The dependence of water vapor thermodynamic characteristics on H_2O molecule vibrational states

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Received July 12, 2001

The dependences of the second and third virial coefficients of water vapor on the H_2O molecule vibrational states are calculated. The model intermolecular Stockmayer potential is used taking into account the dipole-dipole interaction between excited molecules. The strong dependence of virial coefficients on molecular concentration is found. In this case a bending vibrational mode is excited. This also results in significant variations of thermodynamic parameters of water vapor, whose molecules are excited to the bending vibrational states.

Introduction

Knowledge of water vapor characteristics is very important in investigating the Earth's atmosphere, in simulating different physical and chemical processes, and in many other applications. In molecular spectroscopy, the H_2O molecule is classified as nonrigid molecule[1] with complicated intramolecular interactions. The excitation of nonrigid (deformation) oscillation mode results in an anomalously sharp variation of a series of parameters characterizing the vibration-rotation (VR) spectrum of the molecule. Present-day experimental and theoretical methods in the VR-spectroscopy of water vapor are described in Ref. 2. However, in the literature the problem on the influence of intramolecular motions in the H_2O molecule on the intermolecular interactions has not been adequately studied. These interactions manifest themselves both through thermodynamic parameters and through transport coefficients characterizing the gas condition.

In this paper we describe the investigation of the effect of vibrational excitations in the H_2O molecule on the water vapor virial coefficients. Since the H_2O molecule is a polar molecule, primary attention is given to calculation of the variations of virial coefficients at the dipole moment of molecules being varied due to vibrational excitation.

1. Model of the potential of intermolecular interaction

Thermodynamic parameters of a gas medium, such as internal energy, entropy, the Joule–Thomson coefficient, etc. can be expressed through virial coefficients and their derivatives with respect to temperature.[3] The second $B(T)$, third $C(T)$, and so on, virial coefficients are determined through the virial equation of state[3]

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \dots . \quad (1)$$

The second virial coefficient is connected with the forces due to pairwise interaction; the third virial coefficient is connected with the forces due to triple interaction, and so on. The largest contribution to intermolecular interaction forces of polar molecules comes from the dipole-dipole interaction.[4] The quantum-mechanical expression for the energy of interaction of two polar molecules, being in quantum states (n) and (m), has the form[4]

$$E_{dd} = \mathbf{M}_n\, \mathbf{M}_m/R^3 - 3(\mathbf{M}_n\, \mathbf{R})\, (\mathbf{M}_m\, \mathbf{R})/R^5. \quad (2)$$

Here $\mathbf{M}_n = <\Psi_n\, |\, \mathbf{M}\, |\, \Psi_n>$ is the matrix element of the vector of the molecular dipole moment $\mathbf{M}$ based on the complete electronic vibration-rotation wave functions Ψ_n, and the vector $\mathbf{R}$ connects the centers of molecular masses. Projections of M_f of the molecular dipole moment in the space coordinate system ($f = X, Y, Z$) are connected with the projections μ_β of this moment in the molecular system ($\beta = x, y, z$) by the relation $M_f = \sum_\beta \mu_\beta \varphi_{f\beta}$, where $\varphi_{f\beta}$ is the direction cosines connecting the two coordinate systems.

The first approximation, used in this paper, implies that the rotation of a molecule in space is considered from a classical standpoint. This makes it possible to factor out the values connected with the molecular rotation (unit vectors in space coordinate system and $\varphi_{f\beta}$) from the quantum-mechanical mean $< >$. Let us consider next that only one molecular component (for example, $\mu_x = \mu$) differs from zero and we can write that

$$E_{dd} = -\, \mu_n\, \mu_m/R^3\, g(\theta_1, \theta_2, \varphi). \quad (3)$$

The type of the function $g(\theta_1, \theta_2, \varphi)$, determining the relative position of dipoles, is well known.[3] In the matrix element, as it is conventional in the theory of VR molecular spectra,[1–2] one can pass to an effective dipole moment $\tilde{\mu}$ and wave functions $\tilde{\Psi}_n$ of zero approximation for electron and vibrational types of motion. In this paper the dependence of the dipole moment on the rotational operators is not taken into account so that $\tilde{\mu} \approx \mu$. We consider the case when the molecules are in one electron state, so that n and m in Eq. (3) number the vibrational states, i.e., are the generalized vibrational numbers.

