

Methane-water cross second virial coefficient with quantum corrections from an *ab initio* potential

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We present our calculations of the cross second virial coefficient (B_{12}) and of a related quantity, $\phi_{12}=B_{12}-TdB_{12}/dT$, for the methane-water system in the temperature range $T=200-1000$ K. These calculations were performed using one of the *ab initio* potentials developed in previous work [Akin-Ojo and Szalewicz, J. Chem. Phys. **123**, 134311 (2005)]. Quantum corrections of order \hbar^2 were added to the computed classical values. We have estimated the uncertainties in our computed B_{12} and $\phi_{12}(T)$. This allowed evaluation of the quality of the experimental data to which we compare our results. We also provide an analytical expression for $B_{12}(T)$ as a function of the temperature T obtained by fitting the calculated values. This formula also predicts values of $\phi_{12}(T)$ consistent with the directly calculated values. © 2006 American Institute of Physics.
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I. INTRODUCTION

Typically, more than 90% of a given volume of wet natural gas is methane, with the rest being composed of heavier hydrocarbons, water, and small amounts of other compounds. Accurate values of the second virial coefficient (B) of methane-water mixtures are thus useful in the determination of the water dew point of natural gas, i.e., the temperature at which the water vapor in the gas-vapor mixture begins to condense when the mixture is cooled at constant pressure. The second virial coefficient occurs in the virial equation of state, often expressed in terms of powers of the molar volume v as¹

$$\frac{pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots, \quad (1)$$

where p is the pressure, T the temperature, R the molar gas constant, and $B(T)$, $C(T)$, $D(T)$,... are the second, third, fourth,... virial coefficients. For a mixture of ν components, the second virial coefficient is given by¹

$$B(T) = \sum_{i,j=1}^{\nu} x_i x_j B_{ij}(T), \quad (2)$$

where x_j is the mole fraction of the j th species in the mixture. Reliable experimental values of the cross second virial coefficient B_{12} are available for only a few water-gas systems and usually for a limited temperature range. For the $\text{CH}_4\text{-H}_2\text{O}$ system, the available experimental data come from pvT measurements of gas mixtures and from the stud-

ies of the solubility of water (or ice) in methane gas. A third source is from the determination of the excess enthalpies of the gas mixtures, although this method does not give B_{12} directly but instead a related quantity,

$$\phi_{12} = B_{12} - TdB_{12}/dT, \quad (3)$$

from which B_{12} can be extracted based on some assumptions. The values of B_{12} obtained by these methods have rather large uncertainties, and some of these studies do not agree with each other to within the experimental error bars. In this work, we compute the cross second virial coefficient for the $\text{CH}_4\text{-H}_2\text{O}$ system purely from theory and compare our results with experimental work. We use the pair potential energy surface (PES) obtained in Ref. 2 by the symmetry-adapted perturbation theory³⁻⁶ (SAPT) method. We also calculate ϕ_{12} for direct comparison with available experimental results. Our calculations include the quantum corrections of order \hbar^2 .

The paper is divided as follows. The next section discusses the methods used in our calculations, including a derivation of some specific expressions that are needed. This is followed by the section in which we discuss our results and compare with experimental work. We conclude with a summary and suggestions for further work.

II. THEORY AND COMPUTATION

The classical cross second virial coefficient B_{12}^{cl} is given by the expression^{7,8}

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$$B_{12}^{\text{cl}}(T) = -\frac{1}{2} \int \langle e^{-E_{\text{int}}(R, \omega_1, \omega_2)/kT} - 1 \rangle_{\omega_1, \omega_2} R^2 dR, \quad (4)$$

where $E_{\text{int}}(R, \omega_1, \omega_2)$ is the interaction energy of the dimer, with one molecule labeled 1 and the other 2, $\langle \cdots \rangle_{\omega_1, \omega_2}$ denotes the integration over angular orientations, and k is the Boltzmann constant. Explicitly,

$$\langle \cdots \rangle_{\omega_1, \omega_2} = \frac{1}{8\pi^2} \int (\cdots) \frac{d\omega_1 d\omega_2}{2\pi}, \quad (5)$$

