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ON THE THEORY OF MICROWAVE SPECTROMETERS

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A general classification of microwave spectrometers is presented and intrinsic sensitivity limitations of each type are discussed. Thus optimum attainable parameters and methods of their realization are determined for microwave spectrometers.

The intense recent development of microwave spectroscopy methods [1-4] has stimulated a more careful examination of the theory of microwave spectrometers. Review of the results obtained makes possible a general classification of microwave spectrometers, determination of intrinsic sensitivity limits in each type, and definition of optimum attainable parameters and methods for their realization. This is the purpose of the present study.

1. Microwave Spectrometer Structure

The microwave spectrometer is designed for recording of the interaction between frequency-scanned coherent microwave radiation and a specimen of gas, which in the overwhelming majority of cases is in a state of thermodynamic equilibrium. When this interaction occurs the characteristics of both the gas and the radiation change; these changes, applied to the appropriate input channel of the recording device, represent the desired spectrometer output signal. The recording device also inputs information on the radiation frequency, producing a picture of the interaction spectrum. A block diagram of such a spectrometer is depicted in Fig. 1. It is natural to assume that the coherent radiation source characteristics may be chosen, at least in principle, such that optimum spectrometer parameters will be realized. On the other hand, the object of study cannot be varied significantly, and for the future we will assume that it consists of a gas of n molecules* in a state of thermodynamic equilibrium. For the microwave region the most characteristic cases are those in which

$$n_1 - n_2 \ll n_1, n_2 \ll n, \quad (1)$$

where n_1 and n_2 are the respective numbers of molecules in the lower and upper molecular energy states, between which transitions occur under the influence of radiation.

2. Classification of Microwave Spectrometers

Following [5], all microwave spectrometers may be divided into two classes depending on the method employed for separating the desired output signal from the gas lines: in instruments of the first type the

*By doing this we exclude from the present consideration, for example, the double resonance method, etc.

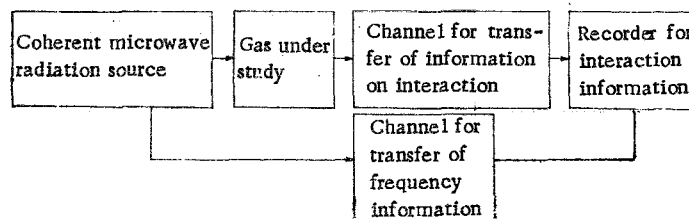


Fig. 1. Block diagram of microwave spectrometer.

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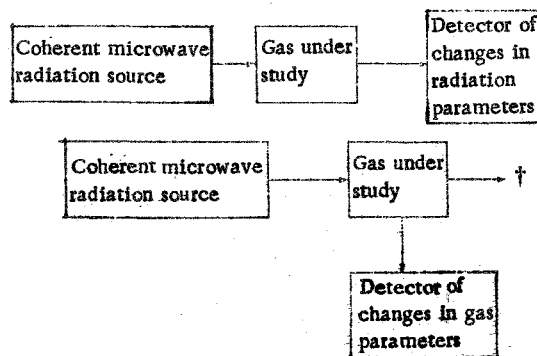


Fig. 2. Spectrometer classification.

desired signal is detected as a change in the parameters of the radiation which has passed through the specimen, while in instruments of the second class the signal is the change in parameters of the specimen itself under the action of the radiation. This situation is depicted in Fig. 2. This classification is in fact quite a profound one. As will be shown below, the advantages and shortcomings of the two basic problems which must be solved to achieve maximum sensitivity in one class of spectrometer are practically absent in the other.

3. Sensitivity Limits of Microwave Spectrometers

The condition for detection of the desired signal at a specified signal/noise ratio (S/N) may be written in the form

$$P_s/P_n \sim S/N, \quad (2)$$

where P_s is the desired signal power at the recorder input and P_n is the noise power within the recorder band width. Depending upon which field or specimen parameter is used as the signal, the concrete expressions of Eq. (2) will vary. Despite such variation, the signal power can still be characterized as the radiation power which is absorbed by the gas, and a general treatment can be conducted from this viewpoint.

