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A COMPUTATIONAL EVALUATION OF THE GAS-PHASE WATER DIMERISATION EQUILIBRIUM CONSTANT IN THE LOW TEMPERATURE REGION WITH PARTICULAR ATTENTION TO THE INTERPRETATION OF GIOTTO AND VEGA FLYBY OBSERVATIONS OF THE COMA OF COMET HALLEY

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ABSTRACT

This study was stimulated by current requirements in the interpretation of water-cluster formation in an expanding cometary atmosphere raised, in particular, by the Giotto and Vega flyby observations of Comet Halley. The equilibrium constant of the gas-phase water dimerisation in the temperature region 100–400 K is evaluated on the base of semi-rigid and flexible water–water potentials. A set of four series of data selected out of twelve considered potentials is suggested, indicating the present reliability interval of the computed values. The selection was based on a comprehensive comparison with the observed thermodynamic data (available for higher temperatures only).

INTRODUCTION

The possible occurrence of various water-group species in a cometary atmosphere has recently been assiduously investigated, especially in connection with the Giotto and Vega flyby observations of Comet Halley, see, for example, refs. 1–10. Computational simulations at appropriate cometary conditions [1,6,10] can help to elucidate various aspects, such as the dimensions of the water clusters formed, their populations, their distribution profile in the cometary coma, etc. These computational simulations require

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the equilibrium constant of the gas-phase water dimer as input information. Moreover, the water dimer has recently been proposed as an important species in the gas-phase chemistry of the coma [1–5], even though its abundance has been subject to conflicting estimates [1,6]. The range of temperatures within a coma is 100–350 K. However, the water-dimer equilibrium constant has never been measured below, still less considerably below, room temperature. The available observational data [11–18] refer to relatively high temperatures and, therefore, the computational evaluations were also primarily directed [19–33] to this temperature region. The present study thus aims at computational evaluation of the equilibrium constants in the low temperature region in order to provide the astrophysical and other research fields concerned with reliable data.

COMPUTATIONS

This study is based on twelve different water–water interaction potentials, namely, the semi-rigid MCY, the flexible BJH and the flexible MCYL family of potentials (four potentials being involved in each family).

The MCY type of water–water (intermolecular) potentials was introduced by Matsuoka et al. [34]. At present, four parametric versions of the *ab initio* potential are available. Originally, two modifications of the MCY potential were derived from the SCF CI results [34], differing in electron-correlation contribution treatment (the full electron correlation is designated MCYI; the intermolecular electron correlation only is designated MCYII). Later, Bounds [35] found a new solution of the MCYII fitting problem leading to a substantial decrease in the mean standard deviation (MCYB potential). Finally, Carravetta and Clementi [36] re-evaluated the electron-correlation contribution, creating the fourth (MCYC) potential. The original MCY-type potentials were rigid, i.e. they considered the intermolecular degrees of freedom only, keeping monomeric-unit geometry fixed at the free-state equilibrium positions. In order to allow intramolecular vibrational motions, the MCY potentials were combined [25,26] with the observed harmonic force field of the gas-phase water molecule. The combined potentials (which, with respect to the harmonic character of the intramolecular parts, can be called semi-rigid or semi-flexible) are coded here by the acronyms MCYI, MCYII, MCYB and MCYC.

There has, however, been a more sophisticated approach to the water–water interaction potentials, namely the so-called central force (CF) model [37–39]. In this approach, the inter- and intramolecular potential parts were described in a uniform form, and three modifications (CF [37], CF1 [38] and CF2 [39]) of the potential were suggested. The flexibility of the potentials were further increased by Bopp and co-workers [40–42], who combined the CF2 intermolecular potential (however, modifying the H–H interaction term

[41]) with a quartic spectroscopic force-field of gas-phase water molecules [43] (BJH/G potential). Moreover, using the water force-field [43] modification, adjusted [40] to liquid water conditions, another flexible potential can be created (BJH/L). Finally, for sake of completeness, the original CF1 and CF2 intermolecular terms can also be combined with the gas-phase intramolecular part [43] (CF1/G and CF2/G potentials).

