



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Line-Shape Study of Deuterated Isotopomer of H₂O by Tunable Diode Laser Spectrometer Around 8.3 μm Wavelength Region

A.A. Mahmoud, R. Zheng, C.X. Duan and G.M. Huang
College of Physical Science and Technology, Central China Normal University,
Wuhan, 430079, People's Republic of China

Abstract: Pressure broadening coefficients and line strength parameters of D₂O vapour were measured with tunable diode laser absorption spectrometer for (010)-(000) band around 8.3 μm wavelength region. The D₂O vapour is produced by passing Ar (>99.999%) through bubbler containing liquid phase sample and it cooled down in the molecular supersonic jet. Lead-salt diode laser source mounted in a liquid-nitrogen cooled Dewar (L5736, laser components) is used to probe the fundamental band transition of D₂O vapour in the center of multipass cell of about 96 passes of the laser beam. In irregular steps temperature was changed to shift the laser's emission wavelength modal. The results of the fitting at 1194.66 cm⁻¹ are presented; the experimental profiles in the same scale for three different pressures are plotted. We used a lock-in detection technique and phase sensitive detection method to get second derivative signal, then Voigt profile is used for fitting and extraction of line-broadening coefficients. Line positions and pressure-broadening coefficients of 6 lines are determined.

Key words: Diode laser spectroscopy, deuterated water vapor, spectroscopic parameters, voigt profile function, line intensities

INTRODUCTION

In view of the importance of deuterated water vapor for absorption spectroscopy in the infrared region, it is necessary that its spectrum should be known as accurately as possible and it therefore seems desirable to publish the new results for comparison with earlier ones.

High resolution Doppler-free laser techniques are used in beam experiments to improve the spectroscopic description of D₂O molecules. High resolution Fourier-transform spectrometer is used to cover and investigate the ν₂ band of D₂O (Toth, 1999; Camy-Peyret *et al.*, 1985). Terahertz laser sideband spectrometer is one of laser technique used to measure rotational transitions of D₂O in the ground state and excited vibrational states, (Michael *et al.*, 2001). Analysis of the rovibrational spectra of the isolated H₂O, D₂O and HDO molecules has been studied by matrix isolation spectroscopy (Fajardo *et al.*, 2004). There is no direct study of deuterated water vapor by diode laser supersonic jet spectrometer and except that in the investigation of rotational-vibrational and infrared spectra of Van der Waals complexes, where the D₂O is used in the formation of molecular complexes (Pugliano *et al.*, 1993). To present knowledge, no tunable diode laser spectroscopic

measurements have been carried out on this transition around the 8.3 μm region.

The supersonic jet molecular beam technique is widely used method in the laser spectroscopy of molecules. The aim was always to look for cooling methods that can adiabatically decrease the internal temperature of the investigated samples. Consequently, very few vibrational and rotational levels of the ground electronic state of the molecule will be populated, which in turn leads to significantly simplified spectra that are possible to resolve and analyze (Herrero and Tanarro, 1999). Study of fundamental spectroscopic parameters of deuterated water vapor molecules in supersonic jet is important. The absorption spectra in infrared regions have been studied in great detail and spectroscopic parameters like line strength, linewidth, line position, line shift, etc., have been extracted by Ray *et al.* (2004) and Grossmann and Browell (1989).

A specie in the molecular beam can be studied under conditions where pressure and Doppler broadening as well as the number of excited vibrational states are reduced (Ponsardin and Browell, 1997). The gases used in molecular beam are composed of D₂O and Ar, which in principle is planed to generate ArD₂O Van der Waals complex.

In most tunable diode-laser spectrometers a single narrow laser line is scanned over an isolated absorption line of the target species to achieve the highest selectivity, analysis is made at low pressure, where the absorption lines are not substantially broadened by pressure (Bohren and Clothiaux, 2006; Bandyopadhyay *et al.*, 2005). This type of measurement has developed into a very sensitive and general technique for monitoring many atmospheric trace species. The main requirement is that the molecule should have an infrared line-spectrum which is resolvable at the Doppler limit, which in practice includes most molecules with up to five atoms together with some larger molecules.

