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A Refined Evaluation of the Gas-Phase Water-Dimerization Equilibrium Constant Within Non-Rigid BJH- and MCY-Type Potentials

Z. Slanina[1,2] **and J.-F. Crifo**[3]

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The flexible BJH- and flexible or semiflexible MCY-type water–water potentials (4 potential modifications in each nonrigid family, i.e., altogether 12 potentials) are used for evaluation of the gas-phase water-dimerization equilibrium constants. The potential-energy term is adjusted for best reproduction of the available experimental equilibrium constants. An independent test using the experimental steam second-virial coefficient isotopic difference shows that the adjustment also improves the computational evaluation of the difference. A set of dimerization equilibrium constants is suggested over a wide temperature interval (based on the BJH/G, MCY-B, or MCYB potential modifications). The best reproduction of the experimental equilibrium constants (in conjunction with good performance for the second-virial isotopic difference) is produced by the BJH/G potential. The results are applicable to various problems such as the formation of water clusters in large-scale natural and artificial water jets (e.g., hydrogen–oxygen rocket motors, orbital capsule water dumps, water ejection from a comet nucleus) or in atmospheric chemistry.

KEY WORDS: clustering; cometary or planetary atmospheres; steam; water-dimerization equilibrium constant; water-dimer populations.

1. INTRODUCTION

The water dimer is one of the best-understood hydrogen-bonded species, this being based on a variety of spectroscopic observations (e.g., Refs. 1–6)

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[1] Max-Planck-Institut für Chemie (Otto-Hahn-Institut), W-6500 Mainz, Federal Republic of Germany.

[2] Permanent address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy, Czech and Slovak Federal Republic.

[3] Institut d'Astrophysique Spatiale, Centre National de la Recherche Scientifique, B.P. 10, F-91371 Verrières Le Buisson Cedex, France.

and a number of theoretical evaluations (for recent contributions, see Refs. 7–11). The water-dimer and other cluster populations are important for the interpretation of atmospheric phenomena [12], fluid studies [13], and problems in solution chemistry [14] and for modeling water recondensation in all kinds of instances. In particular, needs for reliable modeling of recondensation in strongly underexpanded water jets not readily accessible to direct experimentation have appeared recently. One class of such jets are formed during manned spaceflights from exhausts from hydrogen–oxygen thrusters, from vehicle evaporation coolers, and from vehicle overboard liquid dumps [15]. Other examples are the huge impure water jets that form the atmospheres of the comets [16], the interest being enhanced by the Giotto and Vega flyby observations of Comet Halley. Water recondensation is expected to affect the hydrodynamics of these water jets and to affect the photochemistry triggered by solar illumination of the jets [17–24]. Reliable modeling of these jets is required to assess these effects and to optimize future observational programs, such as the future cometary rendezvous missions presently under consideration.

This focuses attention on the small water clusters, and, in the first place, on the dimer, which are the first rungs on the recondensation ladder [21, 25]. A kinetic model is required for the formation of these clusters; in the first approach, microreversibility can be postulated and the equilibrium constants used to relate forward and reverse rate coefficients. The available experimental thermodynamical data [26–32] refer to relatively high temperatures, while the applications deal frequently with the low-temperature region, where computational evaluations [33–45] remain the only source of information. The present report extends previous evaluations, applying the recently introduced flexible BJH-type and semiflexible and flexible MCY-type potentials, however, improving them by a refinement of energetics with respect to available observed thermodynamic terms.

2. COMPUTATIONAL TREATMENT

Recently, nonrigid, flexible interaction potentials have been introduced into water research. One line originated in the so-called central-force (CF) models (CF [46], CF1 [47], CF2 [48]) in which the inter- and intramolecular potential parts were described in a uniform form. Later, Bopp, Jancsó, and Heinzinger [49–51] combined the CF2 intermolecular potential (with a modified H–H interaction term [50]) with a quartic spectroscopic force field of a gas-phase water molecule [52] (BJH/G potential). They also developed [49] a modification of the water spectroscopic potential [52], adjusted to liquid water conditions, leading to the BJH/L flexible water–water potential. Finally, for the sake of completeness, the original

CF1 and CF2 intermolecular terms in conjunction with a gas-phase intramolecular part [52] are considered here, labeled CF1/G and CF2/G.