where $d\omega_j = d\alpha_j d(\cos \beta_j) d\gamma_j$ for $j=1,2$ and the angles $\omega_j = \{\alpha_j, \beta_j, \gamma_j\}$ denote the Euler angles describing the orientation of the j th molecule with respect to space-fixed axes XYZ in a coordinate system such that the vector connecting the centers of mass of the two monomers is always along the Z axis of this system. The distance R is the separation between the centers of mass of the two monomers. In this work, the integration in Eq. (5) was done via Monte Carlo sampling by generating 4×10^6 random orientations and summing over these. This large number of random angular orientations was needed to ensure that the integration error in the calculated cross second virial coefficient was less than $0.05 \text{ cm}^3/\text{mol}$ for each temperature in the range considered. The integration over R was done with the quadrature method of Stenger.⁹ We split the radial integration range (we chose $R=0$ to $R=70 \text{ \AA}$, where $1 \text{ \AA} \equiv 0.1 \text{ nm}$) into $N=15$ subdivisions and used $n=41$ quadrature points in each subdivision. From $R=0$ to $R=10 \text{ \AA}$, we had ten equal subdivisions, two equal subdivisions from $R=10$ to $R=20 \text{ \AA}$, one from $R=20$ to $R=30 \text{ \AA}$, and two equal ones from $R=30$ to $R=70 \text{ \AA}$. Increasing the number of quadrature points per subdivision to $n=81$ did not change the results within a tolerance of $0.0001 \text{ cm}^3/\text{mol}$, indicating that our radial integration is well converged at $n=41$.

Differentiating Eq. (4) with respect to temperature gives

$$-T \frac{dB_{12}^{\text{cl}}}{dT} = \frac{1}{kT} \left(-\frac{1}{2} \right) \int \langle -E_{\text{int}} e^{-E_{\text{int}}/kT} \rangle_{\omega_1, \omega_2} R^2 dR. \quad (6)$$

We computed $-T dB_{12}^{\text{cl}}/dT$ explicitly from Eq. (6) in a similar fashion as the cross second virial coefficient from Eq. (4) and add this to the latter to obtain $\phi_{12}^{\text{cl}}(T)$. There are other ways to calculate the derivative in Eq. (6). One way is to compute the derivative of $B_{12}^{\text{cl}}(T)$ numerically using finite differences. Another way is to fit an analytic function to the computed values of B_{12} and then to differentiate this function. The expression in Eq. (6) is straightforward to compute and is generally more accurate than the other methods.

For the quantum correction $\Delta B_{12}^{(1)}$ of order \hbar^2 , we use the expression^{10,11}

$$\Delta B_{12}^{(1)} = \frac{\hbar^2}{24(kT)^3} \int \left\langle e^{-E_{\text{int}}/kT} \sum_{i=1}^2 \left(\frac{F_i^2}{M_i} + \sum_{s=1}^3 \frac{\tau_{is}^2}{I_s^i} \right) \right\rangle_{\omega_1, \omega_2} R^2 dR, \quad (7)$$

where F_i^2 is the square of the net force acting on molecule i of mass M_i , I_s^i is the s component of the principal moment of inertia of the i th molecule ($s=x, y, z$), and τ_{is} is the s component of the torque on the i th molecule in its principal-axis

frame. This expression resembles one obtainable from Eq. 7 of Ref. 12 and given, e.g., in Ref. 10. Although the former paper emphasized that this expression is not valid for asymmetric top molecules,¹² Wormer has shown¹¹ recently that the correct expression for such molecules has exactly the same form as that given in Ref. 12. Explicitly, $F_i^2 = |\nabla_{\mathbf{R}_i} E_{\text{int}}|^2$ and $\tau_{is} = -\partial E_{\text{int}} / \partial \theta_{is}$, where \mathbf{R}_i is the position vector from the center of mass of the i th molecule to that of the other monomer and θ_{is} is the angle describing the counter-clockwise rotation of the i th molecule about its s th principal axis.

Again, differentiating this expression with respect to the temperature yields

$$-T \frac{d\Delta B_{12}^{(1)}}{dT} = \frac{1}{kT} \left[\frac{\hbar^2}{24(kT)^3} \int \left\langle -E_{\text{int}} e^{-E_{\text{int}}/kT} \times \frac{1}{2} \sum_{i=1}^2 \left(\frac{F_i^2}{M_i} + \sum_{s=1}^3 \frac{\tau_{is}^2}{I_s^i} \right) \right\rangle_{\omega_1, \omega_2} R^2 dR \right] + 3\Delta B_{12}^{(1)}. \quad (8)$$

The quantum correction $\Delta \phi_{12}^{(1)}$ of order \hbar^2 to ϕ_{12} is obtained by adding the appropriate terms, i.e., $\Delta \phi_{12}^{(1)} = -T d\Delta B_{12}^{(1)}/dT + \Delta B_{12}^{(1)}$.