To achieve maximum limiting sensitivity in a microwave spectrometer, as follows from analysis of its structure and from Eq. (2), the following requirements must be satisfied:

- (A) the power absorbed by the gas must be the maximum possible at a specified resolution, and must be maximally transformed into useful signal (the maximum signal condition);
- (B) increase in signal power upon increase in radiation power should not be accompanied by increase in noise power (signal/noise independence condition);
- (C) noise power must be determined by transmission channel noise, which should have the minimum quantity of operational degrees of freedom* (minimum noise condition).

In spectrometers of the first type there are difficulties in satisfying the first two requirements. In fact, to ensure a maximum signal, it is necessary that the radiation field power be close to the power needed for saturation of the spectral line. Not difficult in principle, yet still important, is the fact that when this requirement is fulfilled overloading of the uhf receiver may occur. The main problem is that the signal, a small change in radiation power, is observed against a high background level. As a result, when radiant power is increased, not only the signal, but also the noise level will be increased [6]. Satisfaction of the third requirement presents no difficulties, since the transmission channel is electromagnetic and may be made responsive to a single mode.

In the spectrometers of the second class the situation is reversed. In principle the background signal is absent, and the first two requirements are easily satisfied. All difficulties are connected solely with the third requirement. In fact, the energy absorbed by the gas is initially distributed over $n_1 - n_2$ molecules. Collision relaxation can only lead to redistribution of the energy over n molecules. Since both these numbers are quite large in comparison to unity, it is difficult to realize a channel for transmission of the information on interaction with a small number of degrees of freedom.

*Transmission channel temperature is usually determined by the temperature of the gas specimen, and microwave spectroscopy usually works with polar gases which do not permit deep cooling.

†As in Russian Original - Publisher.

Upon fulfillment of all three requirements the condition for detectability of the desired signal transforms to

$$(P_{\text{abs}})_{P_0 \sim P_{\text{sat}}} \sim \frac{S}{N} kT \Delta f. \quad (3)$$

Here P_{abs} is the power absorbed by the gas at a radiated electromagnetic power of P_0 ; P_{sat} is the saturation power of the observed spectral line; and Δf is the recording instrument bandwidth. We must stress that Eq. (3) describes the limiting sensitivity of microwave spectrometers, independent of their class. A consideration of concrete spectrometer types and a correlation of their sensitivity to the limiting value will be offered below.

4. Microwave Spectrometer Resolving Power

The resolving power of a microwave spectrometer is determined by the width of the spectral lines. Decrease in pressure in the gas cell can narrow the line to the point that Doppler broadening is the deciding factor. Further increase in resolution is achieved by obtaining a narrow sub-Doppler structure. It is interesting that the number of corresponding methods for resolution improvement is greater for spectrometers of the second class. This is true because methods used for the first class are also applicable for the second, while only in spectrometers of the second type is selection by velocity of excited molecules in the information transmission channel possible [2]. We note that the resolving power for a specified modulus of the transition matrix element directly determines the maximum radiation power which can be employed in the spectrometer.

5. Basic Equation of the Microwave Spectrometer

For comparison of concrete spectrometer types it is necessary to have some formal criterion. For this purpose we introduce the concept of the basic equation of the microwave spectrometer.

As is well known, the basic parameters of a gas, defining its interaction with radiation, are the population difference between the resonant levels $n_1 - n_2$, the modulus of the transition matrix element between these levels $|\mu_{12}|$, and the homogeneous half width of the observed spectral line $\Delta\nu$. The first two parameters characterize the intensity of the interaction; the last characterizes the time of the interaction. The relationship between these parameters following from the condition for signal observation with a specified signal/noise ratio, Eq. (2), we will term the basic equation of the microwave spectrometer. The meaning of this basic equation is the following: whatever characteristic might be used in one or the other concrete situation for determination of spectrometer sensitivity, the lower limit of the latter is defined only by the requirement of fulfillment of the basic equation.*

