



Note

Evidence of true bound and metastable dimers and trimers presence in high temperature water vapor spectra



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ABSTRACT

We consider the ratio between true bound and metastable states of small water clusters in water vapor. Reanalysis of water vapor spectra recorded at 650 K and pressures up to 110 atm in the O–H fundamental stretching region was performed using an improved spectroscopic model that revealed manifestations of dimers and trimers in both true bound and metastable states. Dimer and trimer quantities in both states were determined in the model by the corresponding equilibrium constants which were variable coefficients in equations of integrated spectral intensity, of absorption coefficient, and of water vapor thermodynamic state. The obtained constants are in good agreement with the previously known values, including agreement with those obtained from the empirical high-precision thermodynamic water vapor data. The analysis confirms that amounts of bound dimers and trimers are significant even at supercritical temperature.

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1. Introduction

Water dimers (H₂O)₂ are expected to affect the Earth's radiation balance and climate [1–4], homogeneous condensation [5] and atmospheric chemistry [6]. Recent experimental observation of the resolved rotational spectrum of (H₂O)₂ in pure water vapor at room temperature [7] confirms the collisional mechanism of dimer formation [8–10] and dimer presence in the ambient atmosphere. Nevertheless, quantitative characterization of water vapor spectra is not straightforward because of difficult discrimination between the absorption contributions caused by far wings of monomer lines, true bound dimers, metastable dimers and free molecular pairs [11], each of which represents quasi-continuum absorption smoothly varying with frequency.

The present work is a continuation of a series of studies [11–18] aimed at quantitative characterization of different absorption mechanisms in water vapor. A particular goal is evaluation of dimer and trimer

abundances in water vapor at temperature near to the critical one, including separate estimation of their amounts in metastable states.

2. Method of analysis

In our previous work [15] high temperature water vapor spectra initially reported in [16] were retreated using the spectroscopic model taking into account contributions of true bound dimers and trimers. An empirical adjustable parameter related to the water vapor non-ideality was used in the model [15]. In current work we present the improved spectroscopic model, which describes the non-ideality of water vapor at pressures up to 110 atm entirely in terms of formation of true bound and metastable dimers and trimers. Similar to the previous model [15], water vapor is considered as a mixture of water monomers and small water clusters: dimers and trimers. Contrary to the previous case, the new model considers these clusters as ideal gases. Moreover, two more ideal constituents are added, namely metastable dimer and metastable trimer.

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Total pressure (P) of water vapor, integrated intensity of observed spectra (I), and absorption coefficient ($\alpha(\nu)$) are expressed as a sum of the corresponding constituents:

$$P = \sum_i P_i, \quad I = \sum_i I_i, \quad \alpha(\nu) = \sum_i \alpha_i(\nu)$$

where index i is either m , d , t , dm and tm corresponding to monomer, dimer, trimer, metastable dimer and metastable trimer, respectively. Integrated intensity (I) and absorption coefficient ($\alpha(\nu)$) for each constituent is written as:

$$I_i = \frac{P_i}{kT} \cdot \sigma_i, \quad \alpha_i(\nu) = I_i \cdot \Phi_i(\nu)$$

where σ is absorption cross section and $\Phi(\nu)$ is the normalized shape of the absorption band, so that

$$\int_{band} \Phi_i(\nu) d\nu = 1.$$

Total pressure can be expressed through the monomer partial pressure using equilibrium constants (K_i) determining partial pressure of the corresponding constituents:

$$P_d = K_d \cdot P_m^2, \quad P_{dm} = K_{dm} \cdot P_m^2, \quad P_t = K_t \cdot P_m^3, \quad P_{tm} = K_{tm} \cdot P_m^3$$

Bearing in mind that the dimer and trimer molar masses are equal respectively to double and triple mass of the monomer (M), the vapor density ρ can be found as

$$\rho = \frac{M}{RT} (P_m + 2P_d + 2P_{dm} + 3P_t + 3P_{tm})$$

(R is the gas constant) and compared with accurate empirical data [19].