In addition to the above four BJH-type potentials, eight nonrigid potentials related to the water–water (intermolecular) potential originally introduced by Matsuoka, Clementi, and Yoshimine (MCY) [53] are also considered here. At present, four parametric modifications of this intermolecular *ab initio* potential are available (MCYI and MCYII [53], MCYB [54], MCYC [55]). The MCY-type potentials were originally rigid, i.e., the monomeric unit geometry was fixed in the free-state equilibrium positions. As in the BJH case, the MCY potentials were later on combined [56] with (another) quartic gas-phase water force field, namely, the quantum-chemical potential [57]. In the first application Lie and Clementi [56] considered the MCYII intermolecular part, thus creating the so-called MCY-L flexible potential. Following the same approach, the flexible MCY-I, MCY-B, and MCY-C potentials can be introduced.

Selection of a particular intramolecular potential is a matter of choice; cf. Refs. 9, 41, and 58–60. For methodical reasons it is useful, beside the quartic intramolecular potential, to consider a simple harmonic force field [39], too. In that way four additional MCY-type potentials were created (labeled MCYI, MCYII, MCYB, and MCYC), which can be called semiflexible or semirigid for distinguishment from the above flexible MCY-type potentials.

These 12 potential functions were then treated in a unified way described in detail elsewhere [61]. As the first step, energy minimum was located (exhibiting always the C_s point-group symmetry) by means of the analytical energy derivatives. The second energy derivatives were constructed by numerical differentiation of the analytical energy gradient. The differentiation was performed [61] in the so-called quarter precision (about 35 valid decimal digits), thus ensuring the practically exact values of the second derivatives. The latter derivatives were employed in the harmonic vibrational analysis, producing frequencies of the normal vibrational modes. The calculated structural, vibrational, and energy data were then used to evaluate the partition functions of the usual rigid-rotor and harmonic-oscillator quality [39]. Primarily, the dimerization equilibrium constant K_p for the reaction

$$2H_2O(g) = (H_2O)_2\,(g) \qquad (1)$$

was evaluated. However, as some thermodynamic data are also available [31] for the heavy-water dimer, the deutero process

$$2D_2O(g) = (D_2O)_2\,(g) \qquad (2)$$

was considered, too.

In order to compensate some possible imperfections of the potentials as well as of the partition-function approximation, a refinement with respect to the observed data is considered. The potential-energy change ΔE for dimerizations given by Eqs. (1) and (2) is exactly the same (within the generally accepted Born–Oppenheimer approximation). [Differences between both isotopomeric reactions, however, appear when passing to the standard enthalpy changes at the absolute zero temperature (the ground-state energy changes) ΔH_0°.] Thus, the potential-energy change represents a convenient common (temperature independent) parameter which can be varied in order to obtain a best agreement with observed data. Minimization of the sum of squares of experiment–theory differences, $\delta^2 \log K_{\mathrm{p},i}$, in the logarithm of K_p over five observed temperatures T [26, 27, 31] [four and one for reaction given by Eqs. (1) and (2), respectively] is selected as the optimization criterion:

$$\frac{\partial \sum_{i=1}^{5} \delta^2 \log K_{\mathrm{p},i}}{\partial \Delta E} = 0 \qquad (3)$$

The thermodynamic treatment is then repeated using the refined energetics.