We will illustrate the above with an example of an "ideal" microwave spectrometer, the basic equation of which is written in the form of Eq. (3). Considering that

$$(P_{\text{abs}})_{P_0 \sim P_{\text{sat}}} \sim (n_1 - n_2) h \nu \Delta \nu, \quad (4)$$

we obtain

$$(n_1 - n_2) \Delta \nu \sim \frac{S}{N} \frac{kT}{h \nu} \Delta f. \quad (5)$$

First of all, we note that in the basic equation obtained the modulus of the transition matrix element does not appear, i.e., the signal detection criterion is indifferent to this parameter. This result, paradoxical at first glance, is related to the fact that the power used in the spectrometer

$$P_0 \sim P_{\text{sat}} \sim \frac{3}{8\pi} \frac{ch^2 (\Delta \nu)^2 a s}{|\mu_{12}|^2} \quad (6)$$

tends to infinity as $|\mu_{12}| \rightarrow 0$ while the absorbed power remains constant. Here a is the cell section and $s = \sum_M 1$ is the degree of degeneration of the transition with respect to orientation of molecular momentum relative to a fixed coordinate system. It should be understood that the radiation power P_0 available to the experimenter is finite. In the more frequent case where the homogeneous half width of the spectral line is determined by

*It should be noted that minimum detectable values of various concrete characteristics (for example, absorption coefficient) under conditions of spectral line saturation begin to be expressed in terms of the same parameters which enter into the definition of these concrete characteristics. This then produced implicit equations, the analysis of which is difficult.

collisions of molecules with each other, condition (6) at a specified power P_0 fixes an optimum value $\Delta\nu_{\text{opt}}$. In fact, for $\Delta\nu < \Delta\nu_{\text{opt}}$ the signal falls off as n^2 , while for $\Delta\nu > \Delta\nu_{\text{opt}}$ the signal value tends to saturate, and with no increase in signal strength we lose resolving power. With consideration of this fact, and transforming to the relative population difference $\delta_{12} = (n_1 - n_2)/n$ which will be more convenient for further treatment, basic Eq. (5) may be rewritten in the form

$$\delta_{12} | \mu_{12} | \sim \frac{S}{N} \frac{kT \Delta f}{n \nu} \left(\frac{3}{8\pi} \frac{cas}{P_0} \right)^{1/2}. \quad (7)$$

We stress that in Eq. (7) the density of molecules in the gas cell is determined by the power employed in the spectrometer according to Eq. (6).

6. Concrete Spectrometer Types of the First Class

We will consider a spectrometer of the first class, with a signal from the line in the form of a change in radiant power due to interaction with the gas, using a uhf square-law detector as a receiver. A practical example of this class is the Stark spectrometer [6].

For a square-law detector

$$i = \alpha P_{\text{in}}, \quad (8)$$

where i is the detector current and P_{in} is the power at the detector input. As is well known,

$$P_{\text{in}} = P_0 + 2(P_0 P_n)^{1/2} + P_n. \quad (9)$$

It is simple to demonstrate that for any specified P_0 it is desirable to operate with a molecular concentration on the threshold of saturation. As a result, since the signal is the change in radiant power,

$$i_{\text{sig}} = \alpha \Delta P_0 = \alpha P_{\text{abs}} \sim \alpha (n_1 - n_2) h \nu \Delta \nu. \quad (10)$$

The transmission channel can be made to have a single mode response and

$$i_n = 2\alpha (P_{\text{sat}} kT \Delta f)^{1/2}. \quad (11)$$

Consequently, the basic equation is written in the form

$$\delta_{12} | \mu_{12} | \sim \frac{S}{N} \frac{1}{n \nu} \left(\frac{3}{2\pi} kT \Delta f cas \right)^{1/2}. \quad (12)$$

Because the spectrometer under consideration does not in principle fulfill condition B, its limiting characteristic is significantly poorer than that of an ideal spectrometer. In fact, from Eqs. (7) and (12) we obtain

$$\frac{(\delta_{12} | \mu_{12} |)_{\text{start}}}{(\delta_{12} | \mu_{12} |)_{\text{id}}} \sim 2 \left(\frac{P_0}{kT \Delta f} \right)^{1/2} \gg 1. \quad (13)$$

The situation does not change if the square-law detector is replaced by a superheterodyne receiver or uhf radiation balance is employed [7].* In general, at present it is not clear how the complications associated with fulfillment of condition (B) in spectrometers of the first class may be avoided. It is this fact that places the most severe limitation on increasing sensitivity of such spectrometers.