The second approximation, used in the paper, implies that other types of interaction among molecules (dispersion, induction, etc.) are simulated by the Lennard–Jones potential[3,4] with the parameters σ and ε, which do not depend on quantum numbers. Thus, model potential of interaction between the molecules in the vibrational states (n) and (m) used in the calculations has the form

$$U(R,\ n,\ m) = 4\varepsilon\ \{(\sigma/R)^{12} - (\sigma/R)^{6}\} - \\ - \mu_n\ \mu_m/R^3\ g(\theta_1,\ \theta_2,\ \varphi). \qquad (4)$$

This potential is a modified Stockmayer potential[3–5] where the dipole moments of interacting molecules depend on vibrational states. The values of dipole moments in different states $(n) = (v_1,\ v_2,\ v_3)$ (v_i is the vibrational quantum numbers, $i = 1,\ 2,\ 3$) for H_2O molecule were calculated in Refs. 6 and 7; in this case the results are used of the most complete calculations from Ref. 7 ($v_1 \le 4$, $v_2 \le 10$, $v_3 \le 4$). The values $\sigma = 2.65$ Å, $\varepsilon/k = 380$ K for water are taken from Ref. 3 (k is the Boltzmann constant). Note that maximum variation of the dipole moment is 26.4%, according to Ref. 7, and corresponds to the state (0, 7, 0).

2. Second virial coefficient and thermodynamic parameters

The second virial coefficient $B(T)$ for gas, containing molecules in different vibrational states, can be calculated in the same way as for the multicomponent gas mixture

$$B(T) = \sum_n \sum_m x_n\, x_m\, B_{nm}(T), \qquad (5)$$

in this formula x_n is the molecular concentration (states (n)), B_{nn} denotes second virial coefficients for a pure component, i.e., for the gas containing 100% of excited molecules, B_{nm} is the cross virial coefficient determined by the potential (4) with $(n) \ne (m)$. In addition to $B(T)$, the values can be found in the literature of the cited virial coefficient $B^*(T) = B(T)/b_0$, where for water molecule the value of $b_0 = 23.42\ \text{cm}^3/\text{mol}$. The values of B^*_{nm} in the Stockmayer potential model were calculated by the formula[3]

$$B^*_{nm}(\tau) = \left(\frac{4}{\tau}\right)^{\frac{1}{4}}\left[\Gamma\left(\frac{3}{4}\right) - \frac{1}{4}\sum_{j=1}^{\infty}\ \sum_{i=0}^{i\le\frac{j}{2}} \frac{2j}{j!}\, G_i \binom{j}{2i} \times \right. \\ \left. \times\ \Gamma\left(\frac{2j-2i-1}{4}\right)(t_1)^{2i}_{nm}\, \tau^{-\left(\frac{j+i}{2}\right)}\right]. \qquad (6)$$

Here $\Gamma(\ldots)$ is the gamma function, the quantities G_i are connected with the triple integration over angle variables θ_1, θ_2, and φ (Ref. 3), $\tau = \dfrac{kT}{\varepsilon}$, $(t_1)_{nm} = \dfrac{1}{2\sqrt{2}}\ \dfrac{\mu_n \mu_m}{\varepsilon\sigma^3}$.

Analysis of calculations showed that the values of B^*_{nm} vary over wide limits when changing the quantum number v_2. Figures 1a and 1b show the dependences of the second virial coefficients $B_{nn}(T) = B(n,\ T)$ for pure gas components (containing 100% of excited molecules) for the case $n = v_3$ and $n = v_2$, respectively.

