THEORETICAL ANALYSIS OF THE GAS CELL OF A MICROWAVE SPECTROSCOPE WITH AN ACOUSTIC DETECTOR

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Based on the equations of nonequilibrium thermodynamics the problem of processes in the gas cell of a microwave spectroscope containing an acoustic detector is solved. Based on the solution derived, optimization of the parameters of the gas cell is performed.

In order to investigate molecular absorption spectra in the submillimeter range of wavelengths a microwave spectroscope with an acoustic detector has been constructed [1, 2]. The given instrument allows maximum sensitivity with respect to the absorption coefficient of the line ($\gamma_{min} = 2 \cdot 10^{-7}$ cm^{-1}) to be achieved in this range and provides automatic recording of the spectra throughout the entire frequency-tuning interval of the coherent-radiation source (a backward wave tube) without any microwave trimming. During the process of creating the instrument the problem arose of optimizing its parameters and determining its limiting sensitivity. Actually, similar problems have been analyzed successively by a series of authors [3-7], the majority of the results being related to the creation of opticoacoustic receivers and gas analyzers. These results, as a rule, are obtained in a fairly rough approximation without quantitative estimates of the errors which develop under these conditions; in this connection their application is difficult. Therefore an attempt was made to achieve a rigorous solution of the problem involving the processes in the gas cells of a microwave spectroscope based on the equations of nonequilibrium thermodynamics using an electronic computer at a definite stage.

STATEMENT OF THE PROBLEM

In a microwave spectroscope with an acoustic detector (the block diagram is displayed in Fig. 1) the coherent radiation of the source is transmitted through the cell containing the investigated gas. When the frequency of the radiation coincides with the frequency of the spectral line the gas absorbs power, is heated up, and creates an increase in pressure in the cell; it is this increase which constitutes the signal indicating the presence of an absorption line. The signal is recorded by means of an electronic circuit which follows up the position of the membrane that is deformed by the action of the excess pressure. The determination of: a) the optimal parameters of the gas cell and membrane, and b) the limiting sensitivity, which is usually characterized by the minimal detectable gas-absorption coefficient per unit length, is based on solving the problem of finding the maximum signal-to-noise ratio from these parameters. The solution is carried out for a stipulated power of the radiation that has passed through the cell cross section for the case of weak lines.* The parameter domain in which the problem solution proposed below is valid is, in our opinion, most interesting from the point of view of the practical application of the results.

THE DYNAMICS OF THE PROCESSES IN THE GAS CELL OF THE MICROWAVE SPECTROSCOPE

We shall describe the processes that go on in the cell using the equations of nonequilibrium thermodynamics. Thereby we shall limit consideration to processes having a characteristic variation time much longer than the time required for thermodynamic equilibrium to be established in a physically infinitely

*We call a line weak if the relative variation of radiation power in the cell due to gas absorption is small.

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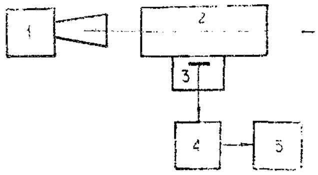

Fig. 1. Block diagram of the microwave spectroscope with an acoustic detector: 1) source of microwave radiation; 2) cell containing the investigated gas; 3) receiver of the pressure change in the cell; 4) amplifier; 5) display device.

small volume (this time has an order of magnitude coinciding with the average time between the collisions of molecules*).

1. Model of a Cell with Rigid Walls

A one-component isotropic rarefied gas occupies a certain closed volume in which heat sources are uniformly distributed. The volume is bounded by a fixed surface which is at a constant temperature.

The model is applicable only in the case when the membrane weakly affects the magnitude of the excess pressure, and this condition is not satisfied for optimal transmission of the signal to the membrane. However, a preliminary analysis of the model given allows the exposition to be simplified in the case when the effect of the membrane is taken into account.

The cell model is described by the system of equations

$$\begin{gathered}\frac{\partial\rho}{\partial t} = -\operatorname{div}\rho\boldsymbol{v},\\ \rho\frac{d\boldsymbol{v}}{dt} = -\operatorname{grad}p + \eta\Delta\boldsymbol{v} + \left(\zeta + \frac{\eta}{3}\right)\operatorname{grad}\operatorname{div}\boldsymbol{v},\\ \rho\frac{du}{dt} = \lambda\Delta T - p\operatorname{div}\boldsymbol{v} + \sigma'_{ik}\frac{\partial v_k}{\partial x_i} + Q,\\ p = p(\rho, T),\quad u = u(\rho, T),\\ T|_S = T_0,\qquad \boldsymbol{v}|_S = 0.\end{gathered}\tag{1}$$

Here ρ, p, T are the density, pressure, and temperature of the gas; v is the mass velocity; u is the density of the internal energy per unit mass; η, ζ are the viscosity coefficients; λ is the coefficient of thermal conductivity†; $\sigma'_{ik} = \eta(\partial v_i/\partial x_k + \partial v_k/\partial x_i - (2/3)\delta_{ik}(\partial v_e/\partial x_e)) + \zeta\delta_{ik}(\partial v_e/\partial x_e)$ is the "viscous" stress tensor; Q is the density of thermal sources per unit volume; T_0 is the temperature of the surface that bounds the volume containing the gas.

