Effect of vibrational excitations on critical parameters in gases of nonrigid polar molecules

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Critical parameters of polar molecules of ammonia and water allowing large-amplitude vibrations are calculated through virial coefficients as functions of the concentration of vibrationally excited molecules. A model potential accounting for the dipole-dipole and dipole-quadrupole (for water vapor) interactions was used. A change in the dipole moment of molecules caused by excitation of a nonrigid vibrational mode is shown to lead to the dependence of critical parameters of gases on the concentration of excited molecules.

Introduction

Ammonia and water molecules fall in the category of nonrigid molecules allowing large-amplitude vibrations. In ammonia, it is inversion, in which the nitrogen atom is tunneled through the plane formed by the hydrogen atoms. In the water molecule, it is a deformation (bending) vibration connected with the HOH angle change. At excitation of the corresponding vibrational modes, some spectroscopic constants, including dipole moments of molecules,[2-4] experiences abnormally sharp changes.[1]

This paper is devoted to studying the effect of excitation of the inversion (for ammonia) and bending (for water) vibrational modes on critical parameters of the corresponding gases. The study is based on the use of the virial equation of the gas state

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

where P is the pressure, V is the molar volume, T is the temperature, R is the universal gas constant. The second $B(T)$ and third $C(T)$ virial coefficients are functions of only temperature and intermolecular potential. The use of this equation for determination of critical parameters (points) of gases is justified, for example, in Ref. 5. For critical points, the following equation is valid[5,6]:

$$(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0. \quad (2)$$

From Eq. (1) (with allowance for only the terms including $B(T)$ and $C(T)$) and Eq. (2) it follows that

$$3C_{cr} = B_{cr}^2, \quad (3)$$

where B_{cr} and C_{cr} are the values of the second and third virial coefficients at the critical point. This equation is used for determination of the critical temperature T_{cr}. The critical volume and pressure are calculated from Eqs. (1) and (3):

$$V_{cr} = -B_{cr}; \quad (4)$$

$$P_{cr} = kT_{cr}/3V_{cr} \quad (5)$$

(k is the Boltzmann constant). Thus, to calculate critical constants, we have to find the second and third virial coefficients. It should be noted here that the coefficients B, C, and critical parameters were calculated many times but with intramolecular motions ignored (see, for example, Refs. 5, 7, and 8).

1. Intermolecular potential

In our calculation of the virial coefficients, we used a coupled model potential

$$\varphi_{12}(r, n, m) = 4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\} -$$
$$\mu_n^{(1)} \mu_m^{(2)}/r^3 g(\theta_1, \theta_2, \phi), \quad (6)$$

where σ and ε are force constants characterizing the nonpolar part of the potential (the Lennard–Jones potential[7,9]); r is the separation between molecules; $\mu_n^{(1)}$ and $\mu_m^{(2)}$ are dipole moments of the first and the second molecules being in the vibrational states (n) and (m), respectively; the form of the function $g(\theta_1, \theta_2, \phi)$ determining mutual arrangement of dipoles is well-known.[7,9] The potential (6) is the model Stockmayer potential,[7,8,10] in which the dipole moments of interacting molecules depend on vibrational states. The values of dipole moments μ_n for different inversion states of ammonia ($n = v_2$ is the inversion quantum number) were calculated in Ref. 2, and the values of μ_n for water ($n = v_2$ corresponds to the bending quantum number) were calculated in Refs. 3 and 4.

In Ref. 8 it was noted that the Stockmayer potential is unsuitable for calculation of the third virial coefficient of the water molecule, especially, at a low temperature. This was connected with the fact that this potential ignores higher multipoles. Therefore, along with the potential (6), we used for H_2O the potential

$$\varphi'_{12}(r, n, m) = \varphi_{12}(r, n, m) -$$
$$- (3/2\mu_n^{(1)}Q/r^3)h - (3/2\mu_m^{(2)} Q/r^3)h', \qquad (7)$$

accounting for the dipole-quadrupole interaction. Here Q is the quadrupole moment identical for all vibrational states, the functions h and h' describe the angular dependence of first molecule's dipole − second molecule's quadrupole and second molecule's dipole − first molecule's quadrupole interactions, respectively:

$$h = h((\mathbf{n}_1, \mathbf{e}_{12}), (\mathbf{n}_2, \mathbf{e}_{12}), (\mathbf{n}_1, \mathbf{n}_2)) =$$
$$= \frac{1}{2} [5(\mathbf{n}_1, \mathbf{e}_{12})^2 (\mathbf{n}_2, \mathbf{e}_{12}) -$$
$$- 2(\mathbf{n}_1, \mathbf{e}_{12}) (\mathbf{n}_1, \mathbf{n}_2) - (\mathbf{n}_2, \mathbf{e}_{12})], \qquad (8)$$

