

ISOMERISM, ENERGETICS, AND THERMODYNAMICS OF (H₂O)₂ AND ITS ROLE IN REAL GAS PHASE OF WATER*

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Recent *ab initio* SCF CI potential energy hypersurfaces of (H₂O)₂ have been systematically investigated with the use of an automatic optimization procedure working with analytically constructed energy gradient with the aim to localize all their stationary points lying in the relevant region. For these stationary points the vibrational analysis has been carried out based on analytically constructed second derivatives of energy with correct respecting of the eight redundancy conditions introduced into the problem by the original choice of the coordinates. Out of the six localized stationary points only one has been found to be a minimum, three of them represent transition states, and the remaining two are higher types of stationary points. Relation of the analytically and the numerically constructed force constant matrices and possibility of the occurrence of extraneous stationary points have been studied. The calculated harmonic vibrational frequencies corresponding to the energy minimum show reasonable agreement with available experimental data. On the basis of the generated molecular parameters of the minimum the thermodynamics of formation of the water dimer has been described within a broad temperature interval, and a good agreement with experimental findings has been obtained. Role of the water dimer in real gas phase of water has been analyzed, and contribution of (H₂O)₂ to value of the second virial coefficient of water vapour has been evaluated. Within the framework of the given quantum-chemical methodological level, this study has led to negation of possibility of isomerism of (H₂O)₂ with respect to equilibrium problems, it has, however, shown the isomerism in the case of kinetics of interconversion of (H₂O)₂.

The story of anomalous water¹ drew the attention² of theoretical chemists to study of stability of the individual water oligomers especially dimers (for reviews see refs^{3,4}). However, essential reason for (H₂O)₂ to become perhaps the most theoretically studied molecular complex (refs³⁻¹⁵) rather consists in an abundance of relevant experimental information (refs¹⁶⁻²⁹) about its properties, which is otherwise a rare situation in the field of weak intermolecular interactions (for a review see ref.³⁰). Semiempirical and non-empirical quantum-chemical calculations⁵⁻¹⁵ enriched that part of our knowledge of water dimers which is not yet accessible experimentally. Thus the former way of filling the gaps in experimental information by assessment and analogy³¹⁻³³ could be abandoned. So far the most complete and precise quantum-chemical description of (H₂O)₂ has been given in the *ab initio* SCF CI results by Matsuoka, Clementi, and Yoshimine⁶ (MCY). The MCY hypersurfaces of potential energy represent a starting point

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of solution of quite a number of problems connected with properties and behaviour of $(\text{H}_2\text{O})_2$. One of such fundamental questions is the problem of isomerism of water dimers. Our former results³⁴⁻³⁸ showed that isomerism must be considered general and regularly encountered feature of multi-molecular clusters, its absence in a particular case being merely an exception. In the case of $(\text{H}_2\text{O})_2$ the problem of isomerism is not clear yet; some results of theoretical studies at various levels indicated its possibility⁴⁻¹⁰, whereas other ones denied it or, at least, did not find it^{4,11-14}. Whereas determination of so called linear structure as a stable formation (*i.e.* its determination as a minimum on the potential energy hypersurface) was repeatedly confirmed⁴⁻¹⁴, literature also treats such structures⁴⁻¹⁰ (*e.g.* bifurcated, cyclic, and closed) the type correspondence of which has not yet been decided within the given hypersurface. Moreover, existence of a single structure representing $(\text{H}_2\text{O})_2$ has also been questioned in experimental study^{25,29}.

This paper aims at contributing to several problems concerning the water dimer using the powerful MCY potential energy hypersurfaces⁶. Following our note¹⁵ three important steps in correct solution of the isomerism problem will be comprehensively analyzed: (i) Location of (all) stationary points on the given energy hypersurfaces, (ii) Their identification using eigenvalues of the force constant matrix, and finally (iii) Test of results by total entropy calculation. At the same time, realization of the steps (i)-(iii) will enable to present, at the MCY methodological level⁶ (which represents the present upper limit of quantum-chemical treatment of the problem), a detailed theoretical description of energetics and thermodynamics of formation of the water dimer and of its role in real gas phase of water.

METHODOLOGY AND RESULTS

I) *MCY Potential energy hypersurfaces.* This work is broadly based on the MCY *ab initio* SCF CI results⁶ obtained by two approaches – besides the configuration-interaction method involving the both inter- and intramolecular correlation contributions (MCY I), the energy surface was also generated by involving only intermolecular correlation corrections (MCY II). The results of detailed mapping of the potential energy hypersurface of the water dimer in any conformation obtained in the both MCY I and MCY II approaches were condensed into an analytic fit. The fitted 22-term expansion was chosen as a function with 10 free parameters and represented a function of total 14 variables. According to the choice⁶, these variables:

$$\mathbf{R}^{(14)} = \{R_i^{(14)}\}, \quad i = 1, \dots, 14 \quad (I)$$

involved nine intermolecular distances between the atoms of the partner monomer units, four intermolecular distances between a H atom of one monomer unit and a certain point at the C_2 axis of the other, and the last, fourteenth variable was the distance between both these points at the C_2 axes. During the whole fitting procedure, rigidity of the monomer units was presumed which was maintained within the experimental

structural parameters of free water molecule. The choice of the coordinate system (1) involving total 8 binding (redundancy) conditions was obviously due to the effort to maintain physical interpretability of the members of the interaction potential. On the contrary, however, this original choice⁶ of the variables (1) represents a severe complication with respect to the below-described procedures II and (especially) III.