3. RESULTS AND DISCUSSION

Table I presents the energetics calculated within the 12 potential modifications for both water-dimer isotopomers within the treatments with and without E-refinement. Clearly enough, the optimal fit given by Eq. (3) mostly requires a smaller depth of the water-dimer potential minimum. However, the depth is scattered, within the 12 potentials, over a rather wide interval, between -25.97 and -17.78 kJ · mol^{-1}. Nevertheless, if we consider from each of the three families only the potential yielding the best fit (vide infra), the interval for ΔE values becomes considerably more narrow.

Comparison of the observed and calculated thermodynamic data is given in Table II. In addition to the K_p values, the sums of squares of experiment–theory differences are considered also for the standard changes of enthalpy H, entropy S, TS term, and Gibbs energy G. The entropy difference sums are not influenced by the E refinement. The Gibbs energy difference sums are, as can be well expected, mostly considerably improved by the refinement. However (as the entropy is not influenced), there are substantial changes (both improvement and deterioration) in the enthalpy difference sums between the treatment with and that without the E refinement. But the equilibrium constant is the quantity of prime interest in our context and agreement between its observed and its calculated values is improved considerably by the potential-energy refinement.

It would be instructive to compare the values from the treatment with and without E refinement for an independent set of experimental data. Recently, such a data set was reported [62], viz., the isotopic difference in the second virial coefficient of steam, $B_2^{\mathrm{H}} - B_2^{\mathrm{D}}$. Within a semiclassical approach (see, e.g., Ref. 63) the isotopic difference is reduced to

$$B_2^{\mathrm{H}} - B_2^{\mathrm{D}} = RT[K_{\mathrm{p}}^{\mathrm{D}} - K_{\mathrm{p}}^{\mathrm{H}}] \tag{4}$$

where $K_{\mathrm{p}}^{\mathrm{H}}$ and $K_{\mathrm{p}}^{\mathrm{D}}$ denote the equilibrium constants of association given by Eqs. (1) and (2), respectively, and R is the gas constant. The sum of

Table I. Survey[a] of the Water-Dimer Energetics[b] in the Semirigid MCY, Flexible BJH, and Flexible MCYL Families of Potentials with and Without[c] *E* Refinement

Term	H isotope	Potential energy ΔE	Ground-state energy ΔH_0°
MCYI	^{1}H	−23.71 (−23.92)	−14.68 (−14.88)
	^{2}D		−16.93 (−17.13)
MCYII	^{1}H	−25.26 (−24.55)	−15.67 (−14.97)
	^{2}D		−18.06 (−17.35)
MCYB	^{1}H	−22.91 (−23.59)	−14.22 (−14.89)
	^{2}D		−16.36 (−17.04)
MCYC	^{1}H	−25.97 (−25.26)	−16.09 (−15.38)
	^{2}D		−18.53 (−17.81)
CF1/G	^{1}H	−19.32 (−26.01)	−11.68 (−18.37)
	^{2}D		−13.46 (−20.15)
CF2/G	^{1}H	−17.78 (−23.56)	−10.62 (−16.40)
	^{2}D		−12.31 (−18.09)
BJH/G	^{1}H	−20.36 (−23.54)	−12.98 (−16.16)
	^{2}D		−14.73 (−17.91)
BJH/L	^{1}H	−19.28 (−23.55)	−13.06 (−17.32)
	^{2}D		−14.49 (−18.76)
MCY-L	^{1}H	−24.04 (−25.01)	−15.88 (−16.84)
	^{2}D		−17.86 (−18.83)
MCY-I	^{1}H	−22.55 (−24.33)	−14.85 (−16.63)
	^{2}D		−16.73 (−18.51)
MCY-B	^{1}H	−21.85 (−23.93)	−14.37 (−16.45)
	^{2}D		−16.18 (−18.26)
MCY-C	^{1}H	−24.77 (−25.68)	−16.28 (−17.19)
	^{2}D		−18.33 (−19.24)

[a] The upper and lower figures refer to the ^{1}H water-isotopomer dimerization $[2\mathrm{H_2O(g)} = (\mathrm{H_2O})_2\,(\mathrm{g})]$ and to the ^{2}D water-isotopomer dimerization $[2\mathrm{D_2O(g)} = (\mathrm{D_2O})_2\,(\mathrm{g})]$, respectively.

