LIGHT ABSORPTION BY AIR AND WATER VAPOR IN THE TRANSMISSION MICROWINDOWS IN THE NEAR IR AND VISIBLE SPECTRAL RANGES

V.A. Kapitanov, Yu.N. Ponomarev, and I.S. Tyryshkin

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk Received July 21, 1997

We present the estimates of absolute cross-sections of light absorption by air and water vapor at laser wavelengths from 0.53 to $1.06 \mu m$. The measurements were performed under controllable conditions using laser spectrometers with long-path cells and high sensitive photoacoustic laser spectrometers.

The problem of anomalous absorption of shortwave radiation in clouds is widely discussed in literature in connection with the climatic models. One of the hypotheses is related to the influence of continuous water vapor absorption. Moreover, the measurements of optical radiation extinction within a wide range from 0.4 to $2.5\;\mu m^{1,2}$ along open atmospheric paths, when excluding the contributions of extinction (measurements aerosol at large meteorological visual ranges) and selective absorption (based on the available banks of spectral lines) have shown value of aerosol extinction to be directly proportional to water vapor concentration, that enabled the authors to evaluate the value of the continuous absorption cross-section.

The measurements under laboratory conditions, when the composition, temperature and pressure of gas medium are controlled and no aerosol component occurs, make it possible to obtain more reliable quantitative results on nonselective absorption of optical radiation by molecular atmospheric components in the transmission microwindows.

In this paper we describe some results of measurements of atmospheric absorption coefficients using laser radiation at some wavelengths in the range from 0.5 to $1.35 \mu m$. These measurements are performed using a highly sensitive methods of laser spectrophotometry and laser optoacoustic spectroscopy.

EXPERIMENTAL TECHNIQUE AND MEASUREMENT PROCEDURE

The measurements of continuous absorption cross sections in gases using the optoacoustic technique are difficult because the signal of optoacoustic detector (OAD) U independent of the radiation source frequency is equally due to the continuous absorption by gas $U_{\rm cont}$ and the absorption of transmitted and scattered radiation by the OAD cell walls and windows $U_{\rm b}$ (Ref. 3).

The level of the background signal $U_{\rm b}$ for the majority of OAD constructions is rather large and the value of equivalent absorption coefficient

 $K_{\rm b} = U_{\rm b}/(\alpha W) \ge 10^{-7} {\rm cm}^{-1}$, (α is the sensitivity of OAD, [V/(W · cm⁻¹)], W is the radiation power, [W]) considerably exceeds the OAD threshold sensitivity expressed in terms of the absorption coefficient $K_{\rm th}(v) = \sqrt{U_{\rm n}^2}/(\alpha W) \ge 3 \cdot 10^{-8} - 4 \cdot 10^{-9} {\rm cm}^{-1}$ (Refs. 3 and 4) (where $U_{\rm n}^2$ is the rms value of noise, V²). In the general case U as a function of radiation frequency v, cm⁻¹, total pressure in the OAD cell P, Torr, and number density of absorbing molecules N, cm⁻³, can be represented as

$$U = \alpha \ W \left[\sigma_{sel}(v, P) \ N + \sigma_{cont}(P) \ N + K_{b}(P)\right], \tag{1}$$

where $\sigma_{sel}(v, P)$ and $\sigma_{cont}(P)$ are the cross sections of selective and continuous absorption, cm^2 .

At a constant pressure of the mixture in OAD cell, P = 0.5-1 atm (the buffer gas pressure is much higher than the absorbing gas pressure), the OAD signal Udepends linearly on the number density of absorbing molecules N and the slope angle of the function U(N)is proportional to the sum of the cross sections of selective and continuous absorption When using narrow band $[\sigma_{sel}(v, P) + \sigma_{cont}(P)].$ tunable lasers the contribution of selective absorption can be decreased by choosing the proper portion of spectrum, far from the absorption lines. In the case of untunable lasers the contribution can be taken into account based on the high resolution spectra available.

The methods described enable us to exclude the background signal and to provide the measurements of continuous absorption with the threshold sensitivity at the level of $3 \cdot 10^{-8} - 4 \cdot 10^{-9}$ cm⁻¹.

Measurements of the cross sections of continuous water vapor absorption were carried out with the use of optoacoustic spectrometers with the ruby ($0.6942-0.6944 \mu m$) and dye ($0.567-0.597 \mu m$) lasers. A detailed description of the spectrometer principle of operation as well as the calibration and measurement procedures are given in Refs. 3 and 4. In all the measurements performed it has not been possible to record the dependence of the OAD signal on water vapor concentration. Figure 1 presents the absorption spectrum of moist and dried air.



