A NEW ATMOSPHERIC ABSORPTION BAND IN THE ULTRAVIOLET

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We have detected a previously unknown atmospheric continious absorption band in the wavelength range 250–320 nm. In contrast to the Hartley O_3 band, the new one is due to the presence of water vapor in the atmosphere.

In Ref. 1, we reported the observation of wide-band atmospheric fluorescence induced by radiation generated by KrF* laser. The fluorescence was quite strong, being at least comparable to Raman scattered signals from nitrogen. The studies described in Refs. 1 and 2 demonstrated that KrF* laser emission can induce water vapor to fluoresce both in the atmosphere and the laboratory.

In the present paper, we describe investigations of the fluorescence properties of the atmosphere and pure water vapor using longer-wavelength laser sources — the fourth harmonic of a Nd:YAG laser, XeCl* and N_2 lasers, and a tunable KrF* laser. We repeated some of the experiments described in Refs. 1 and 2 using the aforementioned lasers in the same setup as before.
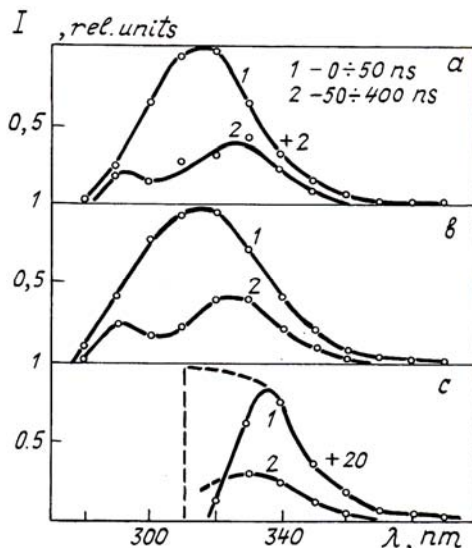

FIG. 1. Fluorescence spectra of H_2O vapor excited by laser radiation at 248 nm (a), 270 nm (b), and 308 nm (c). Curves 1 represent the data obtained during the interval 0 to 50 nsec after pulsed irradiation of cells; curves 2 are obtained in the 50 to 400 nsec interval.

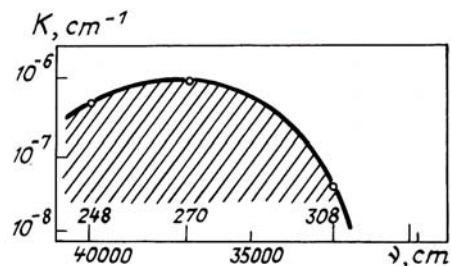It was found from these experiments that fluorescence of both the atmosphere and pure water vapor in evacuated cells could be excited by radiation at $\lambda = 248$ nm, $\lambda = 308$ nm, while the radiation of a molecular nitrogen laser at $\lambda = 337$ nm does not induce fluorescence.

Figure 1 presents the data on the fluorescence spectra of H_2O vapor obtained at different times after excitation by these wavelengths. The spectrum in Fig. 1 (c) is distorted by the long-wavelength wing of the absorption filter placed in front of the monochromator entrance in order to reject spurious light at the laser wavelength diffusely reflected from the cell's windows and walls. The dashed line in this figure presents the short wavelength portion of the H_2O fluorescence spectrum obtained from the distorted one by correcting for the absorption filter responce. It should be noted that the intensity of fluorescence excited by radiation at $\lambda = 308$ nm is 10 times lower than that excited by radiation at $\lambda = 270$ nm. It is quite obvious that radiation at $\lambda = 270$ nm and $\lambda = 308$ nm excites the long-wave wing of the fluorescence band induced by radiation at $\lambda = 248$ nm, hence one may conclude that there exists an absorption band of H_2O vapor, somewhere between 250 and 308 nm, responsible for the fluorescent response of the atmosphere. The long-wave wing of this band vanishes in the vicinity of $\lambda = 320$ nm, which corresponds to the maximum of the fluorescence band. For this reason, N_2 laser radiation is incapable of inducing the fluorescence of H_2O vapor.

FIG. 2. The atmospheric absorption band in the region 320 to 250 nm. Water vapor concentration is $4 \times 10^{17} cm^{-3}$.

Figure 2 presents the shape of the long-wave portion of this absorption band reconstructed from the

above data on fluorescence spectra. The reconstruction was obtained by normalizing the volumes confined by signal surfaces presented in coordinates λ, t, I_F to the laser pulse energy.

The fact that the efficiency of excitation of fluorescence is practically the same for both broadband exciting radiation ($\lambda = 248$ nm) and narrowband radiation ($\lambda = 270$ nm) is Indicative of an absorption band with continious structure. In order to verify this assumption, we rearranged the KrF* laser resonator by inserting into the cavity a grating with 2400 grooves⁄mm, which enabled us in autocollimating mode to obtain an emission line 3 Å wide-tunable, over a 3 Å range. Using this modified laser source, we obtained the absorption spectrum near 250 nm wavelength. The spectrum thus recorded showed no fine structure in this wavelength range.

We see from Figs. 1a and 2 that the shapes of the H_2O absorption and fluorescence bands are the classical ones for the case of absorption due to an electronic transition between the bound ground state ($V'' = 0$) and one that is repulsive (or significantly displaced along the internuclear coordinate r) followed by emission from the repulsive state. The long-wavelength edge of the absorption band found experimentally enabled us to estimate the repulsive term energies, which were to be $E_r = 31000$ cm^{-1} at the right-hand turning point, and $E_e = 37000$ cm^{-1} at the equilibrium position. These values are 10000 cm^{-1} and 3000 cm^{-1} lower than corresponding tabulated values for the potential of the H_2O ground electronic state dissociation. As we can judge from the literature available there are no experimental data known so far that could demonstrate the existence of such a repulsive term in an isolated H_2O molecule. The approximation of this repulsive term to the left-hand turning point indicates that the short-wavelength edge of the absorption band lies near 230 nm.

REFERENCES

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