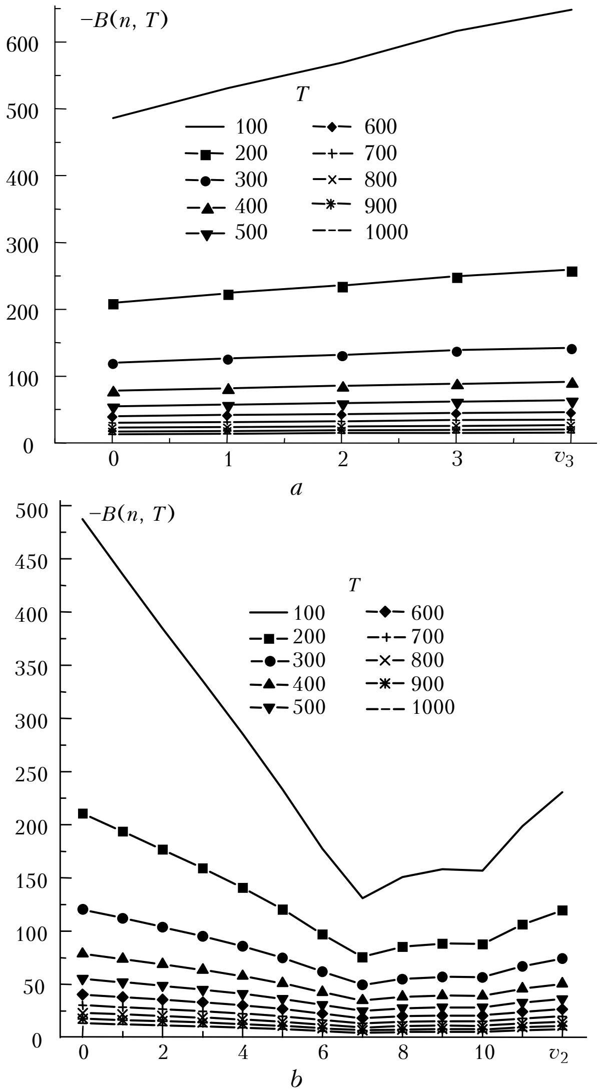

Fig. 1. The dependence of the second virial coefficient $B(n,\ T)$ for water vapor containing 100% of excited molecules (cm^3/mol): (a) quantum number $n = v_3$ (valence vibrational mode); (b) $n = v_2$ (bending vibrational mode) at different temperatures T, °C.

The calculation by formula (5) for the case when the concentrations of x_n are determined by Boltzmann statistics, i.e., $x_n = \exp(-E_n/kT)/Q$ (E_n are vibrational centers, Q is the vibrational partition function) shows that the value of B is close to the value of the second virial coefficient B_0 of water vapor, all the molecules of which are in the ground state ($n = 0$) with $\mu_0 = 1.85$ D. The value of B_0 was calculated repeatedly and compared with the experiment.[3] The dependence of the second virial coefficient B_n on the concentration of excited molecules was calculated by the formula

$$B_n = x_n^2\, B_{nn} + 2(1 - x_n)\, x_n\, B_{n0} + (1 - x_n)^2\, B_0, \quad (7)$$

following from Eq. (5) under the assumption that the water vapor is a two-component mixture consisting of excited molecules (with the concentration x_n) and unexcited molecules (with the concentration $(1 - x_n)$). Figure 2 presents the dependence of the second virial coefficient B_n on the concentration x_n of molecules being in excited states $(n) = (0, v_2, 0)$ at the temperature of 300°C. It is evident that the dependence on v_2 is significant. For example, when transferring 20% of molecules to the excited vibration state (0, 3, 0) the variation of $\Delta B_n = (B_n - B_0)/B_0$ is 4.5%.

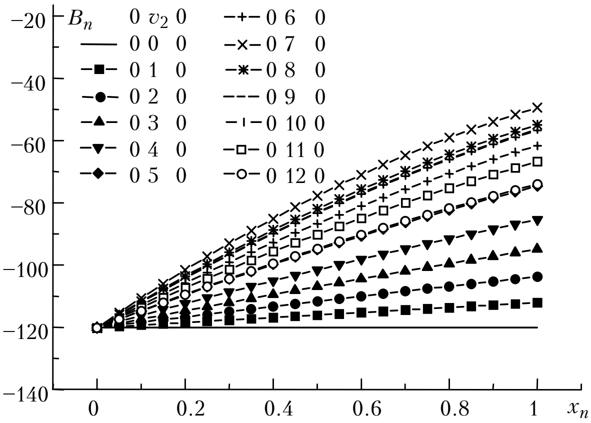

Fig. 2. The dependence of the second virial coefficient $B_n(T)$ (cm^3/mol) of water vapor on the concentration x_n of excited molecules.

Basic contributions to thermodynamic parameters are due to the second virial coefficient and its derivative with respect to temperature. The dependence of these parameters for a pure gas component on vibrational quantum numbers or their dependence on the concentration of excited molecules are similar to the dependences of the second virial coefficient on these values (Figs. 1–2).

3. Third virial coefficient

The calculation of the third virial coefficient is a more complicated problem than calculation of the second coefficient since the interaction of three molecules should be taken into account simultaneously. In this paper, we used the potential (4) and the calculation procedure from Ref. 8 to calculate $C(T)$. Regardless the fact that the Stockmayer potential (4) gives in the calculation of $C(T)$ for water vapor poor agreement with the experimental data,[8] we use it to determine the dependence of $C(T)$ on vibrational excitations, i.e., we are interested not in absolute values of this coefficient, but in its vibration dependence manifested in the dependence of the dipole moments on quantum numbers v_i.

