Measurements of molecular absorption line broadening and shift induced by collisions with selectively excited buffer gas molecules. 1. Experimental setup

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We propose a photoacoustic detector with a differential Helmholtz resonant photoacoustic cell for use in studies of the broadening and shifts of the molecular rotational-vibrational absorption lines due to collisions with selectively excited molecules of a buffer gases. The design and specifications of the photoacoustic laser spectrometer including the laser source for exciting buffer gas molecules at a fixed frequency, tunable narrow-band diode laser for recording absorption line shape and characteristics, as well as the measurement technique are described.

Introduction

One of the important problems in spectroscopy of molecular interactions in gases is the collisional behavior of an absorption line shape of molecules at variations of type and state of colliding partner molecules, gas temperature and pressure, and impacts of external electromagnetic fields. A set of data on spectral line shapes, their collision width and shift allow obtaining a quantitative information on the parameters of intermolecular interaction potential, electrooptical characteristics of absorbing and buffer molecules in excited states, and collision cross sections. These data could be useful in developing the theory of molecular collisions. Analysis of relaxation processes in multi-component molecular mixtures, development of new high-precision methods of analytical spectroscopy, molecular frequency standards, as well as many other applications have an urgent need for such data.

At present, almost all experiments on studying the effect of collisions on the broadening, shift, and profile of molecular absorption lines are being conducted using a weak test field to record the line contour of molecules, undergoing collisions with buffer particles that are in the ground electron-vibrational-rotational state.[1,2] From the experimentally measured values of, for example, shift coefficients of molecular vibrational-rotational lines one can calculate the polarizability of an absorbing molecule in excited vibrational states.[3]

The experiments, which detect the influence of excitation of the buffer gas molecules on the line shape of the absorbing molecule, can help better understanding of the processes of collisions among polyatomic molecules in gases in the presence of channels of quasiresonance energy exchange and favor new methods for estimation of molecular electrooptical characteristics of both absorbing and broadening gases as functions of the excitation energy.

The goal of this work is to discuss the idea of a possible experiment and main steps of the development and realization in practice of a high-sensitive laser photoacoustic (PA) spectrometer for investigation of spectrum of weak absorption of test radiation in the presence of high-power radiation exciting the buffer gas molecules.

The experimental setup

The arrangement of the experiment on estimating the effect of collisions between excited molecules of a buffer gas with absorbing molecules, based on peculiarities of the differential PA detector (PAD) with the Helmholtz resonator is depicted in Fig. 1.

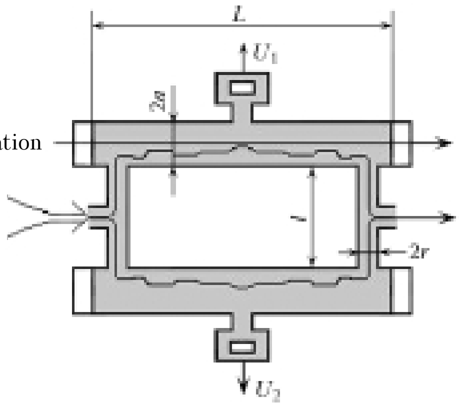

Fig. 1. The schematic layout of the photoacoustic detector with a differential Helmholtz resonator.

In the PAD, two cylindrical cells filled with gas medium under study are connected by two capillaries. A high-sensitive microphone is installed into the side

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wall of each cell. The amplitude of an electric signal U at each microphone output is described as follows

$$U = R(\omega)\, k_v W_0, \quad (1)$$

where $R(\omega)$ is the PAD sensitivity, k_v is the absorption coefficient of the gas under study, W_0 is the laser radiation power at the PAD input, ω is the modulation frequency of laser radiation.

In using a standard measurement procedure, the amplitude (or frequency) modulated laser radiation passes through only one of the PAD absorbing cells. If the modulation frequency coincides with the resonance frequency of the PAD Helmholtz resonator, then the amplitude of electric signal of the microphone in the first cell is[2]:

$$U_1 = R(\omega_p)\, k_v W_0 + U_{ns},$$

and in the second cell

$$U_2 = -R(\omega_p)\, k_v W_0 + U_{ns}, \quad (2)$$

where U_{ns} is the nonselective noise (background) signal. The difference between amplitudes of the electric signals

$$\Delta U = U_1 - U_2 = 2R(\omega_p) k_v W_0 + \Delta U_{ns} \quad (3)$$

is proportional to the absorption coefficient and the power of laser radiation entered into the PAD volume; ΔU_{ns} is the difference between nonselective noise signals, $\Delta U_{ns} \ll U_{ns}$.

As was shown in Refs. 4 and 5, even a single-pass differential PAD of Helmholtz type allows the detection limit for the absorption coefficient to be improved to 10^{-9} W · cm^{-1} · Hz$^{1/2}$ at a signal-to-noise ratio about 1 even with standard commercial microphones (Knowless, for example).

