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Mean Polarizabilities and Second Optical and Density Virial Coefficients of CH_3OH and CCl_2F_2 Between 300 and 355 K

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Dedicated to Prof. Dr. F. Kohler on the occasion of his 65th birthday

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Mean dipole polarizabilities $\alpha_0(\lambda, T)$ as well as second optical (or refractive index) virial coefficients $b_R(\lambda, T)$ and second density virial coefficients $B(T)$ of gaseous CH_3OH and CCl_2F_2 have been determined by precise measurements of the refractive index $n(\lambda, T, p)$ [$543\ \mathrm{nm} \leqslant \lambda \leqslant 633\ \mathrm{nm}$, $300\ \mathrm{K} \leqslant T \leqslant 355\ \mathrm{K}$, $p < 0.25$ bar (CH_3OH) and $p < 3$ bar (CCl_2F_2)]. α_0 is critically compared with the few data in literature. The b_R of these gases was measured for the first time with the cyclic-expansion method. The values of $|B|$ and $b_R = 3160(25)$ $\mathrm{cm^3 \cdot mol^{-1}}$ measured for CH_3OH are considerably greater than the values calculated by Buckingham's statistical-mechanical expressions for a Stockmayer interaction potential. This difference is discussed by assuming dimerization via H bonds, with result $\Delta H_2^0 \approx -(28 \cdots 33)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S_2^0 \approx -(116 \cdots 133)$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the dimerization enthalpy and entropy for standard conditions, respectively. On the other hand, Buckingham's formulae can be used with success to estimate b_R and B of CCl_2F_2.

KEY WORDS: polarizability; refractive index; virial coefficients; CH_3OH; CCl_2F_2.

1. INTRODUCTION

In the past, we have communicated mean polarizabilities α_0 as well as second virial coefficients $B(T)$ and third virial coefficients $C(T)$ of the equation of state of some nonpolar gases in the overall temperature range $230\ \mathrm{K} \leqslant T \leqslant 360\ \mathrm{K}$ (e.g., Refs. 1, 2). These quantities were derived from measurements of the refractive index (RI) $n(\lambda, T, p, x)$ of the gases

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(λ = wavelength, T = temperature, p = pressure, x = mole fraction). The apparatus as well as the methods used for data sampling and data evaluation have been described in detail elsewhere (e.g., Refs. 3, 4). In this paper we communicate for the first time corresponding measurements for polar gases. Gaseous methanol (CH_3OH) and Freon 12 (CCl_2F_2, dichlorodifluoromethane) have been investigated in the temperature range $300\text{ K} \leqslant T \leqslant 355\text{ K}$. Both substances are of great importance in industrial production, research, environmental problems etc. From the viewpoint of intermolecular interactions, the main difference between the two gases is that methanol can undergo hydrogen (H) bonding, but Freon 12 cannot. For instance, this different behavior should be possibly reflected in the virial coefficients. Indeed, in 1963 Everett and Munn [5] have indirectly shown by RI measurements that methanol should have an abnormally high value of the second optical (or refractive index) virial coefficient $b_R(\lambda, T)$, which describes the influence of intermolecular pair interactions on the polarizability α of the two interacting molecules and is therefore incorporated in RI measurements of real gases (see Section 3). Because the b_R of both gases was never determined by experiment, we decided to measure this quantity directly, in order to be able to separate clearly the effects of $b_R(\lambda, T)$ and $B(T)$. α_0, b_R, and B are compared with experimental data from the literature. In addition, b_R and B are estimated by Buckingham's statistical-mechanical expressions for a Stockmayer interaction potential. Dimerization of CH_3OH by H bonding will be discussed assuming chemical equilibrium between monomers and dimers.

2. APPARATUS AND MEASURING PROCEDURES

The refractive index $n(\lambda, T, p, x = 1)$ of gaseous methanol ($p < 0.25$ bar) and Freon 12 ($p < 3$ bar) was investigated with equipment which is described in detail elsewhere [3]. Therefore, it may be sufficient to explain in this section only the essential features of this apparatus with respect to the more difficult investigations of methanol and the new measurements of b_R. In order to prevent condensation of methanol, all gas pipes, valves, pressure transducers, etc., are thermostated and/or insulated from the surroundings. The central part of the apparatus is a two-beam interferometer of the Michelson type, with the gas sample cell in the measuring beam and the evacuated reference cell in the reference beam (see Ref. 3). This interferometer is illuminated with monochromatic light of vacuum wavelength λ ($\lambda = 546.226$ nm of a Hg spectral lamp or $\lambda = 543.51$, $\lambda = 594.11$, and $\lambda = 632.99$ nm of He–Ne lasers; only vacuum wavelengths are considered in this paper). The refractivity $[n(\lambda, T, p) - 1]$ of the gas sample against the vacuum ($n = 1$) is measured for fixed λ and T by changing p [uncertainty $|\Delta(n-1)/(n-1)| \approx 10^{-4}$; see Section 3]. Two kinds of gas sample cells have been used: (a) a single cell of effective geometrical length l (298.15 K) = 61.9470(28) cm (determined with Ar- gas of known n); and (b) a double cell, made up of two identical single cells, A and B, in series one after the other. A and B have the same optical axis and nearly identical volumes and lengths [$l_A = 30.236(2)$ cm, $l_B = 30.226(3)$ cm at 294.97 K]. A and B can be operated either separately or together.

The type of construction of the single cells is described elsewhere [3]. They are manufactured from Duran 50 glass and well thermostated during the measurements ($\Delta T < 10$ mK). T is measured at the two ends of the cells (a and b) with platinum resistance thermometers ($\Delta T < 3$ mK). p is measured with two pressure transducers ($p_{max} = 1$ bar and $\Delta p = 0.6$ mbar for CH_3OH and $p_{max} = 3$ bar and $\Delta p = 1.8$ mbar for CCl_2F_2). As in the previous investigations, these p measurements give the greatest contribution to the uncertainty of the results.

Two kinds of measurements have been performed: (c) "absolute" measurements of n for the determination of the mean dipole polarizability α_0 of the noninteracting molecules, and the difference $B^* \equiv b_R - B$ of the second optical virial coefficient b_R, and the second density virial coefficient B (see Section 3), as was previously done, by pumping the gas completely out of the sample cell (a or b) (see, e.g., Ref. 4); and (d) "difference" measurements of $\Delta n(A, B)$ with the double cell (b) for the determination solely of b_R according to the well-known "cyclic-expansion method" (e.g., Refs. 6, 7). In this method the gas is expanded from one filled single cell (A or B) into the other evacuated single cell (see Section 3).

