MICROWAVE SENSING TECHNIQUE FOR GAS MOLECULES

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ABSTRACT

A new sensor for gases is presented. The device is a microwave spectrometer. Frequency modulated signal,which is proportional to the microwave cavity resonance profile,is displayed on the oscilloscope. At the same time, this signal is compared with the accurate informations of different gases,measured at the same operating conditions. These informations are charged in a computer interfaced with the oscilloscope. This technique is able to identify the gases of types:linear,diatomic,symmetric, and asymmetric polar and non polar molecules. Experimental and calculated results are illustrated. Accuracy and sensitivity of the system are discussed.

INTRODUCTION

In the course of the last five decades,very considerable progress has been made in the investigation of molecular spectra[1-2]. The knowledge of the various properties of the individual molecules,so obtained,allows us to understand and predict physical and chemical properties of gases under consideration. Microwave spectra is one of the main branches of molecular spectroscopy. It is,mainly,concerned with the rotational energy change(in the microwave band)during the absorption of electromagnetic radiation. Molecular spectra have previously been well described from point of view of infrared spectroscopy,but the different frequency range,higher resolution and greater accuracy of microwave spectroscopy make available for study rather different types of phenomena such as hyperfine structure,pressure broadening and Stark and Zeman effects. A big number of molecular absorption spectra of gases in the microwave region above 0.2 mm have been studied[3] .

The purpose of this paper is to present a technique able to study and identify a completely unknown gas specimen. Such identification is based on accurate comparison between the displayed signal(due to the cavity resonance profil caused by the unknown gas specimen)and referenc information for many gases measured at the same operating conditions. Comparison is done using computer type Appel II(with analog to digital interface). It may be useful to search over a wide range of frequencies in order to examine a large variety of gases. The comparison method has been tested by Southern,Morgan,[4] . They only compared the maximum of the signal produced in a spectrometer by

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an absorption line. High resolution is required to identify the lines of a large number of substances in one gaseous mixture and completely unknown gas. Small amount of a gas, for such spectrometer is required to detect absorption. Hence, identification of mixtures of gases for which microwave spectra are known is, in fact, very simple once a sensitive microwave spectrometer is available. More commonly stronger microwave lines of molecules have absorption coefficient near 10^{-5} or 10^{-6} cm^{-1}, so that such a spectrometers could detect a bundances as low as about 10^{-4} or 10^{-3} cm^{-1}. A table of known microwave lines of gases has been prepared[5]and only about 10 cases among more than 1800 lines, listed where two lines of different substances, are closer than 0.25 Mc/s, which is approximately the resolving power of an ordinary spectrometer. The identifications carried out are, for linear, diatomic, asymmetric and symmetric polar and non polar molecules. Frequency of operation is 23,870.11 Mc/s.

EXPERIMENTAL PROTOCOL:

In microwave spectroscopy there are many lines which give very weak absorption even with a cell length of several meters. Changes in power, due to gas absorption of 1 part in a million or less, would have to be observed on the oscilloscope. Therefore the frequency of the microwave signal from the klystron, used here, is square-wave modulated at 31 KHz, and is slowly swept over the cavity resonance by applying a sawtooth sweep voltage from the time base of the oscilloscope(H/P 1715 A), as shown in the experimental block diagram (fig.1). Klystron is protected against vibration and temperature variations using stable air current flow.

To reduce the effect of reflections and standing waves, attenuator is introduced between the klystron and the absorption cell. The cell is evacuated for several days before admitting another vapour into it, and the gas is introduced at the required pressure. A precision pressure gauge(TI type 145)calibrated to a standardize Mc lead gauge, was used for pressure measurements. The range of pressure was determined by the vapour pressure of the sample at room temperature. The cavity was made of polycrystalline copper, was silver plated, and was operated in the TM$_{010}$mode. The cavity temperature was stable to within 1^{0}C.

The radiation transmitted through the cell is detected by means of silicon crystal. The research is carried out at low power level to avoid saturation of the spectral lines. The used modulation frequency signal amplifier has a sufficient gain and sufficiently low noise that the crystal noise is the only limiting factor in the spectrograph sensitivity.

