

Water vapor absorption band nearby 270 nm: intensity borrowing mechanism

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The interaction between the ground \tilde{X}^1A_1 and excited \tilde{B}^1A_1 electronic states of the water molecule has been analyzed, and it was shown that the centrifugal distortion near the linear HOH configuration might lead to a considerable state mixing in the case that both the lower and upper state wave functions are located near the linear configuration. As a result, transitions to the high bending states, such as $(0V_20)$ with $V_2 \sim 20$, within the ground electronic state may be intense due to intensity borrowing. This effect seems to explain the weak 270 nm band experimentally observed earlier in the near UV spectrum.

Introduction

Absorption spectra of the water vapor molecule are of particular interest in atmospheric spectroscopy, because this gaseous constituent of the atmosphere is responsible for about 70% of absorption of the incoming solar radiation. It is for this reason that a large number of papers is devoted to the detailed study of absorption, emission, and Raman spectra of H₂O.

The weak water vapor absorption band nearby 250–300 nm (4.5 eV band) in the near UV region is of certain interest for atmospheric investigations. Atmospheric extinction of solar radiation in this spectral region is determined mostly by ozone, but, as was repeatedly mentioned in the literature, water vapor absorption may contribute markedly to the radiative flux in the atmosphere. Earlier the UV spectra of water vapor were recorded by different methods: fluorescence, absorption, and photoacoustic spectroscopy (the experimental results have been reviewed in Ref. 1). The band of interest was also observed in the electron scattering spectrum.²

Analysis of the totality of experimental data shows that there is the interaction of the UV radiation $\lambda = 300\text{--}250$ nm with water vapor. It was found that this weak band has no any pronounced structure, and the measured absorption coefficients are on the order of $10^{-6}\text{ cm}^{-1}\cdot\text{Torr}^{-1}$. The *ab initio* calculations of the electronic structure of H₂O show that the 300–250 nm cannot be explained by some electronic transition, because the first excited electronic state 3B_1 of the water molecule has the energy of 6.7 eV.

More or less reliable interpretation of the H₂O spectrum nearby 270 nm is lacking yet. In Ref. 3 the potential energy function for the ground and first excited singlet electronic states of H₂O was

calculated, and it was shown that this absorption spectrum may be caused by transitions from the first excited vibrational state (010) to the rovibrational energy continuum above the energy of the dissociation.

The 4.5 eV band can be explained by dissociation of water molecules into H+OH($\tilde{X}^2\Pi$). Fluorescence, in its turn, may be caused by the inverse recombination process. In Ref. 3 it was supposed that transitions to weakly bound states lying above the dissociation threshold can be strong enough thanks to the intensity borrowing from the strong \tilde{A}^1B_1 electronic state. However, it should be mentioned that no calculations allowing interpretation of the experimental data are available by now.

In this paper we propose a hypothesis that can, in our opinion, explain the presence of weak water vapor absorption in the region of 300–270 nm and discuss the mechanism, which can lead to intensification of some H₂O vibrational absorption bands lying near the dissociation threshold. Earlier this hypothesis was discussed in Ref. 7.

Transitions in the region of 250–300 nm fall in the dense rovibrational energy spectrum. The states with the energy of $30000\text{--}40000\text{ cm}^{-1}$ (the H₂O dissociation energy $\approx 41150\text{ cm}^{-1}$) likely have various nature: some of them can be interpreted as overtones of stretching vibrations, while the others are high overtones of the bending vibrations. Note that at excitation of three to four quanta of the bending vibration the so-called anomalous centrifugal distortion is observed, namely, fast increase of the rotational and centrifugal constants. At a higher degree of excitation, when the vibrational energy turns out comparable with the barrier to the linear potential energy function, new (HEL) resonances arise⁴ due to the strong centrifugal distortion of

the rotating molecules near the linear HOH configuration.

Our assumption is that the strong centrifugal distortion in high overtones of the bending vibration, whose energy is comparable with the dissociation threshold, causes the nonadiabatic effect, namely, mixing of RV states belonging to different electronic states, and this can lead to a significant intensity borrowing from strong electronic bands. It is useful to note here that analysis of rovibrational wave functions of 200 highest vibrational states of the water molecule made by Mussa and Tennyson in Ref. 5 showed that among them there are several high overtones of the bending vibration.

1. Mechanism of intensification of the H₂O spectrum nearby 0.27 μm

In Ref. 7 the intensity of H₂O rovibrational bands near the UV region was estimated based on the data calculated by Partridge and Schwenke.⁶ It was shown that this region includes only very weak absorption bands with the intensities about 10⁻⁹ cm⁻² · atm⁻¹, which is much lower than the observed ones.

