

Computed Relative Populations of $D_2(22)$ - C_{84} Endohedrals

with Encapsulated Monomeric and Dimeric Water

Zdeněk Slanina,^{*,a} Filip Uhlík,^b Shigeru Nagase,^c Xing Lu,^d Takeshi Akasaka,^a Ludwik Adamowicz^e

^a*Life Science Center of Tsukuba Advanced Research Alliance,*

University of Tsukuba, Tsukuba 305-8577, Japan

^b*Department of Physical and Macromolecular Chemistry,*

Charles University in Prague, Faculty of Science, Albertov 6, 128 43 Praha 2, Czech Republic

^c*Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan*

^d*State Key Laboratory of Materials Processing and Die & Mould Technology, School of Material Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China*

^e*Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041, USA*

Abstract

The water monomer and dimer encapsulations into $D_2(22)$ - C_{84} fullerene are evaluated. The encapsulation energy is computed at the M06-2X/6-31++G** level and it is found that the monomer and dimer storage in C_{84} yields an energy gain of 10.7 and 17.4 kcal/mol, respectively. Encapsulation equilibrium constants are computed using partition functions based on the M06-2X/6-31G** and M06-2X/6-31++G** molecular data. At high-temperature/high-pressure conditions similar to encapsulation of rare gases in fullerenes, the computed $(H_2O)_2@C_{84}$ to $H_2O@C_{84}$ ratio is close to 1:2.

Just fifty years ago, Harry P. Schultz [1] carried out the very first computational stability evaluations for fullerene or pseudo-fullerene derivatives. He selected cage hydrocarbons (he called polyhedrans) based on Pla-

* Corresponding author; e-mail: zdeneks@email.arizona.edu

tonic or Archimedean polyhedra, including $C_{60}H_{60}$ - fully hydrogenated fullerene C_{60} . His fifty years old predictions based only on a very simple molecular mechanics reasonably agree with the present day advanced calculations [2]. They both point out the well known synthetic hydrocarbon dodecahedrane $C_{20}H_{20}$ as the most stable while $C_{60}H_{60}$ is the third (and comes before another synthetic polyhedrane - cubane C_8H_8). However, his pioneering work has almost entirely been ignored by fullerene historians though otherwise they have properly credited other ancient theoretical works [3-5] on C_{60} (and also computations on smaller carbon clusters [6-8]) that appeared in the fullerene prehistorical era before the C_{60} observation [9] in 1985. In more recent times, the calculations indeed frequently support [10] experiment interpretations. While remembering the Schultz groundbreaking paper [1], it would be thus in his spirit to predict stability of a new species, and it is done here on C_{84} fullerene containing encapsulated water dimer.

Actually, encapsulation of non-metal species inside the fullerene cages has been studied, for example as $N_2@C_{60}$ and $N_2@C_{70}$ [11-13]. Endohedrals with rare gas atoms, in particular with He, were produced using [14-16] high temperatures ($650^\circ C$), high pressures (3000 atm) and a catalyst. Moreover, molecular hydrogen [17] and even a water molecule [18] were placed inside open-cage fullerenes, further on closed synthetically [19,20]. Such fullerene encapsulations of non-metals have also been computed [21-25].

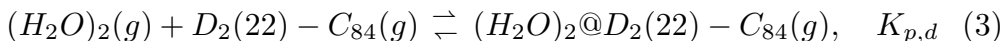
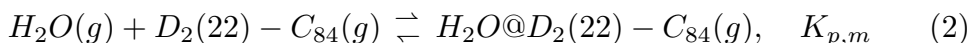
C_{84} has twenty four [26] isolated-pentagon rule (IPR) isomers, two major isomers of D_2 and D_{2d} symmetries are labeled as 22 and 23, respectively, or $D_2(22)-C_{84}$ and $D_{2d}(23)-C_{84}$ (though some minor isomers

are also known [27]). The D_2 and D_{2d} isomers were prepared [28] in a ratio of 2:1 and can be separated by recycling chromatography [29]. The D_{2d} structure has the lowest energy [30] among the C_{84} IPR isomers, however, owing to entropy effects it is still less populated. At a temperature of 1000 K, the $D_2(22)$ - C_{84} isomer is computed [31,32] as 60.3% while the $D_{2d}(23)$ - C_{84} species as only 34.2% in the IPR isomeric mixture. Therefore, the focus here is on the D_2 isomer.