III. RESULTS

Our results are given in Tables I and II together with experimental data and are plotted in Figs. 1–3. The experimental error bars shown in the figures and given in the tables correspond to standard uncertainty with coverage factor of 2 (2σ). The experimental values of the cross second virial coefficient that we compare with are those we extracted from the solubility experiments reported by Oellrich and Althaus,¹³ Kosyakov *et al.*,¹⁴ Mohammadi *et al.*,¹⁵ Chapoy *et al.*,¹⁶ and Gillespie and Wilson.¹⁷ We also use values extracted by Plyasunov and Shock¹⁸ from solubility experiments reported by Olds *et al.*¹⁹ Data from the solubility studies by Rigby and Prausnitz²⁰ are also included, as are results from pvT experiments by Joffrion and Eubank²¹ and those by Abdulgatov *et al.*²² For ϕ_{12} we use the values we extracted from the experiments reported by Wilson and Brady,²³ the values from the excess-enthalpy experiments by Wormald and Lancaster,²⁴ and those determined by us from similar experiments by Lancaster and Wormald²⁵ at higher temperatures than their previous work. Plyasunov and Shock¹⁸ also derived values of B_{12} from Ref. 17 and ϕ_{12} from Ref. 25; their values differ somewhat from those we obtained, but the differences are within the experimental uncertainties we list in Tables I and II. These differences illustrate the inherent ambiguity in deriving these thermodynamic quantities from experimental data. The values of B_{12} indirectly estimated from the excess-enthalpy experiments by Wormald and Lancaster²⁴ are not used by us since these were derived from ϕ_{12} . The procedures we used to obtain B_{12} from solubility data and ϕ_{12} from excess-enthalpy data have been described previously.^{26,27} These procedures require the second virial coefficient for pure water²⁸ and pure methane,²⁹ which were taken from the literature.

TABLE I. Cross second virial coefficient for methane-water. All entries are in cm^3/mol unless otherwise stated. The estimated uncertainty of our calculations is δB_{12} . Experimental uncertainties at the 95% confidence level are in parentheses.

T (K)	B_{12}^{cl}	B_{12}	δB_{12}	Expt.	T (K)	B_{12}^{cl}	B_{12}	δB_{12}	Expt.
233.16	-83.72	-78.77	9.67	-134.4(66.6) ^a	308.11	-45.66	-43.48	6.22	-41.3(65.2) ^b
243.16	-76.77	-72.42	9.03	-102.2(26.9) ^a	313.12	-43.95	-41.86	6.07	-53.5(60.3) ^b
253.15	-70.57	-66.72	8.46	-72.6(14.3), ^a -63.0(36.6) ^c	323.15	-40.72	-38.81	5.79	-54.3(6.2), ^d -46(10) ^e
258.15	-67.70	-64.08	8.20	+17.8(28.3) ^c	344.30	-34.70	-33.09	5.27	-51(10) ^f
263.15	-64.99	-61.57	7.95	-77.4(13.5), ^a -65.4(19.4) ^c	348.15	-33.71	-32.14	5.18	-34.8(6.7), ^f -37(8) ^e
268.15	-62.41	-59.17	7.72	-52.2(14.6) ^c	373.15	-27.85	-26.54	4.68	-30(6) ^e
273.15	-59.96	-56.89	7.50	-71.1(14.6), ^a -48.3(11.6) ^c	377.60	-26.91	-25.64	4.60	-32(4) ^f
277.80	-57.78	-54.86	7.30	-77.0(11.5) ^g	398.15	-22.91	-21.79	4.26	-24.1(11.9) ^h
278.15	-57.62	-54.71	7.29	-55.9(5.4) ^c	410.90	-20.67	-19.64	4.07	-27(2) ^f
279.30	-57.10	-54.22	7.24	-85.8(39.5) ^g	423.15	-18.68	-17.71	3.90	-15.4(9.4), ^d -17.8(9.3) ^h
282.90	-55.50	-52.73	7.10	-66.5(8.4) ^g	444.30	-15.55	-14.69	3.64	-19(8) ^f
283.05	-55.43	-52.67	7.09	-62.3(32.3) ^b	448.16	-15.02	-14.18	3.60	-14.3(5.3) ^h
283.16	-55.39	-52.62	7.09	-38.8(9.3), ^a -55.0(3.4) ^c	460.65	-13.37	-12.58	3.46	-12.7(4.2) ^h
287.70	-53.45	-50.81	6.91	-80.3(14.6) ^g	473.16	-11.83	-11.09	3.33	-11.6(2.7) ^h
288.15	-53.26	-50.64	6.90	-53.1(2.8), ^c -65.9(32.3) ^b	477.60	-11.30	-10.58	3.29	-8.7(17.3), ^d -26(14) ^f
292.70	-51.41	-48.90	6.73	-55.7(9.0) ^g	485.05	-10.45	-9.75	3.22	-10.26(2.6) ^h
293.01	-51.29	-48.78	6.72	-37.0(24.0) ^b	498.16	-9.02	-8.36	3.10	-9.2(1.4) ^h
293.15	-51.23	-48.73	6.72	-51.2(2.5) ^c	510.90	-7.72	-7.10	2.99	-23(22) ^f
297.60	-49.50	-47.10	6.56	-55.4(8.4) ^g	523.16	-6.54	-5.95	2.89	-9.397 ⁱ
298.01	-49.34	-46.95	6.55	-54.0(17.4) ^b	573.16	-2.35	-1.87	2.55	11.143 ⁱ
298.15	-49.29	-46.90	6.54	-63(12) ^c	623.15	1.04	1.45	2.27	19.071 ⁱ
303.11	-47.44	-45.16	6.38	-92.2(61.5) ^b	653.15	2.78	3.15	2.12	15.299 ^j