The amplified output of the crystal is displayed on the cathoderay oscilloscope and it is also fed to the Apple II interface which is the ADALAB carte, to begin signal processing. So the actual line shape is rapidly displayed on the screen, where the horizontal scale of the cathoderay tube(X as shown in fig.2)is a frequency scale and the vertical scale gives a measure of the intensity of absorption. If no absorption occurs, a horizontal line would be obtained on the screen, but when absorption takes place, a peak occurs for each absorbed frequency. The peak is fed through carte ADALAB to the calculator to make accurate evaluation of both the maxima of absorption and the area under the displayed

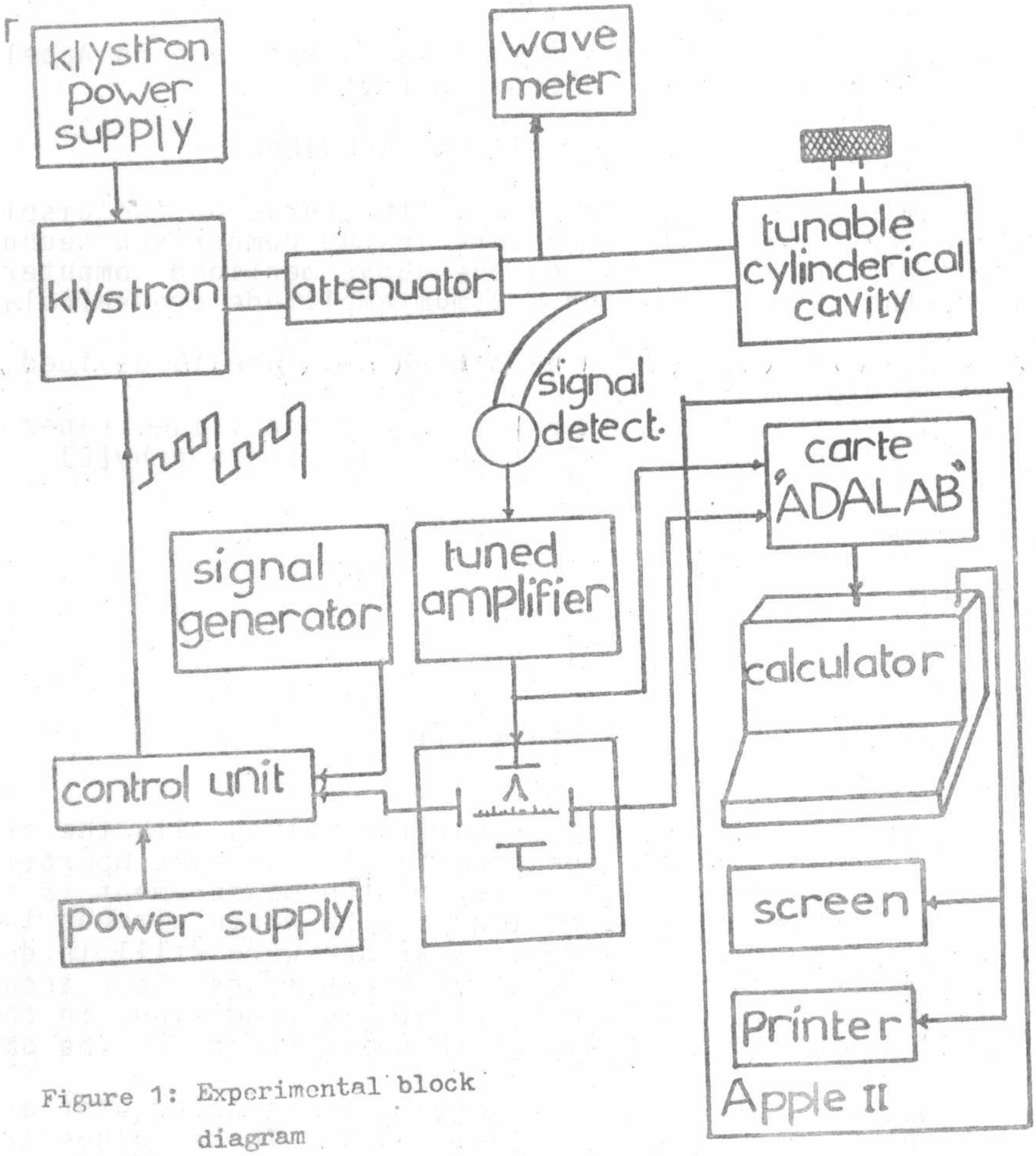

Figure 1: Experimental block diagram

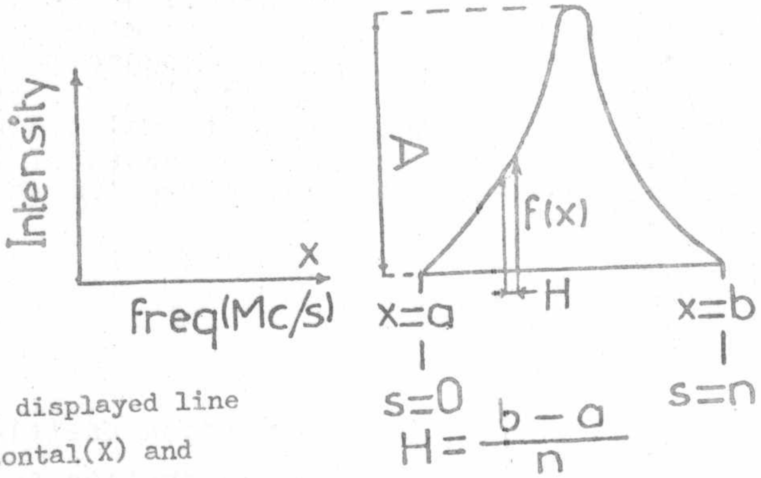

Figure 2: Actual displayed line shape with horizontal(X) and vertical(amplitude) scales.

curve,with accuracy of 2 o/o. Also results are seen on Appel Π screen and obtained at the printer output.

ANALYSIS OF THE COMPARISON TECHNIQUE

Maximum amplitude and area under the curve of the displayed signal are very important parameters in the comparison technique. processing of the signal is done the above mentioed computer type. Area under the curve(fig.2)and maximum amplitude are calculated as follows:

1- The horizontal scale(X)of the cathod ray tube is devided into n element of width H=(b-a)/n

2- To calculate the area whatever its form and value,trapezoidal method is used,and the value,Z,of the area is given by[6] :

$$Z = \int_a^b f(x)\,dx = \sum_{s=0}^{n-1} \int_{a+sH}^{a+H(s+1)} f(x)\,dx = \sum_{s=0}^{n-1} \left(H/2\ f(a+sH) + 1/2\ f(a+H(s+1))\right) \qquad (1)$$

3- The program also compares the calculated values with the standard ones,measured by the same spectrometer at the same operating conditions. The purpose of automation of the measurement is to achieve accuracy that gives indication on line width without interference with other lines. If identifications were still in doubt comparison can be made to the level of Stark lines. Good accuracy depends,mainly,on having stable reproducible conditions in the spectrometer and an adequate signal to noise ratio for the observed line.

The reference standard values,charged in the calculator,are used for identification of the unknown gases. These values are, previously,determined experimentally. To possess high accuracy of these values,updated and modified calculations must be carried out . Polar gases.in microwave band,usually give sharp absorption lines whose widths are narrow(Kc/s to Mc/s). A molecule interacts appreciably with a microwave electromagnetic field to emmit or absorb radiation only if it has an electric or magnetic dipole moment, μ. All the relations used to calculate the intensity of a narrow microwave absorption line of gases of linear,diatomic, symmetric and asymmetric molecules are derived [7]from the well known following relation(2):

$$\gamma_{max} = \frac{8\Pi^2 NF\,|\mu_{ij}|^2 V_o^2}{3CKT\Delta V} \qquad (2)$$

Where: γ_{max} is the maximum absorption coefficient(cm^{-1}),N=number of molecules per C.C in the absorption cell,F=the fraction of these molecules in the lower of the two states involved in the transition, $|\mu_{ij}|^2$=square of the dipole moment matrix element for the transition,summed over three perpendicular directions in space, V=frequency, V_o =resonant frequency of the absorbed line, ΔV is the half width of the line at half maximum, or line breadth parameter, C=velocity of light, K=boltzman constant and T =absolute temperature. Peak absorption of these types of molecules occurs at $V=V_o$.

Usually, for mixtures of more than two gases, the various values of line width parameter $\Delta V_{ij}/P$ will not be known and comparison technique must be adopted. P=pressure and ΔV_{ij} is the half width of the absorption line of molecule i if it were in an almost pure sample of molecule j. Pressure broadening of width of non resonant absorption spectra described by G.Johri [8] is involved in the calculations.