The contribution of monomers, bound dimers and bound trimers to the observed spectra is calculated same as in the work [15], which is shortly described as follows. The effect of line mixing is taken into account for the monomer using the ABC approach having two empirical adjustable parameters [20]. The Lorentz line shape and parameters taken from HITRAN database [21] are employed. Each ro-vibrational band of bound dimer and trimer is approximated by the Lorentz profile with adjustable width. The same width is adopted for all dimer bands. The same width but different from that of the dimers is taken for the trimer bands. Positions and intensities of all dimer and trimer bands within the 3590–3800 cm^{-1} range were taken from the previous studies. Their origin and values can be found in Table 1 of [15].

Metastable dimer and trimer spectra were modeled following the approach used in the work [11]. The metastable dimer is considered as two monomers almost freely rotating near each other. Therefore, its absorption spectrum can be modeled as double absorption of the monomer broadened due to a short lifetime of the metastable molecule. In this work we consider spectra

at pressures ranging from 20 to 110 atm. The corresponding collisional linewidth for water monomer varies within 4–22 cm^{-1} (average pressure broadening is about 0.2 $\text{cm}^{-1}/\text{atm}$), which is in good agreement with the metastable dimer lifetime broadening estimated to be 7–20 cm^{-1} in the work [11]. Therefore, at considered pressures the monomer spectrum shape can be used for the metastable dimer as well.

By analogy, we consider the metastable trimer as a bound dimer and monomer almost freely rotating near each other. This type of the triple molecule is, in our opinion, much more abundant than three monomers almost freely rotating beside each other. Collisional formation of a cluster implies redistribution of translational kinetic energy of colliding molecules into internal degrees of freedom of the cluster [8–10]. Metastable dimer internal energy is already above dissociation. Its collision with a monomer will further increase the dimer internal energy, which more likely entails its dissociation than formation of a triple molecule. Therefore, the metastable trimer absorption spectrum shape can be modeled as a sum of the monomer and bound dimer normalized absorption.

In our analysis we do not consider the absorption caused by an additional transient dipole moment induced by collisions referred to as collision induced absorption (CIA). The CIA contribution to the water vapor rotational spectrum is negligible as shown by calculations [22]. Integrated intensities of rotational and ro-vibrational water bands are of the same order of magnitude [21]. These two facts allow assuming that the CIA can be neglected in the analyzed spectra.

A total of 10 water vapor spectra in the 2500–5000 cm^{-1} range recorded by Vigasin et al. [16] at 650 K and pressures from 20 up to 110 atm were used. Eight adjustable parameters were used to fit the described model to observed spectra, namely bound and metastable dimer equilibrium constants, bound and metastable trimer equilibrium constants, bound dimer ro-vibrational bands width, bound trimer ro-vibrational bands width, and two empirical parameters of the monomer collisional coupling. The same minor adjustments of the monomer, dimer and trimer band integrated intensities within uncertainty limits to which they are known were applied as in the work [15].

Values of equilibrium constants as obtained from the spectra fit are listed in Table 1.

3. Discussion

In general, the new model gives very similar residuals of spectra fitting with the ones of the previous model [15], which can be explained by similarity of the used

Table 1

Values of the dimer and trimer equilibrium constants, as obtained from the 650 K spectra [16] fit, and their comparison with some previous data.

	K_d (atm^{-1})	K_t (atm^{-2})	K_{dm} (atm^{-1})	K_{tm} (atm^{-2})	$K_d + K_{dm}$ (atm^{-1})	$K_t + K_{tm}$ (atm^{-2})
This work	0.7×10^{-3}	3.2×10^{-6}	0.5×10^{-3}	3.8×10^{-6}	1.2×10^{-3}	7.0×10^{-6}
Previous data	0.87×10^{-3} [15]	2.2×10^{-3} [15]	–	–	2.19×10^{-3} [14]	9.06×10^{-6} [14]

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