II) *Location of stationary points.* The technique of automatic optimizations of molecular structures was introduced into the theoretical chemistry in the field of the Consistent Force Field Method (for a review see ref.³⁹) and was modified for purposes of quantum chemistry by Pulay⁴⁰ and by McIver and Komornicki⁴¹. Starting from methodology of these basic works a computer program was developed for location of stationary points at the MCY hypersurfaces. With the aim to remove the above-mentioned 8 binding conditions (and thereby to avoid the necessity of application of the Lagrangian multipliers technique) and to guarantee a reasonably convergent behaviour of the procedure a set of six independent coordinates (2) was chosen for characterization of mutual positions of the both rigid monomer units in $(\text{H}_2\text{O})_2$ according to ref.⁴²:

$$\mathbf{R}^{(6)} = \{R_i^{(6)}\}, \quad i = 1, \dots, 6. \quad (2)$$

This smallest possible coordinate set is formed⁴² by a triad of certain Cartesian coordinates and a triad of the Euler angles introduced in a certain way. The first derivatives of the interaction potential ΔE with respect to the coordinates (2) are given by the expressions:

$$\frac{\partial \Delta E(\mathbf{R}^{(6)})}{\partial R_i^{(6)}} = \sum_{j=1}^{14} \frac{\partial \Delta E(\mathbf{R}^{(14)})}{\partial R_j^{(14)}} \frac{\partial R_j^{(14)}}{\partial R_i^{(6)}}, \quad i = 1, \dots, 6. \quad (3)$$

With respect to the independence of the coordinates (2), location of stationary points at the hypersurface ΔE can be carried out by mere solution of the set of equations:

$$\left(\frac{\partial \Delta E(\mathbf{R}^{(6)})}{\partial R_i^{(6)}} \right)_0 = 0, \quad i = 1, \dots, 6, \quad (4)$$

which was carried out with the use of the variable metric iterative technique⁴³ in the version of ref.⁴¹.

In the computer program used by us the first derivatives of energy (3) were constructed from analytical formulas, which ensured efficiency and precision of location of the stationary points at the MCY hypersurfaces. So far, however, there is no rigorous criterion available for ensuring the completeness of the search for the stationary points. To overcome this drawback we used (besides the all $(\text{H}_2\text{O})_2$

structures considered so far⁴⁻¹⁴) random generating of the starting vectors (2) for the variable metric iterative technique. Overall six stationary points were located on each of the MCY I and MCY II hypersurfaces, their survey is given in Table I and in Fig. 1.

III) *Identification of stationary points and vibrational analysis.* The key part of the problems consists in construction of the matrix of the second derivatives of energy and (in case of the vibrational analysis) construction of the inverse kinetic energy matrix⁴⁴. In the case of redundant coordinates, however, the conventional approach is not immediately applicable⁴⁵, and the problem needs special treatment. Especially essential is proper balancing of the linear force constants. This requirement is dictated by the fact that, generally, the first derivatives of potential energy with respect to members of a coordinate set with redundancy are not equal to zero even in a stationary point. In our case it would be, in principle, possible to take off the redundancy by transition from the coordinates (1) to the system (2). After considering

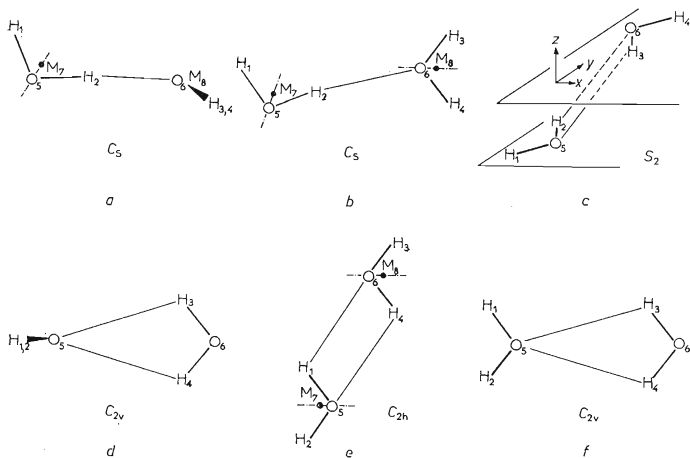


FIG. 1

Schemes of the Stationary Points Found on MCY Hypersurfaces of Potential Energy⁶ of $(\text{H}_2\text{O})_2$ with Given Point Group of Symmetry

(a) Linear, (b) planar linear, (c) closed, (d) bifurcated, (e) cyclic, (f) planar bifurcated; M_7 and M_8 are the points⁶ lying at the C_2 axis of the respective H_2O molecule.

TABLE I
Structural and Energy Characteristics of the Stationary Points Found on MCY Hypersurfaces⁶ of Potential Energy of Water Dimer^a