A non polar gases, ordinarily, do not absorb microwaves. However, if the gas molecules are sufficiently polorizable, some dipole moment may excists during collision[9]. At high pressure, the molecules are in collision for a large part of time, so that an appreciable absorption occurs.

RESULTS AND DISCUSSIONS

The molecules which are chosen for manipulation and evaluation of the presented technique are; sulfor oxide, methyl chloride monofloromethane, aniline, acetamide, benzonitrate, methyl amine, deutrium iodide, acetic acid, benzaldhyde, chloral, hydrogen iodide, methylbutrate, water, toluene, pyridine, propionaldhyde, as polar molecules. Hydrogen, oxygen, carbon sulfide, air, benzene, ethylene, acetylene, acetal, acenaphthene, were chosen as non polar molecules. Working temperature is 300^{ok}.

The range of experimental pressures were determined from the vapour pressure of each molecule at room temperature. Thus each range of pressure varied from molecule to another. Measuring the maximum absorption coefficient(related to the area under the curve)of the processed gas carried and consequently auto comparision is done in order to identify the processed gas. For polar gases, the calculated values of the maximum absorption, γ_{max}, are taken as an ideal measured refererence values. Both measured and reference are presented in table -1. Molecular parameters used in calculations are given indetails in references [10-13]. The difference between the measured and reference values of γ_{max} are quite accurate.

For non polar molecules, the reference values of γ_{max} are previously determined with the same manipolation and experimental conditions. Comparison of refrence and measured values of γ_{max} are listed in table-2.

It is noted from both tables 1 and 2 that, the maximum absorption is different from gas to another. The overall accuracy is not greater than 2 o/o and it depends, mainly on:
(1) Accuracy of the refrence maximum absorption coefficient.
(2) Stability of the reproducible practical conditions, for the same Spectrometer and an adequate signal to noise ratio for the identified gas lines.

It is concluded that the comparison of maximum absorption is a simple and accurate technique to identify gases specialy for quantitative operation. Calculations of area under the curve, corresponding to maximum absorption) increase the accuracy of measuring γ_{max} and then accurate identification is obtained.

Table-1 : Measured and Refrence Values of Maximum Absorption for the Identified Polar Gases.

Measured value of maximum absorption $(cm^{-1}) \times 10^{-5}$	Identified gas	Symbol	Refrence value of maximum absorption $(cm^{-1}) \times 10^{-5}$
15.316	sulfor oxide	SO_2	15.150
14.920	methyl chloride	CH_3Cl	15.106
14.134	monofloromethane	CH_3F	14.327
13.174	aniline	$C_6H_5NH_2$	13.333
13.531	acetamide	CH_3CONH_2	13.736
15.345	benzonitrate	C_6H_5CN	15.060
14.659	methylamine	CH_5N	14.881
15.479	deutrium iodide	DI	15.291
14.796	acetic acid	CH_3COOH	15.015
13.058	benzaldehyde	C_6H_5CHO	13.228
13.865	chloral	C_2HCl_3O	13.699
11.897	hydrogen iodide	HI	12.077
14.417	methylbenzoate	$C_6H_5CO_2CH_3$	14.577
14.616	methylbutrate	$C_3H_7COC_2H_3$	14.793
11.891	water	H_2O	12.048
14.487	toluene	C_7H_8	14.663
13.939	pyridine	C_5H_5N	13.774
13.182	propionaldehyde	CH_3CH_2CHO	13.369

Table-2 : Measured and Refrence Values of Maximum Absorption for the Identified Nonpolar Gases

Measured value of maximum absorption $(cm^{-1}) \times 10^{-5}$	Identified gas	Symbol	Refrence value of maximum absorption $(cm^{-1}) \times 10^{-5}$
11.774	Hydrogen	H_2	11.990
12.036	Oxygen	O_2	11.905
14.748	Carbon sulfide	CS_2	14.970
17.713	Air	N_2(78%) + O_2(22%)	18.051
14.559	Benzene	C_6H_6	14.749
14.652	Ethylene	C_2H_4	14.837
15.044	Acetylene	C_2H_2	14.925
14.496	Acetal	$C_6H_{14}O_2$	14.706
14.625	Acenaphthene	$C_{12}H_{10}$	14.368

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