

He-broadening and shift coefficients of water vapor lines in infrared spectral region

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ABSTRACT

The water vapor line broadening and shift coefficients in the $\nu_1+\nu_2$, $\nu_2+\nu_3$, $\nu_1+\nu_3$, $2\nu_3$, $2\nu_1$, $2\nu_2+\nu_3$, and $\nu_1+2\nu_2$ vibrational bands induced by helium pressure were measured using a Bruker IFS 125HR spectrometer. The vibrational bands $2\nu_3$ and $\nu_1+2\nu_2$ were investigated for the first time. The interaction potential used in the calculations of broadening and shift coefficients was chosen as the sum of pair potentials, which were modeled by the Lennard-Jones (6-12) potentials. The vibrational and rotational contributions to this potential were obtained by use of the intermolecular potential parameters and intramolecular parameters of H₂O molecule. The calculated values of the broadening and shift coefficients were compared with the experimental data.

Keywords: Line broadening and shift coefficients, semi-classical method, intermolecular potential, Fourier spectroscopy.

1. INTRODUCTION

At present the experimental and theoretical helium – broadening coefficients of H₂O transitions in different spectral regions have been obtained [1–12]. In ref.[12] the experimental data of the line broadening (γ) and shift (δ) coefficients were obtained for 9 vibrational bands of H₂O. These data were used to determine the intermolecular interaction potential which was taken as the sum of pair potentials which, in turn, were modeled by the Lennard-Jones potentials.

2. EXPERIMENTAL DETAILS

The experimental setup and line parameters retrieval procedure have been described in detail in [8]. The measurements of the water vapor absorption spectra in 3000-9000 cm⁻¹ region perturbed by pressure of He pressure were performed at the V.E. Zuev Institute of Atmospheric Optics (IAO), SB Russian Academy of Science, using Bruker IFS 125HR high-resolution Fourier transform spectrometer. The spectrometer was equipped with CaF₂ beam splitter, InSb detectors and tungsten halogen lamp as the light source. The Thermo Electron White type multiple reflection absorption cell with BaF₂ windows and with gold-coated mirrors was used for the measurements. This cell was located inside the evacuated sample compartment. The records of the H₂O and H₂O – He absorption spectra were made at room temperature (~18 °C) with the optical path length of 10 m and unapodized resolution 0.01 cm⁻¹, which corresponds to 50 cm of MOPD in the Bruker definition. The pressure of the water vapor varied from 3.22 mbar to 10.05 mbar and was measured with a Baratron gauge with an estimated uncertainty of 0.25%. The pressure of the H₂O – He mixture ranged from 251 mbar to 3193 mbar and was measured with two type of manometers: a DVR-5 capacitance manometer (1100 mbar full scale) and DM501E manometer (10000 mbar full scale) which have a stated uncertainty of 0.5% according to the manufacturer. In this pressure range eight absorption spectra of H₂O and H₂O – He mixture have been recorded.

Determination of the line position, integrated line absorbance, Gaussian and Lorentzian widths and baseline (treated as a linear function) of each spectral lines was obtained from the non-linear least square (NLLS) fitting of the Voigt profiles to the measured values of absorption. The Gaussian width was fixed at the corresponding Doppler width. In this way the values of the halfwidths and the relative line center position, as well as their standard deviations for water vapor lines of ν_1 , ν_3 , $2\nu_2$, $\nu_1+\nu_2$, $\nu_2+\nu_3$, $\nu_1+\nu_2+\nu_3$, $2\nu_2+\nu_3$ and $2\nu_1$ bands at different pressures of H₂O – He mixture have been obtained. The dependencies of the halfwidths and line center positions on He pressure obtained for every spectral line under treatment were plotted and fitted again using a linear function. This latter procedure allowed to obtain the values of the broadening and shifting coefficients for water vapor absorption lines under study, induced by helium pressure. As an example, Fig. 1 shows a example of H₂O measured and calculated line profiles.