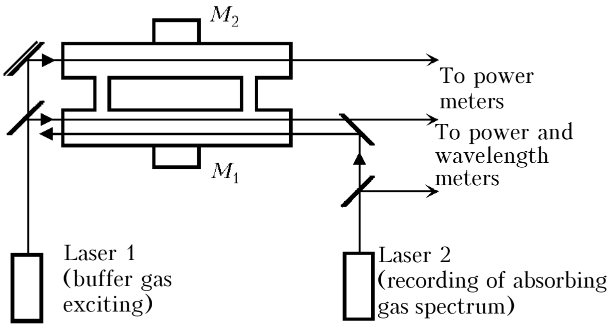

Fig. 2. Schematic layout of experimental setup.

The scheme in Fig. 2 presents the experimental setup for investigation of two-component molecular gas consisting of absorbing molecules, the absorption spectrum of which is recorded with the help of a frequency-tunable narrow-band diode laser, and buffer gas molecules excited by radiation of another laser. A sufficiently high-power discretely frequency-tunable CO_2 laser (~ 10 W) is used in the scheme. The laser's radiation beam is divided into two beams equal in power. The first beam passes the first PAD cell, while the second beam – the second one. Both of the beams excite a definite vibrational state of the buffer gas molecules in the absorption saturation mode (or close to this mode) in order to provide a stationary concentration of the excited buffer gas molecules ≈ 0.1–0.2 of the total number of molecules.

The beam from a frequency-tunable narrow-band laser passes only one PAD cell. In the case of the radiation amplitude modulation, the modulation frequency is tuned to resonance with the PAD fundamental frequency.

Then the electric signal amplitudes in the 1st and 2nd cells are:

$$\begin{aligned} U_1 &= R(\omega_p) k_v W_1 + R(\omega_p) k_{buf} W_2 + U_{ns}, \\ U_2 &= -R(\omega_p) k_v W_1 + R(\omega_p) k_{buf} W_2 + U_{ns}, \end{aligned} \quad (4)$$

and their difference is

$$\Delta U = 2R(\omega_p) k_v W_1 + \Delta U_{buf} + \Delta U_{ns}, \quad (5)$$

where k_{buf} is the absorption coefficient for pumping radiation absorption by buffer gas molecules; ΔU_{buf} and ΔU_{ns} are the differences between signals, corresponding to pumping laser radiation absorption by the buffer gas and noise (background) signals in the 1st and 2nd cells; $\Delta U \gg \Delta U_{buf}$; ΔU_{ns}, and $W_1 \approx W_2$.

Experimental setup (main blocks)

The key elements of the experimental setup are: pulse-frequency CO_2 laser for exciting buffer gas molecules; narrow-band wavelength-tunable near IR diode laser; PAD with differential Helmholtz resonator. Describe briefly the designs of these systems and their main characteristics.

Waveguide CO_2 laser with a discrete wavelength-tuning

The laser housing (tube) is made from stainless steel. It serves a vacuum shell and a base for the optical resonator. Flanges are welded to both ends of the housing, which bear the laser optical elements with vacuum-tight seals.

The metal-ceramic waveguide of the laser (2.2 × 2.2 × 450 mm) is formed of two plane electrodes made from oxidized aluminum and two plane plates made from polished leucosapphire. The lower electrode is connected to the housing; it has a zero potential and is cooled with running water. The upper electrode is insulated from the housing and is cooled due to high heat conductivity of the leucosapphire plates. By applying a high-frequency (HF) voltage to the upper electrode, a capacitive discharge is initiated in the waveguide, which is used to excite the laser gas medium. To equalize the intensity of the HF-field, several inductances are coupled in some places along the electrodes in parallel with them. The HF-generator and loading impedances are matched via a matching circuit. The emission of metal-ceramic waveguide-lasers has linear polarization, whose vector is directed in parallel with the metal electrodes.

To build up the cavity of the tunable waveguide laser an antireflection coated planoconvex lens from

ZnSe was used, instead of a spherical mirror. Its focal length is about doubled relative to that of the corresponding mirror. At a distance of $z_1 = 35$ mm behind the lens, a plane reflecting diffraction grating is set operating in the autocollimation mode. The reflectance of the plane output mirror is 0.96. The cell length is 66 cm, which corresponds to the intermode interval $c/2L = 227$ MHz.

The laser's diffraction grating has a gold coating with a period of 150 mm^{-1}. The efficiency of the grating reflection in the first order of diffraction relative to the incident power is 0.93–0.95 for *s*-polarization.

The grating is installed in the precision rotation unit of a lever type with a lever's length of 80 mm. The grating is rotated with the help of a commercial linear pusher with a stepper-motor drive (8MS00-25 model, EKSMA Co.). The drive parameters are: total stroke of 25 mm, microscrew step of 0.25 mm, 200 steps per turn. Mechanical transmitters of the initial and end positions are installed into the linear pusher, although their accuracy is only about ± 5 steps. To improve the accuracy in determining the zero position of the grating, an optical detector is installed on the drive's shaft, whose positioning accuracy is 1 step. Thus, the angular step of the grating rotation is $\Delta\varphi \approx 16$ μrad/step, that allows a high-precision positioning when tuning the laser emission to generation lines. The pumping laser specifications are given below.

