OPTOACOUSTIC TECHNIQUE FOR MEASURING FAST VIBRATIONAL RELAXATION IN GASES

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Generation of acoustic signals in optoacoustic detectors has certain peculiarities at excitation of molecules of an absorbing gas in its cell with a short laser pulse. The main peculiarities are caused by the influence of natural oscillations of the microphone diaphragm. In this study we have shown that at low pressure ($p \leq 10-100$ Torr) the signal shape is determined by these natural oscillations. Phase shift of the diaphragm natural oscillations is a function of pressure of a gas under study. We propose to measure this pressure dependence of the phase shift for determining VT relaxation time of molecular gases. As an example of the feasibility of this approach, we present some experimental results on the relaxation time of the $\nu_1 + 3\nu_3$ state of H_2O molecule in H_2O-H_2O, H_2O-air, and H_2O-H_2 collisions.

Study of relaxation of selectively excited vibrational states of gas molecules is urgently needed since the relaxation parameters are used in description of the processes of resonance interactions of laser radiation with different substances. Relaxation processes also play an important role in physics of molecular gas lasers and in intermolecular interactions.

Two methods are primarily used for measuring the time of the vibrational–translational (VT) relaxation. One of them, the laser fluorescence method,[1] is based on measurements of time behavior of the fluorescence emission due to transitions of a molecule from an excited vibrational state to lower energy levels. This technique enables the identification of the relaxation channels but is only applicable to studies of relaxation from the levels with high probability of radiative transitions. The second method uses an optoacoustic approach[2] which enables a reliable determination of the total time of a collisional relaxation from an excited state of a molecule due to radiationless transitions. Of course, no identification of the relaxation channels is possible in this case. It seems to be worth combining both these methods by simultaneous recording the fluorescence emission and the acoustic signal initiated in one and the same cell due to absorption of radiation. However, for a number of reasons, this cannot be done for all types of molecules and all types of vibrational–rotational transitions.

At present, time of VT relaxation in molecular gases is measured using several versions of the optoacoustic technique. Among these versions are the phase method,[2,3] the amplitude–frequency method,[12] the technique based on measuring the sensitivity of an optoacoustic detector (OAD) as a function of pressure of a gas in the cell,[4,5] and the method based on measurements of the rise time of the leading edge of the acoustic signal generated in an OAD cell.[6,7]

The main bulk of recent experimental data on the VT relaxation time τ_{VT} for many molecules was obtained just with the above techniques. However, these optoacoustic techniques have certain limitations. Thus, determination of τ_{VT} from measurement data on OAD sensitivity as a function of pressure of a gas in the OAD cell needs for additional information about the coefficient of accommodation of molecules on the cell's walls. This value is, as a rule, unknown or measured insufficiently accurate. For example, in Refs. 4 and 5 its value was taken to be unit and this caused, in our opinion, the disagreement between data of optoacoustic measurements obtained in these studies and data from Ref. 1 obtained using fluorescence technique.

In the technique of τ_{VT} determination from the rise time of the leading edge of an optoacoustic signal recorded at a pressure inside the cell below 10 Torr, it is necessary to know an instrumental delay component occurring due to the microphone diaphragm time lag. Normally, this instrumental characteristic is measured at pressures higher than 10 Torr (Ref. 7). We think that this circumstance can result in an error since the frequency response of a microphone changes with changing pressure. The main drawback of this method, as well as of the phase one, is inability of measuring time intervals shorter than $10^{-5}-10^{-4}$ s because the cutoff frequency of a microphone frequency response is below 100 kHz.

This paper presents a description of an approach to measurements of τ_{VT} values which is a further development of the technique proposed in Ref 14.

THEORETICAL GROUND FOR THE METHOD

Usually, the frequency response of a microphone (the dependence of output signal amplitude on the frequency of input signal) is believed to have a smooth (plane) shape in the frequency range from 1 to 100 kHz, the upper boundary of this range being determined by the diameter of the microphone diaphragm. It is also believed that the shape of a microphone frequency response does not change at pressure inside the OAD cell varying from 0.1 to 760 Torr, so that time behavior of a signal at the output of a wide–band OAD amplifier is entirely governed by the pressure change inside the OAD cell. In fact, at low pressure in an OAD cell ($p \leq 100$ Torr) natural oscillations of the diaphragm induce resonances in the frequency response of the microphone. The amplitude of resonance oscillations increases with decreasing pressure.[10] If a gas in an OAD cell

is excited with a short pulse of radiation ($\tau_p \ll \tau_{VT}$) the acoustic signal from the OAD takes the form of damped oscillations at the fundamental frequency of natural oscillations of the microphone diaphragm. This fact has also been confirmed in the experiments with an additional electrostatic activator.[10]

If an OAD is assumed, according to Ref. 10, to be a multistage serial transducer of the absorbed radiation energy into an electric signal U we can write

$$U = \eta \, x(t) \, , \tag{1}$$

where η is the coefficient of the proportionality between U and the displacement of the diaphragm $x(t)$ with respect to its equilibrium position.