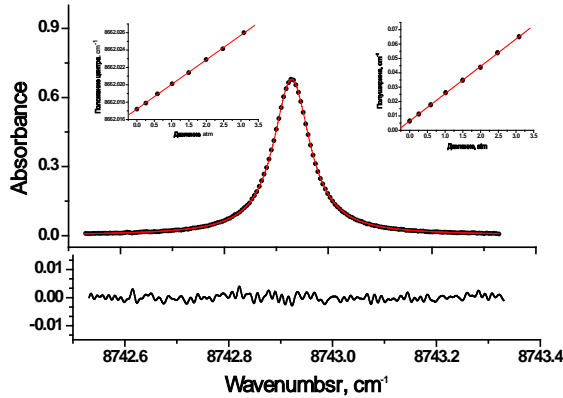


Fig.1. The measured and calculated profiles of line $\nu_1+\nu_2+\nu_3$ [2 1 2] \leftarrow [3 1 3], the line centre position and halfwidth (Lorentzian component) of this line as a function of the helium pressure .

3. CALCULATION OF THE BROADENING AND SHIFT COEFFICIENTS

The line broadening and the line-center shift coefficients, γ and δ , respectively, were calculated in the *RBET* method based on the Robert-Bonamy (*RB*) formalism [14] in which the resonance functions are calculated in the model of exact trajectories (*ET*) [15]. In the *RB* method for the transition $i \rightarrow f$ in the H₂O molecule perturbed by the pressure of mono-atomic gases, the coefficients γ_{if} and δ_{if} are calculated by using the expression

$$\gamma_{if} + i\delta_{if} = \frac{n}{c} \int_0^{\infty} v F(v) dv \int_{r_0}^{\infty} D r_c dr_c [1 - \exp(-iS_1 - S_{2,i}^{outer} - S_{2,f}^{outer*} - S_2^{middle})], \quad (1)$$

Here, n is the density of the buffer gas, c is the speed of light, v is the relative velocity of interacting particles and r_c is the closest approach distance between them. The formula for the parameter r_0 , the Jacobian D of the transition from the variable (b, v) (b is the impact parameter) to the variable (r_c, v) are presented in ref. [15]. The expressions for $S_2(b)$ functions were taken from refs. [15, 16]. In contrast to the original version of the Robert-Bonamy method [14], the *RBET* method uses resonance functions [15] from $S_2(b)$, obtained in the *ET* model. To calculate these functions, as well as $S_1(b)$ and $S_2(b)$, it is necessary to specify the inter-molecular interaction potential. This potential was chosen as the sum of pair potentials

$$V = V_{1,2}^{aa} = \sum_{i=1}^3 \left(\frac{d_i}{r_i^{12}} - \frac{e_i}{r_i^6} \right), \quad (2)$$

which, in turn, were modeled by the Lennard-Jones (6-12) potentials. In formula (2) the index i refers to the i -th atom of H₂O molecule and d_i and e_i are the atomic pair energy parameters. The isotropic part is usually taken in the form of the Lennard-Jones potential

$$V_{isot} = -\frac{C_6}{r^6} + \frac{C_{12}}{r^{12}}, \quad (3)$$

were $C_6 = 4\varepsilon\sigma^6$, and $C_{12} = 4\varepsilon\sigma^{12}$, and ε and σ are the parameters.

Procedure of the broadening coefficients calculation is presented in ref. [12] in more detail. To make possible the calculation of the broadening coefficients γ and δ for vibrational bands the extrapolational formulas for variable parameters σ (in \AA^3), ΔC_6^{vib} (in $D \cdot \text{\AA}^3$) and ΔC_{12}^{vib} (in $D \cdot \text{\AA}^9$) were proposed as

$$\begin{aligned} \sigma &= 2.596 - 0.00837 \cdot v_1 + 0.0067 \cdot v_2 - 0.0062 \cdot v_3, \\ \Delta C_6^{vib} &= 0.1694 \cdot v_1 - 0.00687 \cdot v_2 + 0.191 \cdot v_3, \\ \Delta C_{12}^{vib} &= 147.0 \cdot v_1 + 9.7 \cdot v_2 + 148.5 \cdot v_3. \end{aligned} \quad (4)$$

