Rotational and centrifugal-distortion constants for the $(00V_3)$-type vibrational states of the HD^{16}O molecule

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Rotational-vibrational constants for (006) and (007) vibrational states of the HDO molecule are determined by use of the least squares fitting to experimental rotation-vibration energy levels. All the known rotational constants, as well as integrated band intensities are approximated using the Pade method, and spectroscopic constants of nv_3-type bands are predicted for $n = 8...15$. The calculations showed that the rotational A constant decreases strongly, almost two times, due to the rotational-vibrational interaction.

Introduction

For many reasons, it is interesting to investigate fine structure of the absorption spectra of HD^{16}O molecule in the near IR and visible spectral region. First, absorption by isotopic modifications of H$_2$O molecule should be taken into account in calculating the atmospheric transmission for a narrow-band radiation. This is especially important for assessment of laser radiation absorption in atmospheric transmission windows and microwindows. Second, as was shown in Ref. 1, the total contribution of weak absorption lines, including those of the HD^{16}O molecule, to the total atmospheric absorption is about several percent, and it should be taken into account in estimates of the radiation budget. Third, the HD^{16}O molecule is an asymmetric isotopic modification of the water molecule, it is characterized by some features in the intramolecular dynamics,[5–8] and the study of these features is of particular interest in the theory of rotational-vibrational molecular spectra.

For these reasons, HD^{16}O absorption spectra were studied intensely, and the review of these studies can be found in Ref. 2. Among recent publications, to be noted there are Refs. 4–12, which report new data on the spectra in the near IR and visible range.

The problem of absorption of the near UV radiation by water vapor is well-known (see the review in Ref. 13). Analysis shows that a weak H$_2$O band near 0.27 μm cannot be caused by some electronic transition, while rotational-vibrational transitions in this range are too weak to give rise to a noticeable absorption. Reference 13 puts forward the hypothesis about possible "intensification" of RV transitions because of rotational-vibrational-electronic interaction between the ground and first excited electronic levels. It also seems quite probable that symmetry lowering in HDO because of the isotopic substitution can intensify this effect. Therefore, it is necessary to analyze the available experimental data on HDO weak absorption bands in the shortwave region, in order to extrapolate these data to the near

UV region and to estimate HDO absorption in this spectral range.

The absorption spectra corresponding to HDO nv_3 vibrational bands were studied earlier in Refs. 3–5 and 8. It was shown that this band sequence, the strongest in the HD^{16}O spectrum, corresponds to transitions to almost isolated $(00V_3)$-type vibrational states non-interacting with others. In Refs. 3–5 and 8, the states up to $V_3 = 5$ were studied. In Ref. 11, the spectra of the $(000) \rightarrow (006)$ and $(000) \rightarrow (007)$ bands were analyzed, spectral lines were assigned, and rotational energy levels of the (006) and (007) vibrational states were determined.

In this paper, the rotational-vibrational energy spectrum of the $(00V_3)$-type states is analyzed. The rotational and centrifugal distortion constants for $V_3 \le 5$ were taken from Ref. 2, and for the (006) and (007) states they were determined by use of the least squares fitting to energy levels from Ref. 11. The spectroscopic constants known from the literature and obtained here, as well as the results of high-accuracy variational calculation of the HD^{16}O spectrum[12] were approximated by the Pade method. These results allow us to estimate the line positions and strengths of the HD^{16}O bands in the visible and near UV regions. In this paper, the integral absorption coefficients for the nv_3 bands are estimated.

Rotational and centrifugal distortion constants for the (006) and (007) states

In the HD^{16}O molecule, because of non-symmetric isotopic substitution, harmonic frequencies have significantly different values. Thus, for example, vibrational frequencies $\omega_1 = 2823$ cm^{-1} and $\omega_2 = 1444$ cm^{-1} turn out to be multiple ($\omega_1 \approx 2\omega_2$), thus leading to typical Fermi polyads for the lower vibrational states. However, the frequency $\omega_3 = 3888$ cm^{-1} corresponding to vibrations of the OH bond differs significantly from the first two ones. In this connection, the vibrational levels close in energy to $(00V_3)$ one have far different vibrational quantum numbers; therefore, the $(00V_3)$ states turn out to be

isolated and almost do not interact with the other states.[6] At a high degree of excitation, the rotational-vibrational energy spectrum has no pronounced polyad structure.[8]