A similar degree of sophistication for the intramolecular term used with the BJH-type flexible potentials was also applied to the MCY intermolecular potentials. Lie and Clementi [44] created a so-called MCYL potential by combining the MCYII intermolecular potential with a quartic potential of a free water molecule from calculations [45]. Again, considering the remaining three MCY-type potentials, a four-membered MCYL family of flexible potentials is created (coded here by MCY-X, where X = L, I, B or C, so that distinction is possible from the above semi-rigid MCYX potentials).

The twelve potential functions were then treated in a unified way, described in detail elsewhere [33]. For each of the potentials, its energy minimum was located and harmonic vibrational analysis was carried out within it. In agreement with previous experimental and theoretical results, the water dimer, in all 12 cases, exhibits C_s point-group symmetry and a near-linear hydrogen bond. Using the calculated structural, vibrational and energy data a complete thermodynamics of the gas-phase water-dimer formation has been described (primarily by the dimerisation equilibrium constant K_p), employing the partition functions of the usual rigid-rotor and harmonic-oscillator quality. As some observed thermodynamic data are also available for the heavy water dimer, the treatment was carried out for both ^{1}H and ^{2}D water-dimer isotopomers.

RESULTS AND DISCUSSION

The energetics calculated within the twelve potential modifications for both water-dimer isotopomers is presented in Table 1. The potential energy change, ΔE, for the light water dimerisation

$$2H_2O(g) = (H_2O)_2(g) \tag{1}$$

and the heavy water dimerisation

$$2D_2O(g) = (D_2O)_2(g) \tag{2}$$

is exactly the same (within the generally accepted Born–Oppenheimer approximation). Differences between the isotopomer formations, (1) and (2), appear, however, when passing to the standard enthalpy changes at absolute zero temperature (the ground-state energy changes), $\Delta H_0^{\ominus}$. It is interesting to note the differences between results from related MCYX and MCY-X potentials. In the former case, only six geometrical degrees of freedom were

TABLE 1

Survey [a] of the water dimer energetics [b] in the semi-rigid MCY, flexible BJH and flexible MCYL families of potentials

Potential	H isotope	Potential energy ΔE	Ground-state energy $\Delta H_0^\ominus$
MCYI	^{1}H	−23.92	−14.88
	^{2}D		−17.13
MCYII	^{1}H	−24.55	−14.97
	^{2}D		−17.35
MCYB	^{1}H	−23.59	−14.89
	^{2}D		−17.04
MCYC	^{1}H	−25.26	−15.38
	^{2}D		−17.81
CF1/G	^{1}H	−26.01	−18.37
	^{2}D		−20.15
CF2/G	^{1}H	−23.56	−16.40
	^{2}D		−18.09
BJH/G	^{1}H	−23.54	−16.16
	^{2}D		−17.91
BJH/L	^{1}H	−23.55	−17.32
	^{2}D		−18.76
MCY-L	^{1}H	−25.01	−16.84
	^{2}D		−18.83
MCY-I	^{1}H	−24.33	−16.63
	^{2}D		−18.51
MCY-B	^{1}H	−23.93	−16.45
	^{2}D		−18.26
MCY-C	^{1}H	−25.68	−17.19
	^{2}D		−19.24

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

[b] Either the potential energy change, ΔE, or the ground-state energy change, $\Delta H_0^\ominus$, is presented, both in kJ mol^{-1}.

optimised [25,26]. Thus, a further lowering of the ΔE term is to be expected after the full geometrical optimisation with the MCY-X flexible potentials. Moreover, the monomer/dimer vibrational shifts are rather modest [26,33] in the semi-rigid MCYX potentials while the flexible MCY-X potentials [33] are in reasonable agreement with (the negative) observed shifts. Consequently, an additional lowering (originated in the vibrational zero-point energy) is to be expected with the flexible MCY-X $\Delta H_0^\ominus$ terms in comparison to the semi-rigid MCYX ones.