MATERIALS AND METHODS

Experimental setup: An overall schematic of the experimental apparatus is shown in Fig. 1. One method makes up the scheme of the gases characterization at the College of Physical Sciences and Technology in Central China Normal University. The laser-method that has been employed to the gases is the one of the most useful characterization methods (Camy-Peyret *et al.*, 1985; Werle, 1996; Toth, 1999; Michael *et al.*, 2001). The employment period was one academic semester (4 months) and it was in the end of 2008.

Lead-salt diode laser source placed in a liquid-nitrogen cooled Dewar (Model L5736, laser component).

The laser beam was first collimated by an off-axis parabolic mirror and then the laser is split into 3 parts, one to be pass through the sample jet inside the evacuation chamber, where the detection conditions is optimized and the other 2 parts to pass through the reference cell and the Ge etalon. Spherical mirrors are used for further collimation and focusing the laser beam into the center of a stigmatic multi-pass cell. Mechanical and diffusion pumps are used to get relatively low background pressure of about 10^{-6} m bar. Valve driver (IOTA ONE from Parker Hannifin) is used to control the sample via., the pulsed supersonic jet nozzle (General Valve Series 9). The optimal opening time of the nozzles was about 400 sec and operation frequency of about a 20 Hz gas repetition. The sample molecular beam is directed into the multi-pass cell center and it makes about 90° angles with reflected laser beams as it shown in Fig. 1. After 96 passes through the sample molecular beam the exit laser beam is detected by a liquid-nitrogen cooled HgCdTe detector (Judson technologies). The detector signal is monitored by a lock-in amplifier (Signal Recovery 7280) triggered by the valve driver. The analogue signal is recorded with the help of a 14 bit analogue to digital converter (ADC) (NI PXI-5122) and transferred to the embedded controller for data processing. The embedded controller is used to externally modulate the source controller (L5830, Laser Components). The ADC runs with a maximum sampling rate of about 20 M sample sec^{-1} (mega samples per