[b] Either the potential-energy change ΔE or the ground-state energy change ΔH_0° is presented, both in kJ · mol^{-1}.

[c] Results without E-refinement treatment are presented in parentheses.

squares of experiment–theory differences for the term in Eq. (4) is included in Table II. It is evident that the potential-energy refinement considerably improves the agreement with observation.

The lowest value of the $\sum \delta^2 \log K_{p,i}$ term is found for the MCYB, BJH/L, and MCY-B potential in the semiflexible MCY, BJH, and flexible MCY family of potentials, respectively. In the BJH family, however, the difference with respect to the BJH/G potential (i.e., the second best term) is quite negligible. As the latter potential yields considerably better reproduction of the isotopic virial difference in Eq. (4), it may be reasonable to prefer the BJH/G equilibrium constants to BJH/L ones. In the triad MCYB, BJH/G, and MCY-B the best agreement with the experimental equilibrium constants is produced by the BJH/G potential, which can thus be recommended for evaluations of the water-dimer populations in various applications (however, some additional observed data would be useful for the potential screening).

Table II. Comparison[a] of the Observed Standard Changes of Enthalpy H, Entropy S, TS Term, and Gibbs Energy G as Well as Equilibrium Constant K_p for the Gas-Phase Water-Dimer Formation with Their Evaluations in the 12 Potentials Studied, with and Without E Refinement, and Also the Comparison for the Steam Second-Virial Coefficient Isotopic Difference $B_2^H - B_2^D$

Term	$\sum \delta^2 H_i$[b]	$\sum \delta^2 S_i$[c,d]	$\sum \delta^2 G_i$[b]	$\sum \delta^2 \log K_{p,i}$[e]	$\sum \delta^2 (B_2^H - B_2^D)_i$[f]
MCYI	13.1 (13.1)	47.9 [9.55]	2.82 (2.74)	0.0426 (0.0461)	2657 (3041)
MCYII	20.6 (14.2)	119 [17.6]	4.77 (8.82)	0.0629 (0.104)	2860 (1763)
MCYB	16.1 (13.2)	54.7 [13.4]	2.12 (3.69)	0.0348 (0.0728)	2353 (3652)
MCYC	30.0 (19.3)	189 [28.3]	5.92 (10.3)	0.0745 (0.117)	2936 (1795)
CF1/G	65.6 (71.0)	323 [72.2]	1.11 (227)	0.0194 (3.72)	26.1 (7038)
CF2/G	122 (18.8)	645 [137].	1.96 (176)	0.0262 (2.79)	46.3 (2372)
BJH/G	35.0 (18.1)	153 [36.7]	0.982 (50.9)	0.0188 (0.856)	36.3 (252)
BJH/L	34.8 (35.4)	154 [37.0]	0.751 (91.4)	0.0144 (1.52)	2530 (12401)
MCY-L	22.1 (40.4)	134 [19.8]	4.06 (6.72)	0.0504 (0.128)	15.0 (26.7)
MCY-I	12.4 (28.6)	49.7 [9.45]	2.23 (15.6)	0.0321 (0.293)	22.6 (63.7)
MCY-B	14.8 (22.7)	52.2 [12.5]	1.62 (21.2)	0.0259 (0.384)	25.5 (98.2)
MCY-C	32.2 (54.8)	207 [31.2]	5.16 (7.14)	0.0614 (0.131)	19.6 (74.6)

[a] Results without E-refinement treatment are presented in parentheses (if different). For the observed values see Refs. 26, 27, and 31 and references therein; the standard state–ideal gas phase at 1 atm = 101,325 Pa pressure.

[b] Sum of squares of theory–experiment differences, in $(\mathrm{kJ \cdot mol^{-1}})^2$.

[c] Sum of squares of differences,[b] however, in $(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})^2$.