In order to consider processes of interest to us the system (1) may be linearized near the unperturbed state (Q = 0):

$$\begin{gathered}\rho = \rho_0(1 + r),\qquad T = T_0(1 + \theta),\\ u = u_0(1 + \varepsilon),\qquad p = p_0(1 + \delta).\end{gathered}$$

As a result,

$$\begin{gathered}\frac{\partial r}{\partial t} = -\operatorname{div}\boldsymbol{v},\\ \frac{\partial\boldsymbol{v}}{\partial t} = -c^2\left[\operatorname{grad}\delta - \frac{\eta}{p_0}\Delta\boldsymbol{v} - \frac{\zeta + \eta/3}{p_0}\operatorname{grad}\operatorname{div}\boldsymbol{v}\right],\\ \frac{\partial\varepsilon}{\partial t} = a^2\Delta\theta + \frac{2}{f}\frac{\partial r}{\partial t} + \frac{2}{f}\frac{Q}{p_0},\\ p_0 = \frac{\rho_0}{m_0}kT_0 = c^2\rho_0,\quad \delta = r + \theta,\\ u_0 = \frac{fk}{2m_0}T_0 = \frac{f}{2}c^2,\quad \varepsilon = \theta,\end{gathered}\tag{2}$$

*We have in mind the microwave-spectroscopy value of the average time between collisions. At a pressure of 1 mm Hg its typical value is of the order of 10^{-7} sec.

†The system (1) is written out on the assumption that in the considered interval of variations of the thermodynamic parameters the viscosity and thermal-conductivity coefficients are practically constant during the dynamic process [8].

$$\theta|_S = 0, \quad v|_S = 0.$$

Here $c^2 = (k/m_0)T_0$; $a^2 = (2/f)(\lambda T_0/p_0)$; m_0 is the mass of a gas molecule; k is Boltzmann's constant; f is the number of degrees of freedom which make a contribution to the specific heat at $T = T_0$.

The dynamics depends essentially on the values of the following four dimensionless parameters:

$$\pi_1 = \left(\frac{l_0}{\tau}\frac{1}{c}\right)^2, \qquad \pi_2 = \frac{\lambda T_0}{p_0 l_0^2}\tau,$$

$$\pi_3 = \frac{\eta}{p_0\tau}, \qquad \pi_4 = \frac{\zeta}{p_0\tau},$$

where τ is the characteristic variation time of the amplitude of the sources; l_0 is the characteristic size of the cell.

We shall consider the solution of the problem in the domain*

$$\pi_1 \ll 1, \quad \pi_3 \ll 1, \quad \pi_4 \ll 1.$$

This allows radical simplification of the first two equations of the system (2).

$$v \sim \frac{l}{\tau} r,$$

$$\frac{v/\tau}{c^2(r/l)} \sim \frac{l^2}{\tau^2}\frac{1}{c^2} \leqslant \frac{l_0^2}{\tau^2}\frac{1}{c^2} = \pi_1 \ll 1, \tag{3}$$

$$\frac{(\eta/p_0)(v/l^2)}{r/l} \sim \frac{\eta}{p_0\tau} = \pi_3 \ll 1, \quad \frac{(\zeta/p_0)(v/l^2)}{r/l} \sim \frac{\zeta}{p_0\tau} = \pi_4 \ll 1,$$

where l is the characteristic distance over which the quantities v and r vary. The distance has an order of magnitude not exceeding l_0, since $v|_S = 0$ and $\int r dv = 0$. As a result, we obtain

$$\delta = r + \theta = \mathrm{const}\,(t) \tag{4}$$

instead of the first two equations (i.e., the given approximation corresponds to a quasistatic variation of the pressure in the cell). Determining const (t) by integrating Eq. (4) over the cell volume, we have

$$\delta = r + \theta = \bar{\theta},$$

$$\frac{\partial\theta}{\partial t} - b^2\Delta\theta = s^2\left(\frac{\partial\bar{\theta}}{\partial t} + \frac{Q}{p_0}\right), \tag{5}$$

$$\theta|_S = 0.$$

In principle, one can obtain certain of the results of interest to us from (5). However, here it is more reasonable to go over to a generalization for the case in which the effect of the membrane is taken into account.