To find the view of $x(t)$ function, it is necessary to solve the equation of motion for a diaphragm,[8] assuming that all points of the diaphragm are moving in one and the same way

$$mS \frac{d^2x}{d\,t^2} + q\,\frac{d\,x}{d\,t} + Kx(t) = F(t) = P(t)S \, , \tag{2}$$

where m is the diaphragm mass per unit surface; S is the diaphragm area; q is the coefficient of damping; K is the flexibility of the diaphragm; $F(t) = P(t)S$ is the force applied to the diaphragm; and, $P(t)$ is a pressure change relative to the equilibrium value.

Let us consider two cases, i.e., a confined volume ($D/v_s \le \tau_m$, where D is the diameter of a cell, v_s is the speed of sound, and τ_m is the measurement time) and an open space ($D/v_s \gg \tau_m$).

In the first case, the pressure pulse $P(t)$ occurring due to absorption of a short laser pulse, $\tau_p \ll \tau_{VT}$, can be written, according to Ref. 9, in the following form:

$$P(t) = P_0 \, (e^{-t/\tau_T} - e^{-t/\tau_{VT}}) \, , \tag{3}$$

where τ_T is the characteristic time of thermal relaxation of a gas in the cell.

A solution of the equation (2) with the force (3) entering into it and the initial conditions

$$x(t) \Big|_{t=0} = 0; \quad \frac{d\,x}{d\,t}\Big|_{t=0} = 0 \tag{4}$$

is as follows:

$$x(t) = U_0\gamma + U_0 \, e^{-\beta t} \sqrt{\alpha^2 + \frac{d^2}{\omega^2}} \sin(\omega t - \varphi) \, , \tag{5}$$

where $\omega = \sqrt{\omega_0^2 - \beta^2}$; $\omega_0 = \sqrt{\dfrac{K}{m\,S}}$; $\beta = \dfrac{q}{m\,S} \ll \omega_0$;

$U_0 = \dfrac{P_0}{m}$; $\tan\varphi = \dfrac{\alpha\,\omega}{d}$; $\alpha = \dfrac{\tau_T^2}{a_1} - \dfrac{\tau_{VT}^2}{a_2}$;

$\gamma = \dfrac{\tau_T^2}{a_1} \exp\left(-\dfrac{t}{\tau_T}\right) - \dfrac{\tau_{VT}^2}{a_2} \exp\left(-\dfrac{t}{\tau_{VT}}\right)$;

$d = \dfrac{\tau_T}{a_1} (1 - \beta\,\tau_T) - \dfrac{\tau_{VT}}{a_2} (1 - \beta\,\tau_{VT})$;

$a_1 = 1 - 2\beta\,\tau_T + \omega_0^2\,\tau_T^2; \ a_2 = 1 - 2\beta\,\tau_{VT} + \omega_0^2\,\tau_{VT}^2$.

Under conditions of slow relaxation $\tau_{VT}\omega \gg 1$ and strong damping by the diaphragm ($p > 100$ Torr) $\omega_0 \ge \beta$, the expression (5) takes the form

$$x(t) = \frac{U_0}{\omega^2} (e^{-t/\tau_T} - e^{-t/\tau_{VT}}) + \frac{U_0}{\omega^2}\frac{1}{\omega\,t_{VT}} e^{-\beta t} \sin(\omega\,t - \varphi). \tag{6}$$

The second term of this expression rapidly decreases and reaches the value $1/\omega\tau_{VT}$ times lower than the first term. Under this conditions, the method of determining τ_{VT} from the duration of the leading edge of an OA signal[7,9] is preferable. The OA signal in this case resembles the pressure pulse (3), though it is modulated by an alternating component, which is fed by natural oscillations of the diaphragm. By the way, the authors of Refs. 6 and 9 relate these oscillations to higher−orders resonances of the cell.