The water dimer has vigorously been studied as an H-bond model and also as a component of Earth's [33] and cometary [34,35] atmospheres. It has been established that the dimer mole fraction [36] in saturated steam increases with increasing temperature. It may be a surprising result but in fact it can easily be rationalized. While the equilibrium constant for the dimer formation decreases with temperature, the saturated pressure grows faster. The saturated steam is a well defined system and therefore it is also used here. The water dimer formation will be described by the usual dimerization equilibrium constant $K_{p,2}$ in terms of the partial pressures of the components:



The monomeric and dimeric water encapsulations are similarly described by the encapsulation equilibrium constants $K_{p,m}$ and $K_{p,d}$:



The key term evaluated here is the ratio between the equilibrium populations (expressed by the partial pressures p_i) of the C_{84} endohedrals with the water dimer and monomer:

$$\frac{P_{(H_2O)_2@C_{84}}}{P_{H_2O@C_{84}}} = \frac{P_{(H_2O)_2} K_{p,d}}{P_{H_2O} K_{p,m}} = \frac{K_{p,d}}{K_{p,m}} P_{H_2O} K_{p,2} \quad (4)$$

Under the equilibrium conditions, the monomer pressure roughly equals to the saturated steam pressure P_{sat} , however, more precisely it is the term after the subtraction of the water-dimer molar fraction x_2 , $(1 - x_2)P_{sat}$ (if higher water oligomers are ignored).

The structural and energy data for the encapsulation equilibrium constants are calculated using the M06-2X density functional with the standard 6-31++G** basis set (M06-2X/6-31++G**). The partition functions are of the usual rigid rotor and harmonic oscillator quality and the vibrational frequencies are from simpler M06-2X/6-31G** approach. All the calculations are carried out with the Gaussian program package [37]. The M06-2X/6-31++G** encapsulation energies with inclusion of the basis set superposition error (BSSE/CP2) and so-called steric correction [38] are given in Table 1. Incidentally, the BSSE/CP2 term reduces the gain in the monomer and dimer encapsulation energy by 2.20 and 3.96 kcal/mol, respectively. Although the water-dimer encapsulation gives a larger potential-energy stabilization, the difference is somewhat compensated by the entropy terms. The cage influences the water dimer conformation (Fig. 1) which is otherwise trans for the free species. However, the encapsulated trans arrangement is higher in energy only by 0.08 kcal/mol. The encapsulates in various endohedrals undergo relatively free motions which is responsible for reconstruction of the cage symmetries known from NMR spectroscopy. The fully optimized $H_2O@C_{84}$ and $(H_2O)_2@C_{84}$ aggregates exhibit just C_1 static symmetry. However, in order to reflect the

fast internal motions, it is more realistic to describe the aggregates by the dynamic D_2 symmetry (especially for the $K_{p,m}$ and $K_{p,d}$ terms).

The water dimerization constants are generated [37,39] at a higher, G3&MP2=/AUG-cc-pVQZ computational level. In fact, comparison between the observed and calculated standard Gibbs-energy changes $\Delta G_{T,2}^o$ shows that the calculated curve looks like a best fit through the experimental points. The calculated $K_{p,2}$, $K_{p,m}$, $K_{p,d}$ terms are together with the observed saturated-steam pressures [40] applied in Eq. (4) in order to get the required ratios between the equilibrium populations of the C_{84} endohedrals with the water dimer and monomer (Table 2). The interplay of the equilibrium characteristics produces a relatively uniform picture. In the equilibrium high temperature and high pressure regime the ratio between the endohedrals with dimeric a monomeric water should be close to 1:2.

