Volume 7, Number 3
1004-423X/98/07030190-06

ACTA PHYSICA SINICA
(Overseas Edition)

March, 1998
©1998 Chin. Phys. Soc.

PHOTO-ACOUSTIC MEASUREMENTS OF WATER VAPOR ABSORPTION COEFFICIENT IN UV SPECTRAL REGION

B. A. TIKHOMIROV, V. O. TROITSKII, V. A. KAPITANOV, G. S. EVTUSHENKO, and Y. N. PONOMAREV

Institute of Atmospheric Optics SB RAS. 1 Akademicheskii av., Tomsk 634055, Russia

(Received 9 August 1996; revised manuscript received 26 September 1997)

Data on the absorption coefficient of H_2O in binary mixture with N_2 in UV region of spectra are presented. With the use of the high sensitivity photoacoustic spectrometer, the following values of the absorption coefficient were found: $2.3\times10^{-9}cm^{-1}\cdot Pa^{-1}$ ($\lambda=255$ nm), $0.9\times10^{-9}cm^{-1}\cdot Pa^{-1}$ ($\lambda=271$ nm), and $1.6\times10^{-9}cm^{-1}\cdot Pa^{-1}$ ($\lambda=289$ nm).

PACC: 4337G; 7840; 4390

I. INTRODUCTION

The sun-blind region of wavelengths ($\lambda=250-320$ nm) is prospective for development of remote sensing of the small gas components of the atmospheric air. In particular, the frequency doubled copper vapor laser with the wavelengths 255, 271 and 289 nm is used for ozone remote sensing by the differential absorption technique.[1]

The quantitative data on the absorption and radiation spectra of the gas components under study as well as origin of these spectra are of great significance.

A new band of H_2O absorption spectra discovered in the range of 250 – 320 nm was described in Ref. [2] Then an existence of that band was confirmed experimentally with the use of the laser and other spectrophotometers.[3,4]

It was found[2,3] that the H_2O absorption band has a maximum near the wavelength of 270 nm. The value of the maximal absorption coefficient measured by the fluorescence technique is $\kappa\sim10^{-9}cm^{-1}\cdot Pa^{-1}$; the same value measured by the spectrophotometric technique is $\kappa\sim(1.4-2.2)\times10^{-8}cm^{-1}\cdot Pa^{-1}$. A disagreement in these experimental data can be caused by ignoring of nonradiative channel of energy transfer when analyzing the H_2O fluorescent measurements and by attenuation of radiation due to absorption by the water vapor molecules adsorbed at the surfaces of windows and mirrors in the multipath cells used in the spectrophotometers.

It is known that the photoacoustic (PA) method of spectroscopy is applied to measure the absorption of laser radiation in gas due to radiationless relaxation of excited molecules. A goal of the present work is to measure the water vapor absorption coefficients at the wavelengths of 255, 271 and 289 nm for the binary mixtures of H_2O with N_2 and H_2 using the PA technique.

II. EXPERIMENTAL SETUP

The experimental setup is presented in Fig. 1. The spectrometer consists of the

copper vapor laser with the nonlinear β-BaB_2O_4 crystal which allows UV radiation with power up to 30 mW to be obtained when the pumping power is ~1 W, photoacoustic detector (PAD) with the vacuum system for preparing gas mixtures, PA calorimeter, and electronics to record the signals.

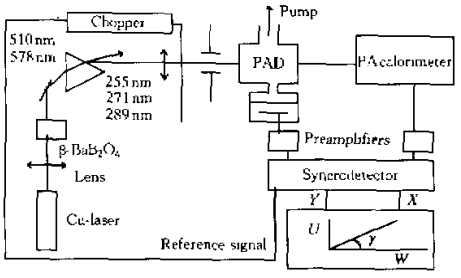

Fig. 1. Experimental setup.

Special features of the spectrometer are the following:

1. For strict control of the PAD microphone sensitivity the electrode-activator[5] was used in the microphone design.

2. Quartz transparent to UV radiation was chosen experimentally as a material for the windows.

3. The electronic system consists of two similar channels with the synchrodetectors having the same integration times for amplification and recording of the signals from the PAD and calorimeter. The signals from the synchrodetector outputs are applied to the inputs "X" and "Y" of the plotter. The values of the absorption coefficient were determined after calibration of the spectrometer when measuring a linear dependence of the PAD detector signal amplitude U on the PA calorimeter signal amplitude W, $\tan\gamma = U/W$. Such a procedure of signals recording allowed us to reduce essentially a spectrometer noise caused by instability in the copper vapor laser power W.

