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Abstract

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DEVELOPMENT OF A METHOD FOR DETERMINING THE RELAXATION TIME OF AN EXCITED VIBRATIONAL STATE OF MOLECULES BY MEANS OF A SPECTROPHONE

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In our work ([1]) we proposed a selective method for determining relaxation time with the aid of the spectrophone of M. L. Veingerov ([2]), i.e., a method that makes it possible to determine this quantity differentially for each type of molecular vibration independently of the others. The present article gives the results of further development of this method.

In the first version of the method it was approximately assumed that the measured phase shifts between the signal developed by the optico-acoustic receiver and the radiation directed into it are related to the relaxation time by a linear dependence; for large values of the measured quantities, corrections were introduced according to the theory of B. I. Stepanov and O. P. Girin ([3]). Here a direct functional dependence is established between the measured phase shifts and the relaxation times over the entire range of their values.

The relaxation time is determined by measuring the phase shift of the signal developed by the optico-acoustic receiver, filled with the gas under investigation, relative to the signal of the reference-voltage generator, using the device described in ([4]). The generator includes a photocell illuminated by light modulated synchronously with the radiation directed into the receiver. Displacement of the photocell along the arc of the circumference of the modulating disk is used to compensate the measured phase shift. The attainment of compensation is noted with the aid of a synchronous detector.

In studying a series of absorption bands it may turn out that the radiation beams emerging from the spectral instrument and entering the receiver are modulated by the disk, for different bands, with some difference in phase because of the nonuniform spatial distribution of energy in these beams. This circumstance is the cause of a systematic error in determining the difference of phase shifts corresponding to different absorption bands. The error is eliminated if the measurements are carried out by rotating the modulating disk first in one direction and then in the other, and taking the mean values of these two measurements.

To eliminate other instrumental phase shifts and to find the dependence of the measured quantities on the relaxation time, one may carry out a treatment analogous to that used in the theory of fluorometers ([5]), and determine the phase

shift of the first harmonic of the Fourier expansion of the function representing the pressure pulsation in the receiver relative to the first harmonic of the modulated radiation.

As shown in ([3]), the rise of pressure during the illumination time and its fall during the darkening time are described, when the relaxation time is negligibly small, by exponential laws. If the relaxation time is finite, then the shape of the curve changes, as a result of which there arises a phase shift of the harmonic components of its expansion in a series and, in partic-

···the phase shift of the first harmonic. We shall denote this phase shift relative to the moment when the radiation enters the chamber by φ_1. The microphone membrane, which senses the pressure pulsation, will oscillate with some additional phase displacement. Therefore one more shift is added to that indicated above; let us call it φ_2. In addition to these shifts, one must take into account the shift caused by the nonidentity of the amplification paths of the receiver and the photocell, and the phase shift of the first harmonic of the photocell signal relative to the moment when the radiation enters the receiver; we shall denote it by φ_3. Thus the total phase shift of the first harmonic of the signal at the output of the amplifier connected to the receiver, relative to the first harmonic of the signal of the reference-voltage generator, is $\varphi = \varphi_1 + \varphi_2 + \varphi_3$.

As a result of expanding in a series the function describing the pressure pulsation in the receiver, it turns out that

$$\varphi_1 = \operatorname{arc\,tg} \frac{\omega(\beta + p)}{\beta p - \omega^2}, \tag{1}$$

where $p = 1/\tau$; τ is the relaxation time; β is a quantity reciprocal to the time constant characterizing the rise of gas pressure in the receiver; ω is the angular frequency of modulation.

Similar arguments were given by A. O. Salle ([6]) and Jakokos and Bauer ([7]). The right-hand side of expression (1) is the sum of two angles: $\varphi_4 = \operatorname{arc\,tg} \frac{\omega}{\beta}$ and $\psi = \operatorname{arc\,tg} \frac{\omega}{p}$, of which the first is the phase shift caused by the thermal inertia of the gas in the receiver ($\varphi_1 = \varphi_4$ when $p = \infty$), while the second is caused by the relaxation time; hence

$$\varphi = \operatorname{arc\,tg} \frac{\omega}{p} + \varphi_2 + \varphi_3 + \varphi_4.$$

The sum $\varphi_2 + \varphi_3 + \varphi_4$ is an instrumental phase shift, which in the general case depends on the concentration of the mixture, since with a change in concentration the density, heat capacity, and thermal conductivity of the mixture take on new values. To determine the absolute value of the relaxation time, this instrumental phase shift must be eliminated.

Two methods of eliminating it may be indicated.