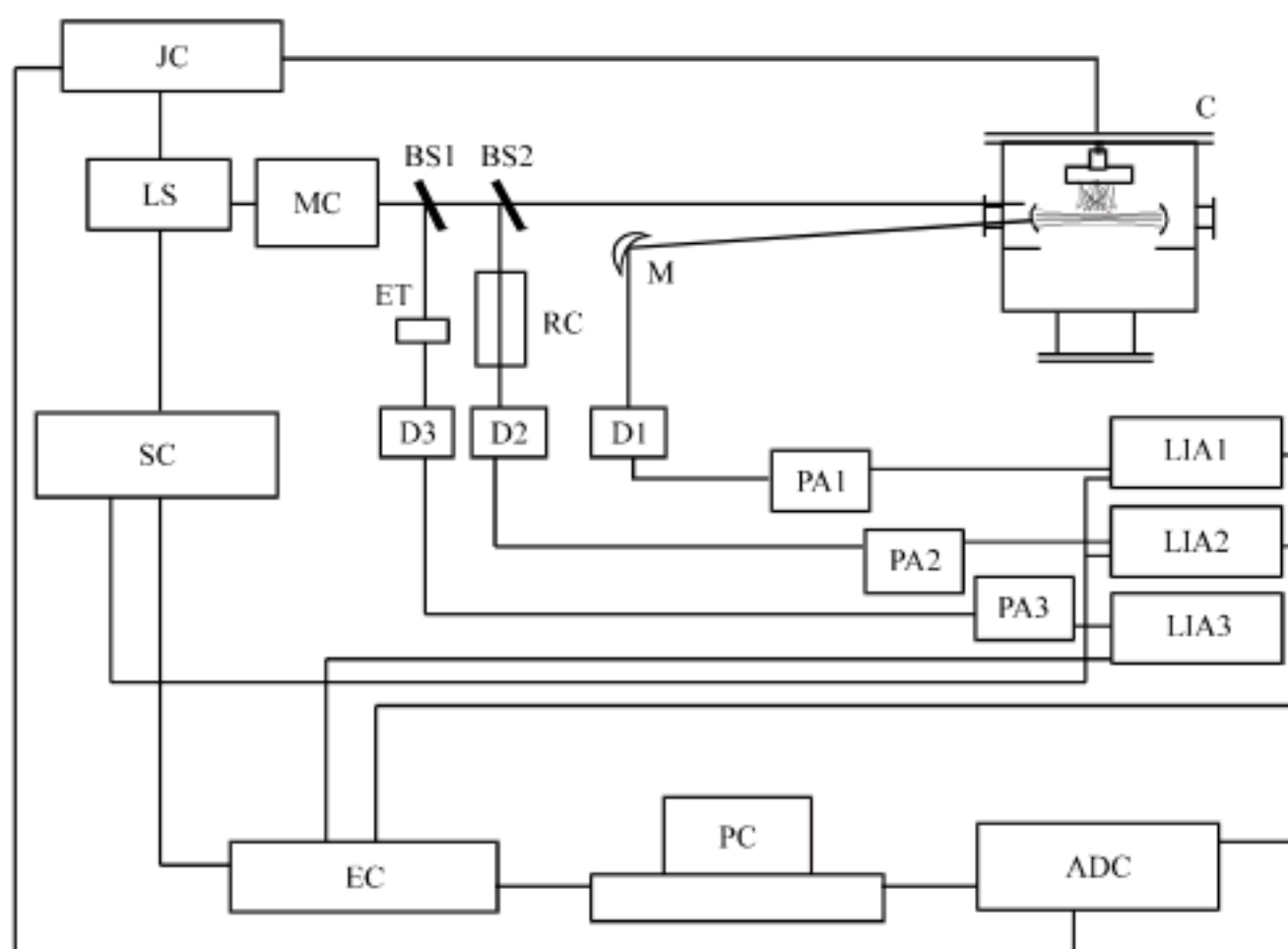


Fig. 1: Depicts the basic setup of the tunable diode laser absorption spectrometer, LS: Laser Source, SC: Source Controller, JC: Jet Controller, LIA: Lock-In Amplifier, D: Detector, PA: Preamplifier, PC: Computer, M: Mirror, BS: Beam Splitter, ET: Etalon, C: Chamber, RC: Reference Cell, ADC: Analog-Digital Converter, EC: Embedded Controller

second), resulting in the acquisition of 10.000 Mbit during the scan interval time. The ADC has one input channel, where the jet signal is permanently connected. Another two (SRS830) lock-in amplifiers are used simultaneously to record the absorption of the reference cell and the etalon fringes (FSR $\sim 0.0485 \text{ cm}^{-1}$). The diode laser current, data acquisition and signal processing is controlled by labview program. During the spectral detection (data collection), the laser frequency increases gradually as the current of the diode laser increases.

Generally, the current supplied to the diode is modulated to vary the wavenumber and swept at a rate of 0.03 mA/step, while the temperature is kept constant. The operational mode of the diode laser is accomplished over a small spectral range of about ($\sim 3 \text{ cm}^{-1}$) at one temperature. The modulation of the laser current is externally ramped from lock-in amplifier at ($f = 40 \text{ kHz}$). Different wavenumber preferences were achieved by varying the temperature of the diode.

The controlled pressure deuterated water vapor is formed in the pulsed supersonic jet expansion diluted in the Ar carrier gas. With a different stagnation pressures the absorption spectrum of D_2O is recorded. The absorption spectrum of D_2O was calibrated against accurate line positions of N_2O from the HITRAN database (Rothmana *et al.*, 2005). The relative uncertainty in line positions was approximately $\pm 0.0001 \text{ cm}^{-1}$.

Detection of the spectrum: The spectrum of D_2O has been obtained in the 8.3 nm wavelength region, using a supersonic slit jet system coupled to a tunable diode laser spectrometer with a spectral resolution of 0.005 cm^{-1} . The spectral range covered by the diode laser is often disturbed with mode hops. The single-mode region is selected by adjusting the current and temperature of the diode laser. The etalon fringes observation with a digital oscilloscope reveal the mode break and single mode region. Only well-separated transitions within a single mode are chosen for line-shape analysis.

