

ANALYSIS OF THE HDO ABSORPTION SPECTRUM BETWEEN 9600–10200 cm^{-1} *

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The absorption spectrum of HD^{16}O was recorded at a resolution of 0.02 cm^{-1} with a Bruker IFS 120HR Fourier Transform Spectrometer in the region of $9600\text{--}10200\text{ cm}^{-1}$. As far as we know it is the first time to record and analyze the HDO spectrum in this region which was assigned as the $\nu_1 + 2\nu_3$ and $2\nu_2 + 2\nu_3$ bands. With the strong resonance interactions between these two bands considered, the spectroscopic parameters were optimized by the nonlinear least squares method.

Keywords: Vib-rotational spectrum, HDO

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I. INTRODUCTION

The investigation of high resolution of H_2O and its major isotopomers is strongly required to interpret the atmospheric spectra and calculations of the absorption due to minor atmospheric constituents in the atmospheric transmittance windows. As an asymmetric isotopic modification of water, the spectrum of HDO is studied and gives additional information to determine the intramolecular potential function of the water molecule. Since the high stretching vibrational states of HDO have the delocalized nature, it has been a focus of significant attention as the molecule to elucidate photofragmentation and chemical reaction dynamics of vibrational quantum state selection^[1]. More high resolution spectroscopic studies are required to realize the goal of the bond selective chemistry reaction.

The first extended study of the HDO infrared spectrum was carried out by Benedict *et al.*^[2] from 2400 to 8000 cm^{-1} . The most extensive study was fulfilled by Toth and co-authors,^[3] which covers the region from 600 to 7700 cm^{-1} . The $3\nu_2$ and $\nu_1 + \nu_2$ bands which in the region of $3900\text{--}4400\text{ cm}^{-1}$ were investigated by Perrin *et al.*^[4] The ν_2 and $\nu_1/2\nu_2$ bands were analyzed by Guelachvili^[5] and Papineau *et al.*,^[6] respectively. Ohshima *et al.*^[7] recorded the spectrum of HDO from 6380 to 6600 cm^{-1} . More spectra^[8] have been analyzed with the wave number higher than 8500 cm^{-1} . But in the region of $9600\text{--}10200\text{ cm}^{-1}$, there has been no discussion on it yet.

The rotational energy levels of the ground vibrational state and spectroscopic constants of the Watson A-reduced Hamiltonian have been reported by Johns^[9] and Papineau *et al.*,^[6] respectively.

We present here the first detailed high resolution Fourier transform spectroscopic observation and the analysis of the HDO spectrum in the region of $9600\text{--}10200\text{ cm}^{-1}$. The observed (022) and (102) states of HDO interact with each other through both the Fermi and the Coriolis interactions. With these resonances considered, a good agreement between the experimental data and the calculated levels is achieved.

II. EXPERIMENTAL DETAILS

The sample of D_2^{16}O was purchased from Beijing Chemical Industry, Ltd. (China). The stated abundance of deuterium was 99.8 %. The sample of HDO was prepared by mixing the D_2O and H_2O equally. The spectrum was recorded at room temperature with the Bruker IFS 120HR Fourier transform interferometer, which was equipped with a multipass gas cell with adjustable path length, a tungsten source, a CaF_2 beamsplitter, and a Si diode detector. The unapodized resolution was 0.02 cm^{-1} , and the apodization function was Blackman-Harris 3-Term. The sample pressure was 1500 Pa , which was measured by a manometer with a stated accuracy of 20 Pa . The total path length was 105 m .

Since there are many absorption lines due to the H_2O and D_2O in the region under the study, we use

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the spectrum of “pure” D₂O, which was also recorded before in our laboratory, and the H₂O lines listed in the Hitran 96 database in this region to identify the absorption lines of HDO. The frequency was also calibrated with these H₂O lines in the Hitran96 database. The estimated precision in positions of unblended lines was $2 \times 10^{-3} \text{ cm}^{-1}$.

III. ROTATIONAL ANALYSIS

The HDO is a prolate asymmetric top molecule of the C_s type symmetry. As a consequence, any of its vibrational-rotational band contains absorption lines arising from transitions of the two types (both A and B).

