



Note

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



T.A. Odintsova*, M.Yu. Tretyakov

Institute of Applied Physics of the Russian Academy of Sciences, 46 Ulyanov str., 603950 Nizhny Novgorod, Russia

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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 (H_2O)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 (H_2O)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.

* Corresponding author. Tel.: +7 831 416 48 66; fax: +7 831 436 37 92.
E-mail address: odintsova@appl.sci-nnov.ru (T.A. Odintsova).

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

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

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 ($\alpha(v)$) for each constituent is written as:

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

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

$$\int_{\text{band}} \Phi_i(v) dv = 1.$$

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]

approaches. For the same reason use of both models resulted in the same widths of bound dimer and trimer ro-vibrational bands constituting 59 and 110 cm^{-1} respectively. Figs. 1–3 demonstrate agreement of the developed model with the experimental data and can be compared with the corresponding figures from the previous work [15]. Fig. 4 presents decomposition of the spectrum observed at 79 atm.

Most interesting is the analysis of the obtained values of equilibrium constants. Currently known values of the bound dimer equilibrium constant were discussed, e.g., in the

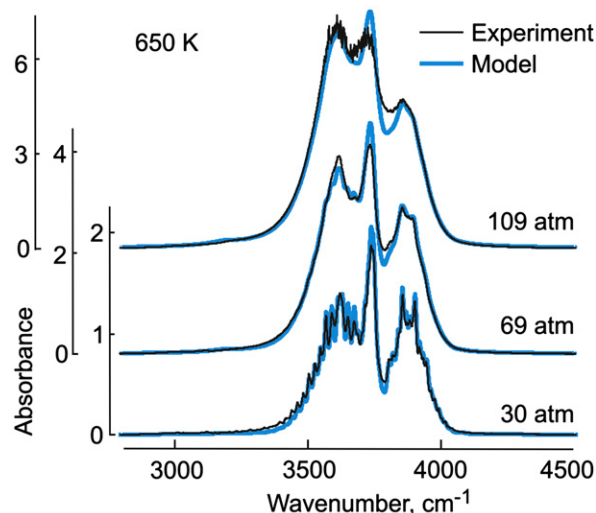


Fig. 1. Comparison of experimental and model spectra of pure water vapor at three characteristic pressures.

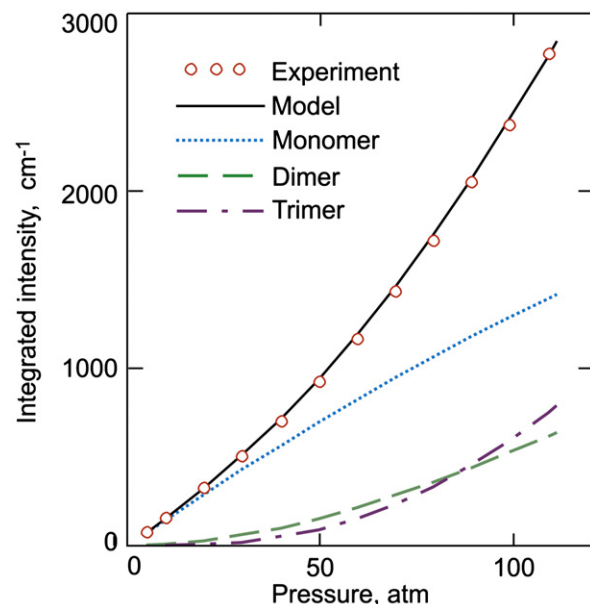


Fig. 2. Decomposition of integrated intensity (given in units of absorbance multiplied by frequency interval) of observed spectra and total integrated intensity of water vapor absorption calculated with obtained parameters. Experimental data are shown by points. Total contributions of bound and metastable species are shown for dimers and trimers.

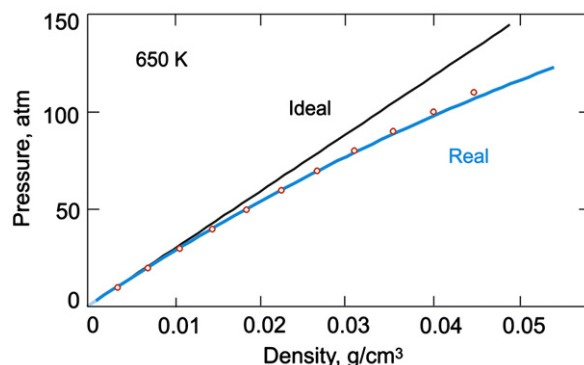


Fig. 3. Correspondence of the model to the equation of state of water vapor. Circles correspond to experimental conditions calculated with obtained parameters. Black (solid) and blue (dotted) curves correspond to the equation of state for ideal and real vapor respectively. Real water vapor data are taken from NIST Chemistry WebBook [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

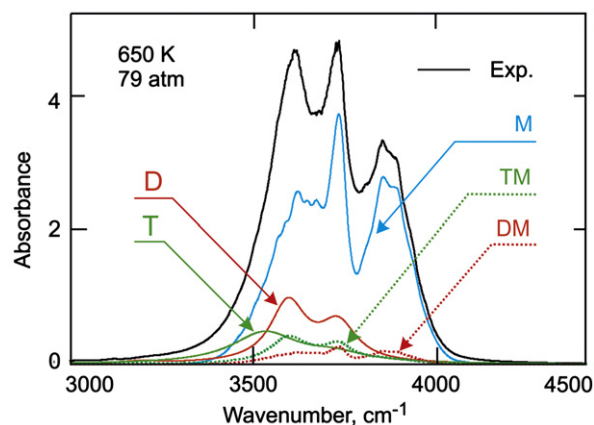


Fig. 4. Decomposition of the experimental absorption spectrum of pure water vapor at 79-atm [16]. Calculated contribution of monomer (M), bound dimer (D), metastable dimer (DM), bound trimer (T) and metastable trimer (TM) are shown.

works [15,23–25]. The new model dimerization constant is about 20% smaller than the previous one [15], which leads to even better agreement with results of the works [24,25]. The total quantity of dimers in both bound and metastable states can be determined by the sum of their equilibrium constants. A similar quantity can be found for the total amount of trimers. These summed values are somewhat smaller than the equilibrium constant values obtained in the work [14] from the second and third coefficients of the water vapor virial equation of state (see Table 1). However, the agreement can be considered reasonable taking into consideration the model approximations.

The relative fraction of bound and metastable dimers determined in this work can be compared with the results of work [18]. Fig. 4 of [18] allows estimating the bound dimers amount relative to the total amount of bound and metastable dimers to be about 15%. The corresponding value can be calculated from Table 1, which yields about 60%. The larger value obtained in this work can be

explained by an uncertainty in discrimination between bound and metastable states of the dimer. In the conditions of the experiment there are many highly excited metastable (or quasi-bound) dimer states with energies higher than the dimer dissociation energy when the energy excess is distributed among internal degrees of freedom of the monomers. Such states include, in particular, rotation of monomers relative to the hydrogen bond, which does not change the bond length. Dimers in such states still have almost the same structure and, therefore, almost the same absorption spectrum but additionally broadened by the state lifetime. Such dimers are indistinguishable in our model from the true bound ones and, therefore, they contribute to the value of the bound dimer equilibrium constant found in this work.

To conclude, the proposed model allowed estimating the abundance of bound and metastable dimers and trimers in high temperature water vapor, which is in reasonable agreement with the previous data. The performed analysis confirms that the number of bound dimers is quite large even at such a high temperature and is comparable with the number of metastable dimers. It is known [11,24,26] that a relative fraction of bound dimers becomes larger with a decrease of gas temperature. The binary collision nature of dimer formation in gases implies that at a given temperature the number of water dimers in the atmosphere is determined just by the concentration of water molecules and this number is the same as in pure water vapor having the same concentration. This confirms the essential contribution of the bound water dimer as one of the components of bimolecular interactions causing the observed atmospheric continuum.

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