Initially, the diode laser current scanned from 820 to 825 mA. The scan reveals strong transition at $1194.03577 \text{ cm}^{-1}$. Figure 2 shows the deuterated water vapor spectrum of this transition. Locking amplifier is used to obtain the second derivative spectra of the fundamental transitions. Absorption lines are broadened by the line shape function. The majority of the broadening can be attributed to many factors such as velocity distribution in the sample, frequency noise on the diode laser and none exactly orthogonal crossings of the slit jet expansion. Although, in the region where very weak lines are observed, we have been able to perform a line-broadening experiment with these transitions. The later transitions strengths have been reported by Toth (1993)

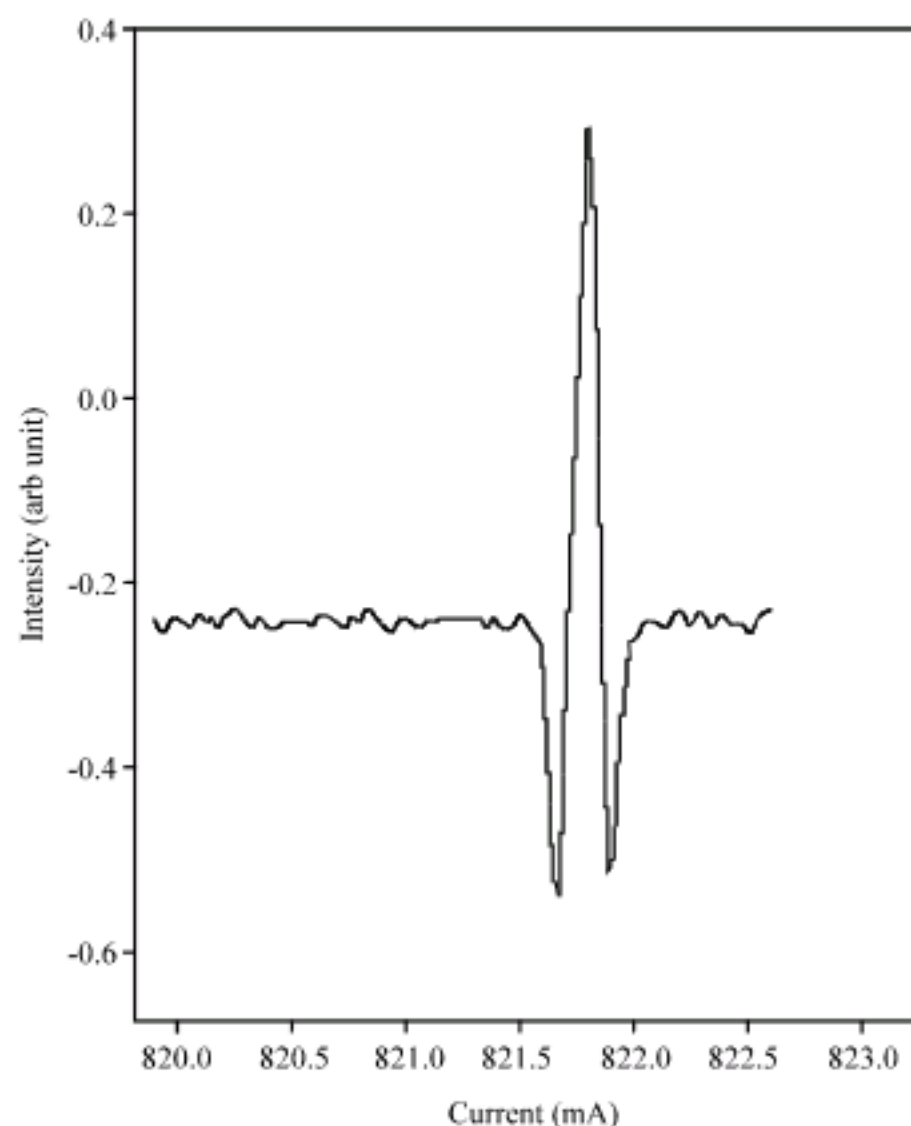


Fig. 2: Spectrum of the D_2O molecule in the ν_2 band region at $1194.0358 \text{ cm}^{-1}$ line