where $\mathbf{n}_1$ and $\mathbf{n}_2$ are unit vectors along dipoles of the first and the second molecules; $\mathbf{e}_{12}$ is the unit vector along r, directed from the first molecule to the second one; $h' = - h((\mathbf{n}_2, \mathbf{e}_{12}), (\mathbf{n}_1, \mathbf{e}_{12}), (\mathbf{n}_1, \mathbf{n}_2))$.

2. Virial coefficients

For a given gas, the parameters T_{cr}, B_{cr}, and C_{cr} are constants. If the distribution of molecules over states is not equilibrium, then such gas is considered as a multicomponent gaseous medium with other values of critical parameters. The second $B(T)$ and third $C(T)$ virial coefficients for this multicomponent gas mixture are calculated as[7]:

$$B(T) = \sum_n \sum_m x_n x_m B_{nm}(T); \qquad (9)$$

$$C(T) = \sum_n \sum_m \sum_s x_n x_m x_s C_{nms}(T), \qquad (10)$$

where x_n is the concentration of molecules in the state (n); B_{nn}, and C_{nnn} are the second and third virial coefficients for the pure component, that is, for the gas consisting of only excited molecules. If the subscripts are different, then B_{nm} and C_{nms} are cross virial coefficients determined by the potentials (6) or (7) with $(n) \neq (m)$. The scheme for calculation of the second virial coefficient is described in Ref. 7, and that for the third virial coefficient in the case of polar molecules is discussed in Ref. 8. In this paper, we use some modifications of these schemes taking into account the fact that dipole moments of molecules may be different. Besides, calculation of the third virial coefficient was generalized for the case that the dipole-quadrupole interaction of molecules is taken into account.

For control, we compared the calculated virial coefficients for ammonia and water vapor consisting of only molecules in the ground vibrational state with $\mu_0 = 1.47$ D (for ammonia) and $\mu_0 = 1.85$ D (for water vapor) with the calculations from Refs. 7 and 8 (the values of σ and ε were taken from the literature). The maximum difference was obtained for water vapor at low temperature: for $T = 373$ K the discrepancy in the second virial coefficient $\Delta B = |(B - B')/B'|$ (B' is the second virial coefficient calculated in Ref. 7) was about

7%, and the discrepancy in the third virial coefficient ($\Delta C = |(C - C')/C|$) was about 13% at $T = 532$ K (C' was calculated in Ref. 8). Calculations of the second virial coefficient for water vapor and ammonia with the more accurate coupled potential and different values of parameters σ and ε in the Lennard−Jones potential are given in Ref. 13.

3. Ammonia

The intramolecular potential of the ammonia molecule has an inversion barrier roughly equal to 2000 cm^{-1} (Ref. 1). This potential barrier disturbs most strongly the inversion pair of levels with $v_2 = 2$ (one of the inversion components is below the barrier, while the another is above the barrier). Transition of the molecule into the excited inversion state with $v_2 = 2$ makes the plane configuration most probable. The same state is characterized by the minimal dipole moment $\mu_{v_2=2} \approx 0.95$ D.