The calculations suggest that the high temperature and high pressure technique [14-16] could also be used for water monomer and dimer encapsulation into higher fullerenes like C_{84} (C_{60} is too small [39] to encapsulate the dimer). The temperatures are likely to go over the critical point (when saturation is not possible and pressures become arbitrary). The high temperatures (and catalyst) allow for a temporary window in the cage, yet they cannot be too high to prevent a larger cage destruction and water dissociation. Although the first observations are to be done in laboratory, the recent final confirmation [41] of C_{60} in the interstellar space allows to search there for fullerene cages with the smallest water droplets inside, too.

Acknowledgements

The reported research has been supported by a Grant-in-aid for Scientific Research on Innovative Areas (No. 20108001, "π-Space") from the Ministry of Education, Culture, Sports, Science, and Technology of Japan; by the Czech Science Foundation/GACR (P208/10/1724); and by the Czech-Norwegian Research Programme (7F14392). An early phase of the research line was supported by the Alexander von Humboldt-Stiftung and the Max-Planck-Institut für Chemie (Otto-Hahn-Institut).

References

1. H. P. Schultz, *J. Org. Chem.* 1965, 30, 1361-1364.
2. Z. Slanina, X. Zhao, F. Uhlík, S.-L. Lee, L. Adamowicz, *Int. J. Quantum Chem.* 2004, 99, 640-653.
3. E. Ōsawa, *Kagaku* 1970, 25, 854-863; Z. Yoshida, E. Ōsawa, *Aromaticity*. Kagaku-dojin, Kyoto 1971, pp. 174-8.
4. D. A. Bochvar, E. G. Galpern, *Doklady Akad. Nauk SSSR* 1973, 209, 610-612; I. Stankevich, M. Nikerov, D. Bochvar, *Russ. Chem. Rev.* 1984, 53, 640-655.
5. R. A. Davidson, *Theor. Chim. Acta* 1981, 58, 193-231.
6. K. S. Pitzer, E. Clementi, *J. Am. Chem. Soc.* 1959, 81, 4477-4485.
7. R. Hoffmann, *Tetrahedron* 1966, 22, 521-538.
8. Z. Slanina, *Radiochem. Radioanal. Lett.* 1975, 22, 291-298.
9. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* 1985, 318, 162-163.
10. Z. Slanina, S.-L. Lee, C.-H. Yu, *Rev. Comput. Chem.* 1996, 8, 1-62.
11. T. Peres, B. P. Cao, W. D. Cui, A. Khong, R. J. Cross, M. Saunders,

- C. Lifshitz, *Int. J. Mass Spectr.* 2001, 210/211, 241-247.
12. T. Suetsuna, N. Dragoe, W. Harneit, A. Weidinger, H. Shimotani, S. Ito, H. Takagi, K. Kitazawa, *Chem. Eur. J.* 2002, 8, 5079-5083.
13. T. A. Murphy, Th. Pawlik, A. Weidinger, M. Höhne, R. Alcalá, J.-M. Spaeth, *Phys. Rev. Lett.* 1996, 77, 1075-1078.
14. M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, R. J. Poreda, *Science*, 1993, 259, 1428-1430.
15. R. J. Cross, M. Saunders, H. Prinzbach, *Org. Lett.* 1999, 1, 1479-1481.
16. R. J. Cross, M. Saunders, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Volume 11 - Fullerenes for the New Millennium*, Eds. K. M. Kadish, P. V. Kamat, D. Guldi, The Electrochemical Society, Pennington 2001, pp. 298-300.
17. M. Carravetta, Y. Murata, M. Murata, I. Heinmaa, R. Stern, A. Tontcheva, A. Samoson, Y. Rubin, K. Komatsu, M. H. Levitt, *J. Am. Chem. Soc.* 2004, 126, 4092-4093.
18. S.-I. Iwamatsu, T. Uozaki, K. Kobayashi, S. Re, S. Nagase, S. Murata, *J. Am. Chem. Soc.* 2004, 126, 2668-2669.
19. K. Komatsu, M. Murata, Y. Murata, *Science* 2005, 307, 238-240.
20. K. Kurotobi, Y. Murata, *Science* 2011, 333, 613-616.
21. Z. Slanina, F. Uhlík, L. Adamowicz, S. Nagase, *Mol. Simul.* 2005, 31, 801-806.
22. Z. Slanina, and S. Nagase, *Mol. Phys.* 2006, 104, 3167-3171.
23. Z. Slanina, P. Pulay, S. Nagase, *J. Chem. Theory Comput.* 2006, 2, 782-785.
24. A. Rodríguez-Forteza, A. L. Balch, J. M. Poblet, *Chem. Soc. Rev.*

- 2011, 40, 3551-3563.
25. A. A. Popov, S. Yang, L. Dunsch, *Chem. Rev.* 2013, 113, 5989-6113.
 26. D. E. Manolopoulos, P. W. Fowler, *J. Chem. Phys.* 1992, 96, 7603-7614.
 27. T. J. S. Dennis, T. Kai, K. Asato, T. Tomiyama, H. Shinohara, T. Yoshida, Y. Kobayashi, H. Ishiwatari, Y. Miyake, K. Kikuchi, Y. Achiba, *J. Phys. Chem. A* 1999, 103, 8747-8752.
 28. K. Kikuchi, N. Nakahara, M. Honda, S. Suzuki, K. Saito, H. Shimomaru, K. Yamauchi, I. Ikemoto, T. Kuramochi, S. Hino, Y. Achiba, *Chem. Lett.* 1991, 20, 1607-1610.
 29. T. J. S. Dennis, T. Kai, T. Tomiyama, H. Shinohara, *Chem. Commun.* 1998, 619-620.
 30. D. Bakowies, M. Kolb, W. Thiel, S. Richard, R. Ahlrichs, M. M. Kappes, *Chem. Phys. Lett.* 1992, 200, 411-417.
 31. Z. Slanina, J.-P. François, M. Kolb, D. Bakowies, W. Thiel, *Fullerene Sci. Technol.* 1993, 1, 221-230.
 32. Z. Slanina, S.-L. Lee, *J. Mol. Struct. (Theochem)* 1995, 333, 153-158.
 33. H. A. Gebbie, W. J. Burroughs, J. Chamberlain, J. E. Harries, R. G. Jones, *Nature* 1969, 221, 143-145.
 34. J. F. Crifo, Z. Slanina, *Astrophys. J.* 1991, 383, 351-355.
 35. J. Crovisier, D. Bockelée-Morvan, P. Colom, N. Biver, D. Despois, D.C. Lis, *Astron. Astrophys.* 2004, 418, 1141-1157.
 36. Z. Slanina, *Z. Phys. D* 1987, 5, 181-186.
 37. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.

- F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Rev. A.02, Gaussian Inc., Wallingford CT, 2009.
38. Z. Slanina, F. Uhlík, S.-L. Lee, L. Adamowicz, T. Akasaka, S. Nagase, *Int. J. Quant. Chem.* 2011, 111, 2712-2718.
39. F. Uhlík, Z. Slanina, S.-L. Lee, B.-C. Wang, L. Adamowicz, S. Nagase, *J. Comput. Theor. Nanosci.* 2015, 12, 959-964; 2015, 12, 2622.
40. W. M. Haynes, D. R. Lide, T. J. Bruno, eds. *CRC Handbook of Chemistry and Physics*, 95th Ed. CRC Press, Boca Raton, FL 2014, p. 6-5.
41. E. K. Campbell, M. Holz, D. Gerlich, J. P. Maier, *Nature* 2015, 523, 322-323.

Table 1. The M06-2X/6-31++G** encapsulation energies ΔE_{enc} for water and water dimer encapsulation into $D_2(22)$ -C₈₄

Endohedral	ΔE_{enc} (kcal/mol)
H ₂ O@C ₈₄	-10.69
(H ₂ O) ₂ @C ₈₄ ^a	-17.37

^a See Fig. 1.

Table 2. The population ratios in the saturated steam for $D_2(22)$ - C_{84} endohedrals with encapsulated water dimer and monomer at selected temperatures T

T (K)	$\frac{P(H_2O)_2@C_{84}}{P_{H_2O@C_{84}}}$
500.0	0.850
600.0	0.690
647.096 ^a	0.637

^a The critical temperature.

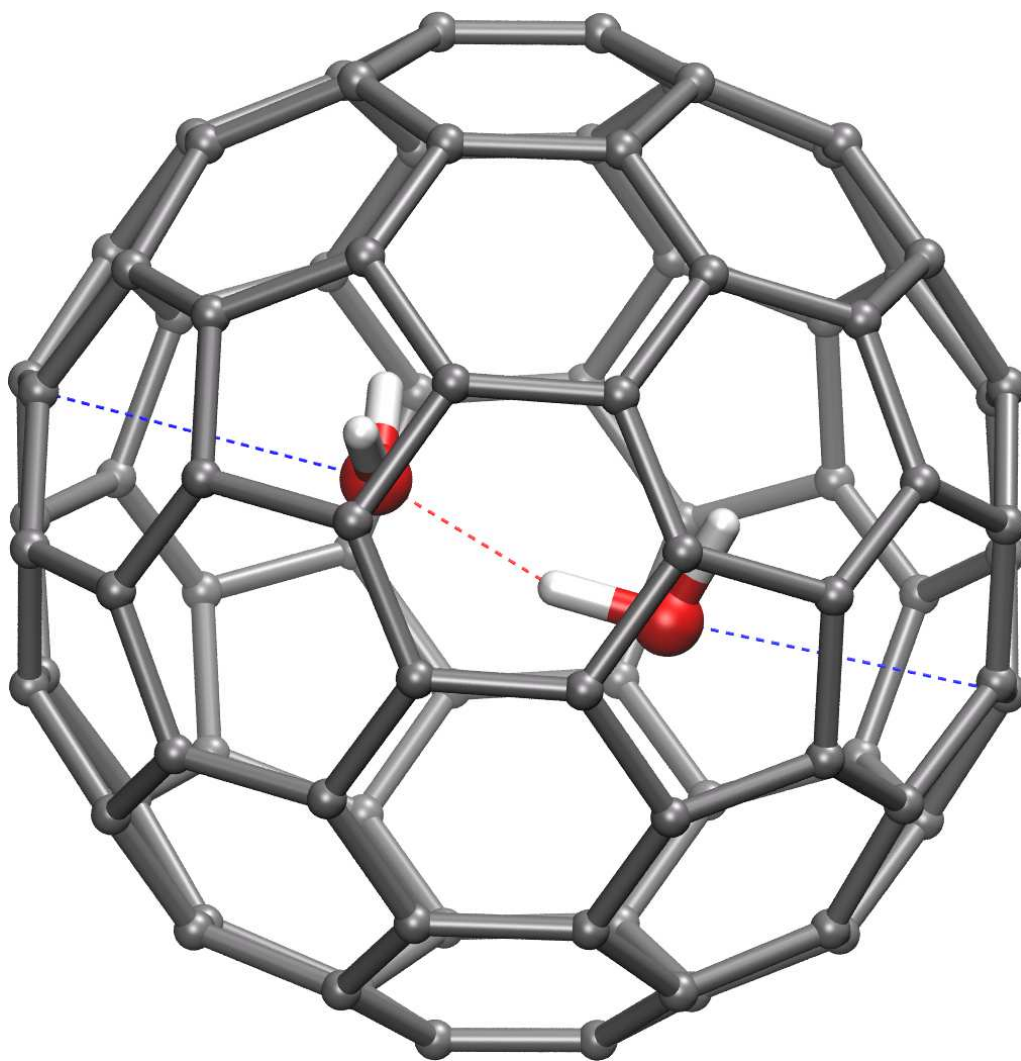


Fig. 1. The M06-2X/6-31++G** optimized structure of $(\text{H}_2\text{O})_2@D_2(22)\text{-C}_{84}$; the hydrogen bond 1.756 Å, the shortest O-C contacts 2.935 and 3.058 Å.

Keywords: Water dimer; $(\text{H}_2\text{O})_2@C_{84}$; $D_2(22)-C_{84}$; Non-metallic fullerene endohedrals; Clusters in saturated vapors; Computational evaluations.

Table of Content text and figure (the figure is the same as Fig. 1):

The smallest water drop in a molecular barrel: Computations predict that the water monomer and dimer can be encapsulated into a C_{84} fullerene cage by means of high temperature and pressure, thus conserving the hydrogen-bond species.