^aExtracted from solubility data of Ref. 14.

^bExtracted from solubility data of Ref. 15.

^cExtracted from solubility data of Ref. 13.

^dExtracted from solubility data of Ref. 17.

^eReference 20.

^fExtracted by Plyasunov and Shock (Ref. 18) from solubility data of Ref. 19.

^gExtracted from solubility data of Ref. 16.

^hReference 21.

ⁱReference 22.

We fitted $B_{12}(T) = B_{12}^{\text{cl}} + \Delta B_{12}^{(1)}$ to the form

$$B_{12} = \sum_{n=1}^6 a_n \left(\frac{T_0}{T} \right)^n, \quad (9)$$

where $T_0 = 599.216$ K is the temperature where $B_{12}(T)$ is zero.

The fit is shown in Figs. 1 and 2 (it can hardly be seen in the figure since it coincides almost perfectly with the calculated values) while ϕ_{12} obtained from it is shown with dotted lines in Fig. 3. The rms error of the fit was $0.091 \text{ cm}^3/\text{mol}$, and the parameters obtained are $(a_1, a_2, a_3, a_4, a_5, a_6) = (109.447, -227.694, 182.497, -80.944, 18.368, -1.673)$.

The unit of each a_n is cm^3/mol . It was estimated in Ref. 2 that the exact global minimum for the $\text{CH}_4\text{-H}_2\text{O}$ dimer would be in the range from -0.98 to -1.08 kcal/mol (where $1 \text{ kcal} \equiv 4.184 \text{ kJ}$). The minimum of our SAPT PES fit is -1.01 kcal/mol . We thus increase and decrease the SAPT PES by $\pm 6\%$ to cover this range (i.e., we scale the whole potential by the factors 1.06 and 0.94, respectively) and plot the resulting B_{12} and ϕ_{12} with dashed lines in Figs. 1–3. This provides us with an estimate of the uncertainties in our reported values, which are given in Table I. Higher-order quantum effects are expected to be much smaller than our estimated uncertainties in the range of temperatures considered. Numerical errors in the integration are also smaller, although

TABLE II. Values of $\phi_{12} = B_{12} - T dB_{12}/dT$ for the methane-water system. All entries are in cm^3/mol unless otherwise stated. The estimated uncertainty of our calculations is $\delta\phi_{12}$. Experimental uncertainties at the 95% confidence level are in parentheses.