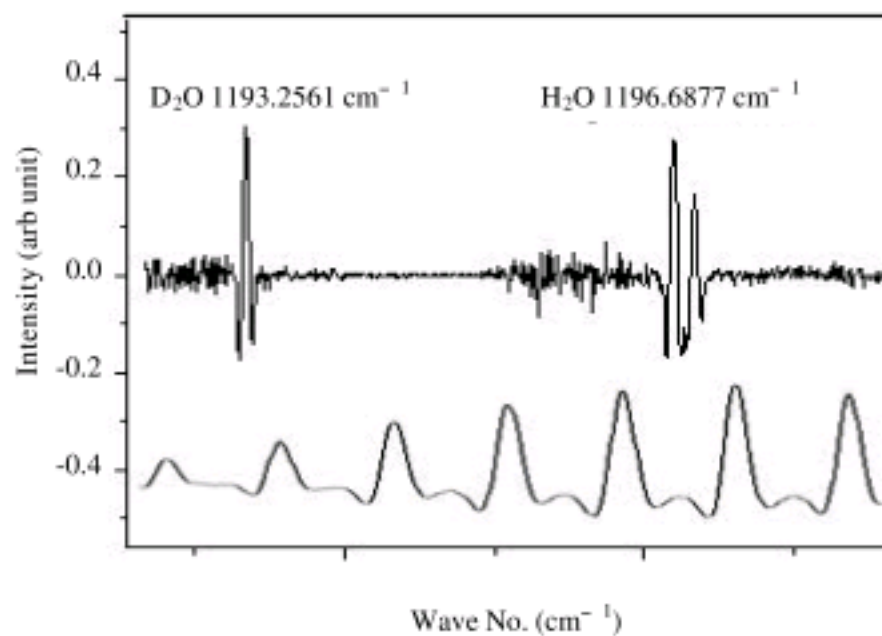


Fig. 3: A part of the scan of second-derivative spectrum of D_2O transitions with simultaneous scan of etalon fringes

are used to confirm lines identification. Figure 3 shows a portion of the observed spectrum of the D_2O line (010)-(000) which contains spectral contamination from the ν_2 H_2O region, in spite of that the lines are considerably sharper in the spectrum. The S/N ratio of the transition at D_2O - $1193.2561 \text{ cm}^{-1}$ is ~ 12 . The sample path length is 4.8 m and the sample pressure is $\sim 3 \text{ mbar}$. In order to optimize S/N ratio in the spectra, the backing pressure were altered, while scanning subsequently over a single D_2O absorption line.

RESULTS AND DISCUSSION

In a conventional direct optical absorption experiment the incident and transmitted intensities (I_0 and I , respectively) of a light beam, propagating through the gas sample medium of path length d , are measured. The absorption of the gas sample is related to the attenuation of the light intensity which is expressed by the well known Lambert-Beer law:

$$I(\omega) = I_0(\omega) \cdot \exp[-\alpha(\omega) \cdot d]$$

where, $\alpha(\omega)$ is frequency dependent absorption coefficient, which is usually given in cm^{-1} .

In general, the line-shape function α is described by a Voigt function, which is the real part of the complex probability function. The second derivative of the experimental spectrum is numerically integrated to obtain the original line shape.

To get the line parameters we apply a nonlinear least-squares fit to the molecular transmission using a Voigt-profile for the modeling of the line shape. The molecular transmission $T(\sigma)$ is obtained from the two signals in two steps. First, the Fabry-Perot signal is used to perform the frequency scaling with a polynomial interpolation on the interference fringes. In a second step, we retrieve the molecular transmission from the direct spectrum A using the relation:

$$A = A_0 T(\sigma)$$

where, A_0 is what would be the laser flux in the absence of absorber in the cell.

A_0 is obtained from A with a polynomial interpolation over full the transmission region of detection. The line position was fitted in order to enhance the residual. The result in the position of weak lines is only relative in relation to the stronger lines in the neighborhoods due to the lack of absolute frequency calibration with a laser spectrometer.

The line intensity $S(T)$ is related to the molecular transmission through the Beer Lambert law. The absorption coefficient at the gas pressure p is modeled using the Voigt profile earlier described by Durry *et al.* (2008), where the molecular parameters of H_2^{16}O , H_2^{17}O , H_2^{18}O and HDO are examined by tunable diode laser spectrometer. They measured these water vapor isotopologues, in the region around 3787 cm^{-1} ($2.64 \mu\text{m}$), while in this case, the observed deuterated water vapor (D_2O) absorption lines are belong to the fundamental ν_2 rovibrational with wavelengths around $8.3 \mu\text{m}$.

