# Comments on the Paper "Detection of the Absorption Spectra of Water Clusters under Atmospheric Conditions"
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### *Pis'ma Zh. Eksp. Teor. Fiz.* **89**, 12 (2009) [JETP Lett. **89**, 10 (2009)]

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A numerical simulation has been performed, indicating that the statement on the detection of water dimer absorption by V.I. Serdyukov et al. in Pis'ma Zh. Eksp. Teor. Fiz. **89**, 12 (2009) [JETP Lett. **89**, 10 (2009)] had been premature. Most of the revealed induced absorption can be attributed to water monomers.

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Recently, V.I. Serdyukov et al. [1] reported the probable detection of the absorption of IR radiation by water dimers in near-saturated vapor under equilibrium gas conditions at room temperature. The detection was performed by comparing the transmission spectra of water vapor in a closed volume in a mixture with air. The spectra were recorded at temperatures smoothly varying from 292 K (conditions close to saturation) to 295 K.

The method used in [1] is based on two assumptions: first, the transmission/absorption spectrum of water monomers remains unchanged when the temperature of the mixture is changed by 2–3 K at a constant content of water vapor and, second, the fraction of water clusters in water vapor increases sharply when it approaches saturation.

Let us analyze whether these conditions are justified.

It is known that the parameters of the molecular spectral lines depend on the temperature (see, e.g., [2]). The numerical simulation indicates that the strongest change in the transmission spectra of water molecules under the conditions of the experiment reported in [1] should be expected from the temperature dependence of the line intensity $S(T)$, which is given by the following expression [2, 3] with a good accuracy:

$$S(T) = S^0 \frac{Q_{VR}(T_0)}{Q_{VR}(T)}$$
$$\times \exp\left[A E_{low}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\left[\frac{1 - \exp(-A\nu/T)}{1 - \exp(-A\nu/T_0)}\right], \quad (1)$$

where $S^0$ is the line intensity measured in cm/molecule at the temperature $T_0$, $Q_{VR}(T)$ is the vibration–rotation partition function, $A \approx 1.43878$ cm K, $E_{low}$ is the energy of the low level of the transition measured in cm$^{-1}$, and $\nu$ is the transition frequency measured in cm$^{-1}$. The temperature dependences of the rotation partition function, $Q_R(T_0)/Q_R(T) = (T_0/T)^{3/2}$, and the populations of the lower level of the transition with the energy $E_{low}$, $\exp[A E_{low}(1/T_0 - 1/T)]$ are dominating in this case, whereas the contribution of the other terms is insignificant.

The temperature dependence of the linewidth $\gamma$ when the collisional broadening prevails (which corresponds to the conditions in [1]) has the form $\gamma \sim (T_0/T)^n$, where the exponent $n$ varies from 0.4 to 0.8 for most of the strong lines of water vapor [3]. The parameters of the pressure-induced shift of the lines and collision coupling (line mixing) parameters also depend on the temperature. However, the manifestation of the shift and line mixing is very insignificant in the case under consideration and a change in the spectrum owing to their temperature dependence can be neglected.
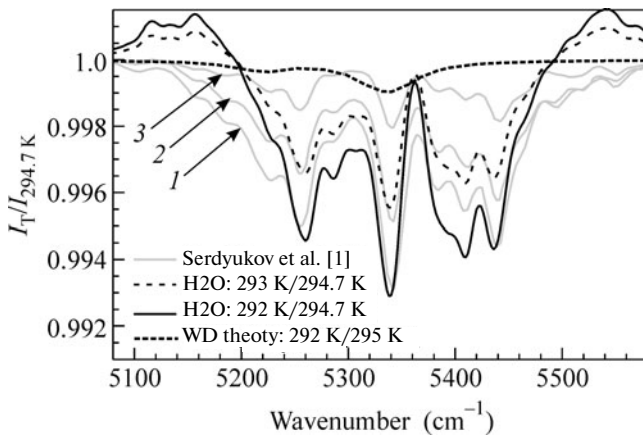
(*1–3*) The "induced transmission" of water vapor determined in [1] as the ratio $I_T/I_{294.7\,K}$ for temperatures from (*1*) ~292 K to (*3*) 294.7 K, which is close to the initial temperature. The solid line and long dashed line are similar calculated ratios of the water monomer transmission spectra at $T = 292$ and 293 K, respectively, to the spectrum at $T = 294.7$ K. The calculation was performed for the conditions close to the experimental conditions in [1]: 16 Torr of $H_2O$ in a mixture with 1 atm of air, the optical path length is 10 m, and the FWHM of the Gaussian instrumental function is 15 cm$^{-1}$. The calculations were performed using the HITRAN-2008 database [3]. The short dashed line is the expected induced transmission of water dimers according to the ab initio calculations of the intensities of dimer transitions [11] in the approximation of the half-width of dimer subbands HWHM = 30 cm$^{-1}$ [12] and with a variation of $K_{eq}$ from 0.061 atm$^{-1}$ (292 K) to 0.057 atm$^{-1}$ (295 K) [6].