2. Model of a Cell with a Membrane

The fixed surface that bounds the volume containing the gas contains a membrane that bends under the action of the excess pressure $p_0\delta$. The relative change in the cell volume is considered to be small under these conditions (i.e., $V = V_0(1 + \sigma)$, $\sigma \ll 1$). The membrane, just as the walls, is maintained at a constant temperature.

The variation of the thermodynamic parameters in the given model due to the action of thermal sources is determined by the following two processes: a) relaxation of heat through the surface of the cell; b) the work performed by the gas on the membrane. The estimates (3), which allow the transition to the approximate equation (4), are invalid for the second process. The point is that the characteristic distance over which the quantity r varies may greatly exceed l_0 in this case. However, it is not difficult to make these estimates for this process too.

*For $l_0 \sim 1$ cm, $p_0 \sim 1$ mm Hg, $\tau \sim 10^{-3}$ sec, $T_0 \sim 300°$K, $c \sim 3 \cdot 10^4$ cm/sec, $\lambda \sim 5 \cdot 10^{-5}$ cal/cm·sec·deg, η, $\zeta \sim 10^{-4}$ g/sec·cm the dimensionless parameters acquire the following values: $\pi_1 \sim 10^{-3}$; $\pi_2 \sim 0.5$; π_3, $\pi_4 \sim 10^{-4}$.

When the membrane is deflected, the gas performs work. The temperature change due to this effect is the following:

$$\theta\left(\frac{1}{\tau}+\frac{a^2}{l^2}\right)\sim\frac{r}{\tau} \quad \text{or} \quad \theta\sim\frac{r}{1+\pi_2}. \tag{6}$$

If $\pi_2 \gg 1$, then the temperature change is small. This corresponds to slow processes during which the temperature is maintained due to the relaxation of heat through the surface. Otherwise there is not enough time for heat relaxation through the surface to take place, and the internal energy of the gas changes. Using (6), we obtain

$$\frac{v/\tau}{c^2(\theta/l)}\sim\frac{\pi_1}{1+\pi_2}<\pi_1\ll 1,$$

$$\frac{(\eta/p_0)(v/l^2)}{\theta/l}\sim\frac{\pi_3}{1+\pi_2}<\pi_3\ll 1, \quad \frac{(\zeta/p_0)(v/l^2)}{\theta/l}\sim\frac{\pi_4}{1+\pi_2}<\pi_4\ll 1,$$

i.e., for the second process the approximate equation (4) is likewise valid. Integrating it over the volume V_0, we have

$$\delta=r+\theta=\bar{r}+\bar{\theta}=-\sigma+\bar{\theta}.$$

In order to make the problem a closed one it is necessary to write the equation of motion of the membrane. We shall consider the case of a tightly stretched circular membrane which operates in a linear quasistatic regime†:

$$x_M=\frac{p_0\delta}{4T^*}(R^2-r_M^2), \quad x=\frac{p_0\delta}{4T^*}R^2.$$

Here [9] x_M is the displacement of the point on the circular membrane having the running radius r_M from the equilibrium state; T^* is the tensile force applied to the edge of the membrane per unit length; x is the displacement of the center of the membrane; R is the membrane radius. As a result, the system (2) is transformed to the following form:

$$\begin{gathered}\delta=\frac{1}{1+m}\bar{\theta}, \quad x=\frac{1}{h_1}\frac{1}{1+m}\bar{\theta},\\ \frac{\partial\theta}{\partial t}-b^2\Delta\theta=s^2\left(\frac{1}{1+m}\frac{\partial\bar{\theta}}{\partial t}+\frac{Q}{p_0}\right),\\ \theta|_S=0,\end{gathered} \tag{7}$$

where $m=h_1/h_2=(\pi/8)(R^4/V_0)(p_0/T^*)$ characterizes the ratio between the vapor pressure of the gas and the elasticity of the membrane ($\delta=h_1x$, $\sigma=h_2x$). The system (5) describing the processes in a cell having rigid walls is derived from (7) for $m\ll 1$.

Since the displacement of the membrane is associated solely with the integral thermodynamic characteristics of the system, we have

$$x(t)=\int_{-\infty}^{t}\bar{G}(t-\tau)\frac{s^2}{1+m}\left(\frac{\partial x}{\partial\tau}+\frac{1}{h_1}\frac{Q(\tau)}{p_0}\right)d\tau, \tag{8}$$

i.e., the problem has been reduced to a one-dimensional linear integrodifferential equation. The Green's function $\bar{G}(t)$ will be calculated below for two particular cases: a) a rectangular cell; b) a cylindrical cell.

