A new mechanism of line narrowing in gas spectroscopes

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A new mechanism is described for obtaining a spectral line with less than Doppler width in gas spectroscopes; the line signal is produced by changing the gas parameters, so that molecules having large frequency shifts are prevented from taking part in producing the signal from the spectral line.

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1. According to the classification given in [1,2] all spectroscopes can be divided into two principal classes on the basis of the method used to observe the signal from the spectral line: by the change in the radiation power passing through the sample (first), and by the change of the parameters of the sample itself under the influence of the radiation (second). A number of advantages of spectroscopes of the second class were considered in [1-3]; in particular, they are presently the most sensitive ones in the microwave region. [3] It is indicated in this note that the principle of signal reception from lines on the basis of changes in the parameters of the investigated sample also provides an additional possibility of controlling the shapes and widths of the observed spectral lines in gas spectroscopes of the second class. The analysis that follows pertains in particular to the case of a gas radiospectrometer with acoustic detector (RAD [1-3]).

2. The signal from the lines in the RAD is produced in the following manner: When the radiation frequency coincides with the frequency of the spectral line, the gas molecule in the cell absorbs a radiation quantum. The adsorbed energy is stored in this case as internal energy of the molecule. Then, when the molecules collide, this internal energy is transformed into molecule translational energy, and this leads to a temperature rise, and hence to an increase of the gas pressure in the cell. It is this pressure increase which is registered by a microphone placed in the cell as the signal from the spectral line. The presence of an intermediate stage of conversion of the internal energy of the gas into thermal energy provides the hitherto-unnoticed possibility of controlling the shapes and widths of the observed lines in spectroscopes of the second class.

Indeed, to obtain a line with a width smaller than the Doppler width it is sufficient to prevent the molecules with large frequency shifts, i.e., those traveling at large angles to the plane radiation front, from taking part in the heating of the gas, i.e., from contributing to formation of the signal, by causing them to collide not with other gas molecules, but say with the walls of a cell of suitable configuration. This can be done in practice by restricting the molecule motion by walls, partitions, etc., placed perpendicular to the radiation propagation directions. Examples are shown in Figs. 1a and 1b. In Fig. 1a, part of the absorbing cell through which the radiation is passed is subdivided into a series of flat intervals by partitions that are transparent to the radiation and are perpendicular to the radiation direction. To make the lines narrower, the following relations must be satisfied between the molecule mean free path l, the radiation wavelength λ, the partition dimension L (and the dimension B of the plane wave front, which is equal to L in this case), and the distance a between the partitions:

$$l \gtrsim (L, B) \gg \lambda, \quad L/a \gg 1. \tag{1}$$

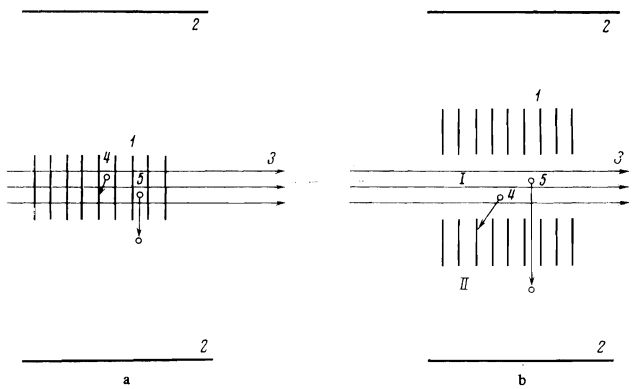

FIG. 1. Possible configurations of RAD cells intended to obtain a spectral line with less-than-Doppler width: 1—partitions with dimensions L, spaced a apart, limit the motion of the molecules; 2—side walls of the cell; 3—radiation of wavelength λ and with dimension of plane wave front B; 4—molecule with large Doppler frequency shift gives up the absorbed energy to the walls; 5—molecule with small Doppler shift gives up the absorbed energy to the gas.