FIG. 1. Absorption spectrum of atmospheric air in the range of the ruby laser temperature tuning. P = 300 mm Hg, (•) correspond to $N_{\text{H}_2\text{O}} = 5.5 \text{ g/m}^3$ and (+) to dried air; the background level is denoted by the dashed curve.

Laser spectrometers with the long-path 30 m and 110 m cells⁵ were used for measurement of absolute values of air absorption at the wavelengths of the following radiation sources: Nd:YAG-laser (1.064 μ m) and its second harmonic (0.532 μ m); ruby laser (0.69 μ m); copper–vapor laser (0.52 μ m; 0.57 μ m).

The radiation spectrum width (Δv) of Nd:YAGlaser and copper-vapor laser did not exceed 0.01 cm⁻¹, as to the ruby laser, $\Delta v \leq 10^{-3}$ cm⁻¹, whose frequency was tuned within $\sim 10 \text{ cm}^{-1}$ limits. The cell was filled with the air using a pipeline through a filter directly from the atmosphere. The air humidity was measured by an aspiration psychrometer of MV-4m type. The measurements were performed at partial pressures of water vapor from 5 to 15 Torr. If the partial pressure of water vapor in the cell was less than the given pressure, before pumping the air to the cell, the water vapor are pumped to the cell using the technique described in Ref. 5 to make the water vapor pressure equals to the given pressure. The filter for air cleaning is a container filled with a hygroscopic wadding, about 2 cm thick layer. The two-layer batiste spacers are located on both sides of the wadding layer.

The gas transmission value is determined from the expression

$$T = (I^{\text{out}} / I^{\text{in}}) / (I^{\text{out}}_{0} / I^{\text{in}}_{0}),$$
(2)

where the indices "out" and "in" correspond to the intensity values at the input and output of the cell, and 0 corresponds to the measurements of the same values at the cell being completely evacuated. The absorption coefficient is determined according to the "ouguer law.

The systems used for intensity recording at the cell input and output as well as the values of the optical path obtained (≤ 4 km) enabled us to record the values of absorption coefficients $K_{\rm cont} \geq 10^{-7}$ cm⁻¹.

The measurements showed that in the range of the ruby laser wavelength tuning from the water vapor

absorption line center ($\lambda = 694.38$ nm) by 5 and more halfwidths as well as at the wavelengths of the above mentioned lasers the value of the cell transmission does not depend on partial pressure of water vapor.

The threshold sensitivity, expressed in terms of the absorption coefficient of optoacoustic spectrometers and spectrophotometers, is much less than 10^{-7} cm⁻¹, and since in all the measurement series the dependence of absorption or transmission on water vapor concentration is not recorded, we can consider the value of the cross sections of continuous water vapor absorption $\sigma_{\rm cont} \leq 0.010$ g⁻¹cm².

The estimates of the absorption cross-section values at all the wavelengths used, as compared to that from Ref. 1 and 2 are given in Fig. 2. These values are half as many values as presented in Ref. 2, and the obtained in Ref. 2 directly proportional dependence of radiation extinction on the water vapor concentration, in our opinion, cannot be explained by the influence of water vapor continuous absorption.



FIG. 2. The atmospheric air absorption cross-sections from Ref. 1 (•), from Ref. 1 with the account for selective absorption (\circ), from Ref. 2 (), and the data presented by the authors (Δ).

REFERENCES

1. C. Tomasi, R. Guzzi, and O. Vittory, J. Atm. Sci. **31**, 255–260 (1974).

2. M.V. Panchenko, V.E. Zuev, S.D. Tvorogov, V.N. Uzhegov, S.I. Nesmelova, Yu.A. Pkhalagov, O.". Rodimova, and N.N. Shchelkanov, ARM, CHAMMP Science Team Meeting, San Antonio, Texas, 1997. 3. A.". Antipov, V.A. Kapitanov, Yu.N. Ponomarev, and V.A. Sapozhnikova, *Optoacoustic Method in Laser Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1984), 128 pp.

4. ".V. "ondarev, V.A. Kapitanov, S.M. Kobtsev, Yu.N. Ponomarev, Opt. Atm. **1**, No. 1, 18–24 (1988).

5. V.N. Aref'ev, V.P. Lopasov, M.M. Makogon, L.N. Sinitsa, A.M. Solodov, and I.S. Tyryshkin, *Applied Spectroscopy of the Atmosphere* (Tomsk, 1988), 262 pp.