LIMITING PARAMETERS OF MICROWAVE SPECTROSCOPES

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We shall estimate the maximum attainable values of sensitivity and the associated resolving powers of gas microwave spectroscopes; we take the limiting factor to be thermal fluctuation processes in the gas. * This problem has become ever more acute in recent times owing to the possibilities that have appeared for the realization of spectroscopes with such characteristics [1].

On the basis of the method used to form the signal from the spectral lines of the gas, existing microwave spectroscopes can be divided into two main classes [1]: in one the signal from the line is observed as a change in the microwave power of the radiation passing through the specimen; in the other, the signal is produced by the change in sample characteristics under the action of microwave radiation. In considering the limiting parameters of an instrument we may assume that the fraction of power absorbed by the sample, P_S is small (i.e., $P_S \ll P_0$, where P_0 is the power of the microwave source). In instruments of the first class, therefore, the useful signal P_S must be observed against the large (noninformative) background P_0, and this is responsible for many phenomena that impair the sensitivity [2]. The second class of instruments is evidently more promising, since it is organically associated with "null" type reception in which only the useful signal P_S is registered. An essentially similar conclusion follows from [3]. Thus in this study we give estimates for the limiting parameters of instruments of the second class; † we assume that the power of the radiation source is adequate for a certain degree of saturation of the investigated transition i.e.,

$$P_0 \sim \frac{h^2 (\Delta\nu)^2 c}{8\pi |\mu_{ij}|^2} S. \tag{1}$$

Here $|\mu_{ij}|^2$, $\Delta\nu$ are the square of the absolute value of a dipole-moment matrix element and the homogeneous half-width of the transition line; S is the cross section of the cell. Here

$$P_S \sim nh\nu\Delta\nu \tag{2}$$

(n is the difference in the number of gas molecules in the energy states between which the transition takes place; ν is the frequency of the transition) and there is no loss of signal owing to inadequate microwave power.

1. The primary effect produced in the gas by coherent radiation is a change in the number of particles at resonance levels as compared with the original Boltzmann distribution. A "number of particles at the level" counter can be used as a selective receiver to register this effect i.e., a device of the quantum-counter type making use, for example, of resonant pumping to transfer particles from the higher of an investigated pair of levels to the very highest (unpopulated) level, with subsequent counting of spontaneously emitted photons. If we assume that (1) is satisfied and that no additional noise is introduced by the process of counting the number of particles at a level, then in this case, of course, it is in principle possible to attain the maximum sensitivity, since individual particles at a level can be registered [4].

It is easy to show that the total threshold equilibrium population of the resonance levels required for registration of a transition has an order of magnitude

* Allowance for thermal fluctuations is fundamental, since the polar gases investigated by microwave spectroscopic methods condense with relative ease (i.e., heavy cooling cannot be used).

† Only the question of the limiting sensitivity of the first class of microwave spectroscopes has received sufficiently complete treatment in the literature [2].

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TABLE 1

$\Delta\nu$, HMz / $\lvert\mu_{ij}\rvert$, debye		10^0	10^1	10^2	10^3
10^0	n	10^5	10^4	10^3	10^2
	γ_{min}, (cM^{-1})	10^{-9}	10^{-11}	10^{-13}	10^{-15}
	$\gamma_{min}(\Delta\nu/\nu)$, (cM^{-1})	$2\cdot10^{-15}$	$2\cdot10^{-16}$	$2\cdot10^{-17}$	$2\cdot10^{-18}$
	P_0, W	$5\cdot10^{-3}$	$5\cdot10^{-1}$	$5\cdot10^{1}$	$5\cdot10^{3}$
10^{-1}	n	10^5	10^4	10^3	10^2
	γ_{min}, (cM^{-1})	10^{-11}	10^{-13}	10^{-15}	10^{-17}
	$\gamma_{min}(\Delta\nu/\nu)$, (cM^{-1})	$2\cdot10^{-17}$	$2\cdot10^{-18}$	$2\cdot10^{-19}$	$2\cdot10^{-20}$
	P_0, W	$5\cdot10^{-1}$	$5\cdot10^{1}$	$5\cdot10^{3}$	$5\cdot10^{5}$
10^{-2}	n	10^5	10^4	10^3	10^2
	γ_{min}, (cM^{-1})	10^{-13}	10^{-15}	10^{-17}	10^{-19}
	$\gamma_{min}(\Delta\nu/\nu)$, (cM^{-1})	$2\cdot10^{-19}$	$2\cdot10^{-20}$	$2\cdot10^{-21}$	$2\cdot10^{-22}$
	P_0, W	$5\cdot10^{1}$	$5\cdot10^{3}$	$5\cdot10^{5}$	$5\cdot10^{7}$

$$N_{thr} \sim \frac{1}{\Delta\nu t}\left[1+\exp\left(-\frac{h\nu}{kT}\right)\right]^2. \tag{3}$$

where t is the photon counting time (we assume that the average number of photons counted is $\sim N\Delta\nu t \gg 1$). Unfortunately, no such quantum-counter equipment has as yet been completely developed for microwave spectroscopy.*

2. A secondary effect produced in the gas by coherent radiation is a change in the macroscopic thermodynamic parameters of the gas. There are existing receivers for registering this effect whose sensitivity can evidently reach the limiting value [1].