3. Calculation of the Green's Function

1) Rectangular cell

$$0\leqslant x\leqslant l_1, \quad 0\leqslant y\leqslant l_2, \quad 0\leqslant z\leqslant l.$$

†We are forced to deal with precisely such membranes in practice [2].

The formal solution of the thermal-conductivity equation

$$\frac{\partial \theta}{\partial t} = b^2 \Delta \theta, \quad \theta|_{t=+0} = \theta_0(x, y, z), \quad \theta|_S = 0$$

is given in [10]. The Green's function used in that paper is the response to a perturbation of the type

$$\theta_0(x, y, z) = 1, \quad x, y, z \in V_0.$$

Hence

$$\overline{G}(t) = \left(\frac{8}{\pi^2}\right)^3 \sum_{p_1 p_2 p_3 = 0}^{\infty} \frac{1}{(2p_1+1)^2} \frac{1}{(2p_2+1)^2} \frac{1}{(2p_3+1)^2} \times \exp\left\{-\pi^2 b^2 \left[\frac{(2p_1+1)^2}{l_1^2} + \frac{(2p_2+1)^2}{l_2^2} + \frac{(2p_3+1)^2}{l^2}\right] t\right\}, \tag{9}$$

$$\overline{G}(0) = 1.$$

2) A cylindrical cell

$$0 \leqslant \rho \leqslant \rho_0, \quad 0 \leqslant z \leqslant l.$$

Applying the same method, we obtain

$$\overline{G}(t) = \frac{32}{\pi^2} \sum_{p=0}^{\infty} \sum_{j=1}^{\infty} \frac{1}{(2p+1)^2} \frac{1}{\mu_{0j}^2} \exp\left\{-b^2 \left[\frac{\mu_{0j}^2}{\rho_0^2} + \frac{\pi^2 (2p+1)^2}{l^2}\right] t\right\}, \tag{10}$$

$$\overline{G}(0) = 1.$$

4. The Approximate Solution of the Equation for Membrane Vibrations

It is inconvenient to work with Green's functions in the form of the infinite series (9), (10). Therefore in the first approximation we place

$$\overline{G}(t) = \exp(-\beta b^2 t),$$

where

$$\beta = \begin{cases} \pi^2 (1/l_1^2 + 1/l_2 + 1/l^2) & \text{— rectangular cell} \\ \mu_{01}^2/\rho_0^2 + \pi^2/l^2 & \text{— cylindrical cell.} \end{cases}$$

In this case Eq. (8) may be transformed to the form

$$\frac{dx}{dt} + \frac{x}{\tau} = \frac{s^2}{1 - s^2 + m} \frac{1}{h_1} \frac{Q}{p_0},$$

where

$$\tau = \frac{1 - s^2 + m}{1 + m} \frac{1}{\beta b^2}.$$

For the density of the thermal sources it is not difficult to obtain the expression*

$$Q(t) = \frac{W \gamma l}{V_0} \eta(t).$$

Here W is the power of the source of electromagnetic radiation; l is the length of the cell along the axis of electromagnetic-field propagation; γ is the absorption coefficient of the gas per unit length; $\eta(t)$ is the modulation function of the thermal sources ($\max \eta(t) = 1$). It is quite sufficient to analyze the harmonic dependence of the sources on time – i.e.,

*It is assumed that the cross section of the electromagnetic-field beam coincides with the cell cross section.

$$\eta(t) \to \varkappa\, 1\,(t)\, e^{i\omega t},$$

where $\varkappa$ is the coefficient of expansion of the periodic modulation function into a Fourier series. As a result, we obtain

$$x(t) = \frac{\varkappa}{4}\frac{W}{T^*}\frac{R^2}{V_0}\gamma l \frac{s^2}{1 - s^2 + m}\frac{1}{\tau^{-1} + i\omega}\left(e^{i\omega t} - e^{-t/\tau}\right). \tag{11}$$

The degree to which a given approximation is substantiated will be determined by comparing the results obtained with the results of an exact calculation for the case of a cylindrical cell.

