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On Theoretical Evaluation of Equilibrium Thermodynamics and Kinetics of the Water Dimer and of the Second Virial Coefficient of Steam*

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A quite recent new fitting of the MCY ab initio SCF CI potential energy hypersurface of $(H_2O)_2$ has been systematically investigated using an automatic geometry optimization procedure employing analytically constructed gradients. The vibration analysis has been carried out for stationary points of the hypersurface based on analytical second derivatives of the energy with proper treatment of the eight redundancy conditions involved. The gas-phase thermodynamics of formation of the water dimer is described within a broad temperature interval on the basis of the thus-generated theoretical structural, vibrational, and energy data. The role of the water dimer in the real gas phase of water is analyzed and the contribution of $(H_2O)_2$ to the second virial coefficient of steam evaluated. Of the stationary points found, three have been identified as transition states in water dimer interconversions (autoisomerizations). The partial and overall activation parameters are evaluated. Relationships between the original and new fit results are studied systematically. The applicability of both fits to various problems is briefly discussed. Throughout the whole study no empirical information was employed (with the exception of atomic masses, fundamental constants, and Coulomb's law).

INTRODUCTION

Since the first treatment by Sokolov[2] several theoretical (e. g., Refs[3–32]) and experimental (e. g., Refs[33–48]) studies have been carried out dealing with the water dimer. In fact, there are several hundreds of papers treating the water dimer. However, we shall refer here only to those related directly to its thermodynamics and/or kinetics. A comprehensive description of the water dimer represents the first necessary step in studies of the real gas[49–51] or liquid[52–54] phases of water within the cluster concept (see, e. g., Refs[55,56]). The description of the gas-phase water dimer itself should be satisfactory within the stationary point representation[57] of its potential hypersurface, while for a meaningful liquid-water description the whole hypersurface seems to be necessary[58–69].

* Part XXVI in the series Multi-Molecular Clusters and Their Isomerism; Part XXV, see Ref. 1.

Theoretical, particularly quantum-chemical calculations have considerably extended our knowledge of the water dimer, supplying information which is not yet accessible experimentally. So far, the most complete and sophisticated quantum-chemical description of $(H_2O)_2$ was given in the ab initio SCF CI study by Matsuoka, Clementi, and Yoshimine[14] (MCY). Their original analytical fit has recently been reanalyzed by Bounds and a new solution to the fitting problem is given in Ref.[68], leading to a considerable decrease in the mean standard deviation (here referred to as the MCY-B fit). In these terms the MCY-B fit represents, so far, the best analytical representation of the original grid of the ab initio SCF CI data, being in the closest contact with it. This communication deals with several problems concerning the treatment of the water dimer using the new MCY-B potential energy hypersurface, i. e. a detailed theoretical description of the structural and vibrational features, energetics, thermodynamics, and kinetics of the water dimer and of its role in the real gas phase of water.

HYPERSURFACE STATIONARY POINTS

The MCY and MCY-B approaches condense the numerical quantum-chemical outputs on the intermolecular potential in $(H_2O)_2$ into the analytical form of a 22-term expansion in terms of a total of 14 geometrical variables and 10 free adjustable parameters — see Ref.[70] for details. Such multi-dimensional hypersurfaces are frequently represented in terms of their stationary points[71], i. e. points fulfilling (in a redundancy-free coordinate set) the following condition on energy E:

$$\text{grad } E = \vec{\mathrm{O}}. \tag{1}$$

The search for stationary points was performed in 6-dimensional space, described in Ref.[23], correctly representing the original 14-dimensional MCY-B hypersurface. The version[23] of the variable metric method supplied by analytically constructed gradient (1) was used for optimizing. Starting points were partly chosen among all the structures considered in the previous studies and partly generated randomly. The force constant matrix was evaluated for each of the six stationary points found. From the second derivatives of the energy in terms of the original 14 variables we passed to the analytical formulae for the second derivatives in mass-weighted Cartesian coordinates, with due attention[72] paid to the eight redundancy conditions involved. Diagonalization of the force constant matrix yielded the number z of its negative eigenvalues, and permitted us to distinguish the minima, the transition states, and the higher types of stationary points having no, one, and two or more negative eigenvalues, respectively. The results for stationary points with $z = 0$ or 1 are surveyed in Table I together with a comparison with the MCY data[23].

In order to carry out vibrational analysis at the stationary points found, the experimental harmonic force field of the free water molecule according to Ref.[74] was used for simulation of intramolecular force constants and added to the MCY-B harmonic intermolecular potential field accordingly. The symmetry of the $(H_2O)_2$ minimum energy structure (C_s — see Table I) enables

TABLE I

A Survey of the Structure and Energy Characteristics of Four Stationary Points[a] Found on MCY and MCY-B Potential Energy Hypersurfaces[b]

Term	Linear	Planar	Closed	Bifurcated
Symmetry	C_s	C_s	S_2	C_{2v}
R_{O-O} (10^{-10} m)[c]	2.87[d]	2.88	2.79	2.96
	2.98[d]	2.98	2.85	3.01
ΔE or $\Delta E^{\neq}$ (kJ/mol)[e]	—24.55	1.13	4.50	9.95
	—23.59	0.95	3.09	7.47
ΔH_0° or $\Delta H_0^{\neq}$ (kJ/mol)[e]	—14.97	—0.03	4.42	6.94
	—14.90	0.04	3.40	5.34
z[f]	0	1	1	1

[a] For schemes of the stationary points — see Ref.[25]
[b] The MCY data are taken from Ref.[23] and presented in the upper line; the MCY-B data are given in the lower.
[c] Oxygen-oxygen interatomic distance.
[d] Observed value according to Refs[42,73] is equal to 2.98×10^{-10} m.
[e] See text.
[f] Number of imaginary normal vibrational frequencies.

symmetry classification of its vibrational motion. The symmetry structure of 12 normal vibrational modes is within the point group of symmetry given by (cf., however, Ref.[75] for a nonrigid approach):

$$\Gamma_{(H_2O)_2,\ C_s} = 8A' + 4A''. \tag{2}$$

Moreover, the vibrational modes can be split into inter- and intramolecular terms. The MCY-B harmonic vibrational frequencies of the $(H_2O)_2$ minimum energy structure are given in Table II. The MCY-B intermolecular frequencies are considerably lower than the MCY values.

THERMODYNAMICS OF WATER-DIMER FORMATION

Knowledge of the structural, vibrational, and energy parameters of $(H_2O)_2$ (see Tables I, II) enables us to construct its partition function within the usual rigid-rotor and harmonic-oscillator approximations (Refs[76–78]) and to describe its thermodynamics, namely the standard thermodynamic terms accompanying the equilibrium process:

$$2\,H_2O\,(g) \rightleftharpoons (H_2O)_2\,(g). \tag{3}$$

The RRHO partition function of a free water molecule was based on the same experimental structural and vibrational data as in Ref.[23] The RRHO approximation is usual in studies of the thermodynamics of $(H_2O)_2$ (as well as other molecular complexes) because at present it is very difficult to obtain information permitting replacement of the RRHO approximation by the approach of a vibrating rotor. It is, of course, true that $(H_2O)_2$ represents a relatively rigid structure compared with the typical van der Waals molecules. This

TABLE II

Harmonic Vibrational Normal Mode Frequencies of the Linear Water Dimer (in cm^{-1})

Symmetry[a]	Intermolecular potential MCY[b]	MCY-B
	Intermolecular frequencies	
A″	114	107
A′	131	117
A″	148	130
A′	183	171
A′	345	311
A″	614	559
	Intramolecular frequencies[c]	
A′	1663	1662
A′	1685	1679
A′	3827	3829
A′	3841	3840
A′	3940	3942
A″	3956	3953

[a] Point group of symmetry — C_s, see Table I.
[b] Taken from Ref.[23]
[c] Corresponding frequencies of the free water molecule are equal to 1649, 3832, and 3942 cm^{-1}.

fact makes the reliability of the RRHO approximation for the MCY evaluation of the $(H_2O)_2$ thermodynamics promising. Table III presents the MCY-B standard enthalpy ΔH_T^o and entropy ΔS_T^o terms for reaction (3) within a broad temperature interval, and their comparison with the original MCY data. Both enthalpy and entropy terms in the MCY-B approach are systematically higher than the MCY values. This difference increases with increasing temperature.

TABLE III

Theoretical Standard Enthalpy ΔH_T^o and Entropy ΔS_T^o Terms for Water-Dimer Formation[a]

T (K)	ΔH_T^o (kJ/mol)		ΔS_T^o (J/K/mol)	
	MCY[b]	MCY-B	MCY[b]	MCY-B
100	—17.25	—16.95	—84.03	—81.01
200	—17.35	—16.89	—85.21	—81.02
298.15	—16.65	—16.07	—82.43	—77.75
300	—16.63	—16.05	—82.37	—77.68
400	—15.54	—14.87	—79.23	—74.31
500	—14.25	—13.53	—76.37	—71.31
600	—12.86	—12.09	—73.83	—68.70
700	—11.40	—10.60	—71.58	—66.40
800	— 9.89	— 9.07	—69.57	—64.35
900	— 8.36	— 7.51	—67.77	—62.52
1000	— 6.80	— 5.94	—66.13	—60.86

[a] The terms presented refer to the equilibrium process $2H_2O\,(g) \leftrightharpoons (H_2O)_2\,(g)$; the standard state is an ideal gas phase at 101325 Pa pressure.
[b] According to Ref.[23]

TABLE IV

Comparison of Theoretical Terms with the Key Experimental Values of the Standard Enthalpy $\Delta H_T{}^o$ and Entropy $\Delta S_T{}^o$ Terms of Water-Dimer Formation[a]

T (K)	$\Delta H_T{}^o$ (kJ/mol)		$\Delta S_T{}^o$ (J/K/mol)	
	theoretical[b]	experimental	theoretical[b]	experimental
373	—15.86	—15.0[c]	—80.06	—77.8[c]
	—15.21		—75.19	
573.15	—13.24	—15.7[d]	—74.48	—74.9[d]
	—12.48		—69.36	

[a] See footnote a of Table III.

[b] The MCY data are taken from Ref.[23] and presented in the upper line; the MCY-B data in the lower.

[c] According to Ref.[41]

[d] According to Refs[79,80].

In connection with the mentioned approximative character of the theoretical results, a careful comparison with existing experimental information on the water-dimer thermodynamics is essential. There are two sufficiently complete sets of observed thermodynamic terms for process (3) in the literature (Refs[41,79,80]). In Ref.[80] the temperature dependence[79] of the observed second virial coefficient B_2 was analyzed using the evaluation of contribution B_f of the free molecules to B_2. However, the evaluation of the B_f term is to be considered as rather arbitrary[41]. Consequently, the $\Delta H_T{}^o$ and $\Delta S_T{}^o$ terms in Ref.[80] cannot be considered as primary observed data. Curtiss *et al.*[41] obtained the enthalpy and entropy of water-dimer formation from measurements of the thermal conductivity of steam. Table IV compares the theoretical and observed enthalpy and entropy terms. While in Refs[79,80] the agreement with the MCY values is better, the other observation[41] favours the new MCY-B results. Moreover, the latter approach also leads to a better agreement with the observed oxygen-oxygen distance (see Table I). Summarizing, the new MCY-B thermodynamic terms for the water-dimer formation should be preferred in further gas-phase applications. This conclusion, however, does not imply that the MCY-B potential should also be better for much more complicated studies of liquid water. In fact, the MCY-B potential was found to give poorer results than the MCY function in the recent liquid-phase test studies[67,68]. Quite recently, Clementi and coworkers[63,69] reevaluated the water-water interaction potential within ab initio SCF calculations with inclusion of correlation energy. Information on the application of the new potential within the presented treatment will be published elsewhere.

For a description of the thermodynamics of the water-dimer the (hypothetical) enthalpy (or internal energy) $\Delta H_0{}^o$ accompanying equilibrium process (3) at absolute zero is of primary interest. The latter term is connected with the corresponding change in the potential energy, ΔE, through the quatum correction to the vibrational zero-point motion, Δ_q:

$$\Delta H_0^{\circ} = \Delta E + \Delta_q . \qquad (4)$$

Remarkably enough, while the MCY and MCY-B ΔE terms differ considerably, the corresponding ΔH_0° terms are quite similar (see Table I).

THE SECOND VIRIAL COEFFICIENT OF STEAM

For practical purposes, the non-ideality of steam is frequently expressed in terms of the virial coefficients, particularly the second virial coefficient, B_2. Therefore, interpretation of the observed values of B_2 represents an important task for theoretical studies. It is useful to decompose the second virial coefficient into a sum of three terms of different natures[81,82]:

$$B_2 = B_f + B_b + B_m \qquad (5)$$

where B_f represents the already mentioned term conditioned by collisions between free molecules, B_b is related to the equilibrium constant for the formation of dimers, and B_m is related to the formation of metastable double molecules. Component B_b can easily be determined on the basis of water-dimer thermodynamics — see, e. g., Ref.[83] Comparison of the MCY-B results with the MCY B_b contributions and with the observed values of B_2 is given in Table V for several selected temperatures. Both the MCY-B and MCY B_b terms are in close agreement with the observed B_2 values; however, while the MCY-B B_b term is systematically lower than the B_2 term, the MCY term is higher. It should also be mentioned that at still higher temperatures than those given in Table V, the agreement becomes progressively poorer. As evaluations of B_f with various potential functions are available[85–87] (cf. also Ref.[68]), the key indefinite term in Eq. (5) is the B_m term. For example, the B_f term for the MCY potential reads[87] —827 and —289 $cm^3\,mol^{-1}$ at 373.15 and 473.15 K, respectively. Thus, for a full understanding of the problem the evaluation of the B_m term seems to be very desirable.

