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## A Note on the Flexible *BJH* and *MCYL* Potentials: A Fair Agreement with the Available Observed Thermodynamic Data on $(\text{H}_2\text{O})_2(\text{g})$ and $(\text{D}_2\text{O})_2(\text{g})$

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The first evaluation of the standard thermodynamic quantities for the gas-phase water-dimer formation and of the steam second-virial-coefficient isotopic difference within the recently developed *BJH* and *MCYL* flexible water potentials is presented. A fair agreement with available observed data is found for both potentials.

### INTRODUCTION

Thermodynamics of the gas-phase water dimer<sup>1</sup> has been evaluated several times<sup>2-14</sup>, however, the new generation of the water-water interaction potentials, viz. the flexible potentials<sup>15-25</sup> was not applied to the problem so far. The flexible potentials allow motions of the atoms in monomeric units and thus, they enable complete description of the water-dimer vibrations, the best results being so far obtained for the flexible *RWK2* potential using quantum simulation<sup>25</sup>. Quite recently Kell *et. al.*<sup>26</sup> augmented the available observed thermodynamic data<sup>27-33</sup> by H/D isotopic difference in the second virial coefficient of water. The present study reports calculations of the thermodynamic terms in the flexible *BJH* (Refs. 19, 20) and *MCYL* (Ref. 23) potentials in order to test applicability of both potentials to the particular situation (in spite of their relatively wide use in several other branches of water research, they have not been so far applied to the gas-phase water dimer).

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## COMPUTATIONAL DETAILS

The *BJH* potential was used in its form given in Refs. 19, 20 with the intramolecular contributions described by the quartic spectroscopic potential of a free water molecule<sup>34</sup>. The *MCYL* potential<sup>23</sup> combines the *MCY* intermolecular part derived from *ab initio* SCF CI results<sup>35</sup> (i. e. the approach employing the intermolecular electron-correlation contribution) with the water quartic force field from the many-body perturbation-theory calculations<sup>36</sup>. Each of the flexible potentials effectively possesses 12 geometrical degrees of freedom; however, the original coordinates sets employed contain several redundancies. In order to avoid complications with the redundancy conditions all differential calculations were carried out in a set of nuclear Cartesian coordinates<sup>37</sup>. The potential energy minimum (exhibiting the usual structure of  $C_s$  point-group symmetry and a near-linear hydrogen bond) was localized using the analytical first derivatives of the potential. In the following vibrational analysis, force constants obtained by numerical differentiation of the potential gradient were used (vibrational results, including various isotopomers, will be published elsewhere<sup>37</sup>, pointing out the successful reproduction of observed monomer/dimer frequency shifts as well as the importance of an accurate minimum location, a careful redundancy treatment, and a proper consideration of all contributions of force constants).

In terms of the *BJH* or *MCYL* structural, vibrational, and energy data, a complete thermodynamics of the gas-phase water-dimer formation



as well as of its deuterio analogue



can be described, employing the partition functions of the usual rigid-rotor and harmonic-oscillator (*RRHO*) quality. In our connections, two kinds of thermodynamic terms for associations (1), (2) are considered, viz. their standard enthalpy  $\Delta H_T^\circ$  and entropy  $\Delta S_T^\circ$  changes.

In addition to the standard terms also the isotopic difference  $B_2(\text{H}) - B_2(\text{D})$  in the water second virial coefficient was evaluated. Within the semi-classical approach (see, e. g. Ref. 8) the isotopic difference is, owing to a favourable cancellation, reduced to:

$$B_2(\text{H}) - B_2(\text{D}) = RT [K_{p2}(\text{D}) - K_{p2}(\text{H})], \quad (3)$$

where  $K_{p2}(\text{H})$  and  $K_{p2}(\text{D})$  denote the equilibrium constants of association (1) and (2), respectively,  $R$  the gas constant, and  $T$  the absolute temperature.