Structure ^b	Point group of symmetry	Type of stationary point ^c	ΔE^d kJ mol ⁻¹	Geometrical parameters ^b 10 ⁻¹⁰ m or °
Linear	C _s	M	-23.92 (-24.55)	$r(\text{O}_5\text{---O}_6) = 2.987$ (2.872); $\angle \text{H}_2\text{O}_5\text{O}_6 = 2.9$ (4.2); $\angle \text{O}_5\text{O}_6\text{M}_8 = 147.6$ (142.4); $r(\text{H}_2\text{---O}_6) = 2.031$ (1.919)
Planar linear	C _s	T	-22.91 (-23.42)	$r(\text{O}_5\text{---O}_6) = 2.993$ (2.881); $\angle \text{H}_2\text{O}_5\text{O}_6 = 6.9$ (6.8); $\angle \text{O}_5\text{O}_6\text{M}_8 = 165.2$ (166.0); $r(\text{H}_2\text{---O}_6) = 2.046$ (1.934)
Closed	S ₂	T	-20.42 (-20.05)	$x_{\text{O}_5} = y_{\text{O}_5} = z_{\text{O}_5} = 0^\circ$; $x_{\text{O}_6} = 0.181$ (0.047) ^e ; $y_{\text{O}_6} = 2.370$ (2.261) ^e ; $z_{\text{O}_6} = 1.564$ (1.629) ^e ; $r(\text{H}_2\text{---O}_6) = r(\text{H}_3\text{---O}_5) = 2.374$ (2.305)
Bifurcated	C _{2v}	T	-15.96 (-14.60)	$r(\text{O}_5\text{---O}_6) = 3.036$ (2.962); $r(\text{H}_3\text{---O}_5) = r(\text{H}_4\text{---O}_5) = 2.565$ (2.494)
Cyclic	C _{2h}	H	-19.93 (-19.35)	$r(\text{O}_5\text{---O}_6) = 2.842$ (2.786); $\angle \text{O}_5\text{O}_6\text{M}_8 = 105.1$ (104.5); $r(\text{H}_1\text{---O}_6) = r(\text{H}_4\text{---O}_5) = 2.388$ (2.327)
Planar bifurcated	C _{2v}	H	-11.73 (-10.33)	$r(\text{O}_5\text{---O}_6) = 3.207$ (3.137); $r(\text{H}_3\text{---O}_5) = r(\text{H}_4\text{---O}_5) = 2.728$ (2.661)

^a Characteristics of the stationary points on the MCY I hypersurface; those on the MCY II hypersurface are given in brackets, if different; ^b For scheme see Fig. 1, for structure parameters of monomeric units see ref.⁶; ^c M means a minimum on the hypersurface, T is the transition state, and H is a higher type of its stationary point; ^d ΔE means potential energy change along the process 2 H₂O = (H₂O)₂; ^e The Cartesian coordinates of the atoms O₅ and O₆ according to orientation of the axes as in Fig. 1c.

the extent of algebraic manipulations necessary for transformation of the force constant matrix and for construction of the inverse kinetic energy matrix in the (unusual in the vibrational analysis) coordinate system (2) it appeared more advantageous to apply the transition to the Cartesian or the mass-weighted Cartesian coordinates⁴⁶⁻⁴⁸.

First of all it was necessary to exclude from the original set (1) those five coordinates which were connected with change of position of the reference point (s) at the C_2 axis of the monomer unit. These reference points have zero mass, which could lead to infinite terms by the transition to the mass-weighted Cartesian coordinates. A system of nine coordinates was chosen for this intermediate step:

$$\mathbf{R}^{(9)} = \{R_i^{(9)}\}, \quad i = 1, \dots, 9, \quad (5)$$

which results from the set (1) after exclusion of the five coordinates in question. For the first derivatives of energy with respect to the coordinates (5) the relation (3) is adequately valid; the second derivatives are given by Eq. (6):

$$\begin{aligned} \left(\frac{\partial^2 \Delta E(\mathbf{R}^{(9)})}{\partial R_i^{(9)} \partial R_j^{(9)}} \right)_0 &= \sum_{k=1}^{14} \left(\frac{\partial \Delta E(\mathbf{R}^{(14)})}{\partial R_k^{(14)}} \right)_0 \left(\frac{\partial^2 R_k^{(14)}}{\partial R_i^{(9)} \partial R_j^{(9)}} \right)_0 + \\ &+ \sum_{k=1}^{14} \sum_{l=1}^{14} \left(\frac{\partial^2 \Delta E(\mathbf{R}^{(14)})}{\partial R_k^{(14)} \partial R_l^{(14)}} \right)_0 \left(\frac{\partial R_k^{(14)}}{\partial R_i^{(9)}} \right)_0 \left(\frac{\partial R_l^{(14)}}{\partial R_j^{(9)}} \right)_0. \end{aligned} \quad (6)$$

The first term in Eq. (6) would disappear in the case of independent coordinates; in the case of redundant coordinates, however, its presence is necessary.

If the problem of $(H_2O)_2$ is to be solved in the Cartesian coordinates, then it is necessary to involve, in proper way, the force relations within each monomeric unit. With the respect to the present state of quantum-chemical information about this problem it is inevitable to use the experimental harmonic force field of free water molecule⁴⁹. For structure unification of variables in the computer program the intramolecular motions in each monomer unit were described by three internal coordinates of the bond stretching type (changes of the O—H bond lengths and of H—H distance in H_2O molecule). Relation between the force constants in this system of internal coordinates and the conventional choice⁴⁹ of the force field of H_2O is given in Appendix. Introduction of the coordinates describing intramolecular motions within each monomer unit extends the coordinate system (5) to:

$$\mathbf{R}^{(15)} = \{R_i^{(15)}\}, \quad i = 1, \dots, 15. \quad (7)$$

Of course the coordinate system (7) still shows three binding conditions, which is

manifested, *inter alia*, in the inequality (8)

$$\left(\frac{\partial \Delta E(\mathbf{R}^{(15)})}{\partial R_i^{(15)}} \right)_0 \neq 0, \quad i = 10, \dots, 15, \quad (8)$$

where the index $i = 10, \dots, 15$ denotes the intramolecular internal coordinates in question. For completeness it must be added that, due to the absence of the respective information, all values of the interaction force constants between the intra- and intermolecular ($i = 1, \dots, 9$) coordinates as well as between the intramolecular coordinates belonging to different monomer units had to be put equal to zero.