For the multicomponent mixture

$$C(T) = \sum_n \sum_m \sum_s x_n\, x_m\, x_s\, C_{nms}(T), \quad (8)$$

where x_n have the same meaning as in Eq. (5), C_{nnn} denotes the third virial coefficients for pure components, and C_{nms} (with a pair of noncoincident indices) denotes the cross virial coefficients. According to Ref. 8, C_{nms} can be presented as a sum $C_{nms} = C + \Delta C_{nms}$, where C is independent of the values of dipole moments of interacting molecules as well as of vibrational quantum numbers. The values of C are determined by the Lennard–Jones potential with the corresponding parameters and have been calculated in the literature (we took these values from Ref. 8) many times. The values of ΔC_{nms}, which determine the difference between the polar and nonpolar virial coefficients, in the model of the Stockmayer potential are determined as

$$*C_{nms} = \frac{3}{2}\, b_0^2 \sum_{j=2}^{\infty} \sum_{i=2}^{j} \frac{2j}{j!} \binom{j}{i}\, \tau^{-1/4(2j+i+2)}\, Q_{j,i}^{(nms)}, \quad (9)$$

where

$$Q_{j,i}^{(nms)} = \frac{1}{3}\left(Q_{j,i}^{nms} + Q_{j,i}^{msn} + Q_{j,i}^{snm}\right), \quad (10)$$

$$Q_{j,i}^{nms} = -\frac{1}{(4\pi)^3}\, \Gamma\left[\frac{1}{4}(2j - i - 2)\right] \times$$
$$\times \int_0^{3/4} \mathrm{d}(y^2) \int_{(1-y^2)^{1/2}}^{1-(1-y^2)^{1/2}} \mathrm{d}x \int_0^{2\pi} \mathrm{d}\varphi_1 \int_0^{2\pi} \mathrm{d}\varphi_2 \int_0^{2\pi} \mathrm{d}\varphi_3 \times$$
$$\times \int_0^{\pi} \mathrm{d}\theta_1 \sin\theta_1 \int_0^{\pi} \mathrm{d}\theta_2 \sin\theta_2 \int_0^{\pi} \mathrm{d}\theta_3 \sin\theta_3 \times$$
$$\times \{A_{j,i}[F_{12}(t_1)_{nm} + \xi^3\, F_{13}(t_1)_{ns} + \eta^3 F_{23}(t_1)_{ms}]^i -$$
$$- B_{j,i}[F_{12}(t_1)_{nm} + \xi^3 F_{13}(t_1)_{ns}]^i -$$
$$- C_{j,i}[F_{12}(t_1)_{nm} + \eta^3 F_{23}(t_1)_{ms}]^i -$$
$$- D_{j,i}[\xi^3 F_{13}(t_1)_{ns} + \eta^3 F_{23}(t_1)_{ms}]^i + F_{12}^i(t_1)_{nm}^i +$$
$$+ \xi^6\, F_{13}^i(t_1)_{ns}^i + \eta^6\, F_{23}^i(t_1)_{ms}^i\}. \quad (11)$$

Determination of the values F_{12}, F_{13}, F_{23}, ξ, η, $A_{j,i}$, $B_{j,i}$, $C_{j,i}$, $D_{j,i}$ are found in Ref. 8 and are not cited in this paper.

The integration over x and y^2 can be only done numerically. In this connection we restricted our consideration to the terms of the series (9) with $2 \le j \le 16$ and $2 \le i \le 8$ as in Ref. 8. Integration was performed using a computer by the Gaussian method with six nodes at six intervals of separation of integration intervals.[9]

Table 1. Integrals $Q_{j,i}$, obtained from Eq. (11) at $(t_1)_{nm} = (t_1)_{ns} = (t_1)_{ms} = 1$

j \ i	2	3	4	5	6	7	8
2	0.4155						
3	0.3368	0.9529					
4	0.3176	0.4378	1.0373				
5	0.2846	0.4514	0.7489	1.0213			
6	0.0958	0.6526	0.6150	1.2419	1.9997		
7	−0.7102	1.170	0.2381	2.0300	1.3140	2.9204	
8	−3.722	2.459	−1.228	3.9951	−0.1707	5.9623	1.0545
9	−14.51	5.855	−6.597	9.014	−5.0478	13.3503	−6.7210
10	−53.08	15.46	−25.67	22.68	−21.566	32.748	−29.369
11	−193.1	44.54	−93.47	62.53	−77.81	87.32	−100.02
12	−714.1	138.4	−338.7	186.5	−272.7	251.04	−328.4
13	−2711	459.9	−1249	595.7	−966	772.6	−1093
14	−10610	1626	−4734	2024	−3511	2530	−3753
15	−42876	6032	−18503	7268	−13173	8763	−13366
16	−178973	23559	−74714	27451	−51153	31968	−49470

To check up the calculations, we compared the values of $Q_{j,i}$ from Ref. 8 and the values of $Q_{j,i}$ obtained from Eq. (11) at $(t_1)_{nm} = (t_1)_{ns} = (t_1)_{ms} = 1$. The comparison has shown that there are some distinctions in the values of several integrals of $Q_{j,i}$. The values of $Q_{j,i}$ obtained are given in Table 1.