7. Concrete Spectrometer Types of the Second Class

We will first consider a spectrometer of the second class, with signal from the line in the form of a change in gas thermodynamic parameters due to interaction with the radiation. A practical example of such a spectrometer is, in particular, a spectrometer with an acoustic detector (RAD) [1, 3].

Through absorption of radiant power the gas changes its energy with a modulation frequency f_m , with maximum oscillation amplitude of

$$\Delta E_s \sim P_{\text{abs}} \frac{\Delta f^{\text{cell}}}{f_m^2 + (\Delta f^{\text{cell}})^2} \frac{1}{2\pi}, \quad (14)$$

where Δf^{cell} is the band of frequencies related to the thermal relaxation time of the gas in the cell. The condition for detectability of this effect against the background of fluctuations in gas energy, and, consequently,

*In the future we will arbitrarily refer to the first class spectrometer in general as a Stark spectrometer.

the effect of change in any thermodynamic parameter, may be expressed as

$$\Delta E_s \sim (\bar{E}_f^2 \Delta f)^{1/2}. \quad (15)$$

Here \bar{E}_f^2 is the spectral density of gas energy fluctuation power in the signal bandwidth Δf . Considering that

$$\bar{E}_f^2 \Delta f^{\text{cell}} \sim (kT)^2 n, \quad (16)$$

and optimizing the detection condition written in the form of Eq. (2) for the parameter Δf^{cell} at a given modulation frequency,* we obtain

$$P_{\text{abs}} \sim \frac{S}{N} 2\pi kT (N \Delta f^{\text{cell}} \Delta f)^{1/2}. \quad (17)$$

As usual, assuming that we operate at a specified power P_0 with a molecular concentration on the threshold of saturation,† we obtain the basic equation of the spectrometer in the form

$$\delta_{12} | \mu_{12} | \sim \frac{S}{N} \frac{kT}{v} \left(\frac{3\pi}{2} \frac{\cos \Delta f^{\text{cell}} \Delta f}{nP_0} \right)^{1/2}. \quad (18)$$

This result could easily be foreseen, since the spectrometer under consideration differs from an ideal one only in the large number of operating degrees of freedom of the transmission channel. The transmission channel here is the gas, and the number of degrees of freedom is proportional to n . From Eqs. (7), (12), (18) we obtain

$$\frac{(\delta_{12} | \mu_{12} |)_{\text{RAD}}}{(\delta_{12} | \mu_{12} |)_{\text{id}}} \sim 2\pi \left(n \frac{\Delta f^{\text{cell}}}{\Delta f} \right)^{1/2} \gg 1; \quad (19)$$

$$\frac{(\delta_{12} | \mu_{12} |)_{\text{Stark}}}{(\delta_{12} | \mu_{12} |)_{\text{RAD}}} \sim \left(\frac{P_0}{P_{\text{cr}}} \right)^{1/2} \frac{n_{\text{RAD}}}{n_{\text{Stark}}}, \quad (20)$$

i.e., excluding technical details and assuming $n_{\text{RAD}} \sim n_{\text{Stark}}$, we find that the RAD is superior to the Stark spectrometer in sensitivity at power levels in excess of a certain critical value, while

$$P_{\text{cr}} \sim \pi^2 n_{\text{RAD}} kT \Delta f^{\text{cell}} \quad (21)$$

is independent of the frequency range.‡

Although we have considered only the least desirable variant of the second class spectrometer (number of degrees of freedom of transmission channel determined by total number of molecules in the gas cell), nevertheless under certain conditions its sensitivity can be better than any spectrometer of the first class. We will now consider the prospects for further increase in sensitivity, i.e., the prospects of decreasing the number of operating degrees of freedom of the transmission channel.