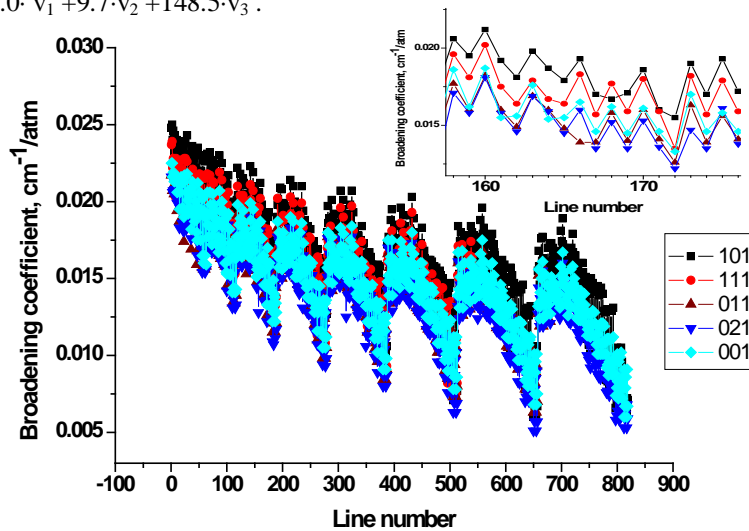


Fig.2. Calculated H₂O–He halfwidths for A-type bands.

The helium broadening coefficients γ and δ were calculated with the optimal sets of potential parameters for the transitions of H₂O vibrational bands with rotational quantum numbers J and K_a up to 14. As an example, the values of the broadening coefficients for five A-type bands are presented on Fig. 2. It is about 20,000 values of γ and δ for T.296 K.

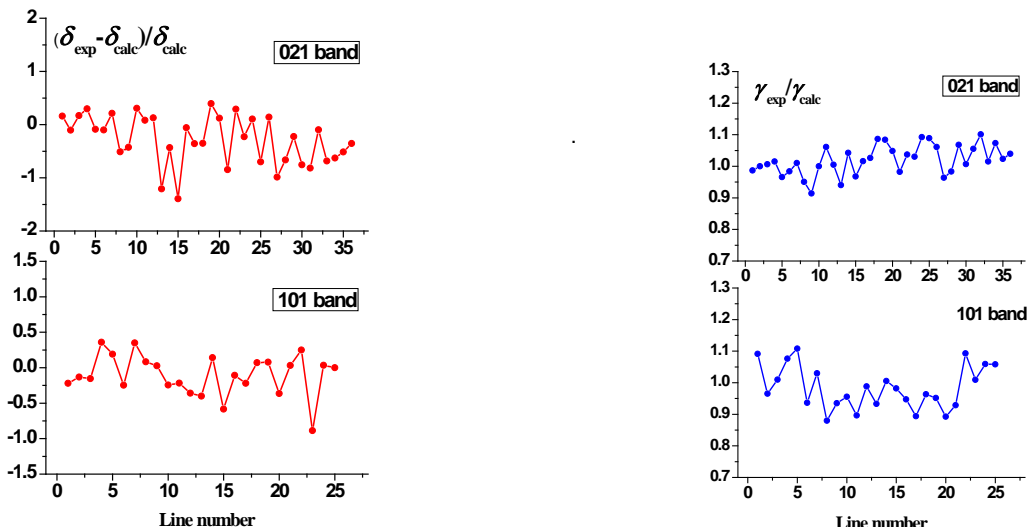


Fig.3. The comparison between experimental and calculated values of broadening coefficients of H₂O lines for 2 vibrational bands

Fig. 3 shows a comparison between experimental and simulated values of broadening and shift coefficients of H₂O lines for $2\nu_2+\nu_3$ and $\nu_1+\nu_3$ vibrational bands, $\text{rms}(\gamma) = 1.8 \cdot 10^{-3} \text{ cm}^{-1}\text{atm}^{-1}$, $\text{rms}(\delta) = 1 \cdot 10^{-3} \text{ cm}^{-1}\text{atm}^{-1}$ for $\nu_1+\nu_3$ and $\text{rms}(\gamma) = 1 \cdot 10^{-3} \text{ cm}^{-1}\text{atm}^{-1}$, $\text{rms}(\delta) = 1.1 \cdot 10^{-3} \text{ cm}^{-1}\text{atm}^{-1}$ for $2\nu_2+\nu_3$ band.

4. CONCLUSIONS

In the present work the optimal set of potential parameters for the model intermolecular potential (3) for H₂O-He system is presented. These parameters allow us to formulate the vibrational dependence in the analytical form (4), and thus to calculate the values of broadening and shift coefficients of water vapor lines induced by helium in wide spectral region.