Figure 3 shows the dependences of the reduced third virial coefficients, $C^*_{nnn} = C_{nnn}/b_0^2$ for pure components in the case when these components contain molecules, in which the bending vibration mode is excited, i.e., $n = v_2$. As one would expect, these dependences are more essential than those for the second virial coefficients $B_{nn}(T)$, Fig. 1*b*.

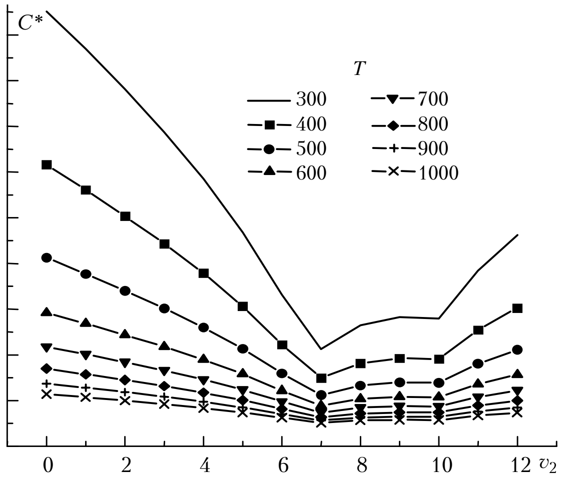

Fig. 3. The dependence of the given third virial coefficient $C^*_n = C^*_{nnn}$ of water vapor, containing 100% of excited molecules, on the vibrational quantum number $n = v_2$ at different temperatures T, °C.

The dependence of the third virial coefficient C_n on the concentration x_n of excited molecules was calculated by the formula

$$C_n = x_n^3\, C_{nnn} + 3(1 - x_n)\, x_n^2\, C_{nn0} + \\ + 3(1 - x_n)^2\, x_n\, C_{n00} + (1 - x_n)^3\, C_{000}, \qquad (12)$$

i.e., as in the case of the calculation of B_n, Eq. (7), it was assumed that water vapor is a two-component mixture of excited and unexcited molecules. Figure 4 shows the dependences of the third virial coefficient C^*_n on the concentration of x_n molecules, being in the excited bending states $(n) = (0, v_2, 0)$ at the temperature of 300°C. Comparing with the coefficient B_n, we can find that the conversion of 20% of molecules to the excited vibrational state (0, 3, 0) changes the coefficient C_n by 5–9% (for B_n this change is 4.5%).

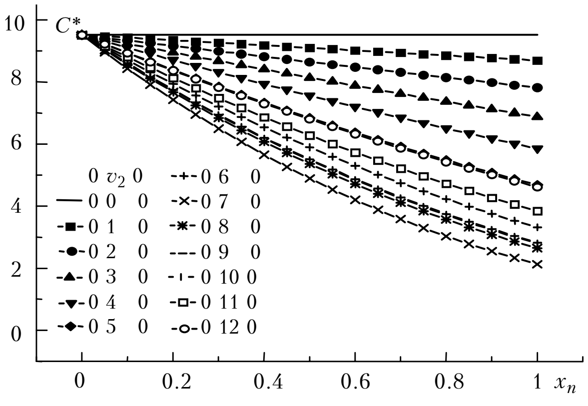

Fig. 4. The dependence of the reduced third virial coefficient C^*_n on the concentration x_n of excited molecules.

4. Discussion

We have shown, by calculations, made with the use of the model intermolecular potential, that the virial coefficients of water vapor depend on the concentration of H_2O molecules in the excited bending vibration states. These dependences are most significant at low temperatures and are clearly defined for the third virial coefficient. Knowledge of virial coefficients enables one to determine thermodynamic characteristics of water vapor containing the molecules in the excited vibrational states. The calculation of the third virial coefficient for the equation of state (1) makes it possible to determine the behavior of critical gas constants depending on the concentration of excited molecules (at a critical point the first and second derivatives of the pressure with respect to gas density (at constant temperature) are equal zero). The results of such calculations for a series of nonrigid molecules will be given in the next paper.

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