In this case only molecules that travel at small angles to the wave front have a high probability of transferring the absorbed energy to other gas molecules. On the other hand, molecules traveling at large angles to the wave front collide with the partition and give up the absorbed energy not to the gas, but to the walls, the heating of which is negligible in comparison with that of the gas, owing to the large specific heat and the large thermal inertia. In the RAD the radiation is customarily modulated with a period of the order of the gas relaxation time in the cell, and the signal is the ac component of the pressure. [1-3] Then, to eliminate the influence of the wall heating, it suffices that the thermal time constant exceed the thermal time constant of the gas in the cell, a condition easy to satisfy. Thus, only the central part of the Doppler line, which is narrower in order of magnitude than the initial Doppler line by a factor L/a, will be observed (at $a \gtrsim \lambda$; if $a < \lambda$, the line width is determined by an expression of the form $\bar{v}/B$, where $\bar{v}$ is the average molecule velocity).

In the case of the configuration shown in Fig. 1b, the partitions do not over the region of the radiation fields. The line-narrowing conditions are

$$l \gtrsim (L+B), \quad B \gg \lambda, \quad L/a \gg 1, \tag{2}$$

but the dimension L is no longer connected with the dimension B of the field region, and can be chosen, for convenience, much smaller than B; Of course, in case 1b the partitions need not even be transparent.

3. Let us calculate the shape of the observed spectral line in the cell configuration shown in Fig. 1b. The problem is assumed to be two-dimensional, i.e., the configuration is independent of the coordinate z; this simplifies

the calculation without changing the gist of the matter. In the absence of partitions that block the molecule motion, the observed spectral line in a sufficiently rarefied gas is determined, as is well known, by the Doppler effect, which is due to the thermal motion of the molecules. Recognizing that a molecule with velocity v_x interacts with radiation propagating along the x axis at a frequency $\omega_c = \omega_0(1 + v_x/c)$, and that the number of molecules with velocities in the interval from v_x to $v_x + dv_x$ is defined by the one-dimensional Maxwellian distribution in the form

$$n(v_x)dv_x = \frac{1}{\alpha\sqrt{\pi}} \exp\left(-\frac{v_x^2}{\alpha^2}\right) dv_x \qquad (3)$$

($\alpha = 2kT/m)^{1/2}$) is the most probable molecule velocity in the gas), it follows that at a sufficiently small homogeneous line width, expression (3) with the substitution

$$v_x = c\frac{\omega_c - \omega_0}{\omega_0} \qquad (4)$$

yields indeed this Doppler line shape. The presence of partitions changes the v_x-distribution of the molecules excited by the radiation field in region I (see Fig. 1b) and traveling into region II without colliding with the partitions, in comparison with the distribution of the type (3). It is precisely these molecules which take part in the heating of the gas in the cell, i.e., in the production of the signal from the spectral line. Therefore to calculate the shape of the observed line it suffices to obtain an expression for this modified distribution, with respect to v_x, of the molecules that had absorbed a radiation quantum in region I and passed without colliding with the walls into region II, and then substitute the value of v_z from Eq. (4).

The condition for unimpeded passage (see Fig. 2, where one of the channels produced by the partitions is shown), for a molecule entering the channel at a point x′ with velocities v_x and v_y, is

$$v_y > \frac{L}{a - x'} v_x, \qquad (5)$$

where the notation is clear from the figure. The fraction of the molecules form (3), passing through the channel without collisions, is then

$$\delta(v_x) = \frac{2}{\alpha^2} \int_{\frac{L}{a-x'}v_x}^{\infty} v_y \exp\left(-\frac{v_y^2}{\alpha^2}\right) dv_y = \exp\left[-\left(\frac{Lv_x}{a\alpha}\right)^2 \frac{1}{(1-s)^2}\right], \qquad (6)$$

where $s = x'/a$, and averaging over the entry points x′ in the interval from 0 to a, we obtain for the v_x-distribution of the molecules that transfer excitation from region I to region II

$$n'(v_x)dv_x = \frac{1}{\alpha\sqrt{\pi}} \exp\left(-\frac{v_x^2}{\alpha^2}\right) dv_x \int_0^1 \exp\left[-\left(\frac{Lv_x}{a\alpha}\right)^2 \frac{1}{(1-s)^2}\right] ds. \qquad (7)$$

