PHOTODISSOCIATION OF WATER VAPOR BY UV LASER RADIATION

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The energy of low electronic states of monomer and dimer water complexes, H_2O and $(H_2O)_2$, has been calculated. It is shown that KrF—laser—induced *photoabsorption of water vapor may be accounted for by the transitions from hot rovibrational levels to quasicontinuum of H_2O states, whereas the fluorescence may be explained by the recombination of the products of monomer water complex disintegration.*

Water vapor fluorescence induced by Kr—F laser radiation has been studied within 250—280 nm (Ref. 1) and 250—400 nm (Refs. 2, 3) spectral ranges. In Refs. 2 and 3 it has been concluded that

1) fluorescence is observed under excitation mode, linear relative to the laser radiant exitance up to 10^7 W/cm^2;

2) there are regions in the fluorescence spectrum with essentially different decay time.

To interpret the observed fluorescence properly, it is necessary to obtain the energy states between which the radiative transitions take place connected with light absorption. The absorption spectra of water vapor in $250 - 350$ nm spectral range has been studied in Refs. 4—7. As has been found, the maximum of absorption band lies at $\lambda = 270$ nm (K = $3 \cdot 10^{-5}$ cm^{-1}), whereas the bottom corresponds to $\lambda = 320$ nm, and the band itself is continual without evident structure. It was concluded that the observed spectra are connected with the novel electronic state of H_2O.

To verify this hypothesis, we have calculated the ground and low electronic states of H_2O and $(H_2O)_2$. For each electronic state the energy has been optimized. The calculations have been made with the MONSTERGAUSS program package.

The key idea in studying the spectroscopic properties of water is the Rydberg character of excited electronic states. The electronic configuration of water ground state can be presented as

$$(1a_1)^2 \; (2a_1)^2 \; (1b_2)^2 \; (3a_1)^2 \; (1b_1)^2 - \tilde{X}^1A_1 \; .$$

Ten excited singlet states result from the electron transition from $1b_1$ orbital to $3s$, $3p$, $4s$, or $3d$ Rydberg orbitals. Some states result from the transition from $3a_1$ orbital. In this paper we consider only low electronic states. In calculations we use the expanded basis including $3s$ and $4s$ orbitals for oxygen atom O, (5211/311), and hydrogen atom H, (211). The calculations have been made for the following transitions: $(1b_1 \rightarrow 3sa_1)^1B_1$ and $(1b_1 \rightarrow 3pb_2)^1A_2$.

The MKSSP method (49 electronic configurations) has been used to calculate the excited states.

To study the low electronic states in detail, the H_2O potential surfaces have been calculated with geometry optimization. Due to the transition from $\tilde{X}^1A_1$ state to the singlet state A^1B_1 ($1b_1 \rightarrow 3sa_1$), the H_2O molecule becomes linear with $R_{OH} = 1.2288$Å and $\alpha = 180°$ that corresponds to the intermediate state from which photodissociation into H and OH occurs. This stationary point of the potential surface lies in the region of nonequilibrium configurations, and any displacement from the region brings in the valley of the disintegration products. The energy corresponding to this stationary point is — 75.32147 a.u.

In the transition $\tilde{X}^1A_1 \rightarrow {}^1A_2$ ($1b_1 \rightarrow 3bp_2$) the molecular geometry is near—linear: $\alpha = 179.7939°$, $R_{OH_1} = 3.2722$Å and $R_{OH_2} = 1.0284$Å. The total energy E equals to 75.4037313 a.u. This state corresponds most likely to the complex with hydrogen bond H … OH. The calculational results for H_2O are shown in Fig. 1.

The total energy of the ground state $\tilde{X}^1A_1$ has been found to be -75.5494 a.u., whereas energy of the vertical transitions into state ${}^1B_1$ and ${}^1A_2$ is -75.26131 and -75.16918 a.u., respectively that corresponds to 7.8 and 10.3 eV, i.e. there is no energy values less than 7 eV for vertical transitions from zero—point vibrational level.

It is not possible, in the present state of the art of both theoretical and computational methods of quantum chemistry, to confirm the hypothesis about the existence of H_2O states intermediate between $\tilde{X}^1A_1$ and A^1B_1. Interpretation of the experimental data obtained is needed to be made within the framework of the present concept concerning the structure of H_2O energy levels. Let us now turn our attention to the diagram presented in Fig.2.

The energy of one quantum of radiation at $\lambda = 248.5$ nm (4.99 eV, 40257 cm^{-1}) is not enough for

