

ANALYSIS OF THE $\nu_2 + \nu_3$ ABSORPTION BAND OF THE MOLECULE OF H_2^{17}O

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An absorption spectrum has been recorded in the 1.9 μm range of a mixture of H_2^{16}O , H_2^{18}O , and H_2^{17}O by a UFS-02 Fourier spectrometer. Individual line positions were determined at an accuracy of 0.005 cm^{-1} . This spectrum is analyzed to retrieve the vibrational-rotational energy levels, rotational and centrifugal constants for the vibrational state (011).

The study of the absorption spectra of the isotope-substituted molecule H_2^{17}O (as well as those of other isotopic derivatives of water — H_2^{18}O and HDO) is important for solving certain problems of atmospheric optics. Indeed, even at those low atmospheric concentrations such as this isotope has (0.00037) its lines may affect absorption in various transparency windows and microwindows. Therefore, the spectral parameters of the H_2^{17}O lines are listed in modern atmospheric line absorption atlases.¹

The absorption spectra of H_2^{17}O are not presently known in sufficient detail. For example, its rotational spectrum was studied in Ref. 2, the ν_2 absorption band — in Ref. 3, and the bands $2\nu_2$, ν_1 , and ν_3 formed by transitions to various states from the first triad of interacting vibrational states — in Ref. 4. In Ref. 5 the vibrational-rotational energy levels belonging to the second triad were determined from an analysis of that molecule's spectrum in the 1.9 μm range. Reference 6 analyzes its absorption spectrum in the 1.4 μm range and energy levels of its (200) and (101) states. In Refs. 5 and 6 the H_2^{17}O absorption spectra were recorded using a classical diffraction grating spectrometer with a spectral resolution of $0.05\text{--}0.07 \text{ cm}^{-1}$.

This paper revises absorption spectra of the H_2^{17}O vapor around 1.9 μm at the higher resolution provided by a high-precision Fourier-spectrometer. The observed spectra are theoretically analyzed.

1. Absorption spectra were recorded at room temperature (295 K) using the experimental setup described in Ref. 7. It includes a UFS-02 Fourier-spectrometer, a White multipass gas cell with a baselength of 125 cm, and an IVK-8 measuring-computing complex. To obtain the needed concentration of H_2^{17}O vapor in the cell, we used a standard sample provided by the All-Union Society "Izotop", consisting of a mixture of H_2^{16}O , H_2^{17}O , and H_2^{18}O , enriched with 17 and ^{18}O , with a content of the principal substance 99.99%. Therefore, the H_2^{17}O lines were recorded against the background of the principal isotopic modification of water H_2^{16}O and the isotope, making possible additional estimates of the accuracy of

the line position measurements for the H_2^{17}O molecule by simply comparing the actually measured line positions and the published data.

TABLE I.

Energy levels of the states (011) and (110) of the H_2^{17}O molecule (cm^{-1}).

J	K_a	K_c	E_{exp}	$\Delta \cdot 10^3$	J	K_a	K_c	E_{exp}	$\Delta \cdot 10^3$
State (011)									
0	0	0	5320.251	-1	5	0	5	5640.474	3
1	0	1	5343.830	1	5	1	5	5641.863	3
1	1	1	5358.540	-1	5	1	4	5720.291	8
1	1	0	5364.145	8	5	2	4	5737.992	1
2	0	2	5389.634	-1	5	3	3	5833.784	3
2	1	2	5400.130	1	5	4	2	5949.003	-1
2	1	1	5416.936	-7	6	0	6	5759.136	-3
2	2	1	5460.569	-1	6	1	6	5759.752	-1
2	2	0	5461.891	1	6	2	5	5873.572	10
3	0	3	5455.402	1	6	2	4	5927.421	5
3	1	3	5461.778	1	6	3	3	5989.918	-4
3	1	2	5495.012	-4	6	4	2	6095.374	1
3	2	2	5533.090	3	6	5	1	6236.217	0
3	2	1	5538.024	-1	7	0	7	5895.386	-4
3	3	1	5617.254	0	7	1	7	5895.645	4
3	3	0	5617.458	1	7	2	6	6028.549	2
4	0	4	5539.244	4	7	3	5	6143.560	0
4	1	4	5541.939	-3	8	0	8	6049.336	-11
4	1	3	5596.874	-5	8	1	7	6199.267	-5
4	2	2	5641.293	-9	8	2	6	6306.227	0
4	3	2	5713.558	-2	9	1	9	6221.047	8
4	3	1	5714.912	-2	State (110)				
4	4	1	5828.074	1	3	3	0	5528.932	-1
4	4	0	5828.101	0	4	3	1	5622.624	-2

The total mixture pressure in the cell ($\text{H}_2^{17}\text{O} + \text{H}_2^{18}\text{O} + \text{H}_2^{16}\text{O}$) was monitored by an oil pressure gauge and varied from 1130 to 2132 Pa. The

total optical beam path in the cell amounted to 1005 cm. The measurements were taken at a resolution of 0.02 cm^{-1} , and the line positions were determined to better than 0.005 cm^{-1} . In the spectrum covering the range 5140 to 5440 cm^{-1} 241 lines were recorded in all, of which 74 were identified as belonging to H_2^{17}O .

2. The spectral line identification procedure was as follows. To identify the principal isotopic modification lines both atmospheric spectra and published data from Ref. 5 were used. Absorption lines of H_2^{18}O were identified on the basis of results from Refs. 5 and 8 and the lines of H_2^{17}O — from spectra presented in Ref. 5, and also from the results of calculations of the transition frequencies, obtained by solving the inverse problem.

As a result of this identification 45 energy levels were revised for the (011) vibrational state of the H_2^{17}O molecule (up to $J \leq 9$ and $K_a \leq 5$), and two energy levels — for the (110) state. These data are presented in Table I together with the values of the difference $\Delta = E_{\text{comp}} - E_{\text{exp}}$.

3. In the solution of the inverse problem for the vibrational states of the second triad Coriolis resonances between the states (011), and (110), and (011) and (030) and the Fermi resonance between the states (110) and (030) must be taken into account. The energy levels and the vibrational-rotational wave functions are determined by the well-known method of diagonalizing the effective rotational Hamiltonian, which takes into account the above random resonances.

$$H = \sum_{\nu, \nu''=5, 6, 7} |\nu\rangle H_{\nu\nu''} \langle \nu''|; \quad (1)$$

$$H_{\nu\nu} = E_{\nu} + \left[A^{\nu} + \frac{B^{\nu} + C^{\nu}}{2} \right] J_z^2 + \frac{B^{\nu} + C^{\nu}}{2} J^2 - \Delta_{\mathbf{kz}}^{\nu} J_z^4 - \Delta_{\mathbf{jkz}}^{\nu} J_z^2 J^2 - \Delta_{\mathbf{j}}^{\nu} J_z^4 + H_{\mathbf{kz}}^{\nu} J_z^6 + H_{\mathbf{kjz}}^{\nu} J_z^4 J^2 + H_{\mathbf{j}}^{\nu} J_z^6 + L_{\mathbf{kz}}^{\nu} J_z^8 + \frac{B^{\nu} - C^{\nu}}{2} J_{xy}^2 - \delta_{\mathbf{k}}^{\nu} \left\{ J_z^2, J_{xy}^2 \right\} - 2\delta_{\mathbf{j}}^{\nu} J_z^2 J_{xy}^2 +$$

$$+ h_{\mathbf{k}}^{\nu} \left\{ J_z^4, J_{xy}^2 \right\};$$

$$H_{56} = F_0^{56} + F_{\mathbf{kz}}^{56} J_z^2 + F_{\mathbf{j}}^{56} J^2 + F_{\mathbf{xyxy}}^{56} J_{xy}^2;$$

$$H_{57} = C_{\mathbf{xz}}^{57} \left\{ J_x, J_z \right\}, \quad H_{67} = C_{\mathbf{xz}}^{67} \left\{ J_x, J_z \right\}; \quad (2)$$

$$5 \equiv (030), \quad 6 \equiv (110), \quad 7 \equiv (011).$$

All of the notation in Eqs. (1) and (2) is standard.

Since the only levels that are determined during the spectral analysis in a number sufficient to solve

the inverse problem, are those of the (011) state, to account for such interactions one needs rather accurate estimates of the rotational and centrifugal constants for the other two vibrational states, and also of the parameters determining the resonance interaction.

