STUDY OF THE WATER VAPOR EXCITATION FUNCTION

V.M. Klimkin, S.F. Luk'yanenko, I.I. Potapkin, and V.N. Fedorishchev

Institute of Atmospheric Optics, Siberian Branch USSR Academy of Sciences, 634055, Tomsk
Received December 26, 1988

The longwave wing of the water vapor excitation function in the range from 270 to 330 nm has been studied with high spectral resolution using a tunable laser with emission linewidth of 0.3 to 0.03 Å.

Till now the fluorescence of water vapor has been observed for the transitions from high electronic states ($E > 8 \times 10^4$ cm^{-1}) excited by two-photon photon absorption of KrF*-laser radiation[1] during the chemical interaction between H_2 and O_2 molecules and by shortwave radiation with $\lambda < 120$ nm (Ref. 3). However, the authors of Ref. 4 have observed in their lidar experiments a broadband fluorescence of H_2O molecules in the region from 280 to 400 nm excited by radiation of KrF*-laser in a single-photon absorption process[5]. It was found later that this fluorescence was produced as a result of absorption of radiation within the H_2O absorption band at wavelengths shorter than 320 nm. This absorption band of the H_2O molecule can be of definite significance, along with the ozone band, in the protection of the Earth's surface from harmful UV solar radiation.

This paper presents results of a detailed experimental study of the UV absorption band of H_2O described in Refs. 3–6 for the first time, using a narrow-band tunable laser.

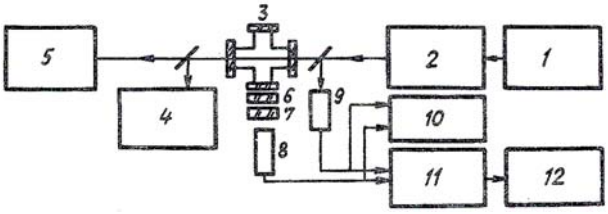

FIG. 1. Block-diagram of the experimental setup.

The arrangement of the experimental setup is depicted in Fig. 1. The frequency-doubled radiation of the dye laser 1 pumped with the second harmonic of the Nd:YaG laser 2 is directed onto the evacuated cell 3 and from there to the average power meter 4. The radiation wavelength is measured with the device 5, which in fact is a small-scale grating monochromator equipped with a photoelectric recording system. The spectrometric unit was calibrated using the mercury lamp spectrum. The error in the laser wavelength measurements made with spectrometer entrance and exit slits of 0.05mm width did not exceed 0.2 nm. The laser delivered pulses of radiation at a repetition rate of 12.5 Hz. Pulse energy was 10 to 50 mJ within the spectral region from 270 to 330 nm. The laser radiation linewidth was between 0.03 and 0.3 nm. Photons scattered in the cell and passed through the iris 6 and filter 7 were detected by the PMT 8. The liquid filters 7 were chosen so that they rejected the second-harmonic radiation diffusely reflected from the cell windows and walls. The PMT's sensitivity spectral range ($\lambda > 340$ nm) included the longwave wing of the H_2O fluorescence band. Pulsed fluorescence signals were observed with the oscilloscope 10 and measured using a stroboscopic peak voltmeter 11 (strobe width of 4 ns) and then plotted by an X-t plotter 12. In our experiments the water-vapor fluorescence signal was obtained as the difference between the fluorescence of the windows and walls of the evacuated cell and that of the cell filled with water vapor at each wavelength within the region from 270 to 330 nm. Typical fluorescence signals are shown in Fig. 2.

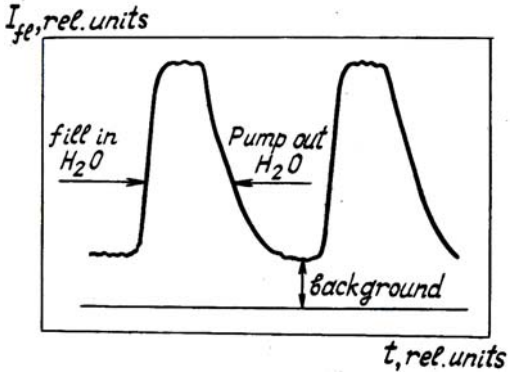

FIG. 2. The recorded H_2O fluorescence signals.

Figure 3 shows the experimentally measured shape of the longwave wing of the H_2O absorption band obtained with the resolution of 0.03 nm. The portions of this band recorded with the higher resolution of 0.003 nm are also presented in this Figure. It is obvious from this Figure that the band intensity is at its maximum at $\lambda = 270$ nm and then decreases monotonically towards longer wavelengths. The longest wavelength at which the signal

due to the fluorescence of H_2O vapor could be distinguished from the background fluorescence of cell windows and walls was about 323 nm. As was shown in Ref. 8, the fluorescence cross-section σ_f at $\lambda = 270$ nm is about 10^{-23} cm^2.

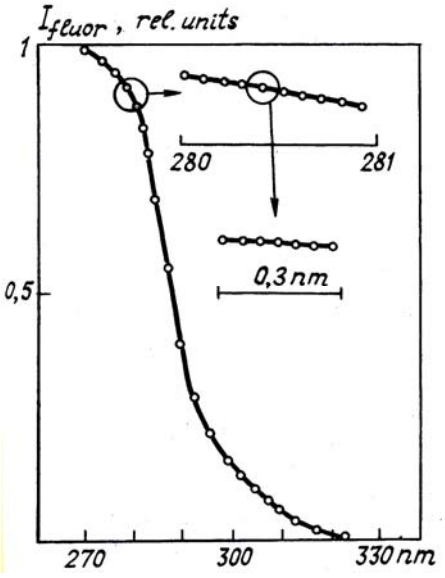

FIG. 3. Longwave wing of the absorption band and segments of it recorded with spectral resolutions of 0.03 nm and 0.003 nm, respectively.

Several 0.3–Å wide portions of the spectrum (that corresponds to the free dispersion spectral range of the Fabry-Perot interferometer installed inside the laser cavity) were recorded with the spectral resolution of 0.003 nm. A fragment of such a spectrum is shown in Fig. 3. Neither in the spectra of the entire wing of the H_2O absorption band made with the 0.03-nm resolution, nor in those portions of it made at a resolution of 0.003 nm was any fine structure typical of a line spectrum revealed.

Thus it was found in this experiments that the absorption band studied is of continuum nature and originates due to the electron transitions from the bound states to the repulsive ones or to the states corresponding to large internuclear distances.

REFERENCES

1. G. Meijen, J.J. Andersen, and A. Bath, J. Chem. Phys., **12**, 1614 (1986).
2. J.A. Blake and G.J. Burns, J. Chem. Phys., **54**, 1480 (1971).
3. L.C. Lee and M. Suto, J. Chem. Phys., **110**, 161 (1986).
4. V.M. Klimkin and V.N. Fedorishchev, Optika Atmosfery, No. 1, **7**, 26 (1988).
5. V.M. Klimkin and V.N. Fedorishchev, Optika Atmosfery, No. 1, **8**, 72 (1988).
6. V.M. Klimkin and V.N. Fedorishchev, Optika Atmosfery, No. 2, **2**, 220 (1989).