If the relaxation is fast, i.e., when $\omega\tau_{VT} \ll 1$, and the damping effect of the diaphragm weakens ($\omega_0 \gg \beta$ at $p < 10$–100 Torr), an approximate solution (5) will take the form

$$x(t) = \frac{U_0}{\omega^2} (1 + e^{-\beta t} \sin(\omega\,t - \varphi)) \, , \tag{7}$$

where

$$\tan\varphi = \frac{\omega_0\,(\tau_T + \tau_{VT})}{1 - \omega_0^2\,\tau_T\,\tau_{VT}} \, , \tag{8}$$

where

$$\varphi = \varphi_{VT} + \varphi_T \, ; \quad \varphi_{VT} = \arctan \omega\tau_{VT}; \quad \varphi_T = \arctan \omega\tau_T \, . \tag{9}$$

It follows from Eq. (8) that phase shifts φ_{VT} and φ_T are additive and if $\omega\varphi_T \gg 1$, $\varphi_T \cong 90°$. Then we have

$$x(t) = \frac{U_0}{\omega_0^2} (1 - e^{-\beta t} \cos(\omega\,t - \varphi_{VT})) \, . \tag{10}$$

The expressions presented above are similar to the expressions derived by Slobodskaya[2,13] in 1948 for describing the phase method. However, in our case we have a pulsed radiation instead of amplitude−modulated radiation and we account for natural oscillations of the diaphragm.

At the same time, instrumental performance of the method could be difficult because in addition to the signal there appear reflections from the cell's walls at a time lag $t_1 = D/v_s$ which causes deterioration of the phase. For example, if we have a cell 3 cm in diameter and a diaphragm 0.635 cm in diameter whose natural frequency $f = \omega_0/2\pi$ is about 60 kHz, such a deterioration of the phase takes place already by the fourth period of the diaphragm oscillations. As a result, the error of φ_{VT} measurements increases.

Let us now consider the second case of an open space. According to Ref. 6, the pressure pulse can be written, neglecting the effects of walls, in the form

$$P(R,\,t) = P_0 \, e^{-t/\tau_{VT}} \int_0^T e^{T'/\tau_{VT}} \, dT' \times$$

$$\times \int_0^\infty e^{-x^2/4} J_0(Rx) \cos(T'\,x)\,x\,dx \, , \tag{11}$$

where $P(t)$ is defined by the following formula:

$$P(t) \simeq \frac{t^2}{\tau_{VT}}\, e^{-t/\tau_{VT}} \ . \qquad (12)$$

Solution of Eq. (2) having expression (12) as its right—hand side and under the initial conditions (4) is as follows:

$$x(t) = (At^2 + Bt + C)\, e^{-t/\tau_{VT}} + De^{-\beta t} \sin(\omega\, t - \varphi) \ . \qquad (13)$$

In the case of $\beta \ll \omega_0$ and neglecting the terms with t_{VT}^4, we obtain

$$x(t) = \left(\frac{\tau_{VT}^2}{(1 + \omega^2\, \tau_{VT}^2)^2}\, t^2 + \frac{4\, \tau_{VT}}{(1 + \omega^2\, \tau_{VT}^2)^2}\, t \right) e^{-t/\tau_{VT}} +$$

$$+ \frac{2\, \tau_{VT}^3}{\omega\, (1 + \omega^2\, \tau_{VT}^2)^3}\, \sin(\omega t - \varphi) \ , \qquad (14)$$

where

$$\tan\varphi = \frac{\omega\, \tau_{VT}\, (3 - \omega^2\, \tau_{VT}^2)}{1 - 3\, \omega^2\, \tau_{VT}^2} \ . \qquad (15)$$

Figure 1 shows time behavior of OA signals. The origin point of the time axis coincides with the leading edge of a laser pulse. Different time lags of OA signals observed at different pressures in a cell are explained by changing speed of sound in the cell's medium ($v_{s_{H_2O}} = 424$ m/s, $v_{s_{H_2O+air}} = 20.067\, T^{1/2}(1 + 0.275\, e/p)^{1/2} = 347$ m/s, where e is the partial pressure of water vapor, and p is the total pressure).
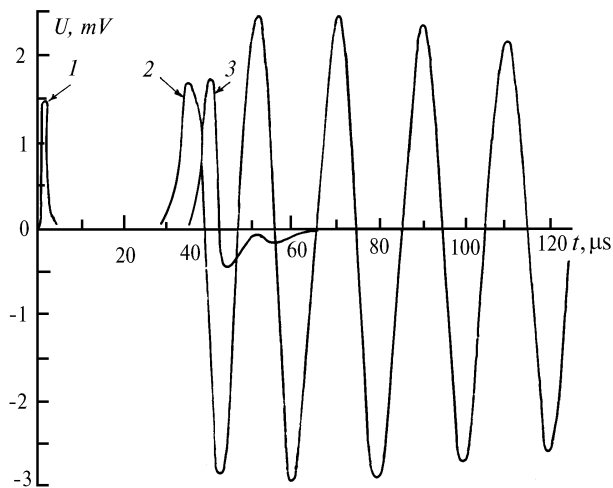