The PAD was calibrated by measuring the PA signal amplitude for CH_4-N_2 mixture with well known value of κ at 3392 nm wavelength using He-Ne laser. Relative concentration of CH_4 in the mixture was equal to 7.22×10^{-3}. The value of the determined PAD sensitivity at CH_4-N_2 pressure of 1.33×10^4 Pa and technical parameters of spectrometer are shown in Table 1. We assume, that if the pressure of absorbing gas (CH_4 or H_2O) is much smaller than the pressure of the buffer gas and the total pressure of gas mixture under study is about of 1.33×10^4 Pa (in this case the collisional relaxation dominates over the radiational one), then the sensitivity of PAD does not depend on the type of absorbing molecules. In the experiments with the copper vapor laser we used the same value of PAD sensitivity determined in the experiments with the He-Ne laser. This assumption is available for the low pressure range ($<10^3$ Pa) when the radiational and collisional relaxation become comparable.

Table 1. Specifications of the PA spectrometer.

Parameter	Value
Mean output power/mW, at 255, 271 and 289 nm	30
Laser pulse repetition rate/kHz	5
Pulse duration/ns	20
PAD sensitivity/(V·cm W^{-1}), at 1.33×10^{4} Pa of pressure	335
Limit detectable value of κ/cm^{-1}	5×10^{-4}
Chopper frequency f/Hz	27
Integration time/s	10
PA cell dimensions:	
Diameter/mm	15
Length/mm	100
Range of gas pressure variations inside the PA cell/Pa	10^{-1} – 10^{5}
Absolute accuracy of measurements of κ/%	≤25

III. MEASUREMENTS OF H_2O ABSORPTION COEFFICIENT

Before the measurements, the PA cell was evacuated up to 10^{-1} Pa. The background PA signal was detected at the wavelengths of 255, 271 and 289 nm when the PA cell was filled with pure N_2 or H_2. Then the measurements were repeated for the binary mixtures of H_2O with N_2 or H_2.

Figure 2 gives the plot of PA signal in the relative units over the pressure range of $0-1.33\times10^{4}$ Pa for pure N_2 and mixture H_2O-N_2. The absolute values of absorption coefficient of H_2O in mixture with N_2 were found using the formula

$$\kappa = \frac{U_1 - U_0}{W_o} = \frac{1}{\alpha}|\tan(\gamma_1) - \tan(\gamma_0)|,$$

where α is the value of PAD sensitivity at the pressure of 1.33×10^{4} Pa, U_0 and U_1 are the amplitudes of PA signals when the cell is filled with 1.33×10^{4} Pa of pure N_2 and with 1.33×10^{4} Pa of the mixture H_2O-N_2, respectively.

It was found that for the binary mixture of water vapor with N_2, the absorption coefficient κ has the following values: 2.3×10^{-9}cm$^{-1}\cdot$Pa^{-1}($\lambda=255$ nm); 0.9×10^{-9} cm$^{-1}\cdot$Pa^{-1}(271 nm), and 1.6×10^{-9}cm$^{-1}\cdot$Pa^{-1}(289 nm) with the uncertainty about 25%.

The background PA signal with high amplitude was produced by the absorption of the cell window in UV radiation region. This absorption consists of two components: the absorption at the window inner surface and in the window volume. A value of the background signal was not stable for the windows made of Ba F_2 or Ca F_2 and was stable enough for the windows made of quartz. We connect the instability of the background signal with absorption of gas molecules at the inner surface of the cell windows. When evacuating the cell, molecules are removed comparatively easy from the surface of the

quartz windows. The windows made of BaF_2 or CaF_2 could not be totally cleared of the adsorbed gases. When the radiation was directed to the polished cell wall, the background signal was not increased apparently. The increase of the background signal value with the decrease in the radiation wavelength (see Fig. 2) is assumed to be due to the spectral dependence of the coefficient of volume absorption in the quartz windows of the cell.

This absorption increases with the decrease of the wavelength within the considered spectrum region and also induces the background signal. The transmission of evacuated PA cell with the quartz windows was established to be the similar function of wavelength as the background signal.

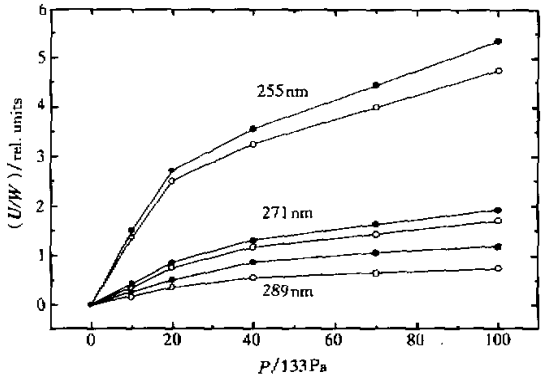

Fig. 2. PA signal as a function of gas pressure in the cell with quartz windows.
• : Mixture of H_2O (7.5%) and N_2 (92.5%), ○ : N_2 (100%).

