

## INVESTIGATION OF ABSORPTION BY WATER VAPOR IN THE REGION 265...350 NM WITH THE HELP OF A SPECTROPHOTOMETER BASED ON THE KSVU-12M SPECTROSCOPIC SYSTEM

S.F. Luk'yanenko, T.I. Novakovskaya, and I.N. Potapkin

*Institute of Atmospheric Optics,  
Siberian Branch of the Academy of Sciences of the USSR, Tomsk  
Received August 21, 1990*

*The spectral absorption coefficient of water vapor was recorded in absolute units in the region 265 ... 350 nm with the help of a spectrometer, based on the KSVU-12M spectroscopic complex, an MDR-6 double monochromator, a multipass cell, and a halogen lamp.*

*The results confirm that the spectral band of water vapor which we studied is diffuse and that it is a band of the water molecule. It is also concluded that the observed band is the sum of at least two overlapping lines (absorption bands).*

In Ref. 1 the absorption spectrum of the UV band of water vapor in the region 270 ... 320 nm was investigated with the help of the discretely tunable second harmonic of a liquid laser. The existence of this band of water vapor was first reported in Ref. 2.

To clarify further the structure of the absorption band of water vapor in the near-UV and to determine how the band is formed it is of interest to obtain a continuous record of the absorption spectrum of H<sub>2</sub>O in the widest possible spectral range without the use of lasers.

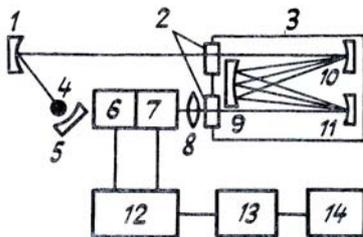


FIG. 1. Schematic diagram of the apparatus.

The experimental apparatus employed for the measurements is shown in Fig. 1. The radiation from a 500 W halogen lamp 4 with a quartz bulb and a spherical reflector 5, was directed with the help of a spherical aluminum-coated forming-mirror 1 (the radius of curvature is equal to 5 m) into a multipass cell 3 with a White optical system (mirrors 9–11). The radius of curvature of the mirrors in the White system is equal to 2 m and the distance between the mirrors is equal to 2 m. The optical system with the aluminum-coated mirrors gave an absorbing layer with a length of  $L = 64$  m without overlapping of spots on the collimator mirror 9 and the radiation from the halogen lamp was attenuated by not more than a factor of 10. The cell 3 had quartz entry and exit windows 2. After leaving the cell the halogen lamp radiation was

focused with a quartz lens 8 onto the input slit of an MDR-6 double monochromator 7 and then recorded with in FÉU-100 photomultiplier 6. The spectroscopic system KSVU-12M (12), and the controlling and processing DVK-3M computers 13 controlled the stepping motor of the monochromator, the power supply to the photomultiplier, and the recording of the signals from the photomultiplier. A trace of the radiation from the halogen lamp was observed on the display of the computer 13. After being processed the measurements were printed out with the help of the printer 14.

Power was supplied to the halogen lamp through a special ac current stabilizer with digital indication of the output voltage. The stabilizer ensured that the radiation flux of the lamp remained constant to within 1%. This made it possible to obtain quite stable results for the absorption coefficient with a single-channel recording system.

The mathematical software for the spectroscopic system made it possible to make repeated traces of the spectrum of the radiation from the lamp in a prescribed region of the spectrum while simultaneously averaging the data and further processing the results (smoothing, normalization, taking the logarithm, etc.).

This made it possible to measure the optical density  $kL$  with an error  $\sigma \approx 0.01 \dots 0.02$  in the wavelength range 400 ... 265 nm. The increase in the values of  $\sigma$  in the short-wavelength region of the spectrum was connected with the rapid decrease in the spectral power of the lamp in this range (Fig. 2) and a corresponding relative intensification of the noise in the photomultiplier. The absorption spectrum was not investigated at wavelengths  $\lambda \leq 265$  nm, because the error in measuring the spectrum increased very sharply at  $\lambda = 260$  nm,  $\sigma \approx 0.1$ .

The experimental procedure was as follows. The investigated range of the spectrum was divided into 20 ... 30 nm intervals. In this case the signals from

the photomultiplier did not drop by more than a factor of 2–5, and there were virtually no additional errors owing to different types of nonlinearities of the transfer function of the photomultiplier. In addition, the limited working memory of the computer made it impossible to store long sections of the spectrum with a sufficiently small ( $\sim 0.1$  nm) step. The spectral step, in turn, was chosen to be equal to or less than the spectral resolution of the monochromator  $\delta$ . The value of  $\delta$  in our experiments was equal to approximately 1 nm in the range 265 ... 280 nm and, respectively, 0.3 and 0.1 nm in the ranges 280 ... 300 nm and 300 ... 360 nm. By varying the instrumental function of the monochromator (by changing the widths of the input and output slits) it was possible to maintain constant the voltage of the photomultiplier (2000 V) in the entire investigated range of the spectrum; this gave more stable results. On the other hand, according to Ref. 3, since the width of the band of interest is quite large ( $> 20$  nm), the instrumental function of the monochromator has virtually no effect on the values, even for  $\delta \sim 1$  nm.