The coordinate set (7) already enables immediate transition to the Cartesian coordinates; for transformations of the first and the second derivatives the relations analogous to (3) and (6) are applied. So far, however, we have not determined the six values of the first derivatives from Eq. (8). The following procedure was used for their determination. The Cartesian coordinates do not show redundancy – they are independent, which implies that transformation of the first derivatives of ΔE from the system (7) to the Cartesian coordinates must result in overall zero values of the first derivatives of ΔE with respect to the latter coordinates. This fact presents an instruction for the choice of the values (8): the six values of the derivatives (8) must be chosen in such way that all derivatives of ΔE with respect to the Cartesian coordinates disappear after the transformation is carried out. This consideration provides a system of linear equations for determination of the six unknown values. In this way we have, in principle, described the algorithm for correct construction of the matrix of the force constants with proper respecting all peculiarities of the original choice⁶ of the coordinate system (I).

This algorithm was used for construction of the matrix of force constants and for analysis of its eigenvalues in all stationary points located on the MCY hypersurfaces. Thereby the stationary points could be divided (Table I) into the minima (no negative eigenvalue), the transition states (just one negative eigenvalue), and higher types of the stationary points (at least two negative eigenvalues).

Having obtained the force constant matrix in Cartesian coordinates, it is easy⁴⁴ to carry out the vibrational analysis with the use of experimental atomic masses⁵⁰. With respect to the equilibrium character of this study we shall restrict ourselves to mere presentation of harmonic vibrational normal mode frequencies of the stationary points of the minimum type (Tables II and III).

IV. Statistical-thermodynamic treatment. It has already been mentioned that the correct solution of the isomerism problem needs an extension of the foregoing two steps by a calculation of thermodynamic quantities (especially the entropy term) and a careful confrontation with available experimental data. Knowledge of the structural parameters and harmonic frequencies of $(\text{H}_2\text{O})_2$ makes it possible

TABLE II
 Harmonic Vibrational Normal Mode Frequencies of Linear Water Dimer^a (cm⁻¹)

Symmetry ^b	Approximate description ^c	Intramolecular potential			
		experimental ^{d,9}	artificially stiff	experimental ^{d,9}	artificially stiff
		intermolecular frequencies		intermolecular frequencies	
		MCY I		MCY II	
A''	H-bond torsion	111.0	111.2	114.4	114.5
A'	in plane H-bond bend	124.8	125.5	131.0	131.8
A''	out of plane H-bond bend	137.9	138.2	148.4	148.9
A'	H-bond stretch	166.9	167.1	182.7	182.9
A'	in plane H-bonds bear	323.2	334.5	345.0	357.4
A''	out of plane H-bonds bear	582.6	583.0	614.5	615.1
		intramolecular frequencies ^d			
A'	acceptor bend	1 663.9	artificially infinite	1 662.8	artificially infinite
A'	donor bend	1 682.1		1 685.0	
A'	donor symmetric stretch	3 828.0		3 826.7	
A'	acceptor symmetric stretch	3 840.5		3 840.9	
A'	donor antisymmetric stretch	3 941.0		3 940.1	
A''	acceptor antisymmetric stretch	3 953.9		3 955.8	

^a Atomic masses of natural isotopic mixtures⁵⁰ were used; ^b Point group of symmetry C_s — see Fig. 1a; ^c For a rough scheme in the case of intermolecular normal mode vibrations — see Fig. 3 of ref. 13; ^d Corresponding frequencies of free water molecule are equal to 1 648.7 (bend), 3 831.6 (symmetric stretch), and 3 942.2 cm⁻¹ (antisymmetric stretch).

to construct its partition function within the rigid rotor and harmonic oscillator approximation (RRHO) (ref.⁵¹). This function along with the RRHO partition function of free water molecule based on experimental structural⁶ and vibrational⁴⁹ parameters and knowledge of energetics of the equilibrium process (A) (Table I) make it possible to describe its thermodynamics:

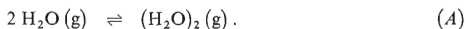


TABLE III
Harmonic Vibrational Normal Mode Frequencies of $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$ (cm^{-1})^a

$(\text{H}_2\text{O})_2$			$(\text{D}_2\text{O})_2$		
MCY I	MCY II	experimental	MCY I	MCY II	experimental
Intermolecular frequencies ^b					
111.0	114.4		80.7	82.9	
124.8	131.0		93.5	97.9	
137.9	148.4		99.4	107.3	
166.9	182.7		155.8	171.3	
323.3	345.0		239.3	255.2	
582.6	614.5		420.8	443.4	
Intramolecular frequencies ^b					
MCY I ^c	MCY II ^c	experimental ^{d,28}	MCY I ^e	MCY II ^e	experimental ^{f,28}
1 664.0	1 663.0	1 653.0	1 216.9	1 216.2	1 208.5
1 682.3	1 685.2	1 671.3	1 229.5	1 231.4	1 220.3
3 828.3	3 827.1	3 717.4	2 761.4	2 760.6	2 687.2
3 840.8	3 841.2	3 800.3	2 770.7	2 771.1	2 740.5
3 941.3	3 940.4	3 880.5	2 887.7	2 887.2	2 836.1
3 954.2	3 956.1	3 899.5	2 896.3	2 897.5	2 856.5

^a Atomic masses⁵⁰ of pure hydrogen and deuterium isotopes were used in the case of MCY I and MCY II potentials; ^b The sequence of symmetries and approximate descriptions is the same as in Table II; ^c Corresponding frequencies of free H_2O molecule are equal to 1 648.9, 3 831.9, and 3 942.5 cm^{-1} ; ^d Corresponding frequencies of monomeric H_2O molecule are equal²⁸ to 1 649.4, 3 808.3, and 3 912.5 cm^{-1} ; ^e Corresponding frequencies of free D_2O molecule are equal to 1 206.1, 2 763.8, and 2 888.7 cm^{-1} ; ^f Corresponding frequencies of monomeric D_2O molecule are equal²⁸ to 1 206.2, 2 746.4, and 2 865.5 cm^{-1} .