Figure 1 depicts the temperature dependence of the reduced third virial coefficient $C_n^* \equiv C_{nnn}/b_0$ ($b_0 = 22.12$ cm$^3 \cdot$mol^{-1}) for 100% concentration of excited molecules ($\sigma = 2.60$ Å, $\varepsilon/k = 320$ K). It can be seen that C_n^* is minimal for $n = v_2 = 2$. Calculation of critical points by Eqs. (3)−(5) for a gas consisting of only molecules in the ground vibrational state gives $T_{cr} = 428$ K, $V_{cr} = 100$ cm^3/mol, $P_{cr} = 116$ atm. The corresponding experimental values are $T_{cr} = 405.5$ K, $V_{cr} = 72.5$ cm^3/mol, $P_{cr} = 111.5$ atm (Ref. 11). Calculation of critical points for the Boltzmann energy distribution of molecules ($x_n = g_n \exp(-E_n/kT)/Q_V$, g_n is degeneration of the vibrational state with the energy E_n, Q_V is the vibrational statistical sum) yields the values close to those given above.
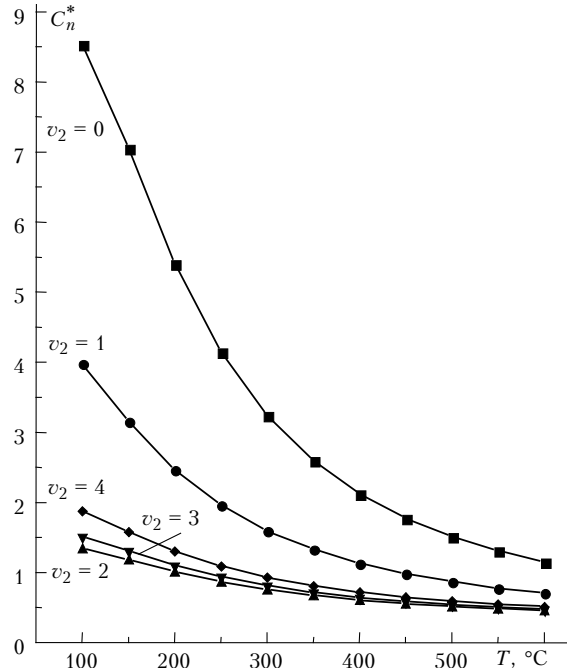

Fig. 1. Temperature dependence of the reduced third virial coefficient of ammonia at 100% concentration of inversion-excited molecules.

Among critical points, the value of V_{cr} changes most quickly as the concentration of excited molecules changes. Figure 2 shows the dependence of the critical volume V_{cr} on the concentration of inversion-excited molecules.
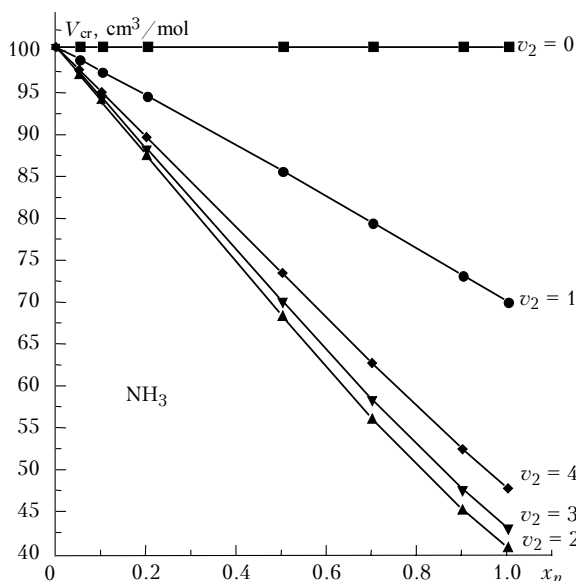

Fig. 2. Dependence of critical volume V_{cr} for NH_3 on the concentration of inversion-excited molecules.

It can be seen that the dependence is strong enough: the transition of 10% of molecules into the first excited state with $v_2 = 1$ changes V_{cr} by 2.5%, and the transition into the excited state with $v_2 = 2$ changes it by 5%.

Figure 3 depicts the dependence of the critical pressure on the concentration of inversion-excited NH_3 and ND_3 molecules for the inversion states with $v_2 = 0$ and 1. At excitation of 10% of molecules into the state with $v_2 = 2$ $(P_{cr})_{NH_3} - (P_{cr})_{ND_3} \approx 2.3$ (atm).

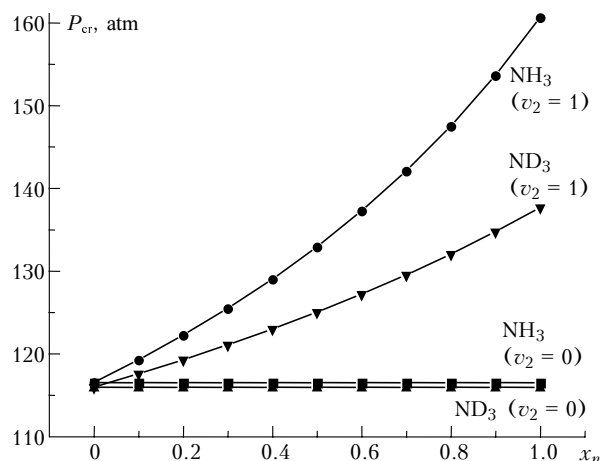**Fig. 3.** Dependence of the critical pressure P_{cr} for NH_3 and ND_3 on the concentration of molecules in the states with $v_2 = 0$ and 1.