According to our hypothesis, the strong centrifugal effect near the linear configuration of the water molecule leads to a mixing of rovibrational states belonging to different electronic states. To estimate the degree of mixing, it is necessary to calculate the mixing coefficients of wave functions:

$$\eta = \eta_{el} \eta_{vr}, \quad \eta_{vr} = \sin \gamma, \quad (1)$$

where η_{el} is the mixing coefficient for electronic states, η_{vr} is the mixing coefficient of rovibrational states,

$$\gamma = \frac{1}{2} \arctan \left(\frac{2 \langle \Psi_{vr}^{(\tilde{X})} | H' | \Psi_{vr}^{(\tilde{B})} \rangle}{E_{vr}^{\tilde{X}} - E_{vr}^{\tilde{B}}} \right), \quad (2)$$

where H' is the perturbation operator; v, v' and r, r' are the vibrational and rotational quantum numbers. The parameter η^2 determines the fraction of intensity borrowed from the strong \tilde{B}^1A_1 band to the weak rovibrational transitions of the ground \tilde{X}^1A_1 electronic state.

The perturbation operator is the operator of kinetic energy of the nuclei and has the form¹²:

$$H' = p_1^2 + p_2^2 + 2b_0 z p_1 p_2 + h_{rb}(\rho_1, \rho_2, z) + h_M(\rho_1, \rho_2, z) + h_y J_y + h_{zx} \{J_x, J_z\}, \quad (3)$$

where

$$p_i = -i\hbar / \partial \rho_i;$$

$$\rho_i = r_i / r_e, \quad z = \cos \theta \quad (0 \leq \rho_i \leq \infty, -1 \leq z \leq 1)$$

are dimensionless vibrational coordinates; r_e is the equilibrium length of the OH bond; θ is the angle between the OH bonds; J_z, J_x, J_y are the components of the angular momentum operator; $\{A, B\} = AB + BA$ is the anticommutator;

$$h_{rb}(\rho_1, \rho_2, z) = \left[\frac{b_1}{\rho_1^2} + \frac{b_2}{\rho_2^2} \right] \times \left[p_z (1 - z^2) p_z + \frac{J_z^2}{2(1+z)} + \frac{J_x^2}{2(1-z)} + \frac{J_y^2}{4} \right]; \quad (4)$$

$$h_y = \frac{1}{2} \left[\frac{b_1}{\rho_1^2} - \frac{b_2}{\rho_2^2} \right] \{ \sqrt{1 - z^2}, p_z \}, \quad (5)$$

$$h_{zx} = -\frac{1}{2} \left[\frac{b_1}{\rho_1^2} - \frac{b_2}{\rho_2^2} \right] \frac{1}{\sqrt{1 - z^2}}, \quad (6)$$

$$h_M(\rho_1, \rho_2, z) = \frac{b_0}{\rho_1 \rho_2} \times \left[\left\{ z, p_z (z^2 - 1) p_z \right\} + \frac{J_z^2}{(1+z)} - \frac{J_x^2}{(1-z)} + z \frac{J_y^2}{2} \right] + b_0 \left(\frac{1}{\rho_2} p_1 + \frac{1}{\rho_1} p_2 \right) \{ 1 - z^2, p_z \} - b_0 \sqrt{1 - z^2} \left(\frac{1}{\rho_2} p_1 - \frac{1}{\rho_1} p_2 \right) J_y; \quad (7)$$

$$b_i = \frac{\hbar}{8\pi^2 c \mu_i r_e^2}; \quad \frac{1}{\mu_i} = \frac{1}{m_i} + \frac{1}{M};$$

$$b_0 = \frac{\hbar}{8\pi^2 c M r_e^2}; \quad J^2 = J_z^2 + J_x^2 + J_y^2. \quad (8)$$

The molecule-fixed coordinate system was taken as follows: the molecule lies in the xz plane and the axis x is directed along the bisector of the HOH angle.

Vibrational states of the type (0V₂0) with the excitation energy near the threshold of the linear configuration are characterized by the centrifugal effect, which is presented by the singular term $J_z^2 / 2(1 + \cos \theta)$ in the Hamiltonian. The centrifugal effect leads, for example, to the fast increase of the rotational constant A and the centrifugal distortion constants of the J_z -series (that is, $\Delta_k, H_k, L_k, \dots, \delta_k, h_k, \dots$) of the effective Watson's rotational Hamiltonian. Moreover, the strong centrifugal effect in the bending vibrational states near the linear configuration may also lead, in mathematical description, to an increase in the off-diagonal matrix elements of the effective Hamiltonian, corresponding to interaction between different vibrational states, which manifest

themselves in strong resonance mixing of wave functions and “transfer” of intensity from strong to weak vibrational bands. Examples of such intensity borrowing are the so-called HEL-resonances in the rovibrational energy spectrum of the lower electronic state of H₂O that give rise to rather intense transitions to the vibrational states like (060), (070), (080), and even (0 10 0) [see Ref. 4].