Absolute n-measurements have been performed by the following two methods (cl and c2).

(cl) The discrete equilibrium p-step method: According to this method the gas is pumped out of the sample cell in N discrete pressure steps $\Delta p_i = p_i - p_{i-1}$ and allowed to reach thermodynamic equilibrium between two consecutive p steps, Δp_i and Δp_{i+1} (e.g., Ref. 1). This method was exclusively used in our previous experiments, but it has many disadvantages in the case of CH_3OH because only some ($N \leqslant 5$) pressure steps or data points (n, T, p) have been realized on account of the necessarily low maximum initial pressure $p_{max} \leqslant 0.25$ bar. On account of these disadvantages, the following method (c2) was developed.

(c2) The continuous quasistatic p method: The gas is continuously, but very slowly pumped out of or filled into the sample cell (both procedures should give the same result, of course). Automatic quick data sampling of (n, T, p) is required and done by a microcomputer (ATARI 1040ST). In this way the number N of equilibrium data points (n, T, p) could be

enormously enlarged ($N \approx 300$), with the result that the standard deviation s of the data fits has been diminished by a factor of about 100 (see Section 4, Tables II and III).

Liquid CH_3OH (purity better than 99.5 vol%, normal boiling point $T_b = 338.15$ K) has been dried by molecular sieve, degassed, and vaporized into the evacuated sample cell. The maximum initial pressure for all measurements was $p_{max} \approx 0.25$ bar.

CCl_2F_2 (purity better than 99 vol%, $T_b = 243.15$ K) from the gas container has been dried and filled into the evacuated sample cell ($p_{max} \leqslant 3$ bar).

3. THE WORKING EQUATIONS

n is determined by the interferometer relation

$$n - 1 = \lambda \Delta f / 2l \tag{1}$$

$\Delta f = |f(p) - f(0)| \geqslant 0$ is the registered interference fringe shift, that is, the difference between the interference fringe order $f(p)$ at pressure p and $f(0)$ at $p = 0$ ($n = 1$). The working equations of the absolute n method (c, c1, c2) and the cyclic-expansion method (d) of Section 2 can be derived by combining the virial expansion

$$(n^2 - 1)/(n^2 + 2)\rho = A_R + B_R \rho + \cdots = A_R(1 + b_R \rho + \cdots) \tag{2}$$

of the Lorentz–Lorenz relation with the virial expansion

$$\rho_0/\rho = 1 + B\rho + \cdots \tag{3}$$

of the equation of state of the gas (e.g., Ref. 4). $\rho \equiv 1/V_m$ is the molar density of the real gas of molar volume V_m and $\rho_0 \equiv p/RT$ is the molar density of the corresponding perfect gas [$R = 8.314510(70)$ $J \cdot mol^{-1} \cdot K^{-1}$ = molar gas constant]. On account of the low initial pressures p_{max} used, third and even higher virial coefficients could not be resolved in the experiments. Therefore, like Eqs. (2) and (3), the resulting combined virial series in powers of ρ_0 may be truncated also after two terms, giving the general working equation for the absolute n measurements (methods c, c1, and c2 of Section 2) [4]:

$$(n^2 - 1)/(n^2 + 2)\rho_0 = A_R(1 + B^*\rho_0 + \cdots) = A_R + A_R B^* \rho_0 + \cdots \tag{4}$$

Because ρ_0 can be measured more easily and accurately than ρ, Eq. (4) is preferred rather than Eq. (2). The first optical virial coefficient A_R and the coefficient B^* have the meanings

$$A_R \equiv 4\pi N_A \alpha_0(\lambda, T)/3, \qquad B^* \equiv b_R - B \tag{5}$$

$N_A = 6.0221367(36) \times 10^{23}$ mol^{-1} is the Avogadro constant and α_0 the mean volume dipole polarizability of the isolated noninteracting molecules (with the dimension of volume). $B_R \equiv b_R A_R$ is sometimes also called the second optical (or refractive index) virial coefficient. For low-density gases one obtains from Eq. (4) another working equation [4]:

$$n - 1 = a_1\rho_0 + a_2\rho_0^2 + \cdots \tag{6}$$

The coefficients a_1 and a_2 are related to A_R and B^* by

$$A_R = 2a_1/3, \qquad B^* = a_2/a_1 - a_1/6 \tag{7}$$

The data points (n, T, p) for CCl_2F_2 ($p_{max} \approx 3$ bar) could be best fitted by Eq. (4), but those for CH_3OH ($p_{max} \approx 0.25$ bar) by Eq. (6).

Second optical virial coefficients b_R (or B_R) have been measured by the cyclic-expansion method (d) of Section 2. On account of the low initial pressures p_{max}, only two consecutive gas expansion steps from cell A $(n_A - 1)$ to evacuated cell B (0) and thereafter from cell B $(n_B - 1)$ to evacuated cell A (0) could be performed. In this case the following working equation holds (e.g., Refs. 6, 7):

$$\begin{aligned} &\Delta n(A \to B)/(n_A - 1) + \Delta n(B \to A)/(n_B - 1) \\ &\quad = (B_n/2A_n^2)[(n_A - 1) + (n_B - 1)] + \cdots \end{aligned} \tag{8}$$

The coefficients A_n and B_n are related to A_R and b_R by

$$A_R = 2A_n/3, \qquad b_R \equiv B_R/A_R = B_n/A_n - A_n/6 \tag{9}$$

Δn is the measured change of n after expanding the gas from one filled cell (A or B) to the other evacuated cell, which means an overall expansion to the double cell (A + B) of nearly the double length $(l_A + l_B)$ and volume (see Section 2). The coefficient B_n can be determined absolutely from Eq. (8), if $A_n = a_1$ is known from absolute n measurements. In the case of CCl_2F_2, $\Delta n = 0$ was observed within the uncertainty of the measurements. Therefore, b_R of this gas was estimated by the following relation (e.g., Ref. 4):

$$b_R = A_R/4 \tag{10}$$

According to Eq. (5), $B(T)$ was finally calculated by

$$B = b_R - B^* \tag{11}$$

4. RESULTS

4.1. CH_3OH

The optical virial coefficients A_R, $B_R \equiv A_R b_R$, and b_R are collected in Table I. They have been measured for three He–Ne laser vacuum wavelengths λ using the double cell (b) of Section 2. A_R is determined by absolute n measurements (cell length $l_A + l_B$), and b_R (or B_R) by the cyclic-expansion method. As usual, standard deviations of the coefficients are given in parentheses.