4. Water vapor

With excitation of the bending vibrational mode, the value of the dipole moment decreases. At $0 \le v_2 \le 4$,

the change $\Delta\mu = |(\mu_{v_2} - \mu_0)/\mu_0|$ is 7.5% (Refs. 3 and 4). This leads to the decrease of the virial coefficients with the growing concentration of the excited molecules. The potentials (6) and (7) were used for calculation of the virial coefficients. Inclusion of the dipole-quadrupole interaction in Eq. (7) leads to significant changes in the third virial coefficient C_n (as compared to the calculations with the use of the potential (6)) at low temperature: for $T = 484$ K the change achieves 50%. With the temperature increase, the values of C_n calculated with the use of Eqs. (6) and (7) almost coincide: at $T = 650$ K the discrepancy between the C_n values is as small as 3.5%.

For the H_2O molecule, the calculated changes in the critical parameters with the varying concentration of excited molecules at low values of the quantum number v_2 are less significant than for ammonia. Thus, for the critical pressure P_{cr} at $0 \le v_2 \le 4$ and the concentration x_n varying from 0 to 20%, the change in P_{cr} does not exceed 1%, while the changes in T_{cr} and V_{cr} achieve 2%.

Figure 4 depicts the calculated dependence of the critical temperature T_{cr} on the concentration of molecules x_n (experimental value[11] is $T_{cr} = 647$ K). The calculation involved the parameters $\sigma = 2.713$ Å and $\varepsilon/k = 350$ K obtained from optimization (by the least-square method) of the calculated values of the second virial coefficient with $\mu_0 = 1.85$ D, $Q = 1.83$ D·Å, and experimental results of Ref. 7.
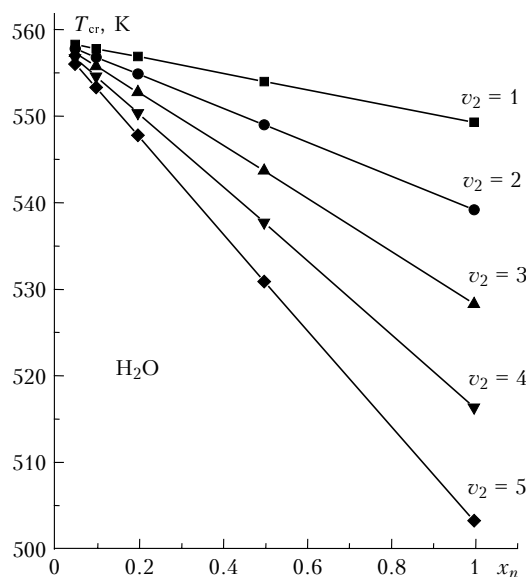

Fig. 4. Dependence of critical temperature of water vapor on the concentration of molecules with the excited bending vibrational mode.

Our aim in this paper was not to determine the optimal parameters σ and ε for the potentials (6) or (7). Such parameters can be determined from experimental data on thermodynamic and transport characteristics of a gas. The obtained values depend on both the experimental data and the method used for reconstruction of parameters. Thus, for example, Ref. 12 presents three sets of parameters σ and ε for the potential (6) of the

H_2O molecule obtained from reconstruction of experimental data on viscosity by different methods. The values of σ in these sets vary from 2.52 to 2.80 Å, and ε/k varies from 260 to 775 K, that is, the value of the parameter ε determining the potential depth varies most widely.

In our case, for example, the experimental value $T_{cr} = 647$ K for the most often used value $\sigma = 2.65$ Å can be achieved in the potential (7) at $\varepsilon/k = 480$ K (it is one variant; the calculation corresponds to the case that all molecules are in the ground vibrational state). It can be seen from Fig. 4 that large variations in T_{cr} take place at high concentrations of excited molecules and at high excitation of the bending vibrational mode. The similar behavior was obtained for V_{cr} as well.

Conclusion

In this paper, we have calculated the dependence of the critical parameters of ammonia and water vapor on the concentration of molecules with excited large-amplitude vibrational mode. The main results are illustrated in Figs. 1–4.

Excitation of the nonrigid vibrational mode leads to the changes in the equilibrium configuration of the molecule and, as a consequence, in its electrooptical parameters, thus resulting in the change of intermolecular interaction forces. These changes should be most significant for polar nonrigid molecules with high dipole moment in the ground state or molecules having no dipole moment in the equilibrium configuration, but acquiring it at excitation of some vibrational mode.

The calculations made in this paper for the critical parameters of ammonia and water vapor show that changes in these parameters in some cases may be significant and, what's more, they can be different for different isotopic modifications of the molecules.

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