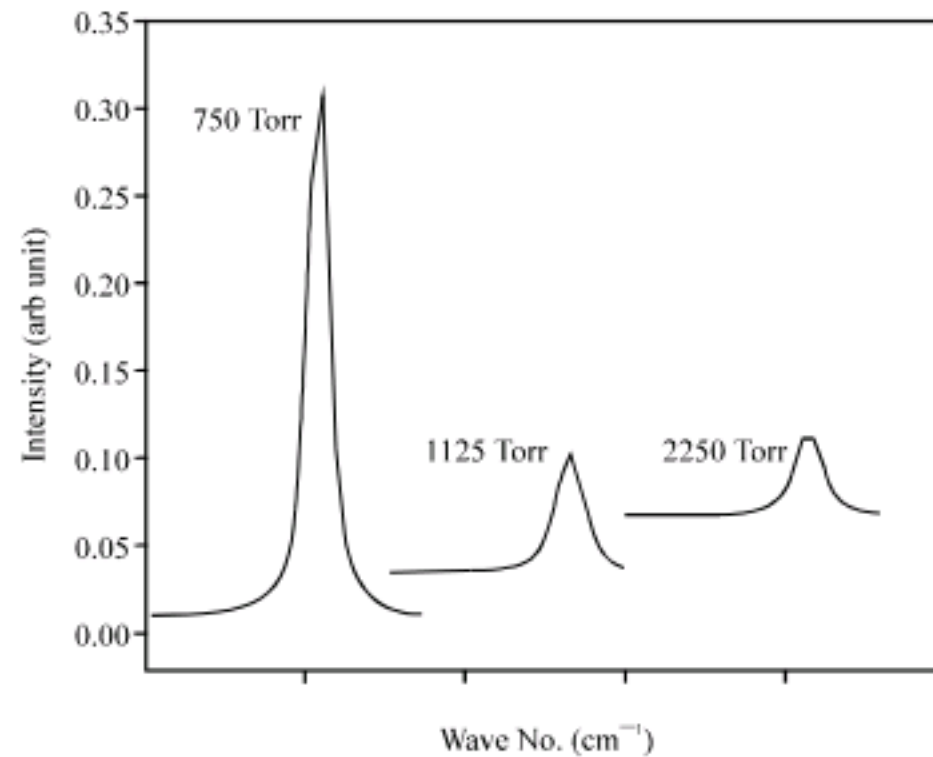


Fig. 4: Experimental profiles for the transition at $1194.6600 \text{ cm}^{-1}$ are presented for three different pressure combinations in the same scale

Table 1: Voigt broadening parameter for D_2O

Observed line position (cm^{-1})	$J' K_a' K_c' \leftarrow J K_a K_c$	Band	Pressure (Torr)	Voigt broadening parameter	Strength (%) (Toth, 1993)
1193.2561	2 1 1 2 0 2	010	750	6.6(7)	1.34E-00
			1125	5.4(4)	
			2250	6.8(2)	
1194.0357	2 0 2 1 1 1	010	750	15.6(1)	5.58E-01
			1125	13.4(1)	
			2250	15.8(7)	
1194.6600	5 2 4 4 3 1	010	750	8.8(1)	1.14E-01
			1125	3.4(1)	
			2250	6.8(3)	
1195.3077	3 1 2 2 2 1	010	750	22.1(2)	8.80E-02
			1125	20.1(1)	
			2250	22.8(6)	
1196.2286	7 5 3 6 6 0	010	750	6.5(3)	6.85E-03
			1125	9.2(2)	
			2250	9.4(1)	
1196.2557	7 5 2 6 6 1	010	750	15.2(3)	3.41E-03
			1125	15.6(3)	
			2250	15.5(1)	

The values in parenthesis are the SD from the fitting process in unit of the last quoted digit

We have presented here the result of fitting for the transition at $1194.6600 \text{ cm}^{-1}$ (Fig. 4) and the experimental profiles plotted in the same scale for three different pressures. All the broadening lines observed at 750, 1125, 2250 Torr are shown in Table 1. The original line shape is fitted with a Voigt profile by using origin software program. For each pressure the Voigt broadening parameter (obtained at jet temperature) in this study are shown in Table 1.

