Journal of Molecular Spectroscopy 265 (2011) 26–38

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

(0 0 0) and (0 1 0) energy levels of the $HD^{18}O$ and $D_2{}^{18}O$ molecules from analysis of their ν_2 bands

An-Wen Liu [a], Ke-Feng Song [a], Hong-Yu Ni [a], Shui-Ming Hu [a], Olga V. Naumenko [b,*], Irina A. Vasilenko [b], Semen N. Mikhailenko [b]

[a] *Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China*
[b] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB RAS, 1, Akademician Zuev Square, 634021 Tomsk, Russia*

ARTICLE INFO

Article history:
Received 21 June 2010
Available online 3 December 2010

Keywords:
Fourier transform spectroscopy
Water molecule
Absorption spectrum
$HD^{18}O$
$D_2{}^{18}O$
Rotation-vibration assignments

ABSTRACT

High-resolution Fourier-transform spectra of water samples enriched by deuterium and oxygen-18 at room temperature are analyzed in the range 969–2148 cm^{-1}. Line positions of about 2470 transitions up to $J_{max} = 22$ and $K_{a\ max} = 12$ of the ν_2 bands of the $HD^{18}O$ and $D_2{}^{18}O$ molecules are reported. This has allowed the determination of extended sets of rotational energies of the (0 0 0) and (0 1 0) vibrational states for both molecules. The generation function model of an effective rotational Hamiltonian was used in the data reduction to account for the strong centrifugal distortion of the rotational levels. Values of effective Hamiltonian parameters have been determined. The RMS standard deviations of the least-squares fits of the energy levels were 2.4×10^{-4} cm^{-1} for 293 energy levels of the ground state and 3.2×10^{-4} cm^{-1} for 281 energy levels of the (010) state of $D_2{}^{18}O$, and 2.6×10^{-4} cm^{-1} for 227 energy levels of the ground state and 4.2×10^{-4} cm^{-1} for 246 energy levels of the (0 1 0) state of $HD^{18}O$. Comparisons of obtained data with the theoretical predictions as well as with other observations are presented.

1. Introduction

Study of the high resolution rovibrational spectra of the water vapor isotopic species is of continuous interest during last two decades. Recently, an exhaustive analysis of the $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, $HD^{17}O$, and $D_2{}^{18}O$ published rotation-vibrational transitions have been performed, and consistent sets of the experimental energy levels have been derived based on the Rydberg–Ritz principle [1–4]. Rare isotopic species of the water molecule, like $HD^{18}O$, and, especially, $D_2{}^{18}O$ are much less investigated compared to other more abundant isotopologues. Complete list of the available studies can be found in [1,3] for $HD^{18}O$ and in [4,5] for $D_2{}^{18}O$. Even for the lowest vibrational states (0 0 0) and (0 1 0), the experimental sets of rotational energy levels were limited (until recent study for $D_2{}^{18}O$ [5]), by $J \leqslant 16$ and $K_a \leqslant 10$. Accurate experimental rotational energy levels of the (0 0 0) and (0 1 0) states represent the initial and essential information for determination of all the upper experimental levels in room temperature spectra. The present study is aimed at improving and enlarging the set of experimental energy levels of the (0 0 0) and (0 1 0) states of the $D_2{}^{18}O$ and $HD^{18}O$ molecules using newly recorded high resolution Fourier transform spectra in the 969–2148 cm^{-1} spectral range combined with all previously published rotation-vibrational transitions of these two water isotopologues. The (0 0 0) and (0 1 0) rotational energy levels have been derived from solution of the system of the Rydberg–Ritz linear equations which includes all validated rotation-vibrational transitions.

2. Experimental details

The spectra were recorded with a Bruker IFS 120 HR Fourier transform spectrometer in Hefei. Experimental details of the measurements have been presented in our previous papers [5,6]. Here we just give a brief summary of the experimental conditions.

The enriched $D_2{}^{18}O$ water sample used in the measurements was purchased from ICON Services. The stated isotopic concentration of ^{18}O is 98%. The spectrum region was extended down to 970 cm^{-1}. A globar source, a liquid nitrogen cooled MCT detector, and a KBr beam-splitter were used. The unapodized spectral resolution was 0.005 cm^{-1}. A 1.5-m base path length adjustable

---

* Corresponding author. Address: Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Russian Academy of Sciences, 1, Akademician Zuev Square, 634021 Tomsk, Russia. Fax: +7 382 2 49 20 86.

E-mail address: olga@asd.iao.ru (O.V. Naumenko).

0022-2852/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2010.10.007

multi-pass gas cell operated at room temperature was used. Total path length for the spectra recording was 15 m. The sample pressure was measured with two capacitance manometers (MKS Baratron 627B) of 1 torr and 20 torr full-scale ranges with an overall accuracy of 0.15%. The sample pressures were 38 and 1520 Pa. Different optical filters were applied to improve the signal-to-noise ratio and to allow the high resolution measurements. The line positions were calibrated using the absorption lines of $H_2{}^{16}O$ and $HD^{16}O$. Their values were taken from the *HITRAN* 2008 database [7]. The accuracy of the line positions of unblended and not-very-weak lines was estimated to be better than 2×10^{-4} cm^{-1}.