5. Rigorous Solution of the Equation for the Membrane Vibrations

Making use of Fourier-transformation, one can obtain the following result from (8):

$$x(\omega) = \frac{1}{h_1}\frac{Q(\omega)}{p_0}\frac{s^2}{1+m}\left\{\frac{\overline{G}'(\omega)}{|\overline{G}(\omega)|^2} + i\left[\frac{\overline{G}''(\omega)}{|\overline{G}(\omega)|^2} - \frac{\omega s^2}{1+m}\right]\right\}^{-1}, \tag{12}$$

where

$$\overline{G}(\omega) = \overline{G}'(\omega) - i\overline{G}''(\omega) = \int_0^\infty \overline{G}(t)\, e^{-i\omega t}\, dt.$$

Let us introduce two correcting multipliers ϑ_1 and ϑ_2, which are defined by the following equations:

$$\beta b^2 \vartheta_1 = \frac{\overline{G}'(\omega)}{|\overline{G}(\omega)|^2}, \quad \omega\vartheta_2 = \frac{\overline{G}''(\omega)}{|\overline{G}(\omega)|^2}. \tag{13}$$

With allowance for (13) one can obtain

$$|x(\omega)| = \frac{|\varkappa|}{4}\frac{W}{T^*}\frac{R^2}{V_0}\gamma l \frac{s^2}{\vartheta_2 - s^2 + \vartheta_2 m}\frac{\tau^*}{[1 + (\omega\tau^*)^2]^{1/2}}, \tag{14}$$

from Eq. (12), where

$$\tau^* = \frac{\vartheta_2 - s^2 + \vartheta_2 m}{1+m}\frac{1}{\vartheta_1 \beta b^2}.$$

The approximate calculation corresponds to $\vartheta_1 = \vartheta_2 = 1$. Thus, the deviation of the correction favors from unity will characterize the degree of deviation of the approximate calculation from the exact one.

Equations (13) treated as equations in ϑ_1 and ϑ_2, depend on four parameters ρ_0, l, ω^2, b^2. However, the number of parameters can be reduced to two:

$$\overline{G}'(\omega) = \frac{32}{\pi^2}\frac{\rho_0^2}{b^2} S(E, D) = \frac{32}{\pi^2}\frac{\rho_0^2}{b^2}\sum_{k=0}^\infty \sum_{n=1}^\infty S[k, n],$$
$$G''(\omega) = \frac{32}{\pi^2}\frac{\rho_0^2}{b^2} EJ(E, D) = \frac{32}{\pi^2}\frac{\rho_0^2}{b^2} E \sum_{k=0}^\infty \sum_{n=1}^\infty J[k, n], \tag{15}$$

where

$$S[k, n] = \frac{1}{(2k+1)^2}\frac{1}{\mu_{0n}^2}\frac{\mu_{0n}^2 + D(2k+1)^2}{[\mu_{0n}^2 + D(2k+1)^2]^2 + E^2},$$
$$J[k, n] = \frac{1}{(2k+1)^2}\frac{1}{\mu_{0n}^2}\frac{1}{[\mu_{0n}^2 + D(2k+1)^2]^2 + E^2}.$$

Under these conditions the following two dimensionless parameters were introduced:

$$D = \pi^2 \rho_0^2 / l^2, \quad E = \omega \rho_0^2 / b^2.$$

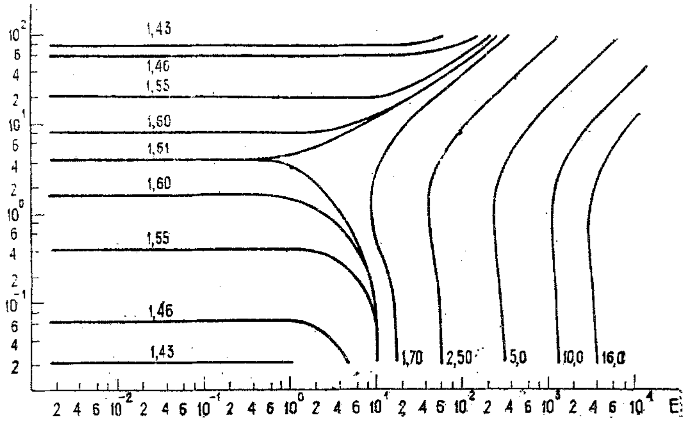

Fig. 2. Field of values of the correction factor ϑ_1 as a function of the dimensionless parameters E and D. The solid lines are lines corresponding to different levels. The numbers denote the numerical value of the quantity ϑ_1.

With allowance for (15), Eqs. (13) for ϑ_1 and ϑ_2 may be written as follows:

$$\vartheta_1 = \frac{\pi^2}{32}\,\frac{S(E,\,D)}{S^2(E,\,D)+E^2J^2(E,\,D)}\,\frac{1}{\mu_{01}^2+D},$$

$$\vartheta_2 = \frac{\pi^2}{32}\,\frac{J(E,\,D)}{S^2(E,\,D)+E^2J^2(E,\,D)}.$$

The calculation of the correction factors was carried out on an electronic computer for the following intervals of parameter variations†:

$$2\cdot 10^{-3}\leqslant E\leqslant 10^4,\quad 2\cdot 10^{-2}\leqslant D\leqslant 10^2.$$

The results of the calculation are displayed in Figs. 2 and 3. Since the correction factors are very slow functions of the parameters of the acoustic system, it follows that the approximate theory provides a qualitatively true reflection of the character of the dependence on these parameters. The exact calculation leads merely to certain quantitative corrections. Because of this, one can assign a simple physical meaning to the quantity $\tau^*(\omega)$ which will be the relaxation time for the action of thermal sources of the type $Q(t) = 1(t)e^{i\omega t}$. In the region near $\omega\tau^* \sim 1$ the character of the dependence of the correction factors on frequency changes, it being true that beginning in this region the role of the quantitative corrections increases with increasing frequency. This is related to the fact that the role of the fast relaxation terms in the expansion of the Green's function (10) begins to increase, and the approximate theory neglects them.