Our numerical simulation indicates that a temperature-induced change in the transmission spectrum of water molecules gives rise to the appearance of "induced transmission" almost identical to that observed in [1] (see figure). The prevailing contribution to the calculated induced transmission spectrum comes from the temperature dependence of the intensity of strong lines ($S^0 > 5 \times 10^{-21}$ cm/molecule), which are responsible for the main features of the monomer spectrum in the given band. The effect of the temperature dependence of the linewidths is smaller and is no more than 10–20% of the resulting induced transmission. The calculations were performed using a line-by-line code [4]. A similar result can be obtained, e.g., using the SPECTRA free network information system [5]. According to the figure, our calculation and the experimental curves [1] coincide to small details corresponding to the features of the low-resolution spectrum of the water molecule and have very close amplitudes. The only exception is the periphery of the band, where the calculated $I_T/I_{294.7\,K}$ ratio is larger than unity. This difference can be attributed to the uncertainty in the base line retrieval when processing the experimental spectra.

Let us now discuss the validity of the second assumption accepted in [1] that the number of water clusters, in particular, water dimers, increases abruptly near the dew point.

It is worth noting that any sharp increase (different from the "classical" dependence of the partial pressure $P_n$ of the clusters of the dimension $n$ in water vapor $P_n = K_{eq,\,n}(T)\,P_1^n$, where $P_1$ is the pressure of the gas of monomers and $K_{eq,\,n}$ is the equilibrium constant for a given cluster) is not implied in modern theoretical calculations of the fraction of small clusters [6], including that in the saturated vapor [7, 8]. Moreover, these calculations for dimers are in very good agreement with the experimental works on the determination of the second virial coefficient in the equilibrium saturated [9] or nearly saturated water vapor [10] up to a temperature of 400 K and a pressure of 4 atm. This means that at these pressures, first, dimers are clusters dominating in the concentration in the equilibrium saturated vapor and, second, any anomalous change, which is not described by classical thermodynamics, should not be expected in the cluster composition of water vapor at the dew point.[1]

The results of our analysis presented in the figure also confirm that the assumption of a sharp increase in the concentration of water dimers when water vapor approaches saturation at subatmospheric pressures and temperatures is unreasonable. Otherwise, the measured induced absorption would noticeably exceed the calculated absorption of monomers. In the absence of a sharp increase in the fraction of dimers, the method that was used in [1] and based on the determination of the induced transmission as the ratio of the amplitudes of two spectra at close temperatures can reveal only a small part of the total absorption by water dimers, which is caused by a temperature change in the dimerization constant $\Delta K_{eq,\,2}(\Delta T)$ and by the corresponding change in the partial pressure of dimers $\Delta P_2 \approx \Delta K_{eq,\,2}(\Delta T)\,P_1^2$. The short dashed line in the figure is the numerically estimated expected spectrum of the induced transmission by water dimers under the conditions of the experiment reported in [1]. This estimate was obtained with the use of the ab initio calculations of the integral intensities of the water dimer vibration–rotation bands [11], the temperature dependence $K_{eq,\,2}(T)$ [6], and the assumption based on [12] that the vibration–rotation subbands of the dimer in the equilibrium water vapor at atmosphere temperatures can be approximated by the Lorentz contour with an FWHM of about 30 cm$^{-1}$.

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[1] We do not consider here the process of formation of large clusters or even microdrops (fog) on various condensation nuclei in the saturated vapor under natural conditions. This phenomenon can reduce the partial pressure of monomers when vapor approaches saturation, but does not promote an increase in the fraction of dimers, the possibility of the spectral observation of which is discussed in this work.

It is also worth noting that our simulation of the induced transmission spectra of the monomer indicates that a decrease in the concentration of monomers under the conditions of the experiment reported in [1], which is due to dimerization when the temperature is reduced by 3°, should result in a negligibly small change in the spectrum of the simulated induced transmission. Indeed, the relative change in the concentration of monomers $\delta n_1$ can be expressed in terms of a change in the dimerization constant as

$$\delta n_1 \approx 2\Delta K_{eq, 2}(\Delta T)P_1. \qquad (2)$$

According to the available information on the temperature dependence of the dimerization constant [12], $K_{eq, 2}(295\ K) \approx 0.04-0.06\ atm^{-1}$, it changes by no more than $7-10\%$ when $T$ is changed by 3°. Thus, $\Delta K_{eq, 2} \sim 0.005\ atm^{-1}$ for the case under consideration. Taking into account that the pressure of saturated vapors under the conditions of the experiment reported in [1] is about 0.02 atm, $\delta n_{H_2O} \approx 0.0002$ follows from Eq. (2). The corresponding change in the monomer spectrum is 30 to 40 times smaller than the calculated induced transmission of monomers presented in the figure.

Thus, the statement on the detection of absorption by water dimers in [1] is premature, because most of the revealed induced absorption can be attributed to water monomers. This circumstance along with the other above reasons can indicate the inconsistency of the assumption of a sharp increase in the concentration of water dimers when the equilibrium water vapor approaches saturation at subatmospheric pressures and temperatures. The possibility of applying the approach proposed in [1] to detect the spectrum of dimers under equilibrium conditions requires a more thorough analysis.

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