TABLE V

Contribution of Water-Dimer Formation to the Second Virial Coefficient B_2 *of Steam*

T (K)	B_2 (cm^3/mol)					
	MCY[a,b]	MCY-B[a]	Experimental[c]			
298.15	—1000	—1388	—1162;	—1165;	—1256	
323.16	— 647	— 915	— 838			
373.16	— 334	— 487	— 451;	— 454		
473.16	— 149	— 228	— 196;	— 197;	— 209;	—215

[a] The contribution B_b — see Eq. (5).

[b] According to Ref.[23]

[c] For references to the original observations, see Refs[23,84].

WATER-DIMER INTERCONVERSIONS

As follows from the above representation of the MCY-B hypersurface by its stationary points, there are three activated complexes involved (Table I). Moreover, all of them can be proved to act as activated complexes (or transition states) in the rate process:

$$(H_2O)_2\,(g) \rightarrow (H_2O)_2\,(g)\,. \tag{6}$$

Thus, the three-fold parallel isomerism of the activated complexes is connected with reaction (6). Using the MCY-B structural, vibrational, and energy (i. e., activation energy $\Delta E^{\neq}$ or activation enthalpy $\Delta H_0^{\neq}$ at absolute zero -- see Table I) data, the partial activation enthalpy and entropy can be evaluated for each of the individual activated complexes. Moreover, their weight factors can be generated[25] and thus also the overall activation terms, to which each activated complex contributes through its weight, can be found. Generally, the overall activation terms should be primarily observed in an experimental

TABLE VI

Temperature Dependence[a] of the Isomerism Corrections $\delta X_{iso}^{\neq}$ and Overall Activation Parameters $\Delta X^{\neq}$ for the Water-Dimer Interconversions[b] ($X = H$ or S)

T (K)	$\delta H_{iso}^{\neq}$ [c] ((kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\delta S_{iso}^{\neq}$ [c] (J/K/mol)	$\Delta S^{\neq}$ (J/K/mol)
100	0.058	—0.201	0.724	—3.974
	0.021	—0.232	0.247	—3.157
200	0.470	—0.535	3.482	—6.360
	0.353	—0.601	2.386	—5.828
298.15	0.905	—0.854	5.261	—7.642
	0.916	—0.767	4.666	—6.511
300	0.912	—0.861	5.286	—7.666
	0.927	—0.770	4.703	—6.521
400	1.251	—1.304	6.268	—8.933
	1.486	—0.975	6.317	—7.104
500	1.505	—1.847	6.838	—10.142
	1.955	—1.289	7.367	—7.801

[a] The MCY-B data are presented in the upper line, the MBY data[25] in the lower.
[b] The terms presented concern the rate process $(H_2O)_2\,(g) \rightarrow (H_2O)_2\,(g)$.
[c] The $\Delta X^{\neq}$ and $\delta X_{iso}^{\neq}$ terms are related through Eq. (7).

study of reaction (6). For a deeper understanding of the relationships between partial $\Delta X_i^{\neq}$ and overall $\Delta X^{\neq}$ activation terms ($X = H$ or S), isomerism corrections $\delta X_{iso}^{\neq}$ can be introduced:

$$\Delta X^{\neq} = \Delta X_{C_s}^{\neq} + \delta X_{iso}^{\neq} \tag{7}$$

where $\Delta X_{C_s}^{\neq}$ denotes the corresponding partial activation term connected with the reaction path through the C_s activated complex. The MCY-B overall activation enthalpy and entropy, as well as the isomerism corrections, are presented in Table VI. Clearly, the isomerism contribution to the overall activation terms of reaction (6) is by no means negligible and may play an important role in understanding the kinetics of this process.

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SAŽETAK

Teorijski proračun termodinamičkih parametara i kinetike dimera molekule vode kao i njegova doprinosa drugomu virijalnom koeficijentu vodene pare

Zdeněk Slanina

Hiperploha potencijalne energije dimera molekula vode konstruirana je s pomoću SCF-CI pristupa, uporabom parametrizacije koju su predložili Matsuoka-Clementi-Yoshimine i Bounds. Analiza hiperplohe omogućuje detaljan opis strukturnih i vibracijskih značajki dimera u plinovitoj fazi. Određeni su termodinamički parametri i kinetika interkonverzije. Procijenjen je doprinos $(H_2O)_2$ drugomu virijalnom koeficijentu vodene pare.