The results of the absolute n measurements are collected in Table II. The quantity N is the number of measured data points (n, T, p) used for data fitting by Eq. (6); s is the standard deviation of these fits. The coefficients A_R and $B^* = b_R - B$ have been calculated by Eq. (7). $B(T)$ was calculated according to Eq. (11) by using the best measured value $b_R = 3171(7)$ $cm^3 \cdot mol^{-1}$ in Table I. Therefore, the uncertainty of B may be estimated to be equal to the uncertainty of B^*. The data set A has been produced with sample cell (a) by the discrete equilibrium p-step method (c1) of Section 2 ($N \leqslant 5$, $s \approx 5 \times 10^{-7}$). The data sets B and C have been produced with sample cell (b) of full length by the continuous quasistatic p method (c2) of Section 2 ($N \approx 300$, $s \approx 3 \times 10^{-9}$). As can be clearly seen, these data sets B and C are more precise and reliable than data set A [see, e.g., the $B(T)$ values]. Therefore, only data sets B and C are considered further in the discussion in Section 5.

4.2. CCl_2F_2

Absolute n measurements have been performed only for $\lambda = 632.99$ nm by the continuous quasistatic p method (c2), using sample cell (b). The results are collected in Table III. The N data points (n, T, p) of each isotherm have been fitted by Eq. (4) with standard deviation s. $B(T)$ was

Table I. Optical Virial Coefficients of CH_3OH

	λ (nm)				
	543.51	594.11	632.99	632.99	632.99
T (K)	303.79(14)	303.09(48)	303.27(15)	332.71(10)	351.12(20)
A_R ($cm^3 \cdot mol^{-1}$)	8.343(4)	8.332(4)	8.427(3)	8.423(3)	8.423(4)
B_R ($cm^6 \cdot mol^{-2}$)	26522(334)	25996(433)	26721(59)	26541(150)	26761(168)
b_R ($cm^3 \cdot mol^{-1}$)	3179(40)	3120(52)	3171(7)	3151(18)	3177(20)

Table II. Experimental Results for CH_3OH According to Eq. (6)
[$\Delta T \leqslant 0.01$ K, $^*b_R = 3171$ cm$^3 \cdot$mol^{-1} in Eq. (11)]

T (K)	N	a_1 (cm^3·mol^{-1})	a_2 (cm^6·mol^{-2})	10^7 s	A_R (cm^3·mol^{-1})	$[b_R - B]$ (cm^3·mol^{-1})	$-B(*)$ (cm^3·mol^{-1})
A (c1)							
546.2 nm							
303.28	5	12.450(5)	54407(11395)	6.4	8.302(3)	4368(915)	1197(915)
318.03	4	12.584(8)	57875(2314)	2.1	8.389(1)	4597(184)	1426(184)
332.61	4	12.519(4)	56712(5820)	8.7	8.339(4)	4528(465)	1357(465)
352.41	4	12.512(6)	39764(4714)	4.6	8.341(6)	3176(377)	5(377)
B (c2)							
546.2 nm							
303.32	271	12.514(6)	63498(412)	0.024	8.343(4)	5072(33)	1901(33)
318.15	319	12.523(4)	57402(314)	0.011	8.349(3)	4582(25)	1411(25)
332.42	287	12.516(4)	51118(150)	0.029	8.344(3)	4082(12)	911(12)
352.30	304	12.515(5)	48404(252)	0.034	8.343(4)	3866(20)	695(20)
C (c2)							
633.0 nm							
303.29	312	12.639(5)	64124(412)	0.029	8.426(3)	5071(33)	1900(33)
318.23	279	12.636(6)	57846(314)	0.024	8.424(4)	4576(25)	1405(25)
332.31	376	12.636(5)	51531(150)	0.013	8.424(3)	4076(12)	905(12)
352.20	213	12.642(6)	48559(252)	0.044	8.428(4)	3839(20)	668(20)

calculated according to Eq. (11). The values of b_R have been estimated by Eq. (10). As mentioned above this was done because the performed cyclic-expansion measurements (d) with CCl_2F_2 gave insignificantly small values of b_R within the experimental uncertainty of about 20 cm$^3 \cdot$mol^{-1} (see Table I). Therefore, the uncertainty of B is estimated to be equal to the uncertainty of B^*.

Table III. Experimental Results for CCl_2F_2 According to Eq. (4)
($\Delta T \leqslant 0.01$ K, $\lambda = 632.99$ nm, $b_R = A_R/4$)

T (K)	N	A_R (cm^3·mol^{-1})	$[b_R - B]$ (cm^3·mol^{-1})	10^3 s (cm^3·mol^{-1})	$-B$ (cm^3·mol^{-1})
303.29	108	17.1482(6)	503(2)	1.5	499(2)
303.53	50	17.1477(2)	503(1)	0.7	499(1)
321.44	77	16.9802(5)	415(1)	1.0	411(1)
321.63	71	16.9805(8)	416(2)	1.3	412(2)
332.28	143	17.0069(5)	355(1)	2.1	351(1)
340.99	42	17.0591(7)	337(2)	1.6	333(2)
341.17	178	17.056(1)	333(3)	6.9	329(3)

Table IV. Mean Polarizabilities $10^{24}\alpha_0(\lambda)$ (in cm^3) of CH_3OH

λ (nm)	This work, RI	Eq. (12) [18], RI		
543.5	3.307(2)	3.336		
546.2	3.308(2)	3.335	3.24 [5], RI	
589.4	—	3.322	3.25 [45L], RI	3.69 [45M], RI
594.1	3.303(2)	3.321		
633.0	3.340(2)	3.312		
∞	—	3.247	3.21 [10, 46], P_E	3.77 [10, 46], P_V
QM	3.05 [20]	3.04 [21]	{0.88, 2.85, 3.21, 3.37} [22]	3.36 [23]