Observed standard enthalpy, $\Delta H_T^\ominus$, and entropy, $\Delta S_T^\ominus$, changes are available for the gas-phase water dimerisation [11,12,16] at five different temperatures, four of which relate to light and one to heavy water dimerisation. In order to facilitate theory–experiment comparisons, the squares of the differences (calculation − observation) were summed over the five tem-

TABLE 2

Comparison of the observed standard [a] changes of enthalpy, H, entropy, S, TS term, Gibbs energy, G, as well as equilibrium constant, K_p, for the gas-phase water-dimer formation with their evaluations in the twelve potentials studied

Potential	$\Sigma\delta^2 H_i$ [b]	$\Sigma\delta^2 S_i$ [c]	$\Sigma\delta^2 (TS)_i$ [b]	$\Sigma\delta^2 G_i$ [b]	$\Sigma\delta^2 \log_{10} K_{p,i}$ [d]
MCYI	13.1	47.9	9.55	2.74	0.0461
MCYII	14.2	119	17.6	8.82	0.104
MCYB	13.2	54.7	13.4	3.69	0.0728
MCYC	19.3	189	28.3	10.3	0.117
CF1/G	71.0	323	72.2	227	3.72
CF2/G	18.8	645	137	176	2.79
BJH/G	18.1	153	36.7	50.9	0.856
BJH/L	35.4	154	37.0	91.4	1.52
MCY-L	40.4	134	19.8	6.72	0.128
MCY-I	28.6	49.7	9.45	15.6	0.293
MCY-B	22.7	52.2	12.5	21.2	0.384
MCY-C	54.8	207	31.2	7.14	0.131

[a] Observed values, see refs. 11, 12, 16, and references therein; the standard state–ideal gas phase at 101325 Pa pressure.

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

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

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

peratures. The summations were carried out for five different thermodynamic terms of the gas-phase water dimerisations, eqns. (1) or (2): enthalpy, H, entropy, S, temperature-entropy product, TS, Gibbs energy, G, and the decadic logarithm of the equilibrium constant, K_p, defined in terms of the partial pressures; for example, for the light water dimer, eqn. (1)

$$K_p = \frac{p_{(H_2O)_2}}{p^2_{H_2O}} \tag{3}$$

The K_p term, eqn. (3), provides input information for numerical cometary simulations [1]. Therefore, let us first consider the sums $\Sigma\delta^2 G_i$ and $\Sigma\delta^2 \log_{10} K_{p,i}$. Clearly, within each of the three potential families both classification terms yield the same ordering of the potential family members (see Table 2), though this is not necessarily valid in general. The best agreement with the observed equilibrium terms is produced by the MCYI, BJH/G and MCY-L potentials within the semi-rigid MCY, flexible BJH and flexible MCYL families, respectively. In fact, in any of the semi-rigid potentials, MCYX, the agreement with the observed K_p terms is better than for the best working member of the other two families. Clearly, this is a result of a rather complex interplay of the various energy and partition-function approximations involved (possibly inclusive of, *inter alia*, enthalpy-entropy compensation). However, the observational data are not considered

[31,33] as particularly precise. Moreover, the observations were reported [11,12,16] for temperatures within the interval from about 370 to about 570 K. It is therefore a more reasonable alternative to select several more reliable potentials out of the full 12-membered set and thus to define an interval of the most reliable calculated K_p values. In order to reflect differences between potential families, the best working potential from each family was selected, i.e. the potentials MCYI, BJH/G and MCY-L. Moreover, in addition to the semi-rigid MCYI values (which rather tend to underestimate the K_p values compared to observations) the MCYB values (i.e. the second best in the MCYX quaternion) were also considered in creating the recommended set as they, incidentally, tend to overestimate the observed values.