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REFERENCES

- [1] Godon, M., Bauer, A., "Helium-broadened widths of the 183 and 380 GHz lines of water vapor," *Chem. Phys. Lett.* **147**, 189–191(1988).
- [2] Goyette, T.M., De Lucia, F.C., "The pressure broadening of the 3₁₃-2₂₀ transition of water between 80 and 600 K," *J. Mol. Spectrosc.* **143**, 346–358 (1990).
- [3] Steyert, D.W., Wang, W.F., Sirota, J.M., Donahue, N.M., Reuter, D.C., "Hydrogen and helium pressure broadening of water transitions in the 380–600 cm⁻¹ region," *J. Quant. Spectrosc. Radiat. Transfer.* **83**, 183–191(2004).
- [4] Claveau, C., Henry, A., Hurtmans, D., Valentin, A., "Narrowing and broadening parameters of H₂O lines perturbed by He, Ne, Ar, Kr and nitrogen in the spectral range 1850–2140 cm⁻¹," *J. Quant. Spectrosc. Radiat. Transfer.* **68**, 273–298 (2001).
- [5] Claveau, C., Valentin, A., "Narrowing and broadening parameters for H₂O lines perturbed by helium, argon and xenon in the 1170-1440 cm⁻¹ spectral range," *Mol. Phys.* **107**, 1417–1422(2009).
- [6] Solodov, A.M., Starikov, V.I., "Broadening and shift of lines of the $\nu_2 + \nu_3$ band of water vapor induced by helium pressure," *Opt. Spectrosc.* **105**, 14–20 (2008).
- [7] Solodov, A.M., Starikov, V.I., "Helium-induced halfwidths and line shifts of water vapor transitions of the $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ bands," *Mol. Phys.* **107**, 43–51 (2009).
- [8] Petrova, T.M., Solodov, A.M., Starikov, V.I., Solodov A.A., "Measurements and calculations of He-broadening and -shifting parameters of the water vapor transitions of the $\nu_1 + \nu_2 + \nu_3$ band," *Mol. Phys.* **110**, 1493–1503(2012).
- [9] Lucchesini, A., Gozzini, S., Gabbanini, C., "Water vapor overtones pressure line broadening and shifting measurements," *Eur. Phys. J. D.* **8**, 223–226 (2000).
- [10] Poddar, P., Mitra, S., Hossain, M.M., Biswas, D., Ghosh, P.N. and Ray, B. "Diode laser spectroscopy of He, N₂ and air broadened water vapour transitions belonging to the (2 $\nu_1 + \nu_2 + \nu_3$) overtone band," *Mol. Phys.* **108**, 1957–1964 (2010).
- [11] Gamache, R.R., Lynch, R., Brown, L.R., "Theoretical calculations of pressure broadening coefficients for H₂O perturbed by hydrogen or helium gas," *J. Quant. Spectrosc. Radiat. Transfer.* **56**, 471–487(1996).
- [12] Petrova, T.M., Solodov, A.M., Starikov, V.I., Solodov, A.A., "Vibrational dependence of an intramolecular potential for H₂O-He system," *J. Quant. Spectrosc. Radiat. Transfer.* **129**, 241–253(2013).
- [13] Starikov, V.I., "Vibration-rotation interaction potential for H₂O-A system," *J. Quant. Spectrosc. Radiat. Transfer.* **155**, 49–56(2015).
- [14] Robert, D., Bonamy, J., "Short range force effects in semiclassical molecular line broadening calculations," *J. Phys. (Paris)* **40**, 923–943(1979).
- [15] Buldyreva, J., Lavrent'eva, N.N., Starikov, V.I. [Collisional Line Broadening and Shifting of Atmospheric Gase. A practical Guide for Line Shape Modeling by Current Semi-classical Approaches], Imperial College Press, London, (2010).
- [16] Labani, B., Bonamy, J., Robert, D., Hartmann, J.-M., Taine, J., "Collisional broadening of rotation-vibration lines for asymmetric top molecules. I. Theoretical model for both distant and close collisions," *J. Chem. Phys.* **84**, 4256–4267(1986).