[d] In the square brackets the sum of squares of differences[b] $\sum \delta^2 (TS)_i$ is presented.

[e] Sum of squares of differences,[b] K_p values in atm^{-1}.

[f] Sum of squares of differences,[b] however, in $(\mathrm{cm^3 \cdot mol^{-1}})^2$.

Table III presents the temperature evolution of the constants in the MCYB, BJH/G, and MCY-B potentials, with and without E refinement (also included are the observed temperatures [26, 27, 31]). The results in Table III are the primary output of this article. The triads of values based on the E refinement represent the present best theoretical prediction of intervals within which the equilibrium constant should lie. At higher temperatures the intervals are sufficiently narrow, while at the lowest temperature the highest/lowest ratio is nearly 4 (without E refinement: 6.5). It should, however, be noticed that the quality of the measured equilibrium constants is not always sufficient; cf. considerably different observed values at practically identical temperatures of 372.4 and 373.0 K. Figure 1 presents

Table III. The Equilibrium Constant K_p of the Gas-Phase Water-Dimer Formation Evaluated[a] in the Semirigid Potential MCYB and in theFlexible Potentials BJH/G and MCY-B with and Without E Refinement

T(K)	$K_p = p_{(H_2O)_2}/p^2_{H_2O}$ (atm^{-1})^a		
	MCYB	BJH/G	MCY-B
100	1.86 (4.21) $\times 10^4$	5.83(267) $\times 10^3$	2.23(27.2) $\times 10^4$
200	1.00 (1.51) $\times 10^0$	6.98 (47.3) $\times 10^{-1}$	1.08 (3.79) $\times 10^0$
298.15	4.32 (5.67) $\times 10^{-2}$	3.88 (14.0) $\times 10^{-2}$	4.51(10.4) $\times 10^{-2}$
300	4.15 (5.45) $\times 10^{-2}$	3.74 (13.4) $\times 10^{-2}$	4.34 (9.99) $\times 10^{-2}$
370.75^b	*1.57 (1.95)* $\times 10^{-2c}$	*1.39 (3.90)* $\times 10^{-2c}$	*1.45 (2.84)* $\times 10^{-2c}$
372.4^b	1.29 (1.61) $\times 10^{-2}$	1.29 (3.59) $\times 10^{-2}$	1.33 (2.60) $\times 10^{-2}$
373.0^b	1.28 (1.59) $\times 10^{-2}$	1.28 (3.56) $\times 10^{-2}$	1.32 (2.58) $\times 10^{-2}$
400	9.37(11.5) $\times 10^{-3}$	9.60 (25.0) $\times 10^{-3}$	9.61(18.0) $\times 10^{-3}$
423^b	7.45 (9.03) $\times 10^{-3}$	7.79 (19.3) $\times 10^{-3}$	7.61(13.8) $\times 10^{-3}$
500	4.14 (4.88) $\times 10^{-3}$	4.58 (9.85) $\times 10^{-3}$	4.20 (6.93) $\times 10^{-3}$
573.15^b	2.83 (3.27) $\times 10^{-3}$	3.26 (6.36) $\times 10^{-3}$	2.86 (4.42) $\times 10^{-3}$
600	2.54 (2.91) $\times 10^{-3}$	2.96 (5.60) $\times 10^{-3}$	2.56 (3.88) $\times 10^{-3}$
700	1.87 (2.10) $\times 10^{-3}$	2.26 (3.90) $\times 10^{-3}$	1.87 (2.68) $\times 10^{-3}$
800	1.54 (1.70) $\times 10^{-3}$	1.91 (3.07) $\times 10^{-3}$	1.53 (2.10) $\times 10^{-3}$
900	1.35 (1.48) $\times 10^{-3}$	1.71 (2.62) $\times 10^{-3}$	1.35 (1.78) $\times 10^{-3}$
1000	1.25 (1.35) $\times 10^{-3}$	1.61 (2.36) $\times 10^{-3}$	1.24 (1.59) $\times 10^{-3}$

[a] Results without E-refinement treatment are presented in parentheses; the standard state choice–ideal gas phase at 1 atm = 101,325 Pa pressure.