5. DISCUSSION

α_0, B_R (or b_R), and B of CH_3OH and CCl_2F_2 are the interesting quantities of this paper. They have been derived from measurements of the refractive index n of the two gases. The results are given in Tables I to V and are discussed in detail in Section 5.1 (CH_3OH) and in Section 5.2 (CCl_2F_2) (λ is the vacuum wavelength). α_0 can be compared with data in the literature by using tables of α_0 itself (e.g., Refs. 8, 9), of the static dielectric polarization $P=(4\pi N_A/3)\alpha_0$ $(\lambda \to \infty, T)$ (e.g., Ref. 10), and of $(n-1)=2\pi N_A(p/RT)\alpha_0(\lambda, T)$ (e.g., Ref. 11). However, a critical review of all the papers, cited in Refs. 8 to 11, shows that only a few different experiments and theoretical calculations, concerning α_0 of CH_3OH (Table IV) and CCl_2F_2 (Table V), have in fact been performed. The situation is even poorer in the case of B_R values. Only one estimated B_R value of CH_3OH [5] and only one pair of measured static dielectric virial coef-

Table V. Mean Polarizabilities $10^{24}\alpha_0(\lambda)$ (in cm^3) of CCl_2F_2

λ (nm)	This work, RI (g)			
633.0	6.7979(2)	6.7315(3)	6.7420(2)	6.7620(6)
(T, K)	(303.41)	(321.54)	(332.28)	(341.08)
488.2	6.78 [35], RI(est)			
514.7	6.76 [35], RI(est)		6.58(4) [36], RI, LS(l, 233K)	
594.1	—		6.53 [37], RI, KE(l, 233K)	
633.0	6.73 [35], RI(est)		6.7(2) [38], SE(est)	
∞	6.34 [10, 39], P_E		7.97 [10, 39], P_V	7.93 [12, 13], P_V
∞	7.78(30) [49], P_V		8.0(5) [38], P_V(est)	

ficients, A_ε [12, 13] and B_ε [12, 14], of CCl_2F_2 are known. On the other hand, a lot of $B(T)$ data of both gases, published up to 1978, are collected in Ref. 15. More recently measured $B(T)$ values seem to exist only for CH_3OH [16].

In the following sections, α_0, B_R, and B of both gases are discussed separately. Special attention is given to the influence of intermolecular interactions, using Buckingham's statistical-mechanical expressions of B_R and B for comparison. In addition, the dimerization of CH_3OH on account of H bonding is discussed in some detail, because there are contradicting statements in the literature.

5.1. CH_3OH

5.1.1. *Mean Polarizability* α_0

Mean dipole polarizabilities $\alpha_0 = a_1/2\pi N_A = 3A_R/4\pi N_A$ of isolated noninteracting molecules have been calculated from the data in Tables I and II. They are compared with the known data from the literature in Table IV. As is indicated in Eq. (5), α_0 should by principle depend on λ and T (e.g., Ref. 8). Although a small increase in α_0, and therefore A_R with increasing T, was observed and discussed previously for some molecular gases (e.g., Refs. 2, 4, 17), this effect cannot be verified clearly by the A_R data in Tables I and II. The reason for this lack may be the smallness of the investigated temperature range. Therefore, the following T-averaged values of A_R (in $cm^3 \cdot mol^{-1}$) have been derived from Tables I and II:

$\lambda = 546.226$ nm: 8.343(36) (Table II, set A), 8.345(3) (Table II, set B);
$\lambda = 632.99$ nm: 8.424(4) (Table I), 8.425(4) (Table II, set C).

These numbers demonstrate the good reproducibility of independent measurements. They have been used for calculating the corresponding α_0 values in the second column in Table IV according to Eq. (5). The α_0 values in the third column are calculated by the perfect-gas approximation Eq. (12):

$$\begin{aligned} \alpha_0(\lambda) &= (kT/2\pi p)(n-1) \\ 10^{24}\alpha_0(\lambda) &= 4.14145/[1.27534 - (10^5\lambda)^{-2}] \end{aligned} \qquad (12)$$

where $\alpha_0(\lambda)$ is in cm^3, and λ in cm. The second expression in Eq. (12) follows from the only known dispersion relation of the refractive index (RI) n of gaseous CH_3OH at standard conditions (perfect gas at $T = 298.15$ K, $p = 1.01325$ bar, $k = 1.380658(12) \times 10^{-23}$ J K^{-1} = Boltzmann constant) [11, 18]. α_0 values according to Eq. (12) have been widely used in the literature (e.g., Refs. 9, 20). They are greater by only about $\Delta\alpha_0 = 2 \times 10^{-28}\,\mathrm{cm}^3$ than the values calculated by the Lorentz–Lorenz relation $\alpha_0 = (3kT/4\pi p)(n^2 - 1)/(n^2 + 2)$ for the perfect gas.

The remaining few experimental data on $\alpha_0(\lambda)$ come from RI measurements [5, 45]. One should notice that the quite often-cited Kerr effect (KE) measurements of Stuart [19] have been evaluated by different authors by using different values of n and k. In Ref. 19 Stuart has obviously used Mascart's value $n = 1.000623$ [45] (589 nm, 273.15 K, 1.01325 bar) and $k = 1.371 \times 10^{-23}\,\mathrm{J\,K}^{-1}$ (e.g., Ref. 45, p. 801), with the result $\alpha_0 = 3.66 \times 10^{-24}\,\mathrm{cm}^3$ according to Eq. (12). Later on Stuart [10] probably used the Lorenz value $n = 1.000549$ [45] for the same conditions and the same k, with the result $\alpha_0 = 3.23 \times 10^{-24}\,\mathrm{cm}^3$. Of course, these α_0-values are smaller by a factor $0.993 = 1.371/1.380658$ than the corresponding values in Table I, indicated by [45M] and [45L], respectively. Finally, Applequist et al. [20] obviously used n of Refs. 11 and 18, with the result $\alpha_0 = 3.32 \times 10^{-24}\,\mathrm{cm}^3$ in Table I, Eq. (12).

The static polarizabilities $\alpha_0(\infty)$ in Table I come from measurements of the static dielectric polarization $P = P_V + P_0 = P_V + a/T \equiv A_\varepsilon$ of the perfect gas [10]. $P_V = P_E + P_A = P - P_0 = C\alpha_0(\infty)$ is the shift polarization and $P_0 = C\mu_0^2/3kT = a/T$ the orientation polarization ($C = 4\pi N_A/3$, $\mu_0 =$ permanent dipole moment). $P_E = 8.1\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ is the electronic and $P_A = 1.4\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ the atomic contribution to P_V of CH_3OH [10, 46]. Additional measurements of P of gaseous CH_3OH are known [47, 48]. Finally, α_0 values from different quantum mechanical (QM) calculations are given in the last row in Table IV (see, e.g., Ref. 9). Their spread is considerable.

