

STUDY OF THE H₂O VAPOR ABSORPTION SPECTRUM IN THE REGION 270–330 NM

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The long-wavelength wing of the H₂O absorption band of H₂O is investigated in the region 270–330 nm with the help of a tunable laser with a linewidth of 0.03 nm and a multipass cell, and the absolute values of the absorption coefficients are determined.

One of the most promising directions for further progress in laser sounding of trace gaseous impurities in the atmosphere is, as is well known, the utilization of the solar-blind range of wavelengths (250–320 nm). In this connection it is very important not only to have a quite accurate knowledge of emission (absorption) spectra of the gaseous components of interest but also to study the spectra and parameters of optically active noise due to laser pumping¹.

It has usually been assumed that in the near-UV there is no appreciable absorption (emission) by atmospheric water vapor excited in a one-photon process.¹ However Klimkin and Fedorishchev discovered² in lidar experiments with a KrF* laser in the region 280–400 nm a wide fluorescence band which they interpreted as a fluorescence band of H₂O. They later established³ that the fluorescence in this region corresponds to a wide absorption band of water vapor in the region $\lambda < 320$ nm. Klimkin et al.⁴ made a detailed study of the long wavelength wing of the new absorption band of H₂O by the method of excitation spectroscopy and they established that it has a diffuse structure.

This work is devoted to a direct determination of the absorption spectrum discovered in Ref. 2–3 of the spectral band of water vapor with the help of a narrow-band tunable laser and a multipass gas cell.

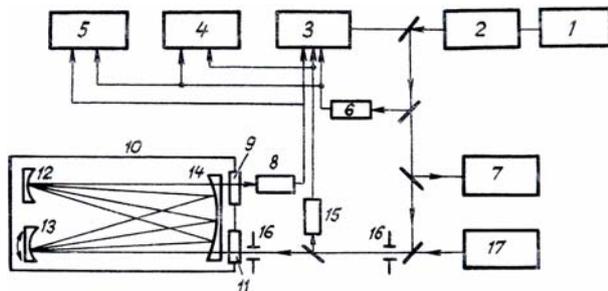


FIG. 1. Schematic diagram of the experimental arrangement.

Figure 1 shows a diagram of the experimental arrangement. The frequency-doubled radiation of the

dye laser 2, pumped by the second harmonic of a YAG laser 1, was directed through a diaphragm 16 and the quartz windows 9 and 11 into a multipass cell 10 with a 2.2 m baseline. The cell was equipped with a White optical system, consisting of three aluminum-coated mirrors 12–14 with identical radii of curvature (~ 2 m). The optical path L_p in the cell was changed from 8 to 160 m by rotating one of the mirrors (13).

The laser pulses (20 ns duration) at the input and output of the cell (the reference channel I_0 and the probe channel I, respectively) were recorded with FEU-100 photomultipliers 15 and 8, observed on a C1-74 dual-beam oscilloscope 3, and separated and recorded with two V9-5 gated digital voltmeters 4 and 5 with a ~ 4 ns gates. The oscilloscope 3 and the voltmeters 4 and 5 were triggered with pulses from a third photomultiplier 6. The multipass cell was aligned with the help of an He-Ne laser 17. The optical path of the beam in the cell L_p was determined from the number of reflections of the radiation of this laser on the collection of mirrors 14 and monitored based on the delay time of the reference signal I_0 and probe signal I on the oscilloscope 3. In our experiments usually $L_p = 104$ m.

The wavelength of the liquid laser was measured with the help of a small MUM diffraction monochromator 7 with a photoelectronic detector whose wavelength scale was referenced beforehand to the emission lines of a mercury lamp. For 0.05 mm wide input and output slits of the monochromator the absolute error in determining the wavelength did not exceed 0.2 nm. The laser operated with a repetition frequency of 12.5 Hz and a per pulse energy of 10–15 μ J. The use of two dyes (rhodamin 6G and 6-aminophenalenone) made it possible to obtain a spectral operating range of 270–330 nm. The width of the emission line $\sigma\lambda$ measured with the Fabry-Perot etalon did not exceed 0.03 nm.

The experimental procedure was as follows. Prior to each measurement of the absorption coefficient the cell 10 was evacuated to a pressure of $\sim 10^{-2}$ torr, and the values of the recorded reference signal I_0 and probe signal I were equalized ($I/I_0 \sim 1$) by adjusting the voltages of the photomultipliers 8 and 15.

After this the values of I/I_0 were selected based on 15–20 realizations, and their average value $\langle I/I_0 \rangle_0$ and variance σ_{I/I_0}^0 were determined. Then after H_2O vapor was injected the corresponding values of $\langle I/I_0 \rangle_{H_2O}$ and $\sigma_{I/I_0}^{H_2O}$ were determined. The absorption coefficient K was calculated from the formula

$$k = [\ln \langle I/I_0 \rangle_{H_2O} - \ln \langle I/I_0 \rangle_0] / L_p$$

The variance of the ratios of the intensities of the reference and probe signals σ_{I/I_0}^0 and $\sigma_{I/I_0}^{H_2O}$ did not exceed 2–3% in the experiments. The error in determining K varied from 10 to 50%, depending on the value absorption coefficient.

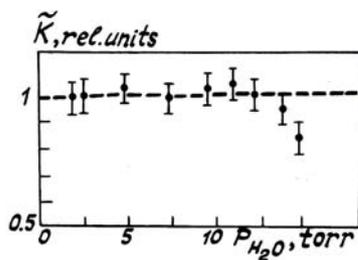


FIG. 2. The normalized absorption coefficient of H_2O at $\lambda = 277.8 \text{ nm}$ ($\tilde{K} = k / P_{H_2O}$). As a function of the total water vapor pressure P_{H_2O} . $T = 21^\circ\text{C}$ and $L_p = 104 \text{ m}$.