Two examples of the recorded spectra near 1176 cm^{-1} (upper panel) and 1583 cm^{-1} (lower panel) with the rotation-vibration assignments are shown in Fig. 1.

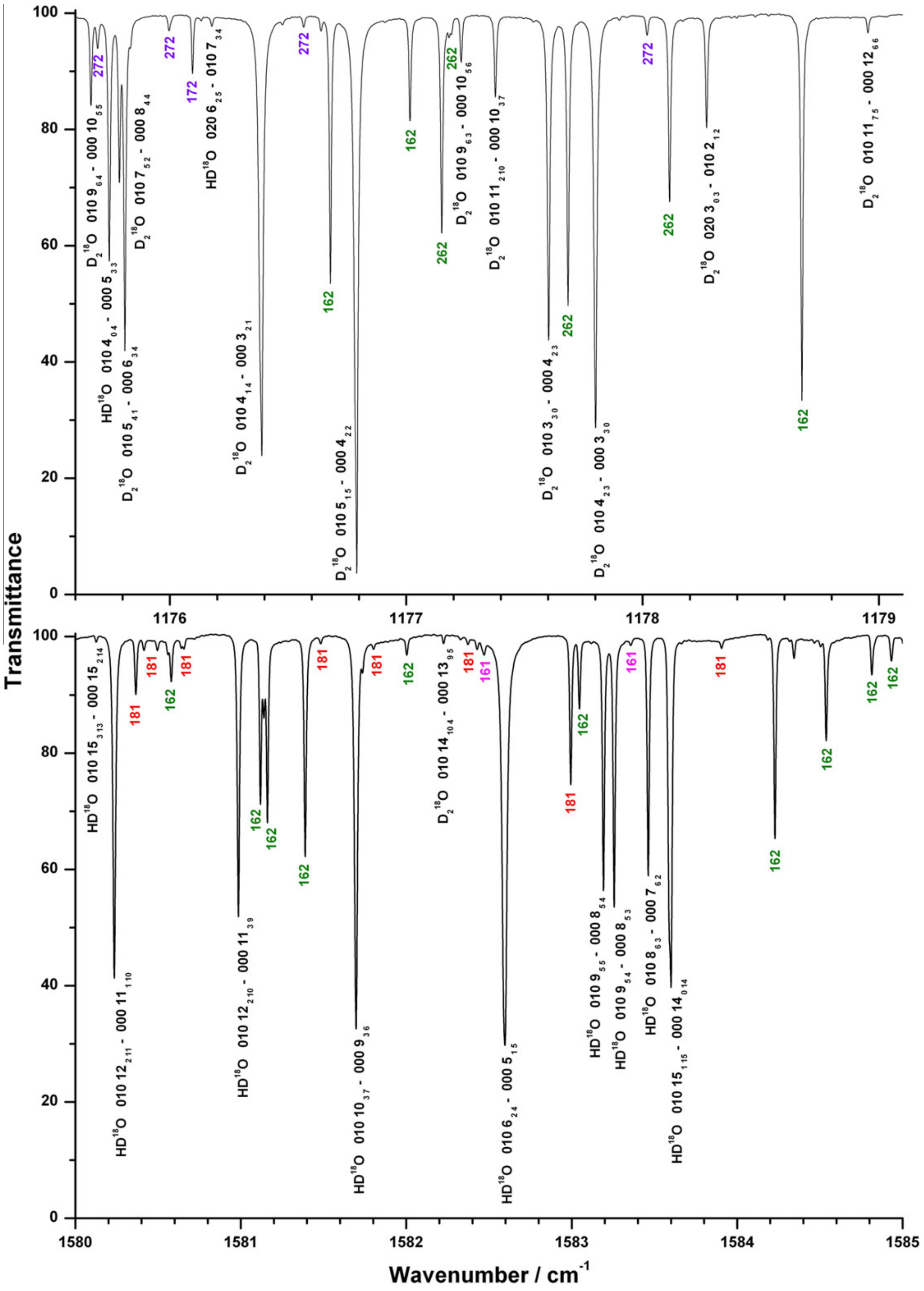

Fig. 1. Part of the spectrum near 1176 cm^{-1} (upper panel) and near 1583 cm^{-1} (lower panel). Rotation-vibration assignments are given for the $HD^{18}O$ and $D_2{}^{18}O$ lines. Lines of other water species are marked by the code of molecule: 161 – $H_2{}^{16}O$, 162 – $HD^{16}O$, 262 – $D_2{}^{16}O$, 181 – $H_2{}^{18}O$, 172 – $HD^{17}O$, and 272 – $D_2{}^{17}O$.