Operation mode	Continuous, pulse-periodic
Spectral range of radiation for $^{12}C^{16}O_2$ isotope, μm	9.2–10.8
Radiation power (W) at lines:	
strong	3–5
weak	no less than 1
Number of radiation lines	no less than 60
Radiation mode	single-mode, single-frequency
Radiation polarization	Linear
Output beam diameter, mm	2
Divergence (full, e^{-2}), mrad	9–10
Power of the pumping HF-generator, W	150
Cooling (emitter + HF-generator)	Water, 2 l/min
Feed/power consumption, V/W	+24/400
Overall dimensions:	
emitter, mm	840×90×150
pumping HF-generator, mm	433×100×42
Weight:	
emitter, kg	10
pumping HF-generator, kg	3

Diode laser for recording the spectra

To record a spectrum and individual absorption line profile, a Sacher Lasertechnik TEC-100 diode laser with exterior cavity is used, operating in the continuous wavelength-tuning mode. Roughly, the range of the wavelength variation is 10–90 nm. In the narrow subranges of the range (0.3–0.5 nm) the wavelength tuning is smooth. The radiation output power at 1.63 μm wavelength reaches 10 mW. Single-mode spectrum width is 10^{-4} cm^{-1}. The laser's wavelength range is 1.595–1.65 μm.

PA detector (PAD) with a differential Helmholtz resonator

The PAD with a differential Helmholtz resonator (DHR) is shown in Fig. 1. It consists of two identical cells with $2a = 7.2$ mm diameter and 150 mm length, connected by similar capillaries ($2r = 5$ mm diameter and 100 mm length). Windows, made from BaF_2 or ZnSe, are vacuum-fitted to the ends of the cells. The filling and evacuation of the PAD is performed through pipes located in the middle of the capillaries. The Knowless EK3027 microphones are installed at the PAD walls. The microphone sensitivity is 20 mV/Pa. The PAD design is described in detail in Ref. 4.

Figure 3 presents the normalized calculated and experimental dependences of the PAD sensitivity on the modulation frequency.

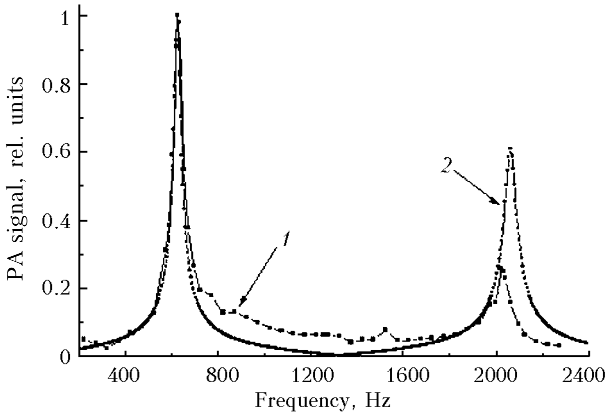

Fig. 3. Normalized dependence of PAD sensitivity on modulation frequency of laser radiation: experiment (*1*); calculation (*2*).

Within the frequency range from 200 to 2300 Hz, two resonances were observed. The width at half-maximum of the most intense resonance was 60 Hz at 627 Hz frequency. The width at half-maximum of the second resonance was 120 Hz at 2020 Hz frequency, and its intensity was three times lower.

The DHR concentration sensitivity is described by the expression[4]:

$$C_{\min} = \Lambda\Delta f^{1/2}/(W_0\sigma), \tag{6}$$

where $\Lambda = (U_n^2)^{1/2}/R$, W · cm^{-1} · Hz$^{1/2}$; $(U_n^2)^{1/2}$ is the root-mean-square value of the PAD noise intensity, V; R is the detector sensitivity, V · W^{-1} · cm; Δf is the transmission band width, Hz; σ is the absorption cross section of the gas molecules.

The PAD threshold sensitivity is $3\cdot 10^{-9}$ W·cm^{-1} × Hz$^{-1/2}$. For gas media absorbing CO_2-laser radiation, such as ethylene, ammonia, sulfur hexafluoride, this sensitivity provides detection at the level of the absorption coefficients ~10^{-9} cm^{-1}.

Conclusion

The photoacoustic detector with differential Helmholtz resonator allows detection of weak absorption line profile against a nonselective background, which exceeds by several orders of magnitude the selective signal from the absorption line. Having in mind this property of the PAD, we propose a new experimental approach to determine the effect of vibrational excitation of buffer gas molecules on the magnitude of the absorbing line shift induced by collisions. The designed laser spectrometer provides a resolution of 10^{-4} cm^{-1} and a minimum detectable absorption coefficient of $\leq 10^{-9}$ cm^{-1}.

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