[b] Temperatures at which observed K_p values are available; the observed K_p values at temperatures *370.75*, 372.4, 373.0, 423, and 573.15 K read (see Refs. 26, 27, and 31, and references therein) *1.19* $\times$ *10*$^{-2c}$, 1.11×10^{-2}, 1.58×10^{-2}, 8.58×10^{-3}, and 3.30×10^{-3} atm^{-1}, respectively.

[c] At the temperature $T = $ *370.75* K, K_p was reported [31] for the ^{2}D water-isotopomer dimerization [$2D_2O(g) = (D_2O)_2\,(g)$], and thus, the theoretical values were evaluated for the heavy-water dimerization (in order to differentiate from the light water-terms, the heavy-water terms are given in italics).

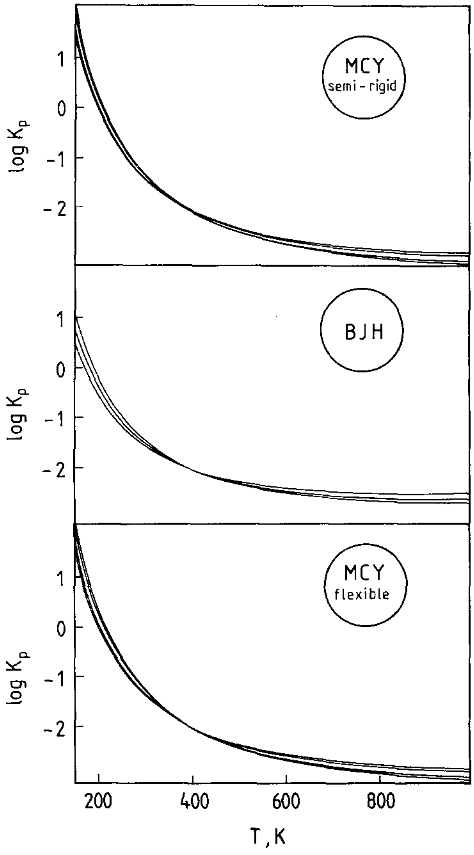

Fig. 1. Temperature dependence of the equilibrium constants K_p (in atm^{-1}) for the dimerization $2H_2O(g) = (H_2O)_2\,(g)$ evaluated within the semi-rigid MCY family of potentials [top: at the end of the considered temperature interval the K_p values decrease in the order MCYB (the highest term), MCYI, MCYII, MCYC (the lowest term)], BJH-type potentials [middle: at the end of the considered temperature interval the K_p values decrease in the order CF2/G (the highest term), CF1/G, BJH/L, BJH/G (the latter two dependencies practically collapse in one, the lowest, curve)], and flexible MCY family of potentials [bottom: at the end of the considered temperature interval the K_p values decrease in the order MCY-B (the highest term), MCY-I, MCY-L, MCY-C (the lowest term)].

the temperature dependence of K_p for the four members of each potential family.

Table IV closes this article with the comparison of calculated and observed values for the isotopic difference $B_2^H - B_2^D$. The comparison is presented for the three potentials from Table III and also for the MCY-L potential yielding the best observation–computation agreement for the isotopic term. Interestingly enough, for the semirigid MCYB potential, even the E refinement does not produce a satisfactory agreement with observation, though it improves the agreement. It can well be seen in Fig. 1 that in each potential family the four curves effectively collapse into one at temperatures around 400 K in order to follow the observed values.

In conclusion, a refinement of the potential energy term based on available experimental data was applied to 12 flexible (or semiflexible) potentials in order to obtain reliable computational evaluations of the gas-phase water-dimerization equilibrium constants. Of these 12 potentials, 4 (the BJH family) are phenomenological, effective (fitted to the properties of bulky water rather than to the gas phase), while the rest are of a nonempirical, ab initio nature (though with various computational approximations involved). Hence, none of the potentials is, strictly speaking, rigorous.