CONCLUSION

In this study, on the absorption line shapes in the ν_2 band we analyzed the spectrum of D_2O vapour from the

line shape function. Line positions and pressure-broadening coefficients of 6 lines have been determined. Voigt profile is used for fitting and extraction of all line-broadening coefficients. The strength results we have obtained with this tunable diode laser spectrometer, associated with molecular beam technique are compared with those of Toth (1993). We believe that the study, we have presented will be helpful in the study of deuterated water vapour absorption spectroscopy in the infrared.

ACKNOWLEDGMENTS

This study has been supported by the National Natural Science Foundation of China (Grant No. 10604019) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

REFERENCES

- Bandyopadhyay, A., A. Ray, B. Ray and P.N. Ghosh, 2005. Line-shape study of argon broadened water vapour overtone transitions in the 818-834 nm wavelength region. *J. Mol. Spectr.*, 234: 93-98.
- Bohren, C.F. and E.E. Clothiaux, 2006. *Fundamentals of Atmospheric Radiation*. 1st Edn., John Wiley and Sons, New York, ISBN: 3-527-40503-8.
- Camy-Peyret, C., J.M. Flaud and A. Mahmoudi, 1985. Line positions and intensities in the ν_2 Band of D_2O improved pumped D_2O laser frequencies. *Int. J. Infrared Millimeter Waves*, 6: 199-232.
- Durry, G., L. Joly, T. Barbu, B. Parvitte and V. Zéninari, 2008. Laser diode spectroscopy of the H_2O isotopologues in the 2.64 μm region for the *in situ* monitoring of the Martian atmosphere. *Infrared Phys. Technol.*, 51: 229-235.
- Fajardo, M.E., S. Tam and M.E. DeRose, 2004. Matrix isolation spectroscopy of H_2O , D_2O and HDO in solid parahydrogen. *J. Mol. Struct.*, 695: 111-127.
- Grossmann, B.E. and E.V. Browell, 1989. Water-vapor line broadening and shifting by air, nitrogen, oxygen and argon in the 720 nm wavelength region. *J. Mol. Spectr.*, 138: 562-595.
- Herrero, V.J. and I. Tanarro, 1999. Production and applications of atomic and molecular beams. *Vacuum*, 52: 3-10.
- Michael, E.A., C.J. Keoshian, S.K. Anderson and R.J. Saykally, 2001. Rotational transitions in excited vibrational states of D_2O . *J. Mol. Spectr.*, 208: 219-223.
- Ponsardin, P.L. and E.V. Browell, 1997. Measurements of $H_2^{16}O$ line strengths and air induced broadenings and shifts in the 815 nm spectral region. *J. Mol. Spectr.*, 185: 58-70.
- Pugliano, N., J.D. Cruzan, J.G. Loeser and R.J. Saykally, 1993. Vibrational and K_a dependencies of the multidimensional tunneling dynamics in the 82.6 cm^{-1} intermolecular vibration of water dimer- d_4 . *J. Chem. Phys.*, 98: 6600-6617.
- Ray, A., A. Bandyopadhyay, B. Ray, D. Biswas and P.N. Ghosh, 2004. Line-shape study of water vapour by tunable diode laser spectrometer in the 822-832 nm wavelength region. *Applied Phys. B.*, 79: 915-921.
- Rothmana, L.S., D. Jacquemart, A. Barbe, D. Chris Benner and M. Birk *et al.*, 2005. The HITRAN molecular spectroscopic database. *J. Quant Spectr., Radiat. Transfer*, 96: 139-204.
- Toth, R.A., 1993. $D_2^{16}O$ and $D_2^{18}O$ transition frequencies and strengths in the ν_2 bands. *J. Mol. Spectr.*, 162: 41-54.
- Toth, R.A., 1999. Air- and N_2 -broadening parameters of HDO and D_2O , 709 to 1936 cm^{-1} . *J. Mol. Spectr.*, 195: 73-97.
- Werle, P., 1996. Tunable diode laser absorption spectroscopy: Recent findings and novel approaches. *Infrared Phys. Technol.*, 37: 59-66.