The integral in (7) cannot be evaluated in terms of elementary functions, but it is easily seen that (7) determines a distribution, with respect to the velocities v_x, which can be much narrower than the initial distribution (3). The first factor in the argument of the exponential under the integral sign is of the form $(Lv_x/a)^2/\alpha^2$, as against v_x^2/α^2 in (3); in addition, the deformation of the velocity distribution, in view of the dependence of the pass-through condition (5) on the entry point, leads to further narrowing of the line. Naturally, the maximum amplitude of the signal from the line (the signal at the line center) remains unchanged, since the partitions do not hinder the motion of the molecules with $v_x = 0$. The

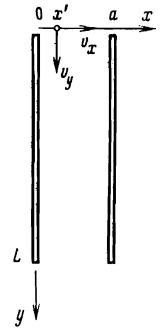

FIG. 2

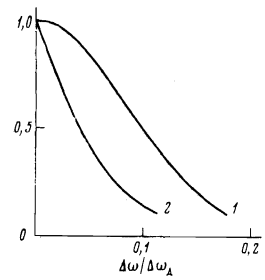

FIG. 3

FIG. 2. Part of Fig. 1b—channel made up of two partitions.
FIG. 3. Form of the function $\exp\left[-\frac{L^2}{a^2}\frac{(\Delta\omega)^2}{(\Delta\omega_D)^2}\right]$ (curve 1) and shape of spectral line determined by (7) (curve 2) at L/a = 10.

line shape at a given ratio L/a can be easily obtained from (7) numerically. We note that at $L/a \gg 1$ we can set the first exponential in (7) equal to unity.

Figure 3 shows a plot of $\exp[-(Lv_x/a)^2/\alpha^2]$ and the line shape corresponding to a distribution with respect to v_x in the form (7), but for L/a = 10. The abscissa axis is in fractions of the half-width of the initial Doppler line in the gas at half-intensity level

$$\Delta\omega_D \approx 0.84\frac{\alpha}{c}\omega_0. \qquad (8)$$

It is seen from Fig. 3 that this cutoff of the velocity distribution sharpens considerably the central peak of the line (the break in the derivative at the center of the line is the consequence of the assumption that the homogeneous line width is negligibly small; actually the central peak is "rounded off" by a homogeneous broadening determined, for example, by the time of flight of the molecules through the region of the radiation field. The half-width of the obtained line at the half-intensity level is, at L/a = 10,

$$\Delta\omega \approx 0.04\,\Delta\omega_D, \qquad (9)$$

and the so-narrowed line has rather steep slopes.

It is important to note that the deviation of the walls and of the radiation propagation direction from perpendicularity in the case of a symmetrical cell construction will obviously not lead to a shift of the center of the observed line, inasmuch as for each molecule that moves in one direction in the gas there exists another, symmetrical molecule moving in the opposite direction. Then the deviation from perpendicularity causes only a symmetrical broadening of the observed line (which in the limit—when the walls and the radiation propagation are parallel—goes over into the usual Doppler broadening).

4. In our opinion, the described method of spectral-line narrowing can serve as a useful adjunct to known high-resolution spectroscopy methods, since it is not connected with nonlinearity, and its realization does not call for passing the radiation through the cell twice, as in the ordinarily used equipment, [4,5], the narrow line is observed from a zero level, and the large sensitivity margin of spectroscopes of the second class [1-3] can ensure a sufficient signal/noise ratio in the course of observation of the lines.

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