T (K)	ϕ_{12}^{cl}	ϕ_{12}	$\delta\phi_{12}$	Expt.
373.15	-107.88	-103.24	11.50	-134(28) ^a
383.15	-102.69	-98.39	11.04	-108(10) ^a
393.15	-97.86	-93.85	10.61	-109(22) ^a
403.15	-93.33	-89.59	10.20	-97(11) ^a
413.15	-89.09	-85.59	9.83	-100(20) ^a
423.15	-85.10	-81.83	9.48	-88(14) ^a
448.16	-76.12	-73.31	8.70	-179(32) ^b
473.16	-68.33	-65.89	8.03	-175(41) ^b
498.16	-61.51	-59.37	7.45	-95(31) ^b
523.16	-55.49	-53.59	6.95	-77(25) ^b
548.16	-50.14	-48.45	6.50	-44(17) ^b
573.16	-45.36	-43.84	6.10	-51(15) ^b
584.00	-43.44	-41.99	5.95	-70(40) ^c
598.16	-41.06	-39.68	5.75	-86(21) ^b
648.16	-33.65	-32.50	5.15	-68(15) ^b
692.00	-28.19	-27.20	4.71	-45(17) ^c
698.15	-27.49	-26.52	4.65	-52(15) ^b
800.90	-17.65	-16.93	3.86	-26(11) ^c

^aReference 24.

^bExtracted from data of Ref. 25.

^cExtracted from data of Ref. 23.

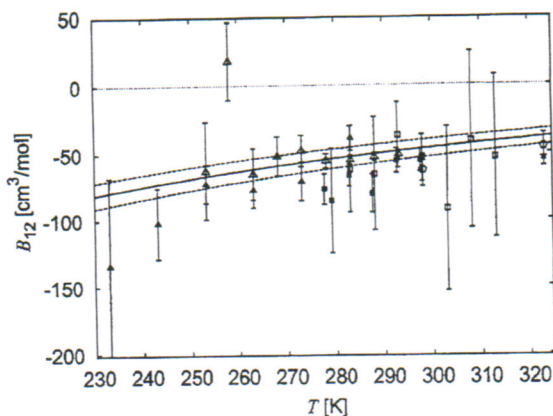


FIG. 1. Cross second virial coefficient B_{12} at low temperature (230–325 K). The solid line is our calculation, while the dotted line was obtained from the fit of Eq. (9). The lower (upper) dashed line, which gives estimates of the uncertainties in our calculations, was obtained by decreasing (increasing) our PES by 6%. All the points are experimental results as follows. Data extracted by us from these solubility experiments reported thus: open triangles—Oellrich and Athaus (Ref. 13); filled triangles—Kosyakov *et al.* (Ref. 14); open squares—Mohammadi *et al.* (Ref. 15); filled squares—Chapoy *et al.* (Ref. 16); and filled upside-down triangles—Gillespie and Wilson (Ref. 17). Open circles are data extracted by Plyasunov and Shock (Ref. 18) from solubility experiments reported by Olds *et al.* (Ref. 19). The open pentagons are from solubility experiments by Rigby and Prausnitz (Ref. 20). Results from pVT experiments: open diamonds—Joffrion and Eubank (Ref. 21); filled diamonds—Abdulgatov *et al.* (Ref. 22).

errors in the fit of the PES to our computed interaction energies could introduce another 2% uncertainty at most.² We consider our calculated uncertainties to be at the 95% confidence level. The expression in Eq. (9), together with the fit parameters, accurately predicts B_{12} for temperatures from 200 to 1000 K, the range used to obtain the fit.

Most of the experimental values of B_{12} and ϕ_{12} shown in Figs. 1–3 agree with one another to within the 2σ error bars shown and also agree with our calculations except for a few points. For B_{12} , our calculations agree best with the pVT experiments by Joffrion and Eubank.²¹ The values extracted by us from the solubility experiments reported by Oellrich and Althaus¹³ also agree well with our calculations except for one point (at $T=258.15$ K) which we consider to be in error. Our worst agreement at lower temperatures (T

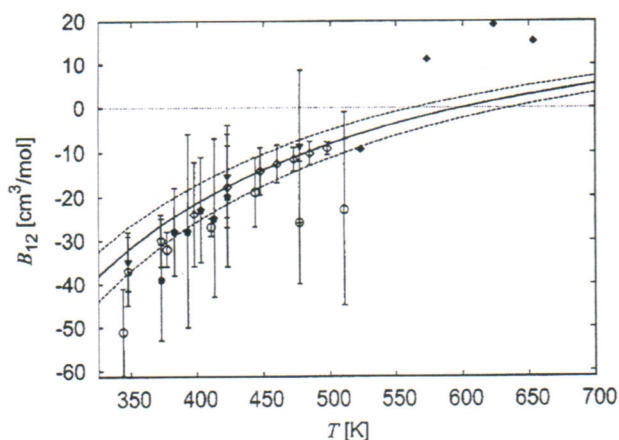


FIG. 2. Cross second virial coefficient B_{12} at high temperatures (325–700 K). The legend is the same as for Fig. 1.

