Computing Metallofullerenes as Agents of Nanoscience: Gibbs Energy Treatment of $Ca@C_{72}$, $Ca@C_{82}$, and $La@C_{82}$

Zdeněk Slanina,*,** Kaoru Kobayashi* and Shigeru Nagase*

*Department of Theoretical Studies
Institute for Molecular Science
Myodaiji, Okazaki 444-8585, Japan
**Institute of Chemistry, Academia Sinica
128 Yen-Chiu-Yuan Rd., Sec. 2
Nankang, Taipei 11529, Taiwan - R.O.C.

ABSTRACT

Three endohedral fullerene systems are simulated computationally, combining the treatments of quantum chemistry and statistical mechanics. Relative concentrations of four isomers of $Ca@C_{72}$, nine isomers of $Ca@C_{82}$, and four isomers of $La@C_{82}$ are evaluated using the Gibbs energy. The results illustrate the enthalpy-entropy interplay in the systems produced under very high temperatures.

Keywords: Carbon-based nanotechnology; molecular electronics; metallofullerenes; optimized syntheses; Gibbs-energy evaluations.

1 INTRODUCTION

Various endohedral cage compounds have been suggested as possible candidate species for molecular memories. One approach is built on endohedral species with two possible location sites of the encapsulated atom [1,2] while another concept of quantum computing aims at a usage of spin states of $N@C_{60}$ [3]. In this work, three systems related to the first approach are simulated computationally, combining the treatments of quantum chemistry and statistical mechanics. Relative concentrations of four isomers of $Ca@C_{72}$, nine isomers of $Ca@C_{82}$, and four isomers of $La@C_{82}$ are computed using the Gibbs energy.

2 COMPUTATIONS

The computations started from the structures [4-6] optimized at the Hartree-Fock (HF) level in a combined basis set: 3-21G basis for C atoms and a dz basis set [7] with the effective core potential on Ca (for the sake of simplicity, denoted here HF/3-21G~dz). Now, the structures are reoptimized using DFT, namely Becke's three parameter functional [8] with the non-local Lee-Yang-Parr correlation functional [9] (B3LYP) with the above basis set (B3LYP/3-21G~dz). The analytical energy gradient was used in the geometry optimizations. All the reported computations are carried out with the Gaussian 98 program package [10].

In the optimized B3LYP/3-21G~dz geometries the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same B3LYP/3-21G~dz optimized geometries a higher-level single-point energy calculation was also performed, using the standard 6-31G* basis set for all atoms (if possible). The electronic excitation energies were evaluated by means of the ZINDO method [11,12], known also as the ZINDO/S method, a semiempirical SCF method combined with the configuration interaction technique and specifically parametrized for calculation of electron excited states. Moreover, in some cases the electronic transitions were also calculated with time-dependent (TD) DFT response theory [13] at the B3LYP/3-21G~dz level. Singlet and triplet excited states were evaluated as they both are relevant for the electronic partition function of a singlet species under the conditions of thermodynamic equilibrium.

Relative concentrations (mole fractions) x_i of m isomers can be expressed [14] through their partition functions q_i and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H^o_{0,i}$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula:

$$x_i = \frac{q_i exp[-\Delta H^o_{0,i}/(RT)]}{\sum_{j=1}^{m} q_j exp[-\Delta H^o_{0,j}/(RT)]} \ , \qquad (1)$$

where R is the gas constant and T the absolute temperature. Eq. (1) is an exact formula that can be directly derived [14] from the standard Gibbs energies of the isomers, supposing the conditions of the inter-isomeric thermodynamic equilibrium. Rotational-vibrational partition functions were constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator approximation. No frequency scaling is applied as it is not significant [15] for the x_i values at high temperatures. The geometrical symmetries of the optimized cages were determined not only by the Gaussian 98 built-in procedure [10] but also by a procedure [16] which considers precision of the computed coordinates. The electronic partition function was constructed by directed summation from the ZINDO or TD electronic excitation energies. In fact, just a few first electronic excited states matter for the partition function. Finally, the chirality contribution [17] was included accordingly (for an enantiomeric pair its partition function q_i is doubled).

3 RESULTS AND DISCUSSION

$Ca@C_{72}$, $Ca@C_{82}$, and $La@C_{82}$ are among the first metallofullerenes to which the combined stability computations have been applied. $Ca@C_{72}$ was isolated [18] though its observed structure is not yet available. It follows from its very first computations [4,19] that there

are four isomers especially low in potential energy. In fact, C_{72} has only one [20] isolated-pentagon-rule (IPR) structure. The endohedral $Ca@C_{72}$ species created by putting Ca inside the sole IPR cage has been labeled [4] by (a). The other three $Ca@C_{72}$ isomers considered in ref. [4] are related to two non-IPR C_{72} cages (b) and (c), and to a C_{72} structure with one heptagon (d).

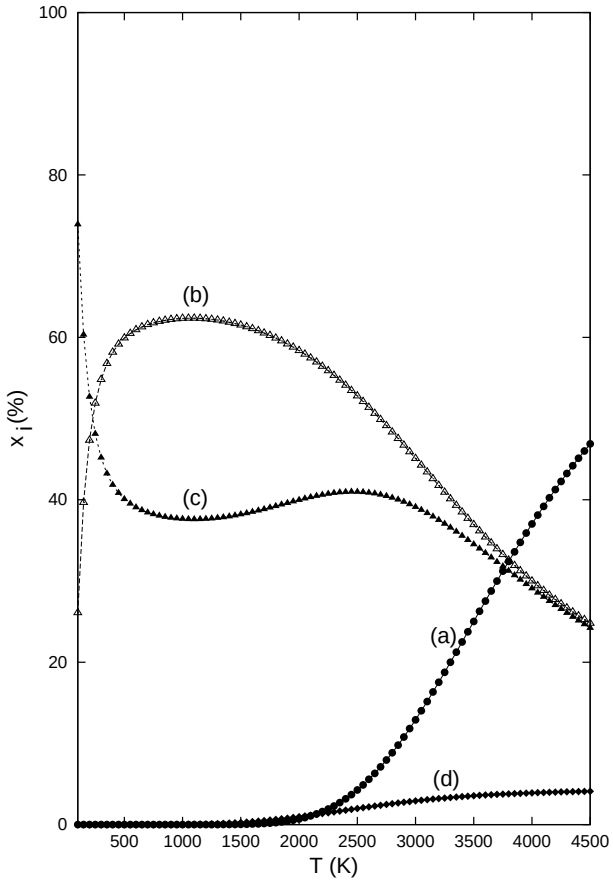

Fig. 1. Relative concentrations of the $Ca@C_{72}$ isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G∼dz entropy.

The extended computations [21] started from the four optimized structures [4] derived using *ab initio* HF treatment with the combined 3-21G∼dz basis set. The structures were reoptimized at the B3LYP/3-21G∼dz level. In the optimized B3LYP/3-21G∼dz geometries the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same geometries single-point energy calculations were also performed at the B3LYP/6-31G* level. The electronic excitation energies were evaluated by means of TD DFT response theory at the B3LYP/3-21G∼dz level.

Fig. 1 presents the temperature development of the relative concentrations of the four $Ca@C_{72}$ isomers in a high temperature region. At very low temperatures (not shown in Fig. 1) the structure lowest in the $\Delta H^o_{0,i}$ scale must be prevailing. However, already at a temperature of 226 K (that has no practical meaning) the relative concentrations of the (c) and (b) structures are interchanged and beyond the point the (b) structure is always somewhat more populated. Even more interesting is the behavior of the IPR-satisfying (a) structure. As the structure is the highest in the potential energy, it must be the least populated species at low temperatures. However, later on the entropy contributions (low symmetry, some lower vibrational frequencies and some lower electronic excitation energies) elevate the (a) isomer into the status of a minor isomer that could also be observed. On the other hand, the (d) isomer has the least chances to be detected. Interestingly enough, the concentration order at high temperatures for $Ca@C_{72}$ is quite similar to that previously computed [22] for $Mg@C_{72}$.