Owing to absorption of the power of the modulated microwave radiation, the energy of the gas varies at the modulation frequency; the maximum amplitude of these oscillations is $\Delta E_S \sim P_S \tau^{cl}$ (provided that $\tau^{cl} \sim \tau^{mod}$, where $\tau^{cl} \sim 1/\Delta f^{cl}$ is the characteristic thermal relaxation time of the gas in the cell; τ^{mod} is the characteristic modulation time). The condition for observability of this effect against the background of the gas-energy fluctuations (and, consequently, the condition for the observability of the effect of a change in any thermodynamic parameter) may be written as

$$\Delta E_S \sim \left[\overline{E_f^2}\Delta f^{rc}\right]^{1/2}, \tag{4}$$

where $\overline{E_f^2}$ is the spectral density of the gas-energy fluctuation power in the signal-reception frequency band (at the modulation frequency); Δf^{rc} is the bandwidth of the reception channel. In order of magnitude $E_f^2\Delta f^{cl} \sim (kT)^2 N$, and

$$P_S \sim kT(N\Delta f^{cl}\Delta f^{rc})^{1/2}, \tag{5}$$

where N, T are the total number of particles in the cell and the gas temperature. The quantity $N^{1/2}$ appears in the right side of the expression because we basically observe the useful signal against the background of fluctuation processes in a gas whose number of degrees of freedom is proportional to N.

From (2) and (5) we find

$$n_{min} \sim \frac{kT}{h\nu\Delta\nu}(N\Delta f^{cl}\Delta f^{rc})^{1/2}. \tag{6}$$

for the minimum detectable value in n.

When the homogeneous line width increases so does the sensitivity with respect to the parameter n, since there is a shift in the line saturation threshold, but at the same time there is a drop in the resolving

* The nearest to this (in principle) is the beam microwave spectroscope which operates according to the following scheme: "beam source → deflecting system (polarizer) → microwave field region → deflecting system (analyzer) → particle counter." Complications inherent in beam methods prevent us from making sufficiently general estimates for this case, however.

power $\Delta\nu/\nu$. Thus to characterize the properties of a spectroscope it is convenient to introduce the parameter $n_{min}(\Delta\nu/\nu)$ for which we obtain the following estimate:

$$n_{\min}\frac{\Delta\nu}{\nu}\sim\frac{kT}{h\nu^2}(N\Delta f^{cl}\Delta f^{rc})^{1/2}. \tag{7}$$

It is clear from (6), (7) that an increase in the working frequency of the spectroscope is very advantageous from the viewpoint of improving its limiting characteristics. As an example, in the submillimeter band, the value of $n_{min}\Delta\nu/\nu$ may be more than two orders of magnitude smaller than for the centimeter band.

In many cases it is more convenient to replace the quantities n_{min}, $n_{min}\Delta\nu/\nu$ by the quantities associated with the least detectable gas absorption coefficient per unit length, γ_{min}. Here

$$\gamma_{\min}\sim\frac{8\pi kT(N\Delta f^{cl}\Delta f^{rc})^{1/2}}{h^2(\Delta\nu)^2 cl}|\mu_{ij}|^2, \tag{8}$$

where l is the length of the cell containing the gas, and

$$\gamma_{\min}\frac{\Delta\nu}{\nu}\sim\frac{8\pi kT(N\Delta f^{cl}\Delta f^{rc})^{1/2}}{h^2\nu\Delta\nu cl}|\mu_{ij}|^2. \tag{9}$$

To conclude, let us examine numerical estimates of the parameters considered. We take the following initial values: $T\sim300°K$, $\nu\sim500$ GHz, $\Delta f^{cl}\sim1$ kHz, $N\sim10^{17}$, $l\sim10$ cm, $S\sim1$ cm^2. Here we fix the parameter $n_{min}\Delta\nu/\nu\sim2\cdot10^{-1}$. The parameters n_{min}, $\gamma_{min}(cm^{-1})$, $\gamma_{min}(\Delta\nu/\nu)(cm^{-1})$, and the corresponding radiation source power P_0 (W) are given in Table 1 for various values of the half-width of the homogeneous line $\Delta\nu$ (MHz) and the absolute value of the dipole-moment matrix element $|\mu_{ij}|$ (debye).

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