1. By measuring the angle φ after adding to the mixture under study a small admixture of a substance that greatly shortens the relaxation time (for example, water vapor), but does not strongly alter the indicated properties of the mixture. The measurement is reduced to finding the difference $\Delta\varphi$ of two values of the angle φ corresponding to some absorption band of the gas for the dry and humidified mixture; then one obtains $\tau = \frac{1}{\omega}\operatorname{tg}\Delta\varphi$.
2. By finding the difference of the values of the angle φ for two absorption bands at two different frequencies of interruption of the radiation (this method is more perfect than the first). For this it is necessary to determine, at the frequency $f = \omega/2\pi$, the difference $\varphi_{\lambda_1} - \varphi_{\lambda_2}$ of the values of the angle φ for two absorption bands λ_1 and λ_2, possessing respectively the relaxation times τ_{λ_1} and τ_{λ_2}. Then the same measurement must be made at the frequency $f' = \omega'/2\pi$. Assuming that the quantity β, which determines the thermal inertia of the gas in the chamber, does not change its value on going from one band to the other, we shall have for the first case
$$\varphi_{\lambda_1} - \varphi_{\lambda_2} = \psi_{\lambda_1} - \psi_{\lambda_2} = \Delta\psi,$$
where $\psi_{\lambda_1} = \operatorname{arc}\operatorname{tg}\frac{\omega}{p_{\lambda_1}}$ and $\psi_{\lambda_2} = \operatorname{arc}\operatorname{tg}\frac{\omega}{p_{\lambda_2}}$, $p_{\lambda_1} = \frac{1}{\tau_{\lambda_1}}$ and $p_{\lambda_2} = \frac{1}{\tau_{\lambda_2}}$.

Analogously, the difference of angles corresponding to the same absorption bands at the frequency $f' = \omega'/2\pi$ is expressed as:
$$\varphi'_{\lambda_1} - \varphi'_{\lambda_2} = \psi'_{\lambda_1} - \psi'_{\lambda_2} = \Delta\psi'.$$

Therefore, since
$$\operatorname{tg}\psi_{\lambda_1} = \omega\tau_{\lambda_1}; \quad \operatorname{tg}\psi_{\lambda_2} = \omega\tau_{\lambda_2}; \quad \operatorname{tg}\psi'_{\lambda_1} = \omega'\tau_{\lambda_1}; \quad \operatorname{tg}\psi'_{\lambda_2} = \omega'\tau_{\lambda_2} \tag{2}$$
and denoting $f'/f = \omega'/\omega = k$; $\operatorname{tg}\Delta\psi = a$; $\operatorname{tg}\Delta\psi' = b$, we obtain
$$\frac{\operatorname{tg}(\psi_{\lambda_1} - \Delta\psi)}{\operatorname{tg}(\psi'_{\lambda_1} - \Delta\psi')} = \frac{\operatorname{tg}\psi_{\lambda_1}}{\operatorname{tg}\psi'_{\lambda_1}} = \frac{1}{k}. \tag{3}$$

The last relation leads to a quadratic equation, whose solution gives the value
$$\tau_{\lambda_1} = \frac{ab\,(k^2-1) + \sqrt{[ab\,(k^2-1)]^2 + 4k(a-bk)(b-ak)}}{2\omega k(bk-a)}. \tag{4}$$

For τ_{λ_2} an analogous expression is obtained, differing from (4) by the sign before the first term in the numerator.

It should be borne in mind that the frequencies f and f^1 must be chosen not too small, so that the tangent dependences entering into (3) cannot be replaced by linear ones; otherwise equation (3) becomes an identity.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The results of applying the method to finding the relaxation time of carbon dioxide molecules in a mixture with nitrogen for the bands 4.3 and 2.7 μ, on the basis of measurements carried out at interruption frequencies of 500 and 1200 cps, are presented in Figs. 1-3.

Fig. 1

Fig. 2

In Fig. 1 are shown the curves of the dependence of the micrometer reading, which displaces the photocell, on the concentration of carbon dioxide in the mixture with nitrogen. Curves 1, 2, 1′, and 2′ were obtained with rotation of the modulating disk in one direction; curves 3, 4, 3′, and 4′, in the opposite direction.

In Fig. 2 are presented the phase-shift values, averaged for the two directions of rotation, expressed in millimeters of micrometer displacement. The zero of the ordinate readings for each pair of curves, corresponding to the 2.7 and 4.3 μ bands for a given interruption frequency, is arbitrary.

Figure 3 presents the dependence of the relaxation time for these bands on the concentration*. It should be borne in mind that the values of τ for the 2.7 μ band at low concentrations are apparently underestimated. The explanation is that, because of insufficient drying, the mixture contains water vapor, which has an absorption band near 2.7 μ. Therefore the signal arising in this region of the spectrum is the sum of the signals corresponding to carbon dioxide and water vapor. Owing to the small relaxation time of water vapor, such superposition leads to a decrease in the measured value of τ.

Results show that collisions of carbon dioxide molecules with nitrogen molecules are, for the 4.3 μ band, considerably less effective than collisions of carbon dioxide molecules with one another. It should be noted that the relaxation time corresponding to the 4.3 μ band is approximately twice as large as that corresponding to the 2.7 μ band in the concentration region where the influence of water vapor is not manifested.

Fig. 3

Fig. 3

Figure 3: Fig. 3

In conclusion I express my gratitude to Prof. M. L. Veingerov for guiding the first stage of the work and for his constant interest in its further development.

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* The points for a concentration of 1% were obtained for both bands from measurements at $f = 230$ Hz and $f^1 = 460$ Hz.

Note: Figure translations are in progress. See original paper for figures.