In the region of $9600\text{--}10200 \text{ cm}^{-1}$, the origins of the $\nu_1 + 2\nu_3$ and $2\nu_2 + 2\nu_3$ bands are predicted by Jensen *et al.*^[10] Since these two bands are located closely, strong resonance interactions exist. So the Hamiltonian model which we used in our theoretical rotational analysis should take into account two interacting vibrational states:

$$H^{\text{eff.}} = \sum_{v,v'} |v\rangle \langle v'| H^{vv'}. \quad (1)$$

Here the diagonal operators H^{vv} ($v = 1, 2$) are the

usual Watson’s operators^[11]:

$$\begin{aligned} H^{vv} = & E^v + \left[A^v - \frac{1}{2}(B^v + C^v) \right] J_z^2 \\ & + \frac{1}{2}(B^v + C^v) J^2 + \frac{1}{2}(B^v - C^v) J_{xy}^2 \\ & - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v J^4 \\ & - \delta_K^v [J_z^2, J_{xy}^2]_+ - 2\delta_J^v J^2 J_{xy}^2 \\ & + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 J^4 + H_J^v J^6 \\ & + [J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J^2 J_z^2 + h_J^v J^4]_+ \\ & + L_K^v J_z^8 + L_{KK}^v J_z^6 J^2 + \dots + P_K^v J_z^{10} + \dots \quad (2) \end{aligned}$$

where $|1\rangle = (022)$, $|2\rangle = (102)$. The $H^{vv'}$ ($v \neq v'$) account for the operators of resonance interactions. In this case, resonance operators $H^{vv'}$ should be written in the form of the sum of two terms

$$H^{vv'} = H_F^{vv'} + H_C^{vv'}, \quad (3)$$

which describes resonance interactions of the Fermi type:

$$\begin{aligned} H_F^{vv'} = & F_0^{vv'} + F_K^{vv'} J_z^2 + F_J^{vv'} J^2 \\ & + F_{KK}^{vv'} J_z^4 + \dots + F_{xy}^{vv'} J_{xy}^2 + \dots \quad (4) \end{aligned}$$

and Coriolis type:

$$\begin{aligned} H_C^{vv'} = & C_y(iJ_y) + C_{yK}^{vv'} [iJ_y, J_z^2]_+ + \dots \\ & + C_{xz}^{vv'} [J_x, J_z]_+ + C_{xzJ}^{vv'} [J_x, J_z]_+ J^2 + \dots \quad (5) \end{aligned}$$