The numerical values presented in Tables IV and V are based on the vibrational characteristics of $(\text{H}_2\text{O})_2$ given in Table II in the columns corresponding to the experimental intramolecular potential.

TABLE IV

Comparison of Theoretical and Experimental Values of Standard Thermodynamic Characteristics of Formation of Water Dimer^a

T, K^b	$\Delta H_T^0, \text{kJ mol}^{-1}$			$\Delta S_T^0, \text{J mol}^{-1} \text{K}^{-1}$		
	MCY I	MCY II	experimental ^{18,19}	MCY I	MCY II	experimental ^{18,19}
423.15	-14.83	-15.25	-15.7	-75.26	-78.54	-74.9
573.15	-12.77	-13.24	-15.7	-71.11	-74.48	-74.9
723.15	-10.56	-11.05	-15.7	-67.68	-71.10	-74.9

^a The changes accompanying the process $2 \text{H}_2\text{O}(\text{g}) \rightleftharpoons (\text{H}_2\text{O})_2(\text{g})$, the standard state is ideal gas phase at 101 325 Pa; ^b Limits of experimental temperature interval¹⁸ and its middle.

TABLE V

Theoretical Standard Thermodynamic Characteristics of Water Dimer Formation^a

T, K	$\Delta H_T^0, \text{kJ mol}^{-1}$		$\Delta S_T^0, \text{J mol}^{-1} \text{K}^{-1}$		$\log K_p^b$	
	MCY I ^c	MCY II ^d	MCY I	MCY II	MCY I	MCY II
100	-17.08	-17.25	-82.00	-84.03	4.64	4.62
200	-17.07	-17.35	-82.42	-85.21	0.15	0.08
298.15	-16.29	-16.65	-79.32	-82.43	-1.29	-1.39
300	-16.27	-16.63	-79.26	-82.37	-1.31	-1.41
400	-15.13	-15.54	-75.98	-79.23	-1.99	-2.11
500	-13.80	-14.25	-73.03	-76.37	-2.37	-2.50
600	-12.38	-12.86	-70.44	-73.83	-2.60	-2.74
700	-10.91	-11.40	-68.17	-71.58	-2.75	-2.89
800	-9.39	-9.89	-66.14	-69.57	-2.84	-2.99
900	-7.84	-8.36	-64.32	-67.77	-2.90	-3.05
1 000	-6.27	-6.80	-62.66	-66.13	-2.95	-3.10

^a Quantities concern the process $2 \text{H}_2\text{O}(\text{g}) \rightleftharpoons (\text{H}_2\text{O})_2(\text{g})$, standard state is ideal gas phase at 101 325 Pa; ^b K_p in (atm^{-1}) , 1 atm = 101 325 Pa; ^c $\Delta H_0^0 = -14.89 \text{ kJ mol}^{-1}$; ^d $\Delta H_0^0 = -14.97 \text{ kJ mol}^{-1}$.

DISCUSSION AND CONCLUSIONS

In our note¹⁵ we have already announced that comprehensive treatment of the MCY *ab initio* SCF CI hypersurfaces of potential energy⁶ leads to negation of possibility of $(\text{H}_2\text{O})_2$ isomerism in relation to equilibrium problems. The primary argument in favour of this statement is the presence of only one minimum among the six stationary points located on each of the MCY I and MCY II hypersurfaces. It has already been mentioned that, so far, no rigorous mathematical method is available enabling an *a priori* determination of number of the stationary points on a given hypersurface. This fact, of course, evokes a question whether some of the stationary points was not omitted by the optimization algorithm used. However, systematic approach of our strategy to the choice of the starting structures for the optimization procedure makes it little likely to omit some of the stationary points in the coordinate area relevant for the weak molecular complex $(\text{H}_2\text{O})_2$. This is particularly true of the stationary points of minimum type; with other types of the stationary points our optimization algorithm could appear less applicable⁵². But, according to our experience, it is more likely that any type of stationary points can be located by the technique used, if the optimization starts from an adequate initial structure. The same follows from the results by Ermer⁵³ concerning the Newton-Raphson procedure. Moreover, in the context of this equilibrium study, location of other stationary points than minima is not crucial, and the conclusions about isomerism of $(\text{H}_2\text{O})_2$ with respect to equilibrium situations cannot be affected. Nevertheless, it is interesting to find three transition states realizing interconversions between the equivalent $(\text{H}_2\text{O})_2$ minima. This varied isomerism of the activated complex, of course, would be manifested in overall values of the respective activation parameters⁵⁴.