FIG. 1. *Time behavior of the electric signal from a microphone of an OAD with open—type cell and the microphone* 0.635 cm *in diameter*: $P_{H_2O} = 8$ Torr *(2)*, $P_{H_2O + air} = 740$ Torr *(3), the pulse of exciting laser radiation (1).*

EXPERIMENT

Measurements of τ_{VT} have been carried out using the proposed technique with a pulsed OA spectrometer[11] (see Fig. 2). The laser used in the experiments delivered the radiation pulses of $5 \cdot 10^{-8}$ s duration with the spectral width $\Delta v = 0.02$ cm^{-1} and 50 mJ energy per pulse. Frequency tuning of the laser emission on resonance with the H$_2$O absorption line at 14397.364 cm^{-1} from the $v_1 + 3v_3$ absorption band has been performed by varying temperature of the resonance reflector which is used as the output mirror of the laser cavity.
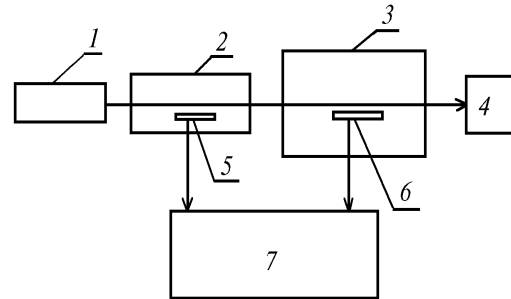

FIG. 2. *Block diagram of an OA spectrometer: 1 — laser, 2 — closed—type OA cell, 3 — open—type OA cell, 4 — power meter, 5 and 6 — capacitor microphones, and 7 — recording system.*

Laser beam was then focused with a 70—cm focal—length lens inside an OA cell. The diameter of a light spot at the focus was about 2 mm.

In this OA spectrometer, we used MK—301 Robotron microphone. Diameter of the microphone is 0.635 cm its pass band exceeds 100 kHz and the resonance frequency $f \sim \omega/2\pi$ is about 60 kHz. The signal from microphone was amplified with an amplifier having 200 to 300 kHz pass band at the amplification coefficient of 10^3. The signal was recorded with a programmable oscilloscope of 20 MHz pass band. Triggering of the recording system is performed with a pulse from FK—19 photodetector that follows the laser pulse.

In these measurements we used two OA cells: one 20 cm long and 3 cm in diameter and other 30 cm long and 30 cm in diameter. In the first cell, the microphone was mounted in a cell's wall at 1.5 cm from the laser beam axis. In the second cell the microphone could be placed at different distance from the beam axis that could be changed from 5 to 10 mm.

Investigations of the phase shift of natural oscillations of the diaphragm have been carried out for pure water vapor at pressures from zero to 6 Torr, for a mixture of water vapor and air at H$_2$O—to—air ratio of concentrations of 1/10 and the total pressure from 0 to 60 Torr, and for H$_2$O—H$_2$ mixture at pressures from 0 to 80 Torr. Prior to filling the cells with a working mixture, they were evacuated down to pressure below 10^{-3} Torr. Water vapor was injected into the evacuated cell by vaporization of doubly distilled water. The mixtures of H$_2$O with air and H$_2$ were first prepared in a mixing vessel of glass.

The data presented for each pressure value were obtained by processing ten signals stored in the memory of the oscilloscope. The phase shift was measured for each half—period with respect to time of a laser pulse emission and taking into account the time lag due to sound travel from the beam to the diaphragm f_0/v_s .

Figure 3a presents data on calculated and experimental values of the phase shift of natural oscillations of the diaphragm as a function of pressure inside the OA cell for the case of a closed cell. The same data, but for the open—type OA cell are shown in Fig. 3b.