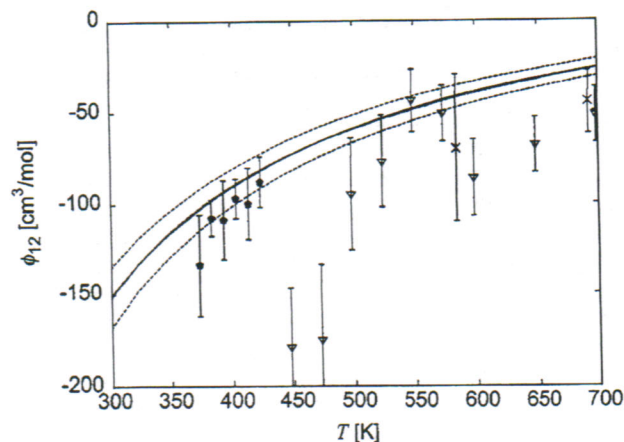


FIG. 3. Values of $\phi_{12}=B_{12}-TdB_{12}/dT$. The solid line is our calculation while the dotted line was obtained from the fit in Eq. (9). The lower (upper) dashed line, which gives estimates of the uncertainties in our calculations, was obtained by decreasing (increasing) our PES by 6%. The filled pentagons are from excess-enthalpy experiments by Wormald and Lancaster (Ref. 24), open upside-down triangles were extracted by us from a newer set of experiments by Lancaster and Wormald (Ref. 25) and the crosses were also extracted by us from experiments reported in Ref. 23.

≤ 325 K) involves the values extracted by us from the solubility experiments reported by Kosyakov *et al.*;¹⁴ we note that this source has also proven to be inconsistent with previous results for the Ar–H₂O (Ref. 27) and H₂–H₂O (Ref. 30) pairs. At higher temperatures ($T > 325$ K), our calculations disagree most with the values extracted by Plyasunov and Shock¹⁸ from the experiments reported by Olds *et al.*¹⁹ (or perhaps the values reported by Abdulgatov *et al.*²² which we cannot critically assess since the authors provided no uncertainties); see Fig. 2. For ϕ_{12} , our best agreement is with values given by Wormald and Lancaster in Ref. 24, while our worst agreement is with those extracted by us from their later work reported in Ref. 25. The numbers we extracted from the experiments reported in Ref. 23 by Wilson and Brady overlap with our calculations within the 2σ error bars shown in Fig. 3 (see also Table II).

The quantum corrections are quite small (see Table I), typically 5%–7% of B_{12} , smaller than the 20% we estimated in Ref. 2 extrapolating from the case of the water–water system. The reason for this smallness lies chiefly in the fact that the PES for the CH₄–H₂O dimer is less anisotropic than that of the H₂O–H₂O dimer; thus, the torques arising in Eq. (7) are smaller for CH₄–H₂O.

IV. CONCLUSIONS

We have obtained the cross second virial coefficient B_{12} and a related quantity, $\phi_{12}=B_{12}-TdB_{12}/dT$, for the methane–water system by using an *ab initio* PES for the CH₄–H₂O dimer. Quantum corrections of order \hbar^2 were included in the calculations of both quantities. We have also determined values of B_{12} and ϕ_{12} from experimental data reported in the literature. The values from most experimental work agree with our calculations within our estimated theoretical uncertainties and using a 95% level of confidence for the former.

Further work could use path-integral Monte Carlo (PIMC) to calculate the quantum corrections to all orders.¹⁰ For the temperature range considered in this work, we believe higher-order corrections, i.e., $\mathcal{O}(\hbar^4)$ and higher, would still be well within our theoretical error bars. In addition, the cross third virial coefficients could be calculated—with and without the assumption of pairwise additivity in the interaction energies between monomers. There are very few experimental results for these; the only known ones are those by Joffrion and Eubank in Ref. 21 and by Abdulgatov *et al.* in Ref. 22.

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