Generally speaking, the same effect can cause mixing of rovibrational states belonging to different electronic states. Figure 1 shows the bending part of the potential energy curve for the ground \tilde{X}^1A_1 and excited \tilde{B}^1A_1 electronic states, the centrifugal distortion energy $K_z^2/2(1 + \cos\theta)$, $K_z = 1$, and the energy levels corresponding to the ground state (bending state near the dissociation threshold) and the excited \tilde{B}^1A_1 state (linear configuration).

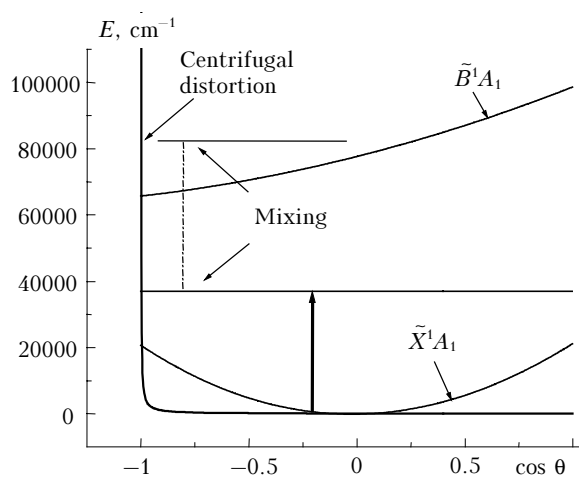


Fig. 1. Potential energy surface (bending coordinate cross section) of the ground \tilde{X}^1A_1 and excited \tilde{B}^1A_1 electronic states and the centrifugal distortion energy.

It can be seen from Fig. 1 that centrifugal distortion can mix the states, in the case when the Frank–Condon factor is rather large, that can occur if the wave functions near $\theta = \pi$ are considered.

The calculations show⁷ that for H₂O molecule the transitions from a state with $V_2 \sim 20$ fall in the region near 270 nm. For such states the rotational constant $A \approx 1200 \text{ cm}^{-1}$ becomes comparable with the vibrational frequencies, and the centrifugal distortion constant is $\Delta_k \approx 400 \text{ cm}^{-1}$ [see Ref. 10]. This is explained by the fact that at excitation by several quanta, multiple of the bending vibration, the corresponding RV wave function is concentrated near the linear configuration HOH.

It is known (see, for example, Refs. 3, 8, 9) that the lower \tilde{X}^1A_1 electronic state of H₂O has the conic cross section in the linear configuration HOH (at $\angle\text{HOH} = 180^\circ$, $r_{\text{OH}_1} = 1.8$, $r_{\text{OH}_2} = 3.1 a_0$, the energy $\approx 6 \text{ eV}$) with the excited \tilde{B}^1A_1 electronic state.

Besides, near the linear configuration the \tilde{B}^1A_1 state is connected, owing to the interaction of the Renner–Teller type with the first excited singlet state \tilde{A}^1B_1 . The interaction of these three states leads, in the mathematical description, to mixing of the adiabatic electronic wave functions and, as was shown in Refs. 8 and 9, this interaction significantly affects the H₂O dissociation process. Speaking generally, this interaction may lead to intensification of transitions to the ground electronic state, for which the probability of achieving the linear configuration is rather high. The coefficient of the mixing electronic wave functions η_{el} depends on the angle HOH and the bond lengths. At the equilibrium values of the bond lengths, η_{el} is equal to 10^{-2} – 10^{-3} [see Ref. 9].

To assess the second factor, η_{vr} , in Eq. (1), we used the simplified one-dimensional model with the fixed OH bonds equal to their equilibrium lengths. We took into account rotation of the molecule about the z -axis, but ignored other perturbation terms including rotation about the x - and y -axes. The operator h_M was ignored as well.

We have estimated the off-diagonal matrix elements of the operator (4) and the mixing coefficients (3), using the wave functions of the bending states ($0V_20$), $V_2'' = 10 \dots 20$, $V_2' = 0 \dots 10$, and the potential energy function from Ref. 11. They were determined by the direct variational method (with the potential functions of the \tilde{X} and \tilde{B} states calculated in Ref. 10). To obtain convergent calculations, we used up to 100 basis functions of the following form:

$$S_V^{(\alpha\beta)}(z) = N_V(1-z)^{\alpha/2}(1+z)^{\beta/2}P_V^{(\alpha\beta)}(z), \quad (9)$$

where N_V is the normalization factor, and $P_V^{(\alpha\beta)}(z)$ are the Jacobi polynomials. The calculations were performed at different values of α and β .

As a result, it was found that the major contribution was due to the centrifugal distortion term $J_z^2/2(1 + \cos\theta)$, while the contributions coming from other terms of the Hamiltonian (4) are negligibly small. The calculated energy levels and matrix elements weakly depend on α and β at their values from 0.1 to 2.