Data calculated by formula (9) (Fig. 3*a*) and formula (15) (Fig. 3*b*) are most close to the experimental results at the following values of the parameter τ_0 :

a) closed—type cell (Fig. 3*a*)

$\tau_0 = 3.8 \cdot 10^{-6}$ s·Torr (H_2O-H_2O), $\tau_0 = 2.2 \cdot 10^{-5}$ s·Torr (H_2O-air);

b) open—type cell (Fig. 3*b*)

$\tau_0 = 1.5 \cdot 10^{-6}$ s·Torr (H_2O-H_2O), $\tau_0 = 1.8 \cdot 10^{-5}$ s·Torr (H_2O-air).

The discrepancies between τ_0 values measured in pure H_2O and in H_2O—air mixture both in (*a*) and (*b*) cases may be explained by a change of τ_T values with increasing pressure.
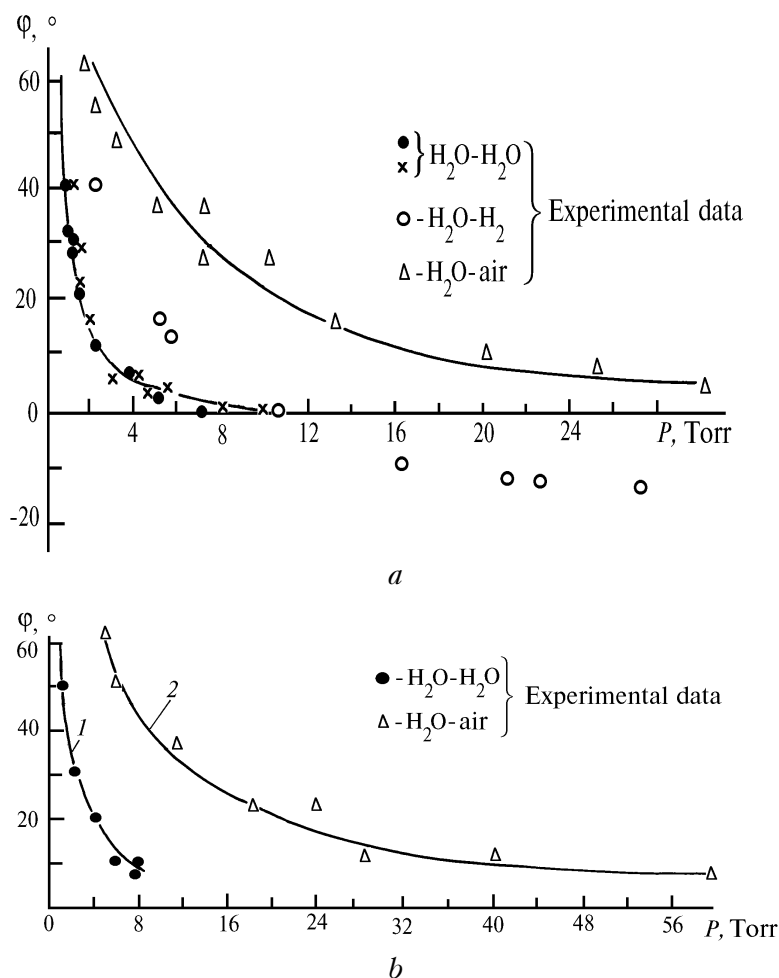

FIG. 3. Dependence of φ on the pressure in an OAD cell of open type (a), solid line corresponds to calculations by Eq. (9), and closed type (b), solid line corresponds to calculations by Eq. (15).

CONCLUSION

Thus, we have shown in this paper that under conditions when a gas at low pressure is resonantly excited in an OA cell with a short pulse of laser radiation the phase of natural oscillations of a diaphragm of a microphone used to detect acoustic signal as a function of pressure inside a cell independent of its diameter. The experiments clearly demonstrated the possibility of determining VT relaxation time of a selectively excited vibrational state of a molecule by measuring pressure dependence of the phase of natural oscillations of a microphone diaphragm. It is preferable to make such measurements using a cell of large diameter since in this case the influence of acoustic waves reflected from windows and walls of the cell is eliminated and, as a result, the accuracy of measurements increases.

The experimental results obtained in this study show new prospects in studying the relaxation times of highly excited vibrational states of molecules, when UV radiation should be used for excitation and when the influence of windows and walls increases not only because of the re—emission of absorbed UV radiation.

Use of a dual—channel optical arrangement of OA measurements with a small— and large—volume cells in the channels could enable measurements not only of VT relaxation time of a certain vibrational level of a molecule, but also assessment (from the signal coming from the small—volume cell) of the rate of deactivation of vibrationally excited molecules at the wall depending on the wall's material and quality of its surface.

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