To find the constants of the rotational and centrifugal distortion of the (006) and (007) vibrational states, the "experimental" energy levels from Ref. 11 were used determined from analysis of high-resolution Fourier transform spectrum. These states were considered as isolated, and the effective rotational Hamiltonian was taken in the following form:

$$H^{[00V]} = E_V + \left(A^V - \frac{B^V + C^V}{2} \right) J_z^2 +$$

$$+ \frac{B^V + C^V}{2} J^2 - \Delta_k^V J_z^4 - \Delta_{jk}^V J_z^2 J^2 - \Delta_j^V J^4 +$$

$$+ H_k^V J_z^6 + \dots + \frac{B^V - C^V}{2} J_{xy}^2 -$$

$$- \delta_k^V \{ J_z^2, J_{xy}^2 \} - 2\delta_j^V J^2 J_{xy}^2 + \dots, \qquad (1)$$

where A^V, B^V, and C^V are the rotational constants, Δ_k^V, Δ_{jk}^V, ... are the centrifugal distortion constants for the vibrational state V; J_x, J_y, J_z are the components of the angular momentum operator (I^r representation), $J^2 = J_x^2 + J_y^2 + J_z^2$, $J_{xy}^2 = J_x^2 - J_y^2$. The spectroscopic parameters obtained, the number of levels involved in the fitting procedure, and the standard deviation of values calculated from the experimental ones are given in Table 1. In fitting the energy levels of the (006) and (007) vibrational states, we had to exclude the levels [515] and [212] with the energies of 20044.5936 cm^{-1} and 22676.5482 cm^{-1}, respectively, because calculated data for them differed significantly from the experimental data. These states are likely perturbed by the resonance interaction.

Table 1. Rotational and centrifugal distortion constants (cm^{-1}) for the (006) and (007) vibrational states of HD^{16}O

Parameter	(006)	(007)
E_V	19836.8777	22625.503
A^V	17.61610±5.38·10^{-2}	16.833644±7.42·10^{-3}
B^V	9.033741±1.90·10^{-2}	9.006203±1.62·10^{-2}
C^V	5.938264±6.60·10^{-3}	5.87544±1.37·10^{-2}
Δ_k^V	7.966175·10^{-3}±7.81·10^{-4}	
Δ_j^V	4.877379·10^{-4}±3.62·10^{-6}	4.954867·10^{-4}±1.08·10^{-5}
δ_j^V	1.808694·10^{-4}±2.53·10^{-6}	
Number of levels	26. $J \leq 5$, $K_a \leq 3$	16. $J \leq 5$, $K_a \leq 2$
Standard deviation	7.4·10^{-3}	1.3·10^{-2}

N o t e . The estimated error in reconstructed spectroscopic constants corresponded to ±1σ confidence interval. The band center E_V was taken equal to the zero level [000] and not varied.

Approximation of the V_3-dependence

The above values of the spectroscopic constants, along with the literature data for other (00V_3) states, can be used to estimate the positions and strengths of lines from other bands of the HD^{16}O molecule in the visible and near UV regions. In addition to the parameters obtained from fitting to the experimental energy levels, it is desirable to use additional data for the states with $V_3 > 7$, which can be obtained through extrapolation, and the results of the high-accuracy *ab initio* calculations.[12] Such calculations have a clear significance for atmospheric spectroscopy.

To determine the dependence of spectroscopic constants on V_3, we used the Pade approximation. As a result, we obtained the following formulas for the rotational constants:

$$A(V_3) = \frac{23.41021 - 1.136596059 V_3 + 0.03775531744 V_3^2}{1 - 0.00432785777 V_3 + 0.001227019016 V_3^2}; \qquad (2)$$

$$B(V_3) = \frac{9.10576}{1 + 0.014265 V_3}; \qquad (3)$$

$$C(V_3) = \frac{6.40778 - 0.02633104 V_3}{1 + 0.0085789 V_3}. \qquad (4)$$

The calculated values of the constants are given in Table 2 and shown in Fig. 1. It can be seen that the constant A for the states with $0 \leq V_3 \leq 15$ changes rather strongly, while the constants B and C vary relatively weakly. This is likely connected with the increase of the mean length of the OH bond at excitation of the ν_3 vibrational mode. It is obvious that the OD bond and the mean value of the HOD angle change only slightly in this case. The asymmetry parameter of the molecule $\kappa = \dfrac{2B - A - C}{A - C}$ varies from −0.68 in the ground state to −0.001 in the (0015) state.

Table 2. Vibrational energy, rotational constants (cm^{-1}), and integral intensities of (00V_3) bands of HD^{16}O molecule

Upper state	E_V	A^V	B^V	C^V	Integral intensity, cm·mol^{-1}
000	0	23.41392	9.1034	6.406281	1.2·10^{-20}
001	3707.46673	22.37621	9.0921	6.328031	1.47·10^{-21}
002	7250.51921	21.36441	9.08021	6.249481	9.44·10^{-23}
003	10631.68	20.37551	9.06556	6.16928	3.48·10^{-24}
004	13853.61856	19.4408	9.05766	6.1053	2.36·10^{-25}
005	16920.02802	18.513613	9.043685	6.012524	2.44·10^{-26}
006	19836.8777	17.616	9.033	5.938	2.01·10^{-27}
007	22625.503	16.834	9.006	5.875	1.11·10^{-28}
008	25268.16	16.03	9.00	5.80	7.72·10^{-30}
009	27773.44	15.31	8.99	5.74	5.33·10^{-31}
0010	30158.07	14.66	8.98	5.69	3.69·10^{-32}
0011	32420.87	14.06	8.97	5.64	2.55·10^{-33}
0012	34566.51	13.52	8.95	5.60	1.76·10^{-34}
0013	36599.55	13.04	8.94	5.58	1.21·10^{-35}
0014	38524.42	12.63	8.93	5.56	8.42·10^{-37}
0015	40345.41	12.27	8.91	5.56	5.82·10^{-38}