H_2O molecule to dissociate into H + OH, if considered are only transitions from zero—point vibrational level 000. However, this quantum energy is practically sufficient for H_2O to dissociate into $O+H_2$ (D_0 = 5 eV), especially when the finite spectral width of KrF laser radiation (~100 cm^{-1}) is taken into account. The energy of 5 eV corresponds to the wavelength λ = 247 nm, consequently, the absorption of radiation with λ > 247 nm is connected with the excitation of rovibrational levels of the ground state of quasicontinuum near the dissociation boundary.
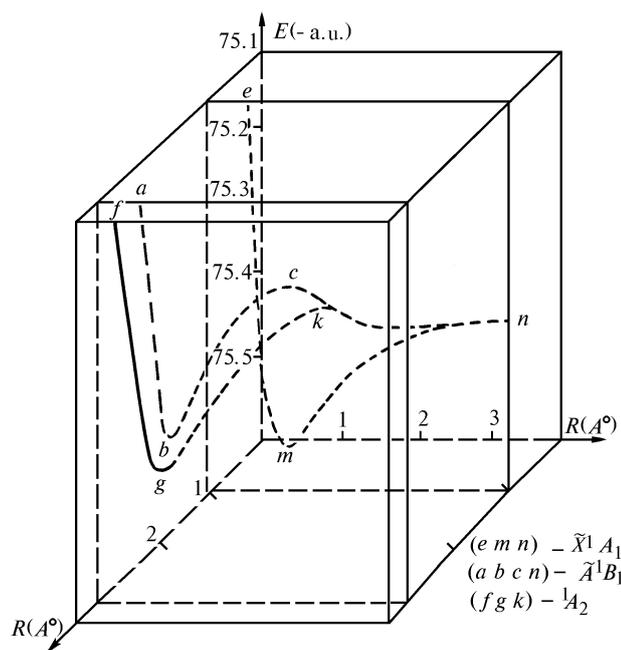
FIG. 1. Potential curves for low electronic states of water monomer H_2O.
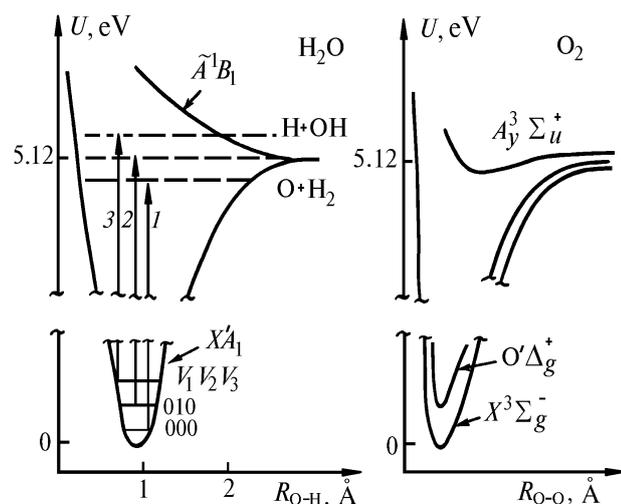
FIG. 2. Diagram of potential curves for H_2O and O_2.

The energy deficit, needed for dissociation to follow the reaction H + OH, amounts to 968 cm^{-1}. Then the transitions, induced by radiation with λ = 248.5 nm, from, for example, virbrational level 010 (1647.59 cm^{-1}) will lead to formation of OH (X^2o) radicals. With excitation of water vapor by radiation at λ = 248.5 nm and taking into account the Boltzmann distribution over the energy levels, the following processes will occur:

$$H_2O + h\nu \xrightarrow{248.5\ nm} H_2O^* \begin{cases} H_2O + M \\ O + H_2 \\ O + OH \\ H_2O + h\nu' \end{cases}$$
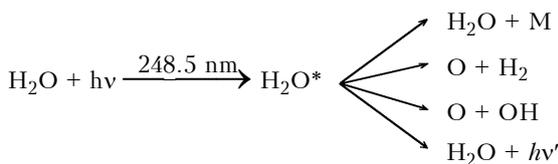
and, consequently, H_2O, H_2O^*, O, and OH can take part in the succeeding fluorescence. It is naturally to suppose that luminescence of excited molecule, H_2O^*, and recombination luminescence appearing in association $O + OH \rightarrow H_2O$ and $O + H_2 \rightarrow H_2O$ are responsible for the fluorescence. This supposition is confirmed by the fact that in pure water vapor the fluorescence can be quenched effectively by molecular oxygen. To explain qualitatively the existence of the fluorescence continuous spectrum recorded,[4-7] the following assumption should be made.

Excitation of H_2O molecules in the quasicontinuum of states lying below the dissociation threshold is low—efficient due to small values of the Frank—Condon factor. The rate of excitation of continuous states lying above the dissociation threshold may be essentially greater due to borrowing intensities from $^1B_1$ state. Then every radiative transition in absorption will be connected with the continuous spectrum of states, whereas the decay of absorption coefficient in the longwave wing of the band will be due to the Boltzmann distribution of energy levels of the ground electronic state.

It should be noted in conclusion that the absorption and the fluorescence observed in experiment are not connected with water vapor dimer, $(H_2O)_2$. The computations we have made in Ref. 8 have shown that only unplane structure (see Fig. 3) has bound ground and S_1 and T_1 excited states with bond energy of 5.5, 2, and 4.4 kcal/mole, respectively. In this case, as compared to the monomer, a shift in absorption takes place to the blue region by the value within 0.65—0.69 eV.
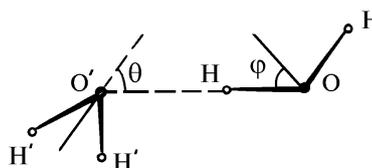
FIG. 3. Geometry of the dimer $(H_2O)_2$ in the equilibrium configuration corresponding to the global energy minimum.

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