It is interesting to note that the dispersion of $\alpha_0(\lambda)$ according to Eq. (12) is normal (increasing α_0 with decreasing λ). This cannot be confirmed clearly by our measurements. Equation (12) gives only the electronic contribution and leads to a static value $\alpha_0(\infty)$, which is of the same order as the value derived from P_E. On the other hand, the atomic contribution P_A is considerable and may be the reason for our measured high value $\alpha_0(633.0\,\mathrm{nm}) = 3.340 \times 10^{-24}\,\mathrm{cm}^3$ (e.g., due to the OH valence vibration at about 2800 nm). The reason for the systematic difference of $\Delta\alpha_0 = (0.02 \cdots 0.03) \times 10^{-24}\,\mathrm{cm}^3$ between α_0 of Eq. (12) and our values is not yet clear and should be investigated by means of additional measurements and by checking the procedure used in Refs. 11 and 18 for reducing the original n measurements to standard conditions.

5.1.2. *Second Optical Virial Coefficients* $b_R = B_R/A_R$

Coming now to the second optical virial coefficients b_R in Table I, one cannot observe a clear dependence on T and λ, as was discussed for other substances only recently [7]. The arithmetic mean of all b_R values of Table I is $b_R = 3160(25)\ \mathrm{cm^3 \cdot mol^{-1}}$, which is comparable with the value $b_R = 3100(100)\ \mathrm{cm^3 \cdot mol^{-1}}$ [5], estimated from B^* according to Eq. (5) by means of $B(T)$ values in the literature. On the other hand, the previously used approximation, Eq. (10), gives $b_R = 2.1\ \mathrm{cm^3 \cdot mol^{-1}}$ and fails completely. Buckingham [24] has derived statistical-mechanical expressions for $B_R = A_R b_R$, which may be schematically written in the following manner:

$$B_R(\text{aniso}) = (3A_R^2/16)\,\varkappa[(1-\varkappa)f_1 + \varkappa f_2] \tag{13}$$

$$B_R(\text{pol}) = (A_R^2/2)[f_3(\alpha) + f_4(\beta) + f_5(\gamma)] = B_R(\alpha) + B_R(\beta) + B_R(\gamma) \tag{14}$$

Equation (13) corresponds to Eq. (4.2), and Eq. (14) to Eq. (4.7), of Ref. 24, respectively. B_R (aniso) is the contribution to B_R due to the anisotropy $\varkappa$ and $B_R(\text{pol})$ due to the polarizability of the molecules [dipole polarizability α, first (β) and second (γ) hyperpolarizabilities]. These equations have been derived for pair interactions between polar molecules according to a Stockmayer potential, and Eq. (13) especially for axially symmetric molecules of anisotropy $\varkappa = (\alpha_{\|} - \alpha_{\perp})/3\alpha(\alpha_{\|}$ and $\alpha_{\perp}$ are the α components parallel and perpendicular to the molecular axis). Although methanol is nonlinear, we have calculated $B_R(\text{aniso})$ by Eq. (13) and $B_R(\text{pol})$ by Eq. (14) for $T = 303.2$ K by using the following molecular parameters: $\alpha = 3.34 \times 10^{-24}\ \mathrm{cm^3}$ (this work), $\beta = 1 \times 10^{-29}$ esu, and $\gamma = 2 * 10^{-35}$ esu (Ref. 24, estimated), $\mu_0 = 1.69$ D [25], central potential parameters $\varepsilon/k = 792$ K and $r_0 = \sigma = 2.76 \times 10^{-8}$ cm [25], $\varkappa = 0.088$ [26] (polarization ratio $\rho_0 = 0.0046$), and $\varkappa = 0.062$ ($\rho_0 = 0.0023$ [26]). The H_n functions in the f_i expressions ($i = 1, \ldots, 5$) are calculated by Eq. (3.6) of Ref. 25. The results are ($A_R = 8.425\ \mathrm{cm^3 \cdot mol^{-1}}$)

$$B_R(\text{aniso}) = 13.31\varkappa[(1-\varkappa)159.38 + \varkappa 164.86]\ \mathrm{cm^6 \cdot mol^{-2}}$$

$$\varkappa = 0.088\text{: } B_R(\text{aniso}) = 187\ \mathrm{cm^6 \cdot mol^{-2}}$$

$$\varkappa = 0.062\text{: } B_R(\text{aniso}) = 132\ \mathrm{cm^6 \cdot mol^{-2}}$$

$$B_R(\text{pol}) = 35.49[15.11 + 34.90 + 6.83]\ \mathrm{cm^6 \cdot mol^{-2}}$$

$$= 2017\ \mathrm{cm^6 \cdot mol^{-2}}$$

and therefore, $b_R = [B_R(\text{aniso}) + B_R(\text{pol})]/A_R = 262\ \mathrm{cm^3 \cdot mol^{-1}}$ ($\varkappa = 0.088$) and $b_R = 255\ \mathrm{cm^3 \cdot mol^{-1}}$ ($\varkappa = 0.062$), respectively. This is only 8% of the observed value. Comparison with the results for CCl_2F_2 in Section 5.2 leads to the conclusion that H bonding gives the main contribution to b_R of CH_3OH. This conclusion is confirmed by the observed $B(T)$ data for methanol, discussed below.

5.1.3. Second Density Virial Coefficients B

In Fig. 1, our low-temperature results are compared with selected data of the literature by using reduced variables $B_r \equiv B/V_c$ and $T_r \equiv T/T_c$ (V_c = critical molar volume, T_c = critical temperature). For the sake of clarity, only the data sets of Kudchadker et al. [15, 27] and Bich et al. [16] have been drawn, which are in accordance with our measurements. The curves 1 to 4 have the following meanings.