We have obtained the same experimental data for H_2 and mixture H_2O-H_2. The background signal recorded for N_2 was one-third of the signal for H_2. It can be explained by the fact that the nitrogen thermal conductivity is one-seventh of the hydrogen one. An amplitude of the PA signal did not increase with rising of H_2O in the mixture H_2O-H_2. Since the nitrogen heat capacity was one-fourteenth of the hydrogen one, and the PA signal amplitude due to radiation absorption in the gas volume was inversely proportional to the gas heat capacity in the cell[5], we could not record an increase in the PA signal with rising H_2O in H_2.

All these results indicate that the difference between the values of the PA signal for the mixture H_2O-N_2 and for pure N_2 is connected with the absorption of UV radiation by H_2O molecules. As distinct from the data of Refs. [2, 3], we obtain a minimum of the absorption coefficient for the wavelength 271 nm. Values of the absorption coefficient obtained in our experiments coincide in the same order of magnitude with the data of Ref. [2] and are one-tenth of the values of the absorption coefficient obtained by the spectrophotometric technique in Refs. [3, 4].

Note, the spectrophotometric measurements, strictly speaking, allow the total

attenuation of radiation in the multipath cell to be measured except the loss at the mirror surfaces, absorption, and scattering in the gas. Parameters of the discovered H_2O absorption band were calculated in Ref. [2] from the signal of fluorescence in assumption that collisional extinction of fluorescence was absent. In the present paper the sensitivity of PAD, determined from the direct measurements of IR radiation absorption, can not be applied for correct calculation of the absorption coefficient within the UV region. For the IR region arising of PA signal in the mixture CH_4-N_2 is due to absorption of radiation at the vibration-rotational transition and subsequent complete collisional relaxation of molecules, but in UV region the PA signal may be also connected with two-photon dissociation of water vapor molecules[6] and absorption of radiation by molecules of radical OH.[7] All these facts can induce the distinction between the data obtained in Refs. [2–4] and in the present paper.

In the future, to increase an accuracy of measurement of absorption by molecular gases in the UV region using the spectrophone, it is necessary to separate the PA signal connected with absorption in the gas volume from the other components, for example, using the PAD with the space-time resolution of the PA signals.

IV. CONCLUSION

Absorption of UV radiation by water vapor in the binary mixtures with N_2 and H_2 at the wavelength 255, 271 and 289 nm was detected and measured by PA spectroscopy. On the basis of comparison of the experimental values of the PA signal obtained for the pure gases N_2 and H_2 and their binary mixtures with H_2O, it was shown that increasing in the amplitude of the signals in the mixture H_2O-N_2 as compared with the amplitude for the pure N_2 was connected with absorption of radiation by water vapor. The PA measurement data on the absorption coefficient at the wavelength 255, 271 and 289 nm for water vapor in the mixture with N_2 are in conformity with the results obtained by the laser fluorescent technique in the same order of magnitude and do not agree with the results of spectrophotometric measurements. The data on the spectral dependence of the absorption coefficient for H_2O, obtained by the PA technique, distinguish from the results of spectrophotometric and fluorescent measurements. It was shown that, when a weak absorption of molecular gases in UV spectral region was measured using the spectrophone, the main problem of experiment was the presence of the background signal caused by absorption of radiation by the cell windows. To solve this problem, we propose to use the pulse lasers of UV region and PA technique with the space-time resolution of the PA signals.

REFERENCES

[1] V.D.Burlakov, V.V.Zuev, G.S.Evtushenko, M.Y.Kataev, S.V.Smirnov and V.O.Troitskii, *Atmospheric and Oceanic Optics*, **7** (1994), 1614.

[2] V.M.Klimkin and V.N.Fedorishchev, *Atmospheric and Oceanic Optics*, **2**(1989), 220.

[3] S.F.Luk'yanenko, T.I.Novakovskaya and I.N.Potapkin, *Atmospheric Optics*, **3**(1990), 1190.

[4] Y.N.Ponomarev and I.S.Tyryshkin, *Atmospheric Optics*, **6**(1993), 360.

[5] A.B.Antipov, V.A.Kapitanov, Y.N.Ponomarev and V.A.Sapozhnikova, Opto-acoustic Method in Laser Spectroscopy of Molecular Gases(Nauka, Novosibirsk, 1984).

[6] C.C.Wang and L.D.Davis, *J. Chem. Phys.*, **62**(1975), 53.

[7] L.A.Kuznetsova, N.E.Kuz'menko, Y.D.Kuzjakov and Y.A.Plastinin, Probabilities of Optical Transitions of Diatomic Molecules. Edited by R.V.Khokhlov (Nauka, Moscow, 1980).