For completeness it should be noted that the equivalent minima of $(\text{H}_2\text{O})_2$ could be differentiated by suitable isotopic labelling of the hydrogen atoms, which would result in a certain isomerism of water dimer. Thus *e.g.* the structures $\text{HOD}\cdots\text{OHD}$ and $\text{DOH}\cdots\text{OHD}$ serve an example representing, in addition, a pair of enantiomers each. This type of isomerism caused by isotopic substitution is widely used for interpretation of experimental data (refs^{22,26,28,29}), it plays, however, no substantial role in the aspects of $(\text{H}_2\text{O})_2$ isomerism dealt with in the present paper.

All the located stationary points show at least one (non-trivial) element of symmetry. Generally, the non-rigidity of $(\text{H}_2\text{O})_2$ would be better classified by the permutation-inversion groups than by the point groups. The adequacy of application of the permutation-inversion group theoretical classification scheme is exemplified by the study⁵⁵ of the tunneling-rotational levels of the water dimer. However, for our purpose the point group formalism is quite sufficient. As for the symmetry properties of the stationary points on the MCY hypersurfaces it should be noted that none of the points is chiral, although this property is relatively frequent with the water oligomers¹³.

All the stationary points given in Table I lie in a region of weak intermolecular interactions, *i.e.* in the region for which the MCY hypersurfaces were suggested⁶. This fact is confirmed by *e.g.* the distances between the oxygen atoms $r(\text{O}_5\text{—O}_6)$ (Table I), the respective values according to the stationary points of the MCY I and MCY II hypersurfaces being $r(\text{O}_5\text{—O}_6) \in \langle 2.842; 3.207 \rangle \cdot 10^{-10}$ m and $r(\text{O}_5\text{—O}_6) \in \langle 2.786; 3.137 \rangle \cdot 10^{-10}$ m, respectively. The MCY hypersurfaces themselves were constructed on the basis of calculation of the structures whose $r(\text{O}_5\text{—O}_6)$ varied within the interval $\langle 2.381; 3.704 \rangle \cdot 10^{-10}$ m and, in some cases, $\langle 2.381; 7.938 \rangle \cdot 10^{-10}$ m. On the other hand, however, it is obvious that outside this parametrization region (*i.e.* particularly in the cases of considerable approach of the monomer units) the MCY hypersurfaces can behave unreasonably and even lead to appearance of extraneous stationary points, *i.e.* those which would not be confirmed by direct quantum-chemical calculation. Recently such possibility was mentioned by Jorgensen¹⁰. His cyclic dimer with $r(\text{O}_5\text{—O}_6) = 1.143 \cdot 10^{-10}$ m obtained by optimization within the C_{2h} point symmetry group^{10,56} does not represent a stationary point in the complete 6-dimensional coordinate space (2). Nevertheless, our optimization procedure starting from the structure given by Jorgensen leads to the stationary point for the distance $r(\text{O}_5\text{—O}_6) = 1.570 \cdot 10^{-10}$ m and $1.559 \cdot 10^{-10}$ m for the MCY I and MCY II hypersurfaces, respectively, the interaction energies being reasonably high. It can, however, be expected that the MCY hypersurfaces will show varied behaviour (with possible appearance of extraneous stationary points) in the region of considerable approach of the monomer units. This fact is connected, first of all, with the circumstance that in the original choice⁶ of the form of analytic potential function for the region of weak interactions of two water molecules it was not necessary to pay attention to the problem of adequate limit behaviour of this potential, *i.e.* to the course at $R_i^{(14)} \rightarrow 0$. In our context, however, the problem of extraneous stationary points in these limit regions can be interesting only from the methodological point of view.

Decision of types of the located stationary points in this paper is based on the analytically constructed elements of force constant matrix. The present studies of weak intermolecular complexes by quantum-chemical methods, however, generally use the numerically constructed matrices of the second derivatives of energy. Therefore, we also evaluated the statements about quality of the individual stationary points on the basis of eigenvalues of the force constant matrix constructed numerically from the changes of the analytically determined first derivatives of energy within the coordinate system (2). Generally speaking, the numerically constructed force constant matrices cannot be considered to be safe means of determination of type of stationary points on the potential hypersurfaces in the region of weak intermolecular interactions (at least so for the used coordinate system). In some cases studied by us the numerical technique did not enable a reliable, unambiguous determination of type of stationary point.

When describing the procedure leading to elimination of the eight redundancy conditions we stressed the necessity of proper balancing of the linear forces, *i.e.* correct treatment of the (generally non-zero) first derivatives of energy in the stationary point of the system described by coordinates with redundancy. Importance of the linear terms is shown by the fact that their neglect can result in appearance of imaginary vibrational frequencies at an evident energy minimum as it was empirically found in this study.

Let us now focus our attention on that one of the six located stationary points which is important for description of equilibrium situations, *i.e.* the minimum. In accordance with the previous theoretical results⁴⁻¹⁴ this structure belongs to the C_s point symmetry group with nearly linear hydrogen bond. Agreement between the theoretical MCY structural parameters and the recent experimental data^{24,27} is reasonable. This is particularly true of the distance $r(\text{O}_5-\text{O}_6)$ which has the value $2.98 \cdot 10^{-10}$ m (by the both experimental techniques^{24,27}). But the difference between the MCY values and experimental findings^{24,27} for the magnitude of the angle between $r(\text{O}_5-\text{O}_6)$ and the proton accepting water axis is greater than 20° .