The calculated results are depicted in Fig. 2. The calculations showed that the mixing coefficients of the rovibrational states increase fast with the growth of V_2'' and achieve several tens of percent.

As a consequence, the total mixing coefficients accounting for the mixing of the electronic states are on the order of 10^{-2} – 10^{-3} . Since the dipole moment of the electronic transition $\tilde{X}^1A_1 \rightarrow \tilde{B}^1A_1$ is large enough ($\sim 0.8 \text{ D}$ [see Ref. 8]), this degree of mixing may prove sufficient to explain the weak 270 nm band.

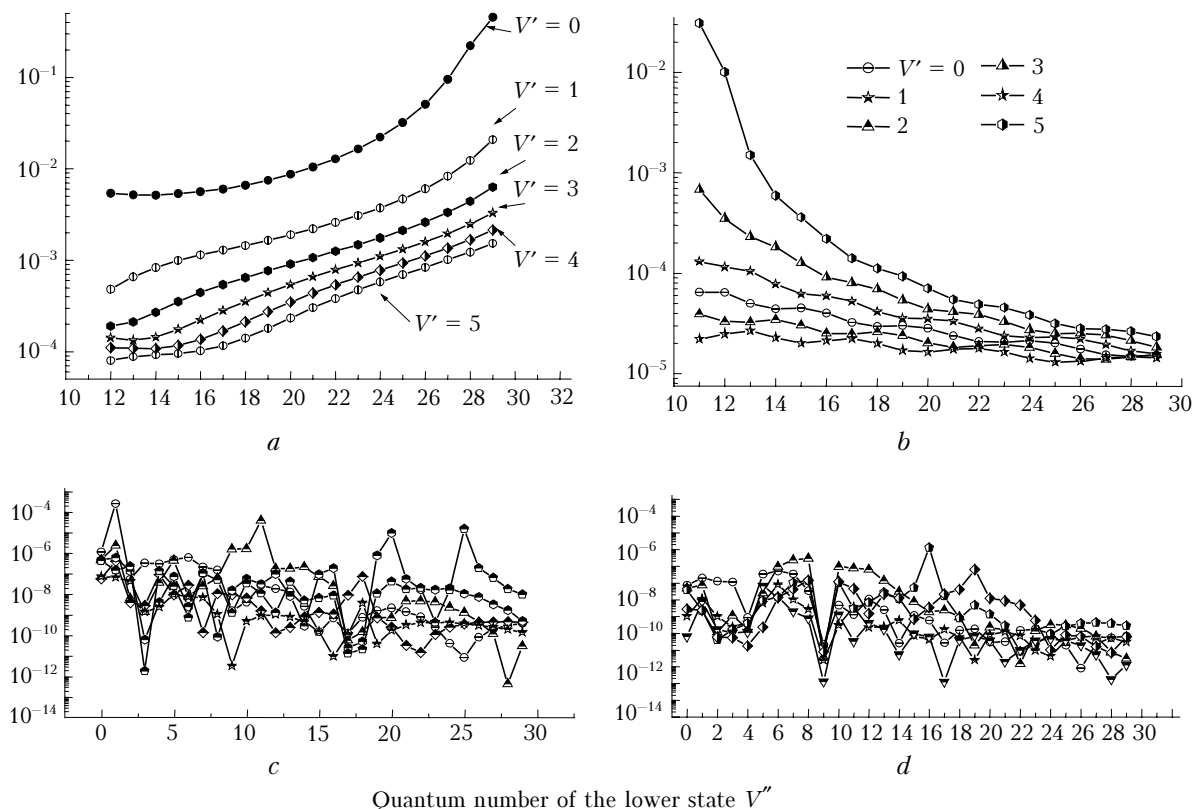


Fig. 2. Mixing coefficient: $K_2 = 1$ (a), 2 (b), 5 (c), and 10 (d).

Conclusions

Thus, the calculations made using a simplified one-dimensional model demonstrate that the centrifugal distortion near the linear configuration in high-excited bending vibrational states of the $(0V_20)$ type of the H_2O molecule can cause strong mixing of rovibrational states in the ground \tilde{X}^1A_1 and excited \tilde{B}^1A_1 electronic states. The fraction of the borrowed intensity is roughly equal to 10^{-6} , and, consequently, the absorption coefficient is on the order of $10^{-6} \text{ cm}^{-1} \cdot \text{Torr}^{-1}$.

This result agrees with the experimental value,¹ at least, qualitatively. Thus, the weak absorption in the 250–300 nm region in the UV spectrum can be interpreted as the absorption due to rovibrational transitions of the water vapor molecule within the ground electronic state; these transitions form the lines that turn out strong enough because of the intensity borrowing from the excited \tilde{B}^1A_1 electronic state.

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