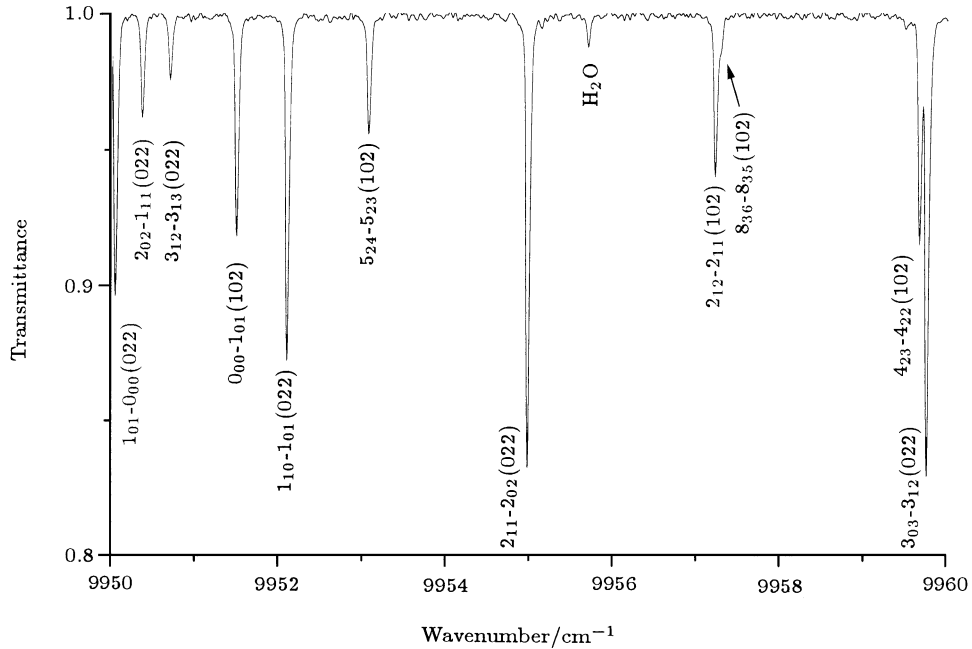


Fig.1. Parts of the spectrum of the (102) and (022) bands of HDO. The label $J'_{Ka'Kc'} - J''_{Ka''Kc''}$ ($n_1 n_2 n_3$) denotes the transitions from the ground state level $J''_{Ka''Kc''}$ to the upper state level $J'_{Ka'Kc'}$ of the upper band ($n_1 n_2 n_3$). Lines marked by “H₂O” are belonged to the absorption of water.

In Eqs.[2]–[5] the following notations are used: $J_{xy}^2 = J_x^2 - J_y^2$, $J^2 = \sum_{\alpha} J_{\alpha}^2$ ($\alpha = x, y$ and z) and $[A, B]_+ = AB + BA$. In our fit, the Hamiltonian in Eq.1 is transformed by a contact transformation to a form in which the leading term in Eq.4 is set to zero, i.e., $F_0^{vv'} = 0$.

Parts of the spectrum of these two bands are illustrated in Fig.2. The expression $J'_{Ka'Kc'} - J''_{Ka''Kc''}$ ($n_1n_2n_3$) denotes the transitions from the ground state level $J''_{Ka''Kc''}$ to the upper state level $J'_{Ka'Kc'}$ of the upper band ($n_1n_2n_3$).

The transitions were assigned by means of the ground state combination differences (GSCD) method. The ground state rotational energies were calculated with the basis parameters taken from Ref.[6].

As a result of our analysis, about 650 transitions were assigned. And 149 upper energy levels were obtained with J' up to 11 and Ka' up to 6, which are listed in Table 1. The spectroscopic parameters listed in Table 2 are obtained by nonlinear least squares fitting.

Table 1. Energy Levels (cm^{-1}) of the (022) and (102) Normal Mode States of HDO.

J	Ka	Kc	(022)			(102)		
			Obs.	Cal.	Obs. - Cal.	Obs.	Cal.	Obs. - Cal.
0	0	0	9934.772	9934.777	-0.005	9967.014	9967.011	0.003
1	0	1	9950.060	9950.066	-0.006	9982.235	9982.237	-0.002
1	1	1	9964.563	9964.565	-0.001	9995.908	9995.902	0.007
1	1	0	9967.617	9967.618	-0.001	9998.878	9998.876	0.002
2	0	2	9980.186	9980.189	-0.003	10012.248	10012.255	-0.008
2	2	0	10043.207	10043.206	0.001	10075.149	10075.147	0.002
2	1	2	9992.028	9992.026	0.002	10023.416	10023.407	0.008
2	2	1	10042.784	10042.786	-0.001	10074.712	10074.710	0.002
2	1	1	10001.161	10001.157	0.005	10032.331	10032.333	-0.001
3	0	3	10024.302	10024.304	-0.002	10056.249	10056.261	-0.012
3	2	1	10090.337	10090.334	0.003	10122.754	10122.757	-0.003
3	1	3	10032.953	10032.953	0.001	10064.418	10064.411	0.008
3	3	1	10160.565	10160.558	0.007	10202.138	10202.143	-0.005
3	2	2	10088.302	10088.305	-0.003	10120.633	10120.632	0.001
3	1	2	10051.100	10051.092	0.009	10082.226	10082.227	-0.001
3	3	0	10160.602	10160.597	0.005	10202.180	10202.182	-0.003
4	0	4	10081.411	10081.413	-0.002	10113.294	10113.306	-0.012
4	2	2	10154.357	10154.350	0.007	10187.539	10187.545	-0.006
4	4	0	10316.904	10316.905	-0.000	10379.055	10379.061	-0.006
4	1	4	10087.080	10087.078	0.002	10118.660	10118.654	0.006
4	3	2	10221.537	10221.541	-0.004	10264.379	10264.378	0.001
4	2	3	10147.722	10147.720	0.002	10181.515	10181.517	-0.002
4	4	1	10316.904	10316.902	0.002	10379.058	10379.058	0.000
4	1	3	10116.937	10116.928	0.008	10149.066	10149.069	-0.003
4	3	1	10221.807	10221.807	-0.000	10264.649	10264.648	0.001
5	0	5	10150.742	10150.745	-0.003	10182.654	10182.663	-0.008
5	2	3	10235.581	10235.577	0.003	10269.949	10269.954	-0.005
5	4	1	10392.821	10392.820	0.001	10456.934	10456.925	0.008
5	1	5	10154.125	10154.123	0.002	10185.868	10185.864	0.004
5	3	3	10297.842	10297.851	-0.008	10342.311	10342.311	0.000
5	5	1				10602.665	10602.665	-0.000
5	2	4	10223.120	10223.123	-0.003	10257.072	10257.075	-0.003
5	4	2	10392.794	10392.794	0.000	10456.906	10456.900	0.006