SPECTRAL THEORY OF FLUCTUATION PROCESSES IN THE GAS CELL OF A MICROWAVE SPECTROSCOPE

The limiting sensitivity of a microwave spectroscope with an acoustic detector is determined by the equilibrium fluctuation processes in the gas cell in view of the smallness of the relative change of the thermodynamic parameters of the investigated gas during the dynamic process. In order to find the limiting sensitivity it is sufficient to know the spectral power density of the fluctuation vibrations of the membrane in the signal-reception frequency range. The calculation will be based on the fluctuation-dissipative theorem (FDT) [11].

6. Spectral Density of the Power of the Fluctuational Vibrations of the Membrane

In the working reception-frequency range the membrane is a noninertial linear oscillator whose characteristics depend on the gas parameters. It is necessary to find the relationship between the average

†For $\lambda \sim 5\cdot 10^{-5}$ cal/cm·sec·deg, $T_0 \sim 300$°K, $p_0 \sim 1$ mm Hg, f = 6, $\rho_0 \sim 1$ cm, $l \sim 5$ cm, $\omega \sim 1000$ rad/sec (160 Hz) the dimensionless parameters take the following values: D ~ 0.5; E ~ 10.

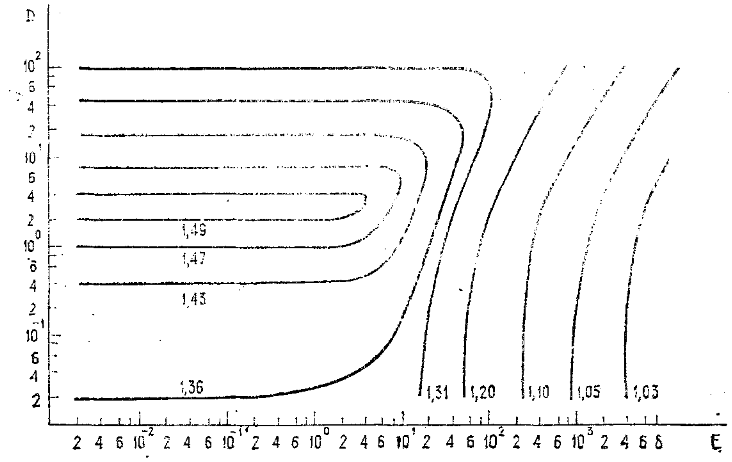

Fig. 3. Field of values of the correction factor ϑ_2 as a function of the dimensionless parameters E and D. The solid lines are lines corresponding to different levels. The numbers denote the numerical value of the quantity ϑ_2.

(over a statistical ensemble) deviation of the oscillator and the force that is linked to this deviation according to the FDT – i.e., to solve the following system of equations:

$$\delta = r + \theta = \bar{r} + \bar{\theta},$$

$$\frac{\partial \theta}{\partial t} - b^2 \Delta \theta = s^2 \left(\frac{\partial \bar{\theta}}{\partial t} + \frac{\partial \bar{r}}{\partial t} \right),$$

$$\theta|_S = 0,$$

$$4\pi T^* x = f + p_0 \pi R^2 \delta,$$

$$r = -\sigma = -\frac{1}{2} \frac{\pi R^2}{V_0} x,$$

where f is the force for which the response must be found. After transformations that are in many ways similar to those used in the case when thermal sources are present, we obtain

$$\left[4\pi T^* (1 + m) \frac{1 + (\omega\tau^*)^2 P}{1 + (\omega\tau^*)^2 P^2} + i 4\pi T^* m s^2 \frac{1 + m}{\vartheta_2 - s^2 + \vartheta_2 m} \frac{\omega\tau^*}{1 + (\omega\tau^*)^2 P^2} \right] x = f,$$

where

$$P = \frac{1 + m}{\vartheta_2 - s^2 + \vartheta_2 m} (\vartheta_2 - s^2).$$

The real part determines the elasticity of the oscillator, while the imaginary part determines its damping coefficient. The weak dependence of the elasticity of the oscillator on frequency is associated with a change in the operating regime of the gas (from isothermal to adiabatic). Using the formulation of FDT, we have