In the calculation of vibrational frequencies at the harmonic level one additional approximation only was made, *viz.* neglect of certain interaction force constants. In the coordinate system (7) it results in decomposition of force constant matrix into three blocks: two blocks 3×3 belonging to the intramolecular coordinates and one block 9×9 belonging to the intermolecular ones. The corresponding inverse kinetic energy matrix, of course, does not possess this block structure, and it is just this matrix which ensures a certain interaction between inter- and intramolecular motions in the vibrational problem of $(\text{H}_2\text{O})_2$. The mentioned neglect of a part of interaction force constants was, of course, necessary, since their values cannot be derived from the MCY hypersurfaces. The SCF calculations by Curtiss and Pople⁵⁷ show that values of the interaction constants between the 3×3 blocks are very close to zero. Nevertheless, their values are important for precise description of changes in the intramolecular frequencies as compared with free water molecule. Some information about mutual influence of inter- and intramolecular motions is obtained from comparison of the values of intermolecular frequencies calculated by two approximations (Table II): besides the intramolecular force field taken from the experiment⁴⁹ a calculation was carried out with artificially stiff monomeric units (*i.e.* the intramolecular force constants were set equal to infinity). A very good agreement between the values of intermolecular frequencies from these two calculations represents an argument in support of the presumption of good separability of the both types of motions in $(\text{H}_2\text{O})_2$.

Symmetry of $(\text{H}_2\text{O})_2$ enables a somewhat finer classification of its vibrational frequencies; the respective structure of representation $\Gamma_{(\text{H}_2\text{O})_2}$ is given by Eq. (9)

$$\Gamma_{(\text{H}_2\text{O})_2} = 8A' + 4A'' \quad (9)$$

For better understanding Table II also gives approximate descriptions of form of the individual normal vibration modes based on the eigenvectors of the vibrational problem. For orientation visualization of these motions the schemes of ref.¹³ can be used.

So far experimental information about intermolecular frequencies of $(\text{H}_2\text{O})_2$ is not available, whereas experimental values of the intramolecular frequencies are known²⁸ (with approximate correction for anharmonicity). The authors²⁸ used the solid nitrogen matrix, which must be taken into account in direct confrontation of their values with the MCY theoretical frequencies. Comparison of the MCY values with the experimental harmonic frequencies²⁸ is relatively good for both $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$ (Table III). The mutual frequency order of the respective vibrational motion within the acceptor and donor molecule was found experimentally the same as that predicted theoretically. Qualitative relations of intramolecular frequencies of the dimer to the corresponding frequencies of free water molecule are only disturbed with the stretching vibration of the acceptor molecule.

Knowing the structural and vibrational characteristics of $(\text{H}_2\text{O})_2$, we can obtain (within the RRHO approximation of partition functions) values of the thermodynamic characteristics of the process (A) at any temperature. Table IV presents a comparison with the experimental data^{18,19}. Four experimental techniques have been employed to study equilibrium thermodynamics of water dimer formation: the analysis of PVT data for nonideality^{18,19}, the maser study of the temperature dependence of water vapour absorptions in the far infrared²⁰, measurement by mass spectrometry and molecular beam sampling techniques²¹, and the study of the pressure dependence of the speed of sound in water vapour²³. But the results^{20,21,23} are incomplete for our purposes. In the studies^{20,23} the enthalpy term only was determined, in the case of the experiment²¹ it is impossible to determine the temperature from the available information sources. The data given in refs^{18,19} are considered¹³ the most complete and, probably, the most accurate and are therefore used for evaluation of quality of MCY thermodynamic quantities. In ref.¹⁹ an analysis was carried out of temperature dependence¹⁸ of the experimental second virial coefficient B_2 of water vapour within the interval 150–450°C using the value of contribution⁵⁸ of free molecules to B_2 which gives a straight plot of ΔG_T^0 of the process (A) against T . This approximate procedure⁵⁸ should eliminate those components from the B_2 value which are not connected with the dimer formation. Linearity of the temperature dependence of ΔG_T^0 , of course, results in constancy of the therefrom derived¹⁹ terms ΔH_T^0 and ΔS_T^0 within a relatively broad temperature interval. Therefore, it seems most reasonable to make the theory *vs* experiment confrontation in the middle of the mentioned interval; Table IV also gives, for comparison, the values for the extreme points of the temperature interval in question. The confrontation of the theoretical and experimental values of ΔH_T^0 and ΔS_T^0 terms at the temperature of 573.15 K is very good for both the MCY I and MCY II hypersurfaces. The

agreement of entropy term is particularly important, as it can be considered¹⁵ an additional argument supporting the negation of $(\text{H}_2\text{O})_2$ isomerism in respect to equilibrium problems which was above based on investigation of the MCY hypersurfaces. Table IV also indicates that within the experimental temperature interval¹⁸ the presumption¹⁹ about constancy of ΔH_T^0 and ΔS_T^0 is fulfilled but only approximately.

Thermodynamic characteristics of the equilibrium (*A*) are evaluated in this paper within the framework of RRHO approximation of partition functions. This approximation is usual in studies of $(\text{H}_2\text{O})_2$ thermodynamics^{13,31-33,59}, because at present it is very difficult to get theoretical or experimental information enabling a substitution of the RRHO approximation by the approximation of vibrating rotator. The problem of calculation of thermodynamic characteristics of van der Waals molecules⁶⁰ is not yet solved. It is, of course, true that $(\text{H}_2\text{O})_2$ represents a relatively rigid structure compared with the typical van der Waals molecules. This fact makes the reliability of the RRHO calculations of thermodynamic characteristics of water dimer promising, especially so at lower temperatures. Furthermore, the agreement between theory and experiment demonstrated in Table IV can be taken as a result of compensation of a number of approximative factors in the theoretical scheme. This aspect would allow to look at our calculation of the thermodynamic characteristics of reaction (*A*) on the basis of the MCY characteristics as at a good extrapolation formula. Thus it is possible to predict the thermodynamic characteristics of water dimerization within a broad temperature interval (Table V). The MCY II hypersurface should be preferred as an information source because of better agreement between theory and experiment. Nevertheless, the correspondence and closeness of results between the MCY I and MCY II hypersurfaces is considerable, being complete in qualitative aspects.