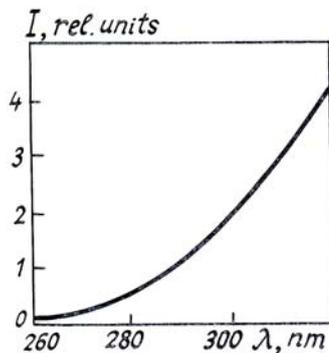


FIG. 2. The spectral, power of the radiation from the halogen lamp in the region 260 ... 320 nm.

The absolute error in referencing the wavelengths  $\sigma_\lambda$  was determined with the help of trial recordings of the emission spectrum of a low-pressure mercury lamp. In the range 260 ... 400 nm it was found that  $\sigma_\lambda \leq 0.01$  nm.

The absorption coefficient of interest was determined using the formula

$$k(\lambda) = -\ln \left[ \frac{\langle I(\lambda) \rangle_n}{\langle I_0(\lambda) \rangle_n \cdot LP_{H_2O}} \right],$$

where  $\langle I_0(\lambda) \rangle_n$  and  $\langle I(\lambda) \rangle_n$  are the spectral distributions, averaged over  $n$  realizations, of the intensity of the radiation of the lamp passing through an evacuated multipass cell and a multipass cell filled with water vapor, respectively;  $P_{H_2O}$  is the water vapor pressure.

Preliminary experiments showed that the total error in determining  $k(\lambda)$  does not exceed  $4 \cdot 10^{-7} \text{ cm}^{-1} \cdot \text{torr}$  in the entire range studied.

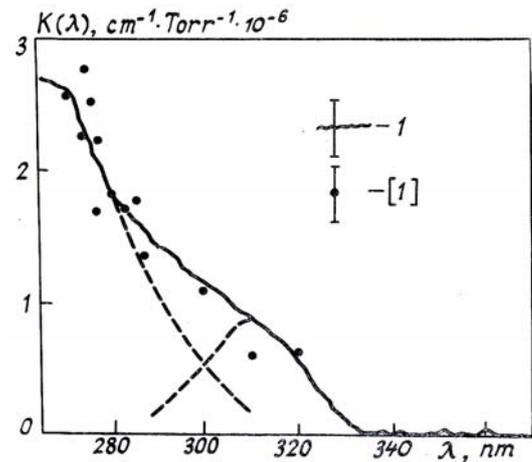


FIG. 3. The spectral absorption coefficient  $k(\lambda)$  of water vapor ( $\text{cm}^{-1} \cdot \text{torr}$ ) in the range 265 ... 350 nm: the solid line shows our data, the dots are the data of Ref. 1, and the dashed lines are the approximate decomposition of the absorption band into separate lines.

The results of investigations of the absorption spectrum of water vapor in the range 265 ... 360 nm are presented in Fig. 3. Figure 3 also shows the data obtained in Ref. 1 with the help of a laser and rescaled to unit pressure. As one can see, the agreement between these data is satisfactory. It also follows from Fig. 3 that the observed absorption band of water is the sum of at least two overlapping bands (lines) centered at about 265 ... 275 nm and 315 ... 320 nm, respectively.

The closeness of the values of  $k(\lambda)$  obtained in Ref. 1 with the help of a laser and in our case, when the width  $\delta$  of the instrumental function is significantly larger, indicates that the water band studied has no fine structure. This conclusion was also drawn in Ref. 3.

Thus our data confirm the fact that absorption by water vapor in the region 265 ... 330 nm is determined not by the interaction of laser radiation with water vapor (photodissociation, etc.), but rather by the fact that the water molecule has a previously unknown electronic transition.

In conclusion we thank V.V. Shlegin for his assistance in arranging and conducting the experiment.

## REFERENCES

1. S.F. Luk'yanenko, T.I. Novakovskaya, and I.N. Potapkin, *Opt. Atm.* **2**, No. 7, 579 (1989).
2. I.N. Klimkin and V.N. Fedorishchev, *Opt. Atm.* **2**, No. 2, 174 (1989).
3. V.M. Klimkin, S.F. Luk'yanenko, I.N. Potapkin, and V.N. Fedorishchev, *Opt. Atm.* **2**, No. 3, 322 (1990).