The second illustrative system, $Ca@C_{82}$, exhibits the richest isomerism among the Ca endohedrals [23-28]. Shinohara *et al.* [25] isolated four isomers of $Ca@C_{82}$ and labeled the isomers by (I), (II), (III), and (IV). Dennis and Shinohara concluded [29] from the ^{13}C NMR spectra of $Ca@C_{82}$(III) its symmetry as C_2. The ultraviolet photoelectron spectra measured by Hino *et al.* [30] support the finding; a similarity with $Tm@C_{82}$(II) was also noted [31]. Very recently, Achiba *et al.* [28] measured the ^{13}C NMR spectra of the all four isomers and assigned the symmetry of isomers (I), (II), (III), and (IV) as C_s, C_{3v}, C_2, and C_{2v}, respectively.

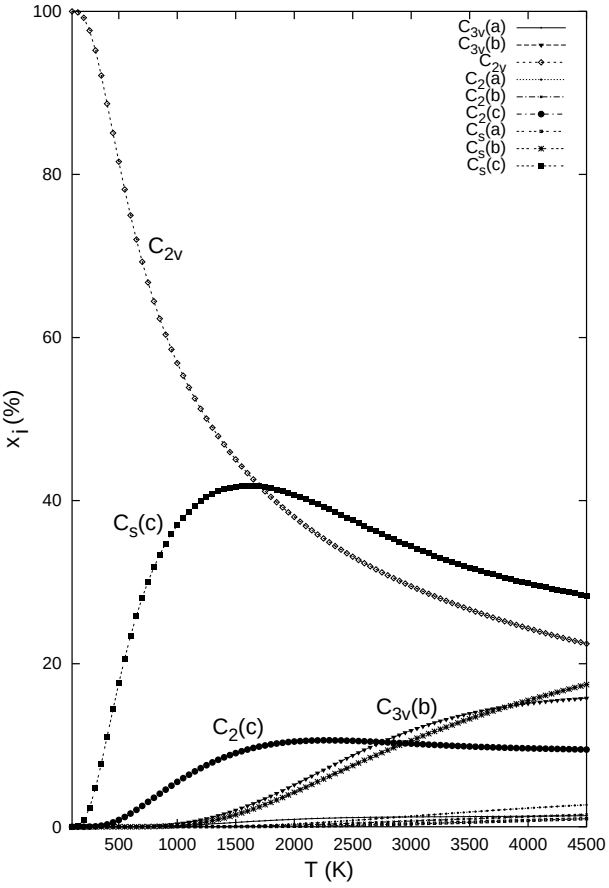

Fig. 2. Relative concentrations of the $Ca@C_{82}$ isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G∼dz entropy.

The $Ca@C_{82}$ structure-energetics relationships were also computed [5] and a qualitative agreement with the experiment found [2]. The computations were performed at the HF and DFT levels and in both cases the C_{2v} structure was the lowest isomer in the potential energy. There were still three other low energy species - C_s, C_2, and C_{3v}. The combined stability computations are now also available for the full set of nine isomers of $Ca@C_{82}$ considered in Ref. [5].

The nine C_{82} IPR structures [20] produce nine $Ca@C_{82}$ cages with the following symmetries recognized [5] at the HF level: C_{3v}(a), C_{3v}(b), C_{2v}, C_2(a), C_2(b), C_2(c), C_s(a), C_s(b), and C_s(c). It has turned out for the structures reoptimized at the B3LYP/3-21G∼dz level that in five cases the original HF structures after the DFT reoptimizations within the same symmetry lead to saddle points with imaginary vibrational frequencies, not to the required local energy minima. When the five saddle points are relaxed and reoptimized, the following local minima are obtained: $C_{3v}(b) \rightarrow C_s$, $C_{2v} \rightarrow C_s$, $C_2(a) \rightarrow C_1$, $C_2(b) \rightarrow C_1$, $C_s(b) \rightarrow C_1$.