Before discussing the recommended values, the following point concerning the MCYI potential must be made. At the time of the evaluations [25,26] the newer observed data [16,17] were not available. It was concluded (on the basis of the then available observed information) [26] that the MCYII results should be preferred. The MCYII results were also preferred in other connections, see refs. 34, 35 and 44. Therefore, in more recent evaluations [31,32] the MCYI potential was not included, more attention being paid to the MCYII and MCYB treatments. Hence, only now is the MCYI output quality explicitly stressed; this also demonstrates the importance of selecting a particular comparison-term as well as a particular set of observational data. Finally, for completeness, it must be mentioned that there are some minor differences between the present MCYI treatment and that of ref. 26: a higher accuracy is used for vibrational frequencies (compare also ref. 31) and pure isotopes (not the natural isotopic mixture) are considered in the present study.

Table 3 represents the primary outcome of this article—the equilibrium constants for water dimerisation, eqn. (1), for the temperature interval relevant to cometary studies. The values are given for the MCYI, MCYB, BJH/G and MCY-L potentials. At the lowest temperatures considered the difference between the highest (MCY-L) and the lowest (MCYI) term is about one order of magnitude. On the other hand, the relative difference between the highest (BJH/G) and the lowest (MCYI) value is considerably smaller at the higher end of the temperature interval.

Figures 1–3 show the temperature evolutions of the equilibrium constants, K_p, within each of the three potential families. Interestingly enough, the intra-family differences are more pronounced in the BJH set than in both MCY-based families. Incidentally, in spite of the temperature decrease of the K_p values, the water-dimer mole fraction, x_2, in saturated steam (composed of monomers and dimers) is still increasing [a] with temperature,

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[a] In fact, the K_p temperature decrease is over-compensated [32] by the temperature increase of the saturated steam pressure.

TABLE 3

The equilibrium constant, K_p, of the light gas-phase water-dimer formation evaluated in the semi-rigid potentials MCYI and MCYB and in the flexible potentials BJH/G and MCY-L

T(K)	$K_p = p_{(H_2O)_2}/p^2_{H_2O}$ (atm^{-1}) [a]			
	MCYI	MCYB	BJH/G	MCY-L
100	3.95×10^{4}	4.21×10^{4}	2.67×10^{5}	3.58×10^{5}
125	6.53×10^{2}	7.04×10^{2}	3.38×10^{3}	3.59×10^{3}
150	4.18×10^{1}	4.56×10^{1}	1.81×10^{2}	1.64×10^{2}
175	5.88×10^{0}	6.47×10^{0}	2.25×10^{1}	1.80×10^{1}
200	1.36×10^{0}	1.51×10^{0}	4.73×10^{0}	3.46×10^{0}
225	4.39×10^{-1}	4.90×10^{-1}	1.42×10^{0}	9.65×10^{-1}
250	1.79×10^{-1}	2.02×10^{-1}	5.46×10^{-1}	3.50×10^{-1}
275	8.70×10^{-2}	9.83×10^{-2}	2.53×10^{-1}	1.54×10^{-1}
298.15	5.00×10^{-2}	5.67×10^{-2}	1.40×10^{-1}	8.18×10^{-2}
300	4.80×10^{-2}	5.45×10^{-2}	1.34×10^{-1}	7.81×10^{-2}
325	2.92×10^{-2}	3.34×10^{-2}	7.90×10^{-2}	4.43×10^{-2}
350	1.93×10^{-2}	2.21×10^{-2}	5.06×10^{-2}	2.75×10^{-2}
375	1.35×10^{-2}	1.55×10^{-2}	3.46×10^{-2}	1.83×10^{-2}
400	9.95×10^{-3}	1.15×10^{-2}	2.50×10^{-2}	1.29×10^{-2}

[a] The standard-state choice ideal gas phase at 1 atm = 101325 Pa pressure.

cf. refs. 6 and 32. Our averaged equilibrium values for x_2, using the saturated steam pressure [46,47], are $(4.4 \pm 2.6) \times 10^{-6}$, $(2.4 \pm 1.3) \times 10^{-4}$, $(2.7 \pm 1.3) \times 10^{-3}$ and $(3.3 \pm 1.4) \times 10^{-2}$, at 200, 250, 300 and 400 K, respectively. These values are in order-of-magnitude agreement with those given in ref. 6 using data [31]. However, both sets of x_2 values are also substantially different from the terms [2] derived from intermediates [31]. The disagreement could be rationalised by the presumption that saturated steam conditions were not considered in the evaluation [2].

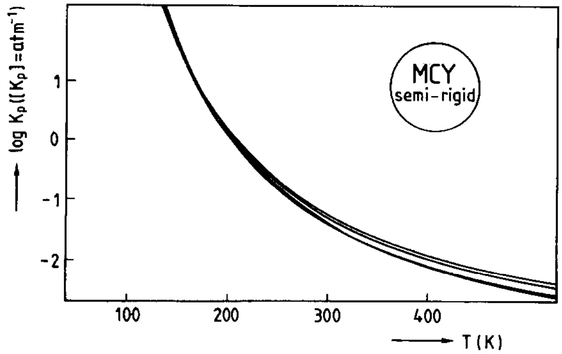

Fig. 1. Temperature dependencies of the equilibrium constants, K_p, for the dimerisation $2H_2O(g) = (H_2O)_2(g)$ evaluated within the semi-rigid MCY family of potentials (at the end of the considered temperature interval, the K_p values decrease in the order: MCYB (the highest term), MCYI, MCYII, MCYC (the lowest term)).

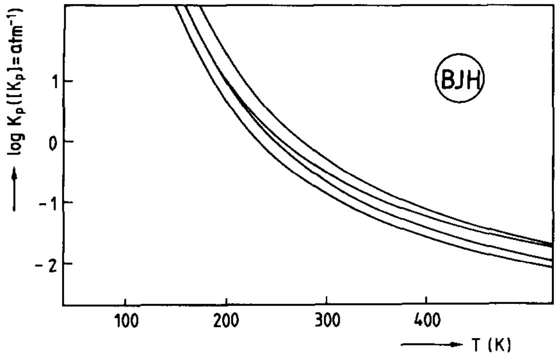

Fig. 2. Temperature dependencies of the equilibrium constants, K_p, for the dimerisation $2H_2O(g) = (H_2O)_2(g)$ evaluated for the four flexible BJH-type potentials (at the end of the considered temperature interval, the K_p values decrease in the order: CF1/G (the highest term), CF2/G, BJH/L, BJH/G (the lowest term)).

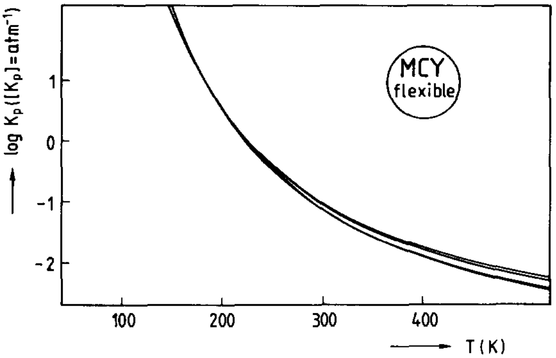

Fig. 3. Temperature dependencies of the equilibrium constants, K_p, for the dimerisation $2H_2O(g) = (H_2O)_2(g)$ evaluated within the flexible MCY family of potentials (at the end of the considered temperature interval, the K_p values decrease in the order: MCY-B (the highest term, MCY-I, MCY-L, MCY-C (the lowest term)).

In concluding, the (presently believed) most reliable computational evaluations of the gas-phase water dimerisation equilibrium constants have been suggested for further use in cometary studies, as well as in other fields of application. The evaluations could be improved by, in particular, including anharmonicity effects in partition functions, or by introducing even more sophisticated water–water potentials. Finally, additional, more precise observed data would certainly also be useful.

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