Table 1. (Continued)

5	1	4	10197.942	10197.938	0.005	10229.862	10229.851	0.011
5	3	2	10298.879	10298.882	-0.003	10343.366	10343.361	0.005
5	5	0				10602.665	10602.665	0.000
6	0	6	10231.957	10231.960	-0.003	10263.998	10264.003	-0.005
6	2	4	10333.798	10333.804	-0.006	10369.910	10369.918	-0.008
6	4	2	10484.177	10484.175	0.002	10550.648	10550.648	-0.000
6	1	6	10233.837	10233.836	0.002	10265.797	10265.793	0.004
6	3	4	10389.394	10389.404	-0.011			
6	6	0				10870.109	10870.110	-0.001
6	5	2				10695.876	10695.873	0.002
6	2	5	10311.933	10311.935	-0.002	10346.953	10346.958	-0.005
6	4	3	10484.046	10484.046	-0.000	10550.526	10550.525	0.001
6	1	5	10293.152	10293.150	0.002	10325.957	10325.939	0.019
6	3	3	10392.337	10392.338	-0.001	10438.882	10438.879	0.003
6	6	1				10870.108	10870.110	-0.001
6	5	1				10695.879	10695.875	0.004
7	0	7	10325.022	10325.025	-0.003	10357.284	10357.285	-0.001
7	2	5	10486.891	10486.896	-0.005	10448.380	10448.395	-0.015
7	4	3	10591.173	10591.171	0.002	10660.403	10660.422	-0.019
7	1	7	10326.018	10326.016	0.002	10358.240	10358.240	-0.000
7	3	5	10496.043	10496.053	-0.010	10544.920	10544.900	0.020
7	5	3				10804.777	10804.772	0.005
7	2	6	10414.398	10414.396	0.002	10450.775	10450.780	-0.005
7	4	4	10590.709	10590.714	-0.005	10659.969	10659.984	-0.015
7	1	6	10401.465	10401.461	0.004	10435.688	10435.671	0.017
7	3	4	10502.773	10502.763	0.011	10551.851	10551.857	-0.006
7	5	2				10804.779	10804.784	-0.005
8	0	8	10430.011	10430.012	-0.001	10462.566	10462.564	0.002
8	2	6	10616.810	10616.826	-0.016	10578.456	10578.471	-0.015
8	1	8	10430.521	10430.517	0.004	10463.058	10463.058	0.000
8	3	6	10620.776	10620.788	-0.013	10669.088	10669.087	0.001
8	4	4				10786.538	10786.517	0.020
8	2	7	10530.130	10530.127	0.003	10568.139	10568.144	-0.004
8	1	7	10521.902	10521.895	0.007	10558.039	10558.035	0.004
8	3	5	10630.602	10630.571	0.031	10682.814	10682.805	0.009
8	4	5				10785.255	10785.265	-0.010
9	0	9	10546.987	10546.988	-0.001	10579.895	10579.892	0.003
9	2	7	10752.794	10752.788	0.006	10722.992	10722.998	-0.006
9	1	9	10547.240	10547.239	0.001	10580.140	10580.142	-0.003
9	3	7				10808.054	10808.053	0.001
9	2	8	10658.773	10658.770	0.003	10698.671	10698.673	-0.002
9	1	8	10653.887	10653.879	0.008	10692.326	10692.328	-0.002
10	0	10	10675.989	10675.990	-0.001	10709.297	10709.296	0.001
10	1	10	10676.113	10676.113	0.000	10709.418	10709.421	-0.003
10	2	9	10800.021	10800.022	-0.001	10842.034	10842.035	-0.001
10	1	9	10797.272	10797.271	0.000	10838.244	10838.250	-0.006
11	2	10	10953.646	10953.644	0.002	10997.965	10997.962	0.003
11	1	10	10952.159	10952.161	-0.002			