## RESULTS AND DISCUSSION

Within the Born-Oppenheimer approximation (generally accepted and used in isotope-chemistry reasoning<sup>38-40</sup>), the potential change  $\Delta E$  is the same for processes (1) and (2) for a given potential. The  $\Delta E$  changes in the *BJH* and *MCYL* potentials are equal to  $-23.54$  and  $-25.01$  kJ/mol, respectively. A next step is transition to the related ground-state-energy changes  $\Delta H_T^\circ$  (i.e., the standard enthalpy changes  $\Delta H_T^\circ$  for

$T = 0$  K). The transition to the  $\Delta H_0^\ddagger$  term actually means (in the harmonic approximation) addition of the zero-point vibrational contribution  $\Delta_0$ :

$$\Delta H_0^\ddagger = \Delta E + \Delta_0 \quad (4)$$

In the *BJH* potential the  $\Delta H_0^\ddagger$  term for the light (1) and heavy (2) water dimerization reads  $-16.16$  and  $-17.91$  kJ/mol, respectively, while in the *MCYL* potential the related values are  $-16.84$  and  $-18.83$  kJ/mol. (It is interesting to note that while at the  $\Delta E$  level the difference between the *BJH* and *MCYL* value is about 1.5 kJ/mol, for the  $\Delta H_0^\ddagger$  term it is reduced to about one half of the former value.)

TABLE I  
Comparison of Calculated and Observed Standard<sup>a</sup> Thermodynamic Characteristics of the Gas-Phase Water-Dimer Formation

Process	T(K)	$\Delta H_0^\ddagger$ (kJ/mol)		
		<i>BJH</i>	<i>MCYL</i>	Observed
2H <sub>2</sub> O(g) = (H <sub>2</sub> O) <sub>2</sub> (g) <sup>b</sup>	372.4	-16.44	-17.71	-15.02 <sup>c</sup>
	373.0	-16.43	-17.70	-13.77 <sup>d</sup>
	423.0	-15.80	-17.10	-14.31 <sup>d</sup>
	573.15	-13.71	-15.08	-15.69 <sup>e</sup>
2D <sub>2</sub> O(g) = (D <sub>2</sub> O) <sub>2</sub> (g)	370.75	-17.02	-18.41	-15.31 <sup>c</sup>
$\Sigma \delta_1^2$ (kJ/mol) <sup>2 f</sup>		18.14	40.40	
		$\Delta S_0^\ddagger$ (J/K/mol)		
		<i>BJH</i>	<i>MCYL</i>	Observed
2H <sub>2</sub> O(g) = (H <sub>2</sub> O) <sub>2</sub> (g) <sup>b</sup>	372.4	-71.80	-80.49	-77.78 <sup>c</sup>
	373.0	-71.78	-80.47	-71.42 <sup>d</sup>
	423.0	-70.19	-78.96	-73.39 <sup>d</sup>
	573.15	-65.98	-74.90	-74.89 <sup>e</sup>
2D <sub>2</sub> O(g) = (D <sub>2</sub> O) <sub>2</sub> (g)	370.75	-72.88	-81.77	-78.12 <sup>c</sup>
$\Sigma \delta_1^2$ (J/K/mol) <sup>2 f</sup>		153.0	133.7	

<sup>a</sup> The standard state-ideal gas phase at 101325 Pa pressure.

<sup>b</sup> <sup>1</sup>H isotope in the calculation.

<sup>c</sup> Ref. 32.

<sup>d</sup> Ref. 32, and therein quoted references.

<sup>e</sup> Refs. 27, 28.

<sup>f</sup> Sum of squares of differences between theory and experiment.

Observed  $\Delta H_0^\ddagger$  and  $\Delta S_0^\ddagger$  terms employed in Table I for testing quality of the potentials are not of a uniform origin. They were obtained either from studies<sup>32,33</sup> of thermal conductivity of H<sub>2</sub>O and D<sub>2</sub>O vapour, or extracted<sup>27,28,32</sup> from different measurements of the second virial coefficient of steam. (There are also other, partial data available<sup>29-31</sup>, however with respect to their incomplete nature they were not considered for the Table I purpose.) In order to compare results from the *BJH* and *MCYL* potentials, the sums of squares of differences between calculations and observations were carried out over five temperatures of observation (i.e., the only one observed value for reaction (2) was treated on an equal basis with the data for association (1)),

separately so for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  series. Generally speaking, agreement with observations is quite good for both potentials. With the enthalpy term the *BJH* potential yields considerably lower values of the sum of squares. (It should be noted that not all the observation may have same accuracy – cf. considerably different  $\Delta H^\ddagger$  terms of reaction (1) at the two lowest temperatures though the temperatures are practically identical.) However, for the entropy changes just the opposite is true (i.e., the *MCYL* data yield a better agreement) albeit the sums of squares are closer, in comparison with the enthalpy case.

In the *BJH* potential the enthalpy terms are, comparing with the observations, mostly underestimated (i.e., lower) while entropy terms are mostly overestimated (i.e., higher). In the *MCYL* potential, however, both enthalpy (with one exception) and entropy terms are underestimated. Consequently, a favourable compensation of the differences with respect to the observations can take place at level of the Gibbs free energy in the case of the latter potential.

TABLE II

*Isotopic Differences,<sup>a</sup>  $B_2(H) - B_2(D)$ , between the Second Virial Coefficient of Water and Heavy Water Evaluated in the *BJH* and *MCYL* Flexible Potentials*

<i>T</i> (K)	<i>BJH</i>	<i>MCYL</i>	Observed <sup>b</sup>
423.15	25.3	16.8	15 ± 7
448.15	16.8	11.0	10 ± 5
473.15	11.3	7.4	3.9 ± 1
498.15	7.7	5.1	3.1 ± 0.5
523.15	5.3	3.5	1.8 ± 0.3
548.15	3.5	2.5	1.6 ± 0.3
573.15	2.3	1.7	0.5 ± 0.4
598.15	1.4	1.1	1.7 ± 0.3
623.15	0.7	0.7	0.6 ± 0.3
648.15	0.2	0.4	0.6 ± 0.3
673.15	-0.2	0.2	0.6 ± 0.3
698.15	-0.5	0.02	0.0 ± 0.3
723.15	-0.7	-0.1	0.2 ± 0.2
748.15	-0.9	-0.2	0.1 ± 0.2
773.15	-1.1	-0.3	0.0 ± 0.2
$\Sigma \delta_1^2$ (cm <sup>3</sup> /mol) <sup>2</sup> <sup>c</sup>	252.0	26.7	

<sup>a</sup> In cm<sup>3</sup>/mol.

<sup>b</sup> Ref. 26.

<sup>c</sup> Sum of squares of differences between theory and experiment.

A surprisingly good agreement between the computations and observed values<sup>26</sup> was found for the isotopic difference in the second virial coefficient of steam  $B_2(H) - B_2(D)$  (Table II). Both potentials reproduce correctly the order of magnitude and temperature course of the term. However, the *MCYL* potential produces a better reproduction of the observation. Both potentials indicate a change of sign of the isotopic difference at higher temperatures, while in the observation this is possible only within the range of experimental errors. It turns out that the realistic, quartic, intramolecular potential is essential for the fine agreement with observation. If the harmonic intramolecular potential<sup>7,8</sup> is used instead, the  $B_2(H) - B_2(D)$  term is sig-

nificantly overestimated throughout the temperature interval. It should finally be noted that the conventional expression for the second virial coefficient, not considering the formation of bound dimers (i. e., integration over the whole configurational space with integrand involving the interaction potential but no reference to the mass of particles), cannot at all distinguish between isotopic modifications of a vapour.

In spite of their different origin (as well as different functional form) the *BJH* and *MCYL* flexible potentials similarly yield a fair agreement with the observed data. There is certainly some cancellation of the errors introduced by, e.g., the *RRHO* approximation. However, the cancellation is primarily significant with the isotopic difference in the second virial coefficient rather than with standard thermodynamic terms of associations (1), (2). The question of the nature of the *BJH* and *MCYL* potential success with the gas-phase water dimer is to be settled only after evaluation of anharmonicity effects on the terms studied. Anyhow, the reported findings imply that the *BJH* and *MCYL* potential can be equally well used within the *RRHO* treatment for a reliable evaluation of the gas-phase water dimer thermodynamic characteristics.

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### SAŽETAK

**Bilješka o fleksibilnim potencijalima BJH i MCYL: dobro slaganje s iskustvenim termodinamičkim podacima za  $(\text{H}_2\text{O})_2(\text{g})$  i  $(\text{D}_2\text{O})_2(\text{g})$**

Z. Slanina

Po prvi puta proveden je proračun standardnih termodinamičkih veličina ( $\Delta H^\circ$ ,  $\Delta S^\circ$ ) za nastajanje dimera vode drugih virijalnih koeficijenata za izotope vodika. Za račun su s podjednakim uspjehom upotrebljeni potencijali BJH i MCYL. Slaganje proračuna s eksperimentom određenim vrijednostima.