Within the gas cell, $n_1 - n_2$ molecules interact with the radiation and absorb energy. An attempt may be made to consider excited molecules only, i.e., to use a receiver in the form of a counter which counts particles at a certain level. Since it will be necessary to count against a background of the equilibrium population of the level, the number of degrees of transmission channel freedom will be proportional to n_2 (or n_1), which is significantly less than n . Unfortunately, at the present time a quantum counter technology for the microwave spectrum has not been developed completely. Moreover, it is not clear what approach could be used other than reradiation of energy absorbed by the molecules. In order to eliminate the pump field it would be necessary to separate the processes of absorption and reradiation either in time or space. Normal spontaneous radiation is not useful for this purpose because of its negligible intensity in the microwave spectroscopy frequency range. However, the reradiation process occurs significantly more rapidly in the case of spontaneous coherent radiation [8]. The essence of this process is the following.

The radiation field induces a polarization wave in the gas specimen. If the field is removed or the interacting molecules are moved out of the field region without distortion of the polarization out of the field region without distortion of the polarization wave phase front, the polarization wave will radiate energy in the same field mode as that in which it was excited. The intensity of this coherent spontaneous radiation is proportional

*The modulation frequency is limited on the low side by technical noise. The optimization condition gives $\Delta f^{\text{cell}} \sim \sqrt{3f_m}$.

†We stress that in principle the RAD can operate only under the condition that the homogeneous half width of spectral lines is determined by collisions between molecules.

‡We note that since for a specified cell configuration $\Delta f^{\text{cell}} \sim 1/n$, P_{cr} is independent of the number of particles in the cell.

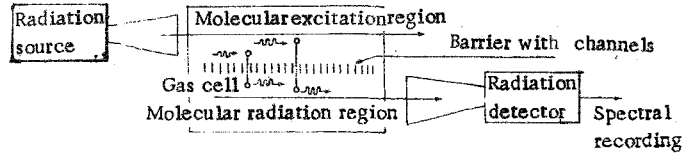


Fig. 3. Spectrometer with spatial separation using coherent spontaneous molecular radiation.

to the square of the number of excited molecules. Although with realization of this method we achieve our goal, namely, we have a single mode signal transmission channel to the recorder, we pay for this achievement because of the low coefficient of conversion of absorbed energy to reradiated energy, i.e., condition (A) will not be fulfilled. Below we will perform an evaluation of a spectrometer with time division (STD) and a spectrometer with space division (SSD).

A practical example of an STD is the centimeter spectrometer described in [9]. An SSD has yet to be constructed. In the evaluations we will assume that in the STD the modulation period is chosen to be of the order of magnitude of the lifetime of the excited state, and that signal reception is accomplished in a narrow bandwidth at the modulating frequency. As for the SSD, it might apparently be constructed on the basis of the sub-Doppler second class spectrometer proposed in [2] (Fig. 3). With these assumptions the treatment of both spectrometers practically coincides. We note that as a rule the excited state lifetime is much less than the reradiation time.

The reradiated power may be expressed in the form

$$P_{\text{rad}} \sim 2\pi E_{\text{abs}} \Delta \nu_{\text{rad}}. \quad (22)$$

Here E_{abs} is the mean power absorbed by the molecules over the period of interaction with the field; $\Delta \nu_{\text{rad}}$ is the half width of the reradiated line. The power of the radiation source should ensure transformation of the system of molecules interacting with the field into the superradiative state.* Then

$$E_{\text{abs}} \sim \frac{1}{2} (n_1 - n_2) h \nu, \quad (23)$$

and for the half width of the reradiated line we have

$$\Delta \nu_{\text{rad}} \sim \frac{1}{\eta} (n_1 - n_2) \Delta \nu_{\text{sp}}, \quad (24)$$

where the coefficient $1/\eta$ considers the fraction of molecules participating in reradiation (due to scattering over interaction time with the field, over quantum number M , etc.†), and

$$\Delta \nu_{\text{sp}} \sim \frac{(2\pi)^2 \nu^3}{hc^3} |\mu_{12}|^2 \quad (25)$$

is the half width of the spontaneous radiation line of an isolated molecule.

