replace all other analytical tools. It does, however, have unique characteristics that make it a very powerful technique for analysis of relatively light molecules with appreciable dipole moments and vapor pressures. Microwave spectroscopy is very sensitive when used on strong absorbers, for which it provides limits of detection below 1 ppm. Its unique resolution makes possible rapid, simple, and definitive identifications. It is capable of quantitative analyses with accuracies less than 1% for cases in which measurements of half-widths are not required; generally, accuracies of a few percent are typical. Measurements are nondestructive and require little time and little sample.

Considerable progress has been made in the development of microwave spectroscopy as an analytical instrument. Several different procedures promise to be effective. More pioneering work is needed, however, to make practical comparisons of the techniques based on the α- and Γ-coefficients and to answer questions regarding each one. For instance, it is not yet clear which is the most inconvenient, the necessity associated with α of working at low powers or the necessity associated with Γ of working at maximum signal. One can guess that there is no general answer but that various conditions associated with a particular situation will dictate an answer. However, guidelines based on experience would be useful. It is not certain that the Γ-procedures do, in fact, require maximum signal. It is possible that commercial spectrometers, designed with the capability of analysis using the Γ-coefficient, have made measurements of α_0 and $\Delta\nu$ sufficiently convenient that procedures based on α will prevail. Furthermore, electronically measured line areas may spotlight analysis using the integrated line intensity. These are only some of the indications that more study must come before standard and routine procedures can emerge.

Microwave spectroscopists have clearly demonstrated the feasibility of microwaves in analytical chemistry. Nevertheless, microwave spectroscopy has not yet gained the widespread acceptance of analytical chemists. There is little doubt that this will come in time. The National Bureau of Standards is compiling a catalog of spectral lines, and the usefulness of microwaves in qualitative analysis will grow as this catalog grows. Rather than waiting for spectroscopists to routinize the techniques, analytical chemists can speed development by stepping in, despite the initial high cost of equipment and lack of familiarity with the technique, and putting the proposed procedures to practical tests. At this stage, the most productive use of the microwave spectroscopy as an analytical tool is undoubtedly in isotopic analysis and in determining or monitoring a specific molecule, rather than in the analysis of very general analytical problems of complex mixtures. Perhaps full use of microwave spectroscopy is waiting for automatic analysis by computer-controlled spectrometers. This appears to be coming.

ACKNOWLEDGMENTS

The authors wish to thank Dr. L. H. Scharpen of Hewlett-Packard for kindly providing us with spectra taken on the H.P. 8460A spectrometer. We would also like to thank T. K. Avirah for help in obtaining some of the illustrative spectra we have used.

In addition, we would like to thank Dr. T. B. Malloy, Jr. and J. A. Wells for providing us with their spectra prior to publication.

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