$$\langle (x^2)_\omega \rangle = \frac{1}{\pi} \frac{1}{4\pi T^*} \frac{m s^2}{(1 + m)(\vartheta_2 - s^2 + \vartheta_2 m)} \frac{\tau^*}{1 + (\omega\tau^*)^2} k T_0,$$

where $\langle (x^2)_\omega \rangle$ is the spectral power density of the fluctuation vibrations of the membrane. Consequently, the mean-square deviation of the membrane in the frequency band $\Delta\omega \ll 1/\tau^*$ is determined from the expression†

$$[\langle (x^2)_\omega \rangle 2\Delta\omega]^{1/2} = \frac{s}{\sqrt{2}\pi} \left[\frac{1}{T^*} \frac{m}{(1 + m)(\vartheta_2 - s^2 + \vartheta_2 m)} \frac{\tau^* \Delta\omega}{1 + (\omega\tau^*)^2} k T_0 \right]^{1/2}. \tag{16}$$

†For $m \sim 1$, $\omega\tau^* \sim 1$, $T^* \sim 10^4$ dyn/cm, $\tau^* \sim 10^{-3}$ sec, $T_0 \sim 300$°K, $\Delta\omega \sim 1$ rad/sec, $s = 0.5$ we obtain $[\langle (x^2)_\omega 2\Delta\omega \rangle]^{1/2} \sim 2 \cdot 10^{-4}$ Å.

DETERMINATION OF THE OPTIMAL PARAMETERS OF THE GAS CELL AND THE MEMBRANE. LIMITING SENSITIVITY

Determination of the optimal parameters of the gas cell and membrane, and determination of the limiting sensitivity are based on solving the problem of finding the signal-to-noise ratio maximum from these parameters for a stipulated power of the radiation transmitted through the cell cross section. The noise at the system output is determined both by the thermal vibrations of the membrane and by the intrinsic noise of the electronic circuit. Two versions will be considered: in the first the dominant role is played by the thermal vibrations of the membrane; in the second the noise of the electronic circuit dominates.

7. First Version of Determining the Optimal Parameters. Limiting Sensitivity

We shall assume that the magnitude of the output signal is linearly related to the displacement of the membrane – i.e., $y(\omega) = R(\omega)x(\omega)$, where $y(\omega)$ is the amplitude of the output signal. Then

$$\frac{S}{N} = \frac{2\mid y(\omega)\mid}{[\langle(y^2)_\omega\rangle 2\Delta\omega]^{1/2}} = \frac{2\mid x(\omega)\mid}{[\langle(x^2)_\omega\rangle 2\Delta\omega]^{1/2}}.$$

Using Eqs. (14) and (16), we obtain

$$\frac{S}{N} = 2\sqrt{\pi}s|\varkappa|\,W\gamma l\left(\frac{1+m}{\mathcal{Э}_2 - s^2 + \mathcal{Э}_2 m}\,\frac{\tau^*}{\Delta\omega}\,\frac{1}{N_0}\right)^{1/2}\frac{1}{kT_0}. \tag{17}$$

Here $\Delta\omega$ is the width of the output-signal frequency band; N_0 is the total number of molecules in the cell. For the analysis, which we shall perform for the case of a cylindrical cell, Eq. (17) is conveniently transformed to

$$\frac{S}{N} = \frac{2\mid\varkappa\mid}{\sqrt{\mathcal{Э}_1}\mu_{01}}W\gamma\left(\frac{1}{\lambda T_0}\,\frac{1}{kT_0}\right)^{1/2}\left(\frac{l}{\Delta\omega}\right)^{1/2}\left[\frac{1}{1+(\pi^2/\mu_{01}^2)(\rho_0^2/l^2)}\right]^{1/2}.$$

Obviously, it is advantageous to increase the length of the cell. Under these conditions it follows that if one ignores the effects associated with the variation of the relaxation time $((\pi^2/\mu_{01}^2)(\rho_0^2/l^2) \ll 1)$, the growth of the signal-to-noise ratio is proportional to $l^{1/2}$. This is associated with the fact that efficient thermal noise sources, unlike the thermal sources of the signal, are not correlated with each other.