Fig. 2 presents the temperature development of the relative concentrations of the nine $Ca@C_{82}$ isomers in a wide temperature region. At very low temperatures the structure lowest in the $\Delta H^o_{0,i}$ scale must be prevailing. However, at a temperature of 1700 K the relative concentrations of the $C_{2v} \rightarrow C_s$ and C_s(c) structures are interchanged and beyond the point the C_s(c) structure is always somewhat more populated. The C_s(c) isomer and also C_2(c) exhibit a temperature maximum. Then, there are still two other structures with significant populations at high temperatures: $C_{3v}(b) \rightarrow C_s$ and $C_s(b) \rightarrow C_1$. Although the former species is a bit more populated, their concentrations are rather close. Fig. 2 is in a reasonable agreement with the qualitative population information [25,28] in a relatively wide temperature interval though the fifth isomer has not been observed yet.

The third illustrative case deals with $La@C_{82}$, i.e., an electronic open-shell system. The $La@C_{82}$ metallofullerene is one of the very first endohedrals that was macroscopically produced [32] and solvent extracted. $La@C_{82}$ has attracted attention of both experiment [33-42] and computations [43-49]. Recently structures of two its isomers were clarified [41,42] using ^{13}C NMR spectra of their monoanions generated electrochemically. The major isomer [41] was thus assigned C_{2v} symmetry and the minor species [42] C_s. The C_{2v} structure was moreover confirmed by an X-ray powder diffraction study [40]. Two isomers could also be extracted [34,36,50] for $Sc@C_{82}$ and $Y@C_{82}$. The findings stand in a contrast to $Ca@C_{82}$ with four known isomers. Computations at *ab initio* HF and DFT levels pointed out [6] just three IPR cages with a sufficiently low energy after La atom encapsulation: C_{2v}, C_{3v}(b), and C_s(c). The fourth lowest La endohedral species, C_2(a), is actually already rather high in energy to be significant in experiment.

An agreement with experiment can be reached (Fig. 3) for temperatures roughly from 1000 to 1300 K when the C_{2v} species is the major isomer followed by an isomer that undergoes C_{3v}/C_s symmetry reduction while the genuine C_s species comes as a still less populated third product. It is possible that the C_{3v} isomer is suppressed in the condensed phase by higher reactivity, however, some additional data are needed.

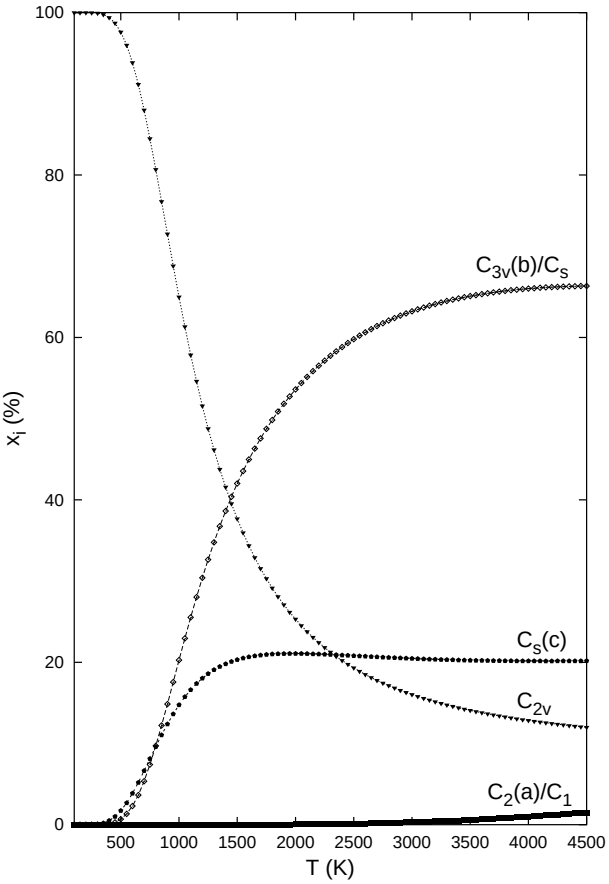

Fig. 3. Relative concentrations of the $La@C_{82}$ isomers based on the B3LYP/6-31G*∼dz energetics and the B3LYP/3-21G∼dz entropy.