The high-temperature data of Ref. 16 could be fitted quite well by a (12–6–8–3) potential [16], yielding curve 3. One observes strong deviation of the measured low-temperature data for $T_r < 0.65$ (or $T < 335$ K), what has to be attributed to association of the methanol molecules by H bonding (see below). The reference curves 1 and 2 have been calculated assuming monomer species only. These curves are used later for the calculation of the dimerization constant K_2 according to Eq. (22). Curve 2 represents the frequently used Berthelot relation (e.g., Refs. 28, 29):

$$B_r(T_r) = (9RT_c/128p_cV_c)[1 - 6/T_r^2] = 0.31977[1 - 6/T_r^2] \tag{15}$$

The following critical constants have been used: $T_c = 513.15$ K[29], $p_c = 79.64$ bar[29], and $V_c = 117.8\ \text{cm}^3 \cdot \text{mol}^{-1}$ [43]. Curve 1 fits the smoothed $B(T)$ data of CH_4 and C_2H_6 in the overall temperature range 110 K $\leqslant T \leqslant$ 600 K [15]. CH_4 and C_2H_6 have been selected as monomeric reference substances according to the principle of corresponding states. Curve 1 is represented by the polynomial

$$B_r(T_r) = -10.333 + 18.828T_r - 13.477T_r^2 + 4.302T_r^3 - 0.504T_r^4 \tag{16}$$

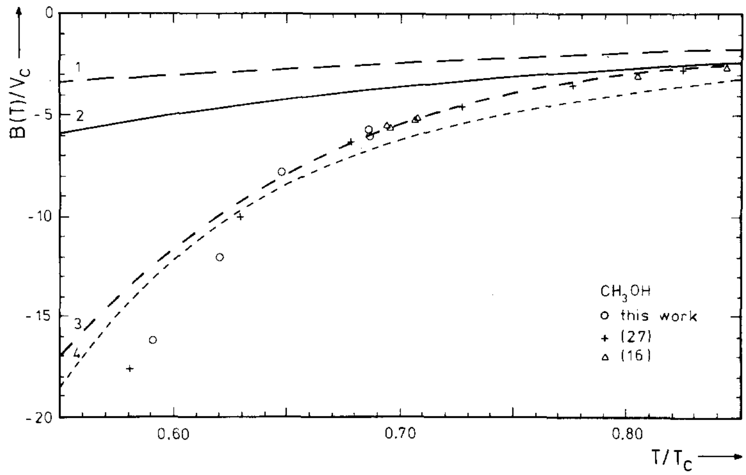

Fig. 1. Second virial coefficient of CH_3OH (reduced representation; see text).

The standard deviation of this fit is $|\Delta B_r| = 0.274$ (but only $|\Delta B_r| = 0.15$ in the T_r range shown in Fig. 1). The following critical data have been used [44]:

$$CH_4: \quad T_c = 190.53\ \text{K}, \qquad V_c = 98.54\ \text{cm}^3 \cdot \text{mol}^{-1};$$

$$C_2H_6: \quad T_c = 305.42\ \text{K}, \qquad V_c = 146.3\ \text{cm}^3 \cdot \text{mol}^{-1}.$$

In addition, $B(T)$ was calculated by the statistical-mechanical expression, Eq. (3.9), of Ref. 25 for polarizable permanent point dipole molecules (expanded to α^2 terms) by using the above given molecular parameters. This calculation was performed in steps of $\Delta T = 2$ K for the temperature range $270\ \text{K} \leqslant T \leqslant 470\ \text{K}$. The result is represented by curve 4 and the following fitting polynomial (standard deviation $|\Delta B_r| = 0.343$):

$$B_r(T_r) = -834.29 + 4007.94 T_r - 7342.50 T_r^2 + 6029.38 T_r^3 - 1864.84 T_r^4 \tag{17}$$

In each case, one observes systematic deviations of the measured $B(T)$ data from the curves for $T_r < 0.65$ (or $T < 335$ K), and this must be attributed to dimerization of the methanol molecules via H bonds.

The effect of dimerization on the second virial coefficient $B(T)$ of a gas was discussed by Schäfer and Foz Gazulla [30] and later on by several authors (e.g., Refs. 29, 31, 32). The dimerization of a species X (e.g., methanol) may be described by the dimerization-dissociation equilibrium $2X_1 \rightleftharpoons X_2$. In the case of $n = n_1 + 2n_2 = 1$ mol (N_A) molecules X in the gas phase, there are $n_1 = 1 - \alpha$ mol of monomers X_1, $n_2 = \alpha/2$ mol of dimers X_2, and $n^* = n_1 + n_2 = 1 - \alpha/2$ mol of particles (X_1, X_2) ($\alpha = 2n_2/1$ = fraction of molecules X forming dimers X_2). By using partial pressures $p_i = x_i p$, mole fractions $x_1 = n_i/n^*$ and total pressure p, one gets the following expression for the dimerization constant K_2:

$$K_2 = p_2/p_1^2 = x_2/px_1^2 = \alpha(1 - \alpha/2)/2p(1 - \alpha)^2 \approx \alpha/2p \tag{18}$$

Sometimes (e.g., Refs. 29, 30) the dissociation constant $K_2' = 1/K_2$ is considered. The approximation in Eq. (18) holds for $\alpha \ll 1$. However, if the exact Eq. (18) is solved for α, one obtains

$$\alpha = 1 - (1 + 4K_2 p)^{-1/2} \approx 2K_2 p \tag{19}$$

The approximation in Eq. (19) holds for $4K_2 p \ll 1$. The virial equation of state of the low-density vapor is then given by

$$pV_m = n^*(RT + Bp) \approx n^*RT + B_1 p \approx RT + B_0 p \tag{20}$$

B_0 is the observed second virial coefficient of the vapor:

$$B_0 = B_1 - RTK_2 \tag{21}$$

The approximations in Eq. (20) and therefore Eq. (21) hold as long as $n^* = n_1 + n_2 \approx n_1 \approx 1$ mol and $n^* = 1 - \alpha/2 \approx 1 - K_2 p$ according to Eqs. (18) and (19). Solving Eq. (21) for K_2 gives

$$K_2 = (B_1 - B_0)/RT = \exp[\Delta S_2^0/R - \Delta H_2^0/RT] \tag{22}$$

This expression may be used to calculate α by Eq. (19) as well as the molar entropy ΔS_2^0 and enthalpy ΔH_2^0 of dimerization for standard conditions by the usual straight-line representation:

$$\ln K_2 = \Delta S_2^0/R - \Delta H_2^0/RT \tag{23}$$

The reference coefficients B_1 of the monomer X_1 may be calculated either by the corresponding-states relation, Eq. (16), or by the Berthelot relation, Eq. (15), used also by Lambert et al. [29]. With the data $B_0 \equiv B$ in Table II (sets B and C) and B_1 according to Eq. (15), one obtains from Eq. (23) (correlation coefficient $r = 0.9915$):

$$\Delta H_2^0 = -33(3)\ \text{kJ} \cdot \text{mol}^{-1}, \ \Delta S_2^0 = -133(38)\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

On the other hand, with B_1 according to Eq. (16) one obtains ($r = 0.9931$)

$$\Delta H_2^0 = -28.5(1.4)\ \text{kJ} \cdot \text{mol}^{-1}, \qquad \Delta S_2^0 = -116(8)\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Using B_1 of Eq. (15), K_2 varies from 0.055 bar^{-1} at 303 K to 0.010 bar^{-1} at 352 K. Therefore, with $p = p_{\max} = 0.25$ bar, $\alpha = 2K_2 p$ varies from 0.028 to 0.005, which confirms the approximations used for $\alpha \ll 1$.

Lambert et al. [29] observed variation of the apparent ΔH_2^0 between $-13.4\ \text{kJ} \cdot \text{mol}^{-1}$ at about 403 K and $-30.6\ \text{kJ} \cdot \text{mol}^{-1}$ at about 313 K, but they did not report any ΔS_2^0 value. ΔH_2^0 (313 K) $= -30.6\ \text{kJ} \cdot \text{mol}^{-1}$ agrees quite well with our values. On the other hand, Weltner and Pitzer [33] have performed calorimetric measurements of the heat capacity C_p of methanol vapor between 345 and 521 K at pressures p of about 0.33, 0.66, and 1.0 bar. Only at the lowest temperature, 345 K, did they observe a strong nonlinear pressure dependence of $C_\text{p}(p)$, which could be best represented by a polynomial $C_\text{p} = C_p^0 + ap + cp^{n-1}$ with $n = 4$, $a = K_2\, \Delta H_2^{02}/RT^2$, and $c = K_n\, \Delta H_n^{02}/RT^2$ [33]. This result was interpreted by the authors of Ref. 33 as indicating, beside dimers and monomers, the presence of tetramer rings, formed by four O–H..O single bonds. By using the p–V–T-data of Eucken and Meyer [34] and fitting these data by the corresponding pressure virial equation of state $pV_\text{m} = RT + Bp + Dp^{n-1}$, Weltner and Pitzer [33] arrived at equations $B = b - RTK_2$ (covolume $b = 80\ \text{cm}^3 \cdot \text{mol}^{-1}$) and $D = -(n-1)RTK_n$ ($n = 4$) for the second (B) and fourth (D) pressure virial coefficients with the thermodynamic constants [33]

$$\Delta H_2^0 = -13.5\ \mathrm{kJ \cdot mol^{-1}}, \qquad \Delta S_2^0 = -69.1\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$$

$$\Delta H_4^0 = -101.3\ \mathrm{kJ \cdot mol^{-1}}, \qquad \Delta S_4^0 = -340.4\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$$

These values of ΔH_2^0 and ΔS_2^0 are about one-half of our values gives above, but ΔH_2^0 agrees quite well with $\Delta H_2^0(403\ \mathrm{K}) = -13.4\ \mathrm{kJ \cdot mol^{-1}}$ of Lambert et al. [29]. On the other hand, from ΔH_4^0 one calculates a single H-bond energy of $-25.4\ \mathrm{kJ \cdot mol^{-1}}$, which is in fair agreement with our values of ΔH_2^0 and is of the same order of single H-bond energies assumed by many people. In the last part of this section we make an attempt to explain this somewhat confusing situation.

At first, one should remember that only the density virial coefficients, and not the pressure virial coefficients, are directly correlated with interactions of molecule pairs, triples, etc. This means that D is a more complicated expression of different K_n, as was shown, e.g., by Woolley [31]. In addition, on account of this special polymerization model of Weltner and Pitzer, the values $B = (80 - RTK_2)$ calculated with the parameters given above (ΔH_2^0, ΔS_2^0) from Ref. 33, deviate significantly from all the reported measured $B(T)$ data. Because we could not resolve in our measurements any higher virial coefficient than B, we believe that our results for ΔH_2^0 and ΔS_2^0, which are about twice Weltner's values, but are in accordance with Lambert's ΔH_2^0 (313 K), may be the more reliable ones. We therefore assume that under the given experimental conditions, only monomers X_1 and dimers X_2 may exist, and not tetramers X_4. The T dependence of ΔH_2^0, observed by Lambert et al. [29], may then be explained by the change of the composition of the binary mixture (X_1, X_2) with changing temperature. This means that mixing rules for B and ΔH_2^0 have to be considered, which are completely neglected so far. On account of the calculated low values of α, a binary mixture of monomers and dimers is obvious. However, one may also think about a mixture of single-bonded and double-bonded dimers. This last mixture model may be employed by assuming, on account of the results in Ref. 33, that dimers are formed at high temperatures by a single O–H..O bond with a binding energy of about $-13.5\ \mathrm{kJ \cdot mol^{-1}}$ but, at lower temperatures, by the possible double bond with a binding energy of about $-30\ \mathrm{kJ \cdot mol^{-1}}$. Although this model seems to be unusual, it is interesting to note that Weltner and Pitzer [33] have explicitely excluded the existence of the postulated tetramer rings in the case of actually existing double-bonded CH_3OH dimers. However, the results of this paper are by no means unique proof of actually existing double-bonded dimers. These have to be established by other methods (e.g., by spectroscopic methods).

5.2. CCl_2F_2

The experimental results in Table III for A_R and $B^* = b_R - B$ according to Eq. (4) demonstrate the good reproducibility of the independent RI measurements at $\lambda = 633.0$ nm. As mentioned above, B was calculated by using the approximation, Eq. (10), for b_R. A weak increase in A_R with increasing T can be observed, if the data at 303 K are excluded.

5.2.1. *Mean Dipole Polarizabilities* α_0

In Table V our arithmetic mean values of $\alpha_0 = 3A_R/4\pi N_A$ are compared with the known data in the literature. Obviously, additional measurements of $\alpha_0(\lambda)$ of CCl_2F_2 in the gas phase (g) do not exist. The data in Ref. 35 are estimated by interpolating measured RI data for gaseous CCl_4 and CF_4 (the corresponding data in Ref. 9 are in SI units and not in the stated esu unit cm^3). The data in Refs. 36 and 37 have been derived from RI measurements of liquid (l) CCl_2F_2 at about 233 K in conjunction with light-scattering (LS) and Kerr effect (KE) measurements. The value α_0 (633.0 nm) in Ref. 38 was estimated from the RI data [36] for liquid CCl_2F_2 at 514.7 nm by means of semiempirical (SE) calculations. The static values $\alpha_0(\infty)$ have been derived from the polarization $P = P_V + P_0 = C\alpha_0(\infty) + a/T \equiv A_\varepsilon$ measured for the gas [10, 13, 39, 49] (see Section 5.1). The estimated high atomic contribution of about 20% to $\alpha_0(\infty)$ is obviously due to the F atoms ($P_\varepsilon = 16.0\ cm^3 \cdot mol^{-1}$ and $P_A = 4.1\ cm^3 \cdot mol^{-1}$ [10, 39]).