Table 2. Spectroscopic Parameters of the (022) and (102) Vibrational States of HDO Molecule (in cm^{-1})^a.

Parameter	(022)	(102)
E	9934.7756(31)	9967.0114(33)
A	23.8225(24)	22.6201(22)
B	9.2185(12)	9.10905(43)
C	6.1222(13)	6.11087(24)
$\Delta_K \times 10^2$	4.850(37)	-0.296(30)
$\Delta_{JK} \times 10^2$	0.3216(46)	-0.1901(80)
$\Delta_J \times 10^2$	0.04491(28)	0.04391(37)
$\delta_K \times 10^2$	0.4508(39)	0.1027(50)
$\delta_J \times 10^2$	0.01979(16)	0.01354(20)
$H_K \times 10^5$	32.8(21)	12.6(14)
$H_{KJ} \times 10^5$	-7.88(23)	10.51(76)
$H_{JK} \times 10^5$	0.24 ^b	0.24 ^b
$H_J \times 10^5$	0.0039 ^b	0.0039 ^b
$h_K \times 10^5$	14.48(31)	-16.73(50)
$h_{JK} \times 10^5$	0.10 ^b	0.10 ^b
$h_J \times 10^5$	0.0021 ^b	0.0021 ^b
$L_K \times 10^7$	98.6(31)	-64.0(20)
$L_{KKJ} \times 10^7$	0.86 ^b	-19.3(20)
$l_K \times 10^7$	-1.9 ^b	-1.9 ^b
$P_K \times 10^9$	0.58 ^b	0.58 ^b
Fermi Type Interactions		
$F_K^{022-102}$	1.7503(22)	
$F_J^{022-102}$	0.08225(69)	
$F_{xy}^{022-102}$	0.12400(83)	
$F_{KK}^{022-102}$	0.005050(44)	
Coriolis Type Interactions		
$C_y^{022-102}$	-0.925(21)	
$C_{xz}^{022-102}$	-0.575(10)	

^a Values in parentheses are the 1σ statistical confidence intervals in the last significant digit. Parameters presented without confidence intervals were fixed to their initial values (see text and footnotes below for details).

^b Fixed to the values of corresponding parameters of the ground vibrational state from Ref.[6].

A statistical analysis of the residuals shows a satisfactory agreement between the observed and calculated energies. For 149 levels which we used to fit the (022) and (102) states,

$\delta \leq 0.005$	67.8% of the levels
$0.005 \leq \delta \leq 0.01$	21.5% of the levels
$0.01 \leq \delta \leq 0.02$	8.7% of the levels
$0.02 \leq \delta \leq 0.04$	2.0% of the levels

with $\delta = |E_{\text{obs.}} - E_{\text{cal.}}|$ (in cm^{-1}). We can see that 98% of the energy levels are reproduced by our fit with errors less than 0.02 cm^{-1} , which is the unapodized resolution of the spectrum.

In our fit, the transformed Hamiltonian we used leads to a mixing of the rotational and coupling constants, so that the initial vib-rotational and resonance parameters cannot be determined well, and the upper state energy levels with high Ka quantum number are not able to be predicted well.

To resolve this problem, first the low J energy levels with $Ka = 0, 1$ are assigned, then these levels are used to fit the interaction parameters. After these interaction parameters are obtained, the higher J and Ka energy levels are predicted well. Then more lines are assigned and more levels are involved to fit more high-order parameters.