ACKNOWLEDGMENTS

The reported research has been supported by a Grant-in-aid for NAREGI Nanoscience Project, Scientific Research on Priority Area (A), and Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and also by the Japan Society for the Promotion of Science.

REFERENCES

[1] J. K. Gimzewski, in *The Chemical Physics of Fullerenes 10 (and 5) Years Later*, Ed. W. Andreoni, Kluwer, Dordrecht, 1996, p. 117.

[2] K. Kobayashi and S. Nagase, in Endofullerenes - A New Family of Carbon Clusters, Eds. T. Akasaka and S. Nagase, Kluwer Academic Publishers, Dordrecht, 2002, p. 155.

[3] W. Harneit, M. Waiblinger, C. Meyer, K. Lips and A. Weidinger, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Vol. 11, *Fullerenes for the New Millennium*, Eds. K. M. Kadish, P. V. Kamat and D. Guldi, Electrochemical Society, Pennington, 2001, p. 358.

[4] K. Kobayashi, S. Nagase, M. Yoshida and E. Ōsawa, J. Am. Chem. Soc. 119, 12693, 1997.

[5] K. Kobayashi and S. Nagase, Chem. Phys. Lett. 274, 226, 1997.
[6] K. Kobayashi and S. Nagase, Chem. Phys. Lett. 282, 325, 1998.
[7] P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299, 1985.
[8] A. D. Becke, J. Chem. Phys. 98, 5648, 1993.
[9] C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785, 1988.
[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh, PA, 1998.
[11] D. R. Kanis, M. A. Ratner, T. J. Marks and M. C. Zerner, Chem. Mater. 3, 19, 1991.
[12] R. D. Bendale and M. C. Zerner, J. Phys. Chem. 99, 13830, 1995.
[13] M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, J. Chem. Phys. 108, 4439, 1998.
[14] Z. Slanina, Int. Rev. Phys. Chem. 6, 251, 1987.
[15] Z. Slanina, F. Uhlík and M. C. Zerner, Rev. Roum. Chim. 36, 965 1991.
[16] M.-L. Sun, Z. Slanina, S.-L. Lee, F. Uhlík and L. Adamowicz, Chem. Phys. Lett. 246, 66, (1995).
[17] Z. Slanina and L. Adamowicz, Thermochim. Acta. 205, 299, 1992.
[18] T. S. M. Wan, H.-W. Zhang, T. Nakane, Z. Xu, M. Inakuma, H. Shinohara, K. Kobayashi and S. Nagase, J. Am. Chem. Soc. 120, 6806, 1998.
[19] S. Nagase, K. Kobayashi and T. Akasaka, J. Mol. Struct. (Theochem) 462, 97, 1999.
[20] P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
[21] Z. Slanina, K. Kobayashi and S. Nagase, Chem. Phys. Lett. 372, 810, 2003.
[22] Z. Slanina, X. Zhao, X. Grabuleda, M. Ozawa, F. Uhlík, P. M. Ivanov, K. Kobayashi and S. Nagase, J. Mol. Graphics Mod. 19, 252, 2001.
[23] L. S. Wang, J. M. Alford, Y. Chai, M. Diener, J. Zhang, S. M. McClure, T. Guo, G. E. Scuseria and R. E. Smalley, *Chem. Phys. Let.* 207, 354, 1993.
[24] Y. Kubozono, T. Ohta, T. Hayashibara, H. Maeda, H. Ishida, S. Kashino, K. Oshima, H. Yamazaki, S. Ukita and T. Sogabe, Chem. Lett. 457, 1995.
[25] Z. D. Xu, T. Nakane and H. Shinohara, J. Am. Chem. Soc. 118, 11309, 1996.