5.2.2. *Second Density Virial Coefficients* B

As mentioned in Section 4, b_R of CCl_2F_2 could not be resolved from the performed cyclic-expansion measurements and was therefore estimated by Eq. (10) for the calculation of $B(T)$ of Table III. These $B(T)$ values are compared with selected data from the literature [15, 40, 41] in Fig. 2, which is analogous to Fig. 1 [the obviously wrong value B (333 K) = $-385.8\ cm^3 \cdot mol^{-1}$ in Refs. 15 and 41 was corrected to $-365.8\ cm^3 \cdot mol^{-1}$]. The following critical data of CCl_2F_2 have been used for this reduced representation [44]: $T_c = 385.15$ K, $V_c = 217\ cm^3 \cdot mol^{-1}$, and $p_c = 41.06$ bar. Again, as in Fig. 1, curve 1 is represented by the corresponding-states relation Eq. (16), and curve 2 by the Berthelot equation

$$B_r(T_r) = 0.25271[1 - 6/T_r^2] \tag{24}$$

which corresponds to Eq. (15). Curve 3 was obtained by fitting our $B(T)$ data for $T < 342$ K and the $B(T)$ data from Ref. 40 for $T > 342$ K to the statistical-mechanical expression, Eq. (3.9), in Ref. 25 [the $B(T)$ data from

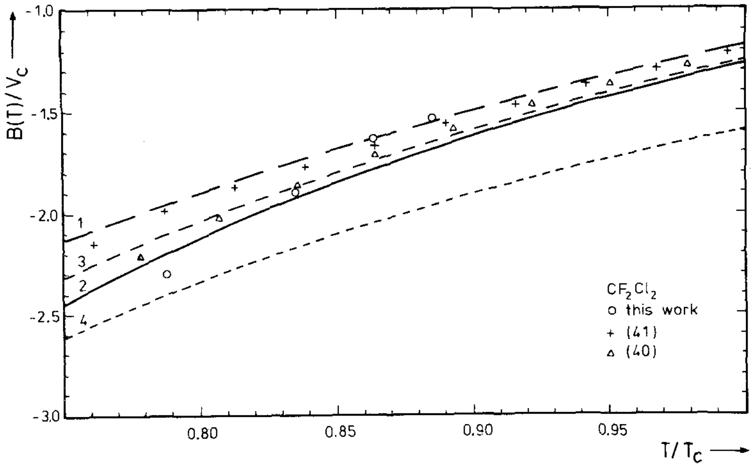

Fig. 2. Second virial coefficient of CCl_2F_2 (reduced representation; see text).

Ref. 40 for $T < 342$ K are more positive than our values; see Fig. 2]. $\alpha_0 = 6.73 \times 10^{-24}\,\mathrm{cm}^3$ (this work) and $\mu_0 = 0.51$ D [38, 39] are used as input parameters. The resulting output parameters of the (12, 6)-central part of the Stockmayer potential for the best fit are $r_0 = 6.60 \times 10^{-8}$ cm and $\varepsilon/k = 207$ K. The corresponding fitting curve 3 can be quite well represented by the following polynomial (standard deviation $|\Delta B_{\mathrm{r}}| = 0.0043$):

$$B_{\mathrm{r}}(T_{\mathrm{r}}) = -14.83 + 31.67T_{\mathrm{r}} - 25.61T_{\mathrm{r}}^2 + 7.52T_{\mathrm{r}}^3 \qquad (25)$$

However, using the values $r_0 = 4.57 \times 10^{-8}$ cm and $\varepsilon/k = 412$ K from Ref. 14 (Table IV), one obtains curve 4, which is too low.

5.2.3. Second Optical Virial Coefficients $b_R = B_R/A_R$

On the other hand, using these last values for r_0 and ε/k and, in addition, $\beta = -2.58 \times 10^{-31}$ esu [38, 42], $\gamma = 6.1 \times 10^{-37}$ esu [38, 42], and $\varkappa = 0.1075$ [35], the following results have been obtained for B_{R} (300 K) according to Eqs. (13) and (14) ($A_{\mathrm{R}} = 16.98\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$): $B_{\mathrm{R}}(\mathrm{aniso}) = 54.06\varkappa[(1-\varkappa)0.0087 + \varkappa 0.0079]\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2} = 0.050\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2}$, $B_{\mathrm{R}}(\mathrm{pol}) = 144.16[0.6747 - 0.0002 + 0.0001]\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2} = 97.252\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2}$, giving B_{R} (300 K) $= 97.3\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2}$ and b_{R} (300 K) $= 5.7\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. These values are smaller than the uncertainty of the present cyclic-expansion measurements (see Table I) and the only measured dielectric second virial coefficient $B_\varepsilon = 235(140)\,\mathrm{cm}^6 \cdot \mathrm{mol}^{-2}$ or $b_\varepsilon = 14(8)\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, but comparable with the estimation, Eq. (10), $b_{\mathrm{R}} = A_{\mathrm{R}}/4 \approx 4.3\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, used in Table III. b_{R} is even smaller for the optimized parameters

$r_0 = 6.60 \times 10^{-8}$ cm and $\varepsilon/k = 207$ K: $B_R(\text{aniso}) = 54.06\varkappa[(1-\varkappa)0.00063 + \varkappa 0.00057]$ $\text{cm}^6 \cdot \text{mol}^{-2}$ = 0.0037 $\text{cm}^6 \cdot \text{mol}^{-2}$ and $B_R(\text{pol})$ = $144.16[0.1502 - 0.00005 + 0.00002]$ $\text{cm}^6 \cdot \text{mol}^{-2}$ = 21.648 $\text{cm}^6 \cdot \text{mol}^{-2}$, giving $B_R(300\text{ K}) = 21.652$ $\text{cm}^6 \cdot \text{mol}^{-2}$ and b_R $(300\text{ K}) = 1.3$ $\text{cm}^3 \cdot \text{mol}^{-1}$. These results demonstrate that the simple estimation $b_R = A_R/4$ according to Eq. (10) can be used with success in the case of the polar gas CCl_2F_2 and perhaps also for other polar gases in the absence of H bonds.

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