Thus, at excitation of the OH bond vibrations, the rotational energy spectrum becomes similar to the spectrum of a top molecule with the highest asymmetry.
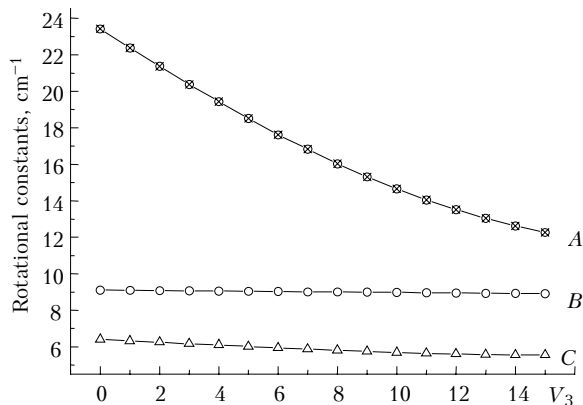
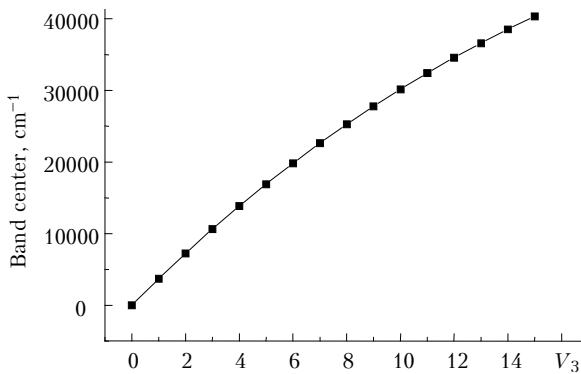**Fig. 1.** Rotational constants vs. quantum number V_3.

Fig. 2. Band centers vs. quantum number V_3.

Fig. 3. Extrapolation of the HD^{16}O integral absorption coefficient to the UV region. The calculations made took into account relative content of the HD^{16}O in water at the water vapor partial pressure of 17 Torr.

Thus, the 0.27-μm band cannot be explained by HD^{16}O absorption. It can likely be explained by the fine effects of rotational-vibrational-electronic interaction with the excited electronic states. However, the estimates obtained here may prove to be useful in calculating the HDO photodissociation rate for the OH bond.[4] It also seems useful to estimate absorption by other H$_2$O isotopic modifications in this interval.

Acknowledgments

The band centers shown in Fig. 2 were calculated by the equation

$$E_{\rm v}(V_3) = \frac{-1920.123607 + 3847.029603 V_3 - 13.56480422 V_3^2}{1 + 0.019402 V_3 + 0.0002 V_3^2}. \quad (5)$$

The dependence of the integral intensity of the $n\mathrm{v}_3$ bands on the quantum number V_3 was also determined (see Table 2). As the initial data, we used the HD^{16}O line strengths calculated by Schwenke[12] for the states (000), (001), …, and (006). The integral intensity was determined as a sum of strengths of individual lines. For the integral intensities, we obtained the following equation:

$$S(V_3) = \exp(-45.65896 - 2.67181\ V_3). \quad (6)$$

Equations (2)−(6) allow the HDO absorption in the region of 25000−40000 cm^{-1} to be estimated. Table 2 and Fig. 3 give the obtained estimates of the integral intensity of the bands and the integral absorption coefficient.

In Fig. 3, the vertical bar separates our calculations and the Schwenke data on the integral intensities of the bands. It should be noted that the approximation obtained predicts a monotonic decrease of line intensities when moving into the UV region. The integral absorption coefficient for the (0013) band, closest to the spectral interval of our interest, is about 10^{-14} cm^{-1}, what is obviously insufficient for even partial explanation of water vapor absorption in this interval.
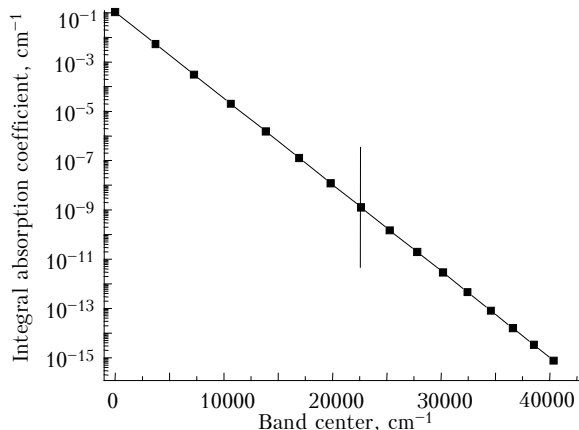
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