Before studying the absorption spectrum of H_2O performed methodological experiments associated

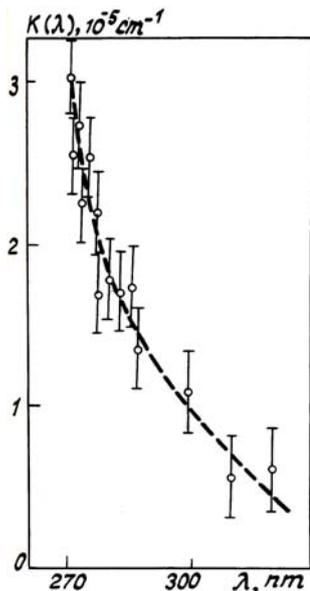


FIG. 3a. The values of the absorption coefficient at $P_{H_2O} = 10 \text{ torr}$ for wavelengths in the $\lambda \in [270, 330] \text{ nm}$. $L_p = 104 \text{ m}$ and $T = 21^\circ\text{C}$.

with the possible effect of beam deflection at the cell outlet, which could happen when gas is injected (owing to the change in the refractive index) and with variations of the transmission of the cell due to changes in the reflection coefficients of its mirrors owing to settling of H_2O molecules on them, on the indications of the photomultiplier. Measurements of the ratios $\langle I/I_0 \rangle$ as a function of the pressure of dried nitrogen gas injected into the cell (at a fixed wavelength λ) showed that, at least up to pressures $N_2 - P_{N_2} \sim 400 \text{ torr}$ the values of $\langle I/I_0 \rangle_{N_2}$ were stable within the limits of error of the experiment. Figure 2 shows the absorption coefficient of H_2O at the wavelength $\lambda = 277.8 \text{ nm}$, scaled to unit pressure ($K = K / P_{H_2O}$), as a function of the total pressure P_{H_2O} in the cell and the temperature of the surrounding medium $T \sim 21^\circ\text{C}$. These experiments showed that the value of \tilde{K} remained practically constant (i.e., the absorption coefficient of water vapor increased linearly with the increase of P_{H_2O}) at least up to pressures $P_{H_2O} \leq 12 \text{ torr}$. For pressures $P_{H_2O} \geq 15 \text{ torr}$ the reduced absorption coefficient decreased (owing to an increase in the reflection coefficient of the mirrors). The absorption spectrum of water vapor was then studied at $P_{H_2O} = 10 \text{ torr}$.

The values of the absorption coefficient $K(\lambda)$ measured in the range 270–330 nm are presented in Fig. 3a. As in Ref. 4, the maximum absorption coefficient was observed at $\lambda = 270 \text{ nm}$ and it had the value $K_{270} = (3 \pm 0.4) \cdot 10^{-5} \text{ cm}^{-1}$.

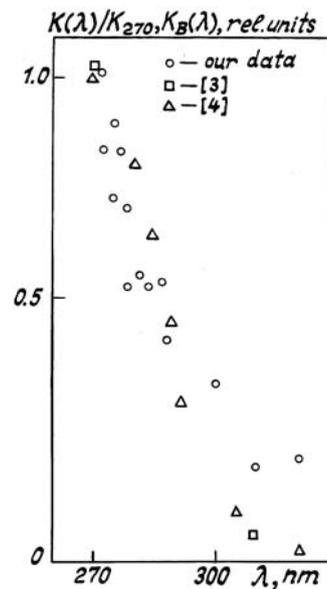


FIG. 3b. Comparison of the obtained data on absorption (in the normalized form $K(\lambda)/K_{270}$) with the results of the investigation^{3,4} of the excitation function of H_2O ($K_e(\lambda)$).

The lower limit of the absorption coefficient at $\lambda = 270$ nm determined in Ref. 3 based on H₂O fluorescence data (under the assumption that the quantum yield of fluorescence η is equal to 100%), is equal to 10^{-6} cm⁻¹ (the concentration of molecules $N_{\text{H}_2\text{O}} \sim 4 \times 10^{-17}$ cm⁻³). Comparing this quantity with our data made it possible to determine the real value of the quantum yield of fluorescence of H₂O at the pump wavelength $\lambda = 270$ nm: $\eta_{270} \sim 0.03$.

Our results are shown (in normalized form) in Fig. 3b where they are compared with the data from an investigation of the excitation function of H₂O vapor K_e .^{3,4} As one can see, all results agree qualitatively with one another, but there is nonetheless some discrepancy (especially in the region $\lambda \geq 300$ nm) in the shapes of the contours of the absorption and excitation bands.

The obtained data on the absolute values of the absorption coefficients of H₂O make it possible to determine the UV transmission F of water vapor. If the H₂O pressure in the lower atmosphere is assumed to be equal to ~ 10 torr and the effective thickness of a vertical column of water vapor $L_p \sim 3-5$ km, then

for $\lambda = 270$ nm $F_{\text{H}_2\text{O}} \sim 10^{-4}-10^{-7}$. In spite of the fact that in this region of spectrum the degree of attenuation of light by ozone is usually significantly higher ($F_{\text{O}_3} \sim 10^{-18}$), in many cases H₂O can apparently also have a definite effect on the UV radiation.

In conclusion we thank V.M. Klimkin and V.N. Fedorishchev for useful discussions.

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