As a result, the basic equation of the spectrometer takes on the form

$$|\delta_{12}| |\mu_{12}| \sim \left(\frac{S}{N} \right)^{1/2} \frac{1}{2\pi n \nu^2} \left(\frac{\eta}{\pi} kT \Delta f c^3 \right)^{1/2}. \quad (26)$$

From Eqs. (12), (18), and (26) we obtain

$$\frac{(\delta_{12} | \mu_{12})_{\text{Stark}}}{(\delta_{12} | \mu_{12})_{\text{STD(L)}}} \sim \left(\frac{S}{N} \right)^{1/2} \frac{\nu}{\nu_{\text{cr}}} \frac{n_{\text{Stark}}}{n_{\text{STD(L)}}}; \quad (27)$$

$$\frac{(\delta_{12} | \mu_{12})_{\text{RAD}}}{(\delta_{12} | \mu_{12})_{\text{STD(L)}}} \sim \left(\frac{S}{N} \right)^{1/2} \frac{\nu}{\nu_{\text{cr}}} \left(\frac{P_{\text{cr}}}{P_0} \right)^{1/2} \frac{n_{\text{STD(L)}}}{n_{\text{RAD}}}. \quad (28)$$

where

$$\nu_{\text{cr}} \sim c \left(\frac{\eta}{6\pi^2 a s} \right)^{1/2}, \quad (29)$$

$$P_{\text{cr}} \sim \pi^2 n_{\text{RAD}} kT \Delta f^{\text{cell}}$$

*The condition for the lower limit of source power practically coincides with Eq. (6), where as the homogeneous half width of the line we take the half width related to the finite duration of the interaction with the field.

†It should be understood that the calculation of this coefficient differs for the cases of STD and SSD.

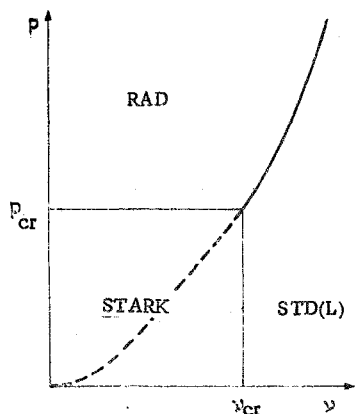


Fig. 4. Regions of superiority in maximum sensitivity for spectrometer types considered herein. Dashed line shows continuation of boundary between RAD and STD (L).

8. Evaluation of Results

Equations (20), (21), (27)–(29) permit an approximate, but very useful examination of the regions of superiority in maximum sensitivity of the various spectrometer types. Remarkably, in the final analysis (assuming $n_{\text{Stark}} \sim n_{\text{RAD}} \sim n_{\text{STD (L)}}$) the most important parameters are radiated power used in the spectrometer, and spectrometer operating frequency. Numerical evaluations give

$$\nu_{\text{cr}} \sim 1 - 25 \text{ GHz (for } a \sim 3 \text{ cm}^2, \eta \sim 10 - 10^2, s \sim 10^2 - 1),$$

$$P_{\text{cr}} \sim 1 \text{ W (for } a \sim 3 \text{ cm}^2, l \sim 10 \text{ cm, } T \sim 300^\circ \text{K)}$$

(where l is the length of the spectrometer gas cell).

A diagram is shown in Fig. 4, indicating the regions of superiority in maximum sensitivity for the spectrometer types studied herein for observation of signals with $S/N \sim 1$. We note that with increased signal/noise ratio requirements the range of superiority of the STD (L) increases. Examination of this diagram permits the conclusion that the region of superiority of spectrometers of the first class practically coincides with the "classical" range of centimeter microwave spectroscopy with low power radiation sources. It is important that in the region of superiority of second class spectrometers the absolute sensitivity of the instruments also increases.

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