Let us determine the limiting sensitivity of the microwave spectroscope from the absorption coefficient of the gas per unit length. We shall assume that this quantity is defined as that absorption coefficient γ_{min} for which $S/N = 1$:

$$\gamma_{min} = \frac{\sqrt{\mathcal{Э}_1}\mu_{01}}{2\mid\varkappa\mid}\,\frac{1}{W}(\lambda T_0 kT_0)^{1/2}\left(\frac{\Delta\omega}{l}\right)^{1/2}\left(1+\frac{\pi^2}{\mu_{01}^2}\,\frac{\rho_0^2}{l^2}\right)^{1/2}. \tag{18}$$

In the case when the modulating function is a "meander" (randomly initiated) and $\lambda \sim 5\cdot10^{-5}$ cal·cm^{-1}·sec^{-1}·deg^{-1}, $T_0 \sim 300$°K, $l \sim 10$ cm, $\omega\tau^* \sim 1$, $(\pi^2/\mu_{01}^2)(\rho_0^2/l^2) \ll 1$, $\Delta\omega \sim 1$ rad/sec, one can write

$$\gamma_{min}\,(\text{cm}^{-1}) \approx \frac{3\cdot10^{-11}}{W\,(\text{watt})}$$

instead of (18). Note that in the given type of microwave spectroscope, the sensitivity increases in direct proportion to the power of the electromagnetic-radiation source; this way of increasing sensitivity is very promising [2].

8. The Second Version of Determining the Optimal Parameters

In this version, the problem can be reduced to finding the maximum of the output signal. The use of the results of the solution allows the initial requirements governing the electronic circuit to be eased. Under these conditions the results will depend on what parameter characterizing the state of the membrane the electronic circuit follows up. We shall consider the case when the displacement of the center of the membrane is this parameter.

We transform Eq. (14) to a more convenient form – namely:

$$|x| = \frac{s\,|\varkappa|}{\pi\mu_{01}} \frac{1}{\sqrt{2Э_1}} \gamma W \left(\frac{1}{\lambda T_0} \frac{l}{\omega T^*}\right)^{1/2}$$
$$\times \left[\frac{\omega\tau^*}{1+(\omega\tau^*)^2}\right]^{1/2} \left[\frac{m}{(1+m)(Э_2 - s^2 + Э_2 m}\right]^{1/2} \left[\frac{1}{1+(\pi^2/\mu_{01}^2)(\rho_0^2/l^2)}\right]^{1/2}. \tag{19}$$

We require fulfillment of the conditions

$$\omega\tau^* = 1, \quad m = \left(\frac{Э_2 - s^2}{Э_2}\right)^{1/2}, \quad \frac{\pi^2}{\mu_{01}^2}\frac{\rho_0^2}{l^2} \ll 1. \tag{20}$$

Under these conditions the three last multipliers in (19) reach a maximum and

$$|x| = \frac{s\,|\varkappa|}{2\pi\mu_{01}} \frac{1}{\sqrt{Э_1}} \frac{1}{\sqrt{Э_2} + \sqrt{Э_2 - s^2}} \gamma W \left(\frac{1}{\lambda T_0} \frac{1}{\omega T^*}\right)^{1/2}.$$

The entire subsequent analysis requires consideration of the engineering requirements. We shall not do this,† but shall merely formulate certain fairly general conclusions.

1) For fulfillment of the matching conditions (20). The signal increases only as $\omega^{-1/2}$ with increasing frequency. Therefore one can always find a certain minimal frequency $\omega_{\min}$ below which it is disadvantageous to go due to the growth of engineering noise.

2) The working pressure p_0 of the gas is fairly rigidly stipulated by the requirements of the experiment. Consequently, we obtain the optimal value of the gas-cell radius from the condition $\omega\tau^* = 1$.

3) For stipulated membrane parameters the magnitude of the signal increases with increasing cell length only to a length determined by the condition $m \sim 1$; for a further increase in length the magnitude of the signal saturates.

4) The dependence of the matching conditions on gas pressure leads to a dependence on output-signal pressure. In the region of the collisional absorption width it is not difficult to obtain

$$\frac{|y(p_0)|}{|y_{\mathrm{opt}}|} = \frac{2\left(\frac{p_0}{p_0^*}\right)^{1/2}}{1+\frac{p_0}{p_0^*}} \frac{\left(2\frac{p_0}{p_0^*}\frac{p_0^*}{p_0^{**}}\right)^{1/2}}{\left[1+\left(\frac{p_0}{p_0^*}\frac{p_0^*}{p_0^{**}}\right)^2\right]^{1/2}}, \tag{21}$$

where p_0^{**}, p_0^* are, respectively, the pressures at which the matching conditions $\omega\tau^* = 1$ and $m = 1$ are fulfilled; $|y_{\mathrm{opt}}| = |y(p_0 = p_0^* = p_0^{**})|$. The given property is a shortcoming of a microwave spectroscope with an acoustic detector. The curves (21) can be smoothed by spacing the points p_0^* and p_0^{**}.

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†We refer interested readers to [2] where such an analysis has been performed on the basis of the results obtained here.

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