Table IV. Isotopic Differences, $B_2^H - B_2^D$, Between the Second Virial Coefficient of Water and Heavy Water Evaluated[a] in the Semirigid Potential MCYB and in the Flexible Potentials BJH/G, MCY-I, and MCY-B, with and Without E Refinement, and Their Comparison with Observation[b]

T (K)	MCYB	BJH/G	MCY-L	MCY-B	Observed[b]
423.15	38.4 (46.5)	10.3 (25.3)	12.7 (16.8)	11.2 (20.3)	15 ± 7
448.15	29.4 (35.3)	7.1 (16.8)	8.5 (11.0)	7.8 (13.6)	10 ± 5
473.15	23.3 (27.6)	5.0 (11.3)	5.8 (7.4)	5.5 (9.4)	3.9 ± 1
498.15	18.9 (22.2)	3.6 (7.7)	4.0 (5.1)	4.0 (6.6)	3.1 ± 0.5
523.15	15.7 (18.3)	2.5 (5.3)	2.8 (3.5)	2.9 (4.6)	1.8 ± 0.3
548.15	13.3 (15.4)	1.8 (3.5)	2.0 (2.5)	2.1 (3.3)	1.6 ± 0.3
573.15	11.4 (13.1)	1.2 (2.3)	1.4 (1.7)	1.5 (2.3)	0.5 ± 0.4
598.15	9.9 (11.4)	0.7 (1.4)	0.9 (1.1)	1.1 (1.6)	1.7 ± 0.3
623.15	8.8 (10.0)	0.4 (0.7)	0.6 (0.7)	0.7 (1.1)	0.6 ± 0.3
648.15	7.9 (8.9)	0.1 (0.2)	0.4 (0.4)	0.5 (0.7)	0.6 ± 0.3
673.15	7.1 (8.0)	−0.1 (−0.2)	0.2 (0.2)	0.3 (0.4)	0.6 ± 0.3
698.15	6.5 (7.3)	−0.3 (−0.5)	0.02 (0.02)	0.1 (0.2)	0.0 ± 0.3
723.15	5.9 (6.6)	−0.4 (−0.7)	−0.1 (−0.1)	−0.03 (−0.04)	0.2 ± 0.2
748.15	5.5 (6.1)	−0.6 (−0.9)	−0.2 (−0.2)	−0.1 (−0.2)	0.1 ± 0.2
773.15	5.1 (5.7)	−0.7 (−1.1)	−0.3 (−0.3)	−0.2 (−0.3)	0.0 ± 0.2

[a] In $cm^3 \cdot mol^{-1}$; results without E-refinement treatment are presented in parentheses.
[b] From Ref. 62.

Moreover, they have been applied within an approximative partition-function scheme. Our energy refinement can be understood as an effective way to compensate for various approximations involved and to create a sophisticated interpolation formula through the observed data available. The refinement yields not only a considerable improvement of the observation–computation agreement for the equilibrium constant but also of the (independent) experimental isotopic difference in the steam second-virial coefficient. In each of the three potential families considered, the most reliable potential modification was selected (MCYB, BJH/G, and MCY-B potentials). The selected potentials suggest an interval of values within which the equilibrium constant should lie. In the latter triad, the best agreement with the experimental equilibrium constants is produced by the BJH/G potential, which can thus be recommended for evaluations of the water-dimer populations. The proposed computed equilibrium constants represent the most reliable set so far available in literature, useful in a wide spectrum of problems ranging from, for example, atmospheric spectroscopy [12] to hydrodynamics of shuttle-orbiter water releases [15, 64, 65]. Nevertheless, more precise experimental data would still be useful for further improvements as well as allowance for anharmonicity corrections to partition functions.

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