[26] F. G. Hopwood, K. J. Fisher, P. Greenhill, G. D. Willett and R. Zhang, J. Phys. Chem. B 101, 10704, 1997.
[27] T. Kimura, T. Sugai and H. Shinohara, Int. J. Mass Spectrom. 188, 225, 1999.
[28] T. Kodama, R. Fujii, Y. Miyake, K. Sakaguchi, H. Nishikawa, I. Ikemoto, K. Kikuchi and Y. Achiba, Chem. Phys. Lett. 377, 197, 2003.
[29] T. J. S. Dennis and H. Shinohara, Appl. Phys. A 66, 243, 1998.
[30] S. Hino, K. Umishita, K. Iwasaki, M. Aoki, K. Kobayashi, S. Nagase, T. J. S. Dennis, T. Nakane and H. Shinohara, Chem. Phys. Lett. 337, 65, 2001.
[31] T. Kodama, N. Ozawa, Y. Miyake, K. Sakaguchi, H. Nishikawa, I. Ikemoto, K. Kikuchi and Y. Achiba, J. Am. Chem. Soc. 124, 1452, 2002.
[32] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, R. E. Smalley, J. Phys. Chem. 95 (1991) 7564.
[33] R. D. Johnson, M. S. de Vries, J. Salem, D. S. Bethune, C. S. Yannoni, Nature 355 (1992) 239.
[34] S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, Y. Achiba, J. Phys. Chem. 96 (1992) 7159.
[35] S. Bandow, H. Kitagawa, T. Mitani, H. Inokuchi, Y. Saito, H. Yamaguchi, N. Hayashi, H. Sato, H. Shinohara, J. Phys. Chem. 96 (1992) 9609.
[36] M. Hoinkis, C. S. Yannoni, D. S. Bethune, J. R. Salem, R. D. Johnson, M. S. Crowder, M. S. De Vries, Chem. Phys. Lett. 198 (1992) 461.
[37] K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, Y. Achiba, Chem. Phys. Lett. 216 (1993) 67.
[38] C. S. Yannoni, H. R. Wendt, M. S. de Vries, R. L. Siemens, J. R. Salem, J. Lyerla, R. D. Johnson, M. Hoinkis, M. S. Crowder, C. A. Brown, D. S. Bethune, L. Taylor, D. Nguyen, P. Jedrzejewski, H. C. Dorn, Synth. Met. 59 (1993) 279
[39] K. Yamamoto, H. Funasaka, T. Takahasi, T. Akasaka, T. Suzuki, Y. Maruyama, J. Phys. Chem. 98 (1994) 12831.
[40] E. Nishibori, M. Takata, M. Sakata, H. Tanaka, M. Hasegawa, H. Shinohara, Chem. Phys. Lett. 330 (2000) 497.
[41] T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, E. van Caemelbecke, K. M. Kadish, J. Am. Chem. Soc. 122 (2000) 9316.
[42] T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, X. Gao, E. van Caemelbecke, K. M. Kadish, J. Phys. Chem. B 105 (2001) 2971.
[43] S. Nagase, K. Kobayashi, T. Kato, Y. Achiba, Chem. Phys. Lett. 201 (1993) 475.
[44] S. Nagase, K. Kobayashi, Chem. Phys. Lett. 228 (1994) 106.
[45] W. Andreoni, A. Curioni, Phys. Rev. Lett. 77 (1996) 834.
[46] K. Kobayashi, S. Nagase, Chem. Phys. Lett. 282 (1998) 325.
[47] J. Lu, X. W. Zhang, X. G. Zhao, S. Nagase, K. Kobayashi, Chem. Phys. Lett. 332 (2000) 219.
[48] K. Kobayashi and S. Nagase, in Endofullerenes - A New Family of Carbon Clusters, eds. T. Akasaka, S. Nagase, Kluwer Academic Publishers, Dordrecht, 2002, p. 155.
[49] K. Kobayashi, S. Nagase, Mol. Phys. 101 (2003) 249
[50] E. Nishibori, M. Takata, M. Sakata, M. Inakuma, H. Shinohara, Chem. Phys. Lett. 298 (1998) 79.