The results in Table V also present an illustration of some general features of thermodynamic characteristics of van der Waals molecules which has been discussed recently^{36,37,61,62}. Both the ΔH_T^0 and ΔS_T^0 terms corresponding to reaction (*A*) show a non-monotone temperature dependence with a minimum. Due to mutual compensation of the two terms this feature is not transferred into the temperature dependence of equilibrium constant of reaction (*A*). It is typical of thermodynamics of the associations leading to formation of van der Waals molecules (ref.³⁶) that the entropy term markedly co-determines their low stability, especially so at higher temperatures. From Table V it is seen that at about 200 K the values of the ΔH_T^0 and $-T\Delta S_T^0$ terms are equal – except for their sign – which results in approximately zero value of the corresponding $\log K_p$. Above this temperature, contribution of $T\Delta S_T^0$ to ΔG_T^0 becomes gradually decisive.

Experimental values of the second virial coefficient of water (for a review see refs^{17,63}) represent an important information about non-ideality of water vapour but also about properties of water dimer^{16,19,31}. Therefore, interpretation of B_2 as a primary experimental information represents an important task for theoretical

chemistry. It is possible to analyze the second virial coefficient as a sum of three interactions between molecular pairs⁶⁴:

$$B_2 = B_f + B_b + B_m, \quad (10)$$

where B_f arises from collisions between free molecules, B_b is related to the equilibrium constant for the formation of dimers, and B_m is related to formation of metastable double molecules. The component B_b can easily be determined on the basis of the

TABLE VI

Magnitude of Contribution of Formation of Water Dimer to the Second Virial Coefficient B_2 of Water Vapour

T, K	$B_2, \text{cm}^3 \text{mol}^{-1}$		
	MCY I	MCY II	experimental ^a
298.15	-1 257.6	-1 000.3	-1 162 ^a ; -1 165 ^a ; -1 256 ^a
323.16	- 822.9	- 647.1	-838.3 ^b
373.16	- 433.0	- 334.0	-451.0 ^b ; -453.6 ^b
473.16	- 199.3	- 149.4	-196.1 ^b ; -196.7 ^b ; -209 ^{b,c} ; -215 ^{b,d}

^a For original references see review⁶³; ^b For original references see critical compilation¹⁷; ^c $T = 473.17$ or 473.18 K; ^d $T = 473.12$ K.

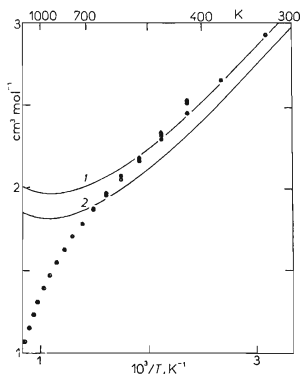


FIG. 2

Temperature Dependence of Contribution of Formation of $(\text{H}_2\text{O})_2$ Cluster to Value of the Second Virial Coefficient B_2 of Water Vapour with Given ● Experimental B_2 Values¹⁷

1 MCYI, 2 MCYII; y axis: $\log(-B_2)$, $\{B_2\} = \text{cm}^3 \text{mol}^{-1}$.

results given in this paper. Comparison of the MCY results with experimental information summarized in the critical compilation¹⁷ is given in Fig. 2. Numerical values for several chosen temperatures (not only for the case of results involved in the critical compilation¹⁷ but also for those of review⁶³) are given in Table VI. From the presented temperature dependences it can be concluded that, in the range of lower temperatures, the contribution of formation of water dimer agrees reasonably with the overall B_2 value, whereas in the range of higher temperatures its course begins to differ markedly from the experimental temperature dependence of B_2 .

In conclusion it should be stated that this study indicates a necessity of further coordinated efforts of theory and experiment directed to investigation of a number of open problems concerning the water dimer.

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APPENDIX

Relations between force constants f_r , f_α , f_{rr} , and $f_{r\alpha}$ corresponding to conventional choice⁴⁹ (r_1, r_2, α) of internal coordinates of the XY_2 molecule and force constants f_{R_1} , f_{R_2} , f_{R_3} , $f_{R_1R_2}$, and $f_{R_1R_3}$ in the base of three stretching coordinates ($R_1 = r_1$; $R_2 = r_2$; R_3) are expressed in Eqs (11)–(14), where r_0 is the equilibrium bond length X–Y and R_3 corresponds to the distance Y–Y.

$$f_{R_1} = f_{R_2} = f_r + \frac{t\alpha}{r_0} \left(-2f_{r\alpha} + \frac{f_\alpha t\alpha}{r_0} \right) \quad (11)$$

$$f_{R_3} = f_\alpha r_0^2 \cos^2(\alpha/2) \quad (12)$$

$$f_{R_1R_2} = f_{rr} + \frac{t\alpha}{r_0} \left(-2f_{r\alpha} + \frac{f_\alpha t\alpha}{r_0} \right) \quad (13)$$

$$f_{R_1R_3} = f_{R_2R_3} = \frac{1}{r_0 \cos \alpha/2} \left(f_{r\alpha} - \frac{f_\alpha t\alpha}{r_0} \right) \quad (14)$$

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