Those high-order parameters, such as H_{Jk} , H_K , h_{Jk} , h_J , and P_K , cannot be significantly determined and are fixed to their ground state values.

IV. DISCUSSION

The highly excited vibrational states (102) and (022) of HD¹⁶O have been investigated. Line assignments and energy levels are determined and rotational constants of the Watson A - reduced Hamiltonian are obtained. We can see that the obtained parameters have successfully reproduced the upper state levels.

The Fermi and the Coriolis type resonances are significant since the difference of the two band origins is small. It is also shown that there exist resonances in the (n_1, n_2, n_3) and $(n_1 - 1, n_2 + 2, n_3)$ bands because the wave numbers of ν_1 and $2\nu_2$ are close to each other ($\nu_1 = 2723.6795 \text{ cm}^{-1}$ and $2\nu_2 = 2792.0115 \text{ cm}^{-1}$).^[6] Ohshima *et al.*^[7] got the interaction parameters F_0 , F_K , and C_y by studying the (101) and (021) bands. Perrin *et al.*^[4] recorded the $3\nu_2$ and $\nu_1 + \nu_2$ bands and got the interaction parameters F_0 , F_K , F_J , F_{xy} , C_y and C_{xz} .

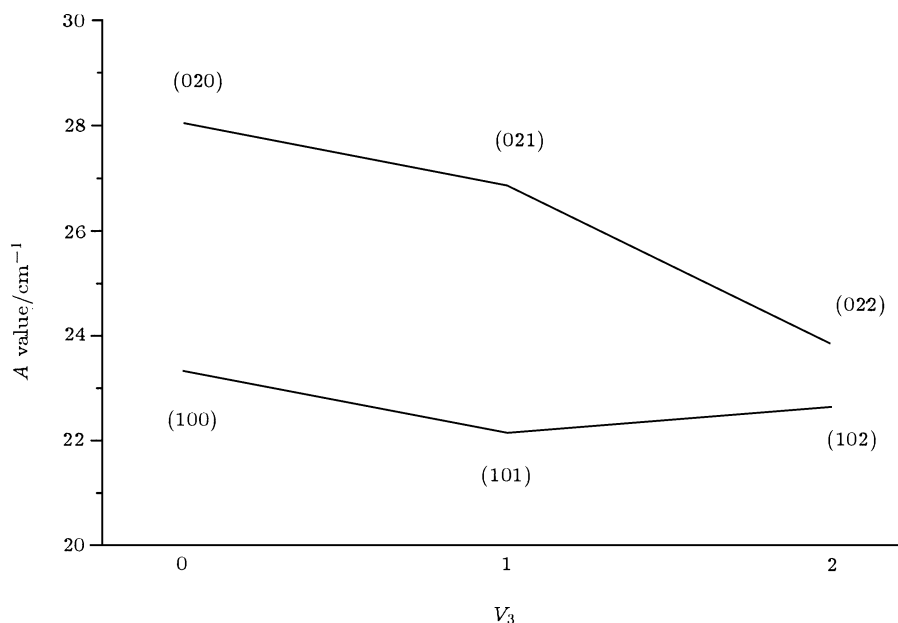


Fig.2. The rotational constant A of the (100), (101), (102), (020), (021) and (022) bands. The dots which denotes the bands with the same ν_1 and ν_2 quantum number are linked by one line.

In our present work, the interaction parameters F_K , F_J , F_{xy} , F_{KK} , C_{xz} and C_y are fitted, while the parameter F_0 is not included in the fitting and is set to zero. If we compare the rotational constant A with those obtained by Papineau *et al.*^[6] and Ohshima *et al.*^[7], we can see that the change of the value of the rotational constant A does not obey the α -relations (Fig.2): the lines linking different dots which have the same ν_1 and ν_2 quantum number are not straight.

The reason is that the contact transformed Hamiltonian leads to a mixing of the rotational and coupling constants. The vib-rotational parameters got via this method are the effective values. Because different F_0 initial values mean different contact transformations of the Hamiltonian, we suggest the parameter F_0 should be considered in the global fitting rather than in this case.

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