Such estimates have been obtained using the isotopic relation in the form of the well-known Fraley-Rao rule⁹

$$A_{17} = (A_{18} - A_{16})k + A_{16}, \quad (3)$$

The constant $k = 0.52977$ here was retrieved from the energy levels 101 of the (011) vibrational state for H_2^{16}O , H_2^{17}O , and H_2^{18}O . The parameters of the Hamiltonian (1), (2) were denoted in Ref. (3) as A_{17} , A_{18} , and A_{16} for the respective water isotopic modifications. Parameters of the Hamiltonian for the second triad of H_2^{17}O were calculated from Eq. (3). The initial data needed for such calculations (i.e., the constants A_{18} and A_{16}) may be found in Refs. 8 and 10. Estimates of the rotational, centrifugal, and resonance constants, as well as the parameters E_{ν} are given in Table II in the column labelled "Calculations".

It should be stressed that the estimates thus obtained appear to be rather accurate: computations of the energy levels from Table I yield an average retrieval error of about 0.06 cm^{-1} . This set of constants was then used as an initial approximation in the solution of the inverse problem. Constants for the Hamiltonian, obtained by least squares fit to the energy levels of the vibrational states (011) and (110), taken from Table I, are given in Table II together with their respective 68% confidence intervals.

To solve the inverse problem all the constants for the states (110) and (030) as well as the resonance constants C_{xz}^{57} , F_0^{56} , and $F_{\mathbf{k}}^{56}$, and the constants $H_{\mathbf{k}}$, $H_{\mathbf{j}}$, and $L_{\mathbf{k}}$ for the (011) state were set to their initial values. This made it possible to account for the effect of the resonances and for high centrifugal constants during the computations of the (011) vibrational state energy levels.

The set of parameters from Table II describes the vibrational-rotational energy levels at the level of accuracy of our experiment: the corresponding standard deviation is 0.0048 cm^{-1} . The differences $\delta = |E_{\text{exp}} - E_{\text{comp}}|$ are distributed as follows:

$$\delta \leq 5 \cdot 10^{-3} \text{ cm}^{-1} \text{ for } 85 \% \text{ of all the levels,}$$

$$5 \cdot 10^{-3} < \delta \leq 11 \cdot 10^{-3} \text{ cm}^{-1} \text{ for } 15 \% \text{ of the levels.}$$

Recording and analysis of the H_2^{17}O spectra has resulted in retrieving the energy levels of the (011) state at an accuracy level better than that achieved in Ref. 5. In particular, one may note that the levels 441, 440, and 542, given in Ref. 5, are in error by 0.03 to 0.07 cm^{-1} , and levels 414 and 423 are incorrect.

TABLE II.

Spectroscopic constants for the H₂¹⁷O states (011), (110) and (030) (cm⁻¹)

Parameter	(011)		(110)	(030)
	Computation	Inverse problem	Computation	Computation
E	5320.253	5320.25011 ₉ (72)	5218.720	4666.057
A	29.3372	29.342590 ₆ (99)	29.9575	41.8093
B	14.6108	14.608663 ₅ (56)	14.4756	14.9726
C	8.9743	8.976829 ₃ (31)	8.9312	8.8135
$\Delta_k \cdot 10^2$	4.838	4.92889 ₂ (58)	5.230	24.047
$-\Delta_{Jk} \cdot 10^3$	7.474	7.6003 ₅ (28)	7.370	13.745
$\Delta_J \cdot 10^3$	1.427	1.43497 ₄ (32)	1.429	1.716
$\delta_k \cdot 10^3$	3.269	3.2188 ₄ (52)	3.735	14.599
$\delta_J \cdot 10^4$	6.008	5.6236 ₆ (27)	5.936	7.452
$H_k \cdot 10^4$	2.342	2.6038 ₉ (27)	2.983	41.890
$-H_{kJ} \cdot 10^5$	3.519	fixed	3.265	6.933
$H_J \cdot 10^7$	5.962	fixed	11.164	0
$h_k \cdot 10^5$	6.409	5.619 ₁ (40)	7.863	19.045
$-L_k \cdot 10^6$	0.880	fixed	1.196	63.060

$$C_{xz}^{(011)-(030)} = -0.1442, \quad C_{xz}^{(011)-(110)} = -0.29847₉ (23),$$

$$F_0^{(110)-(030)} = 70.98, \quad F_k^{(110)-(030)} = -0.363$$

Note: 68% confidence intervals in parentheses (for the last two figures of respective values)

The energy levels and parameters of the Hamiltonian we have obtained may now be used to estimate the parameters of H₂¹⁷O absorption lines around 1.9 μ m.

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