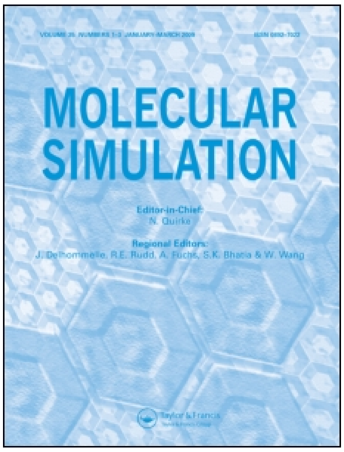

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Computing fullerene encapsulation of non-metallic molecules: $N_2@C_{60}$ and $NH_3@C_{60}$

Z. Slanina[a]; F. Uhlík[b]; L. Adamowicz[c]; S. Nagase[d]
[a] Institute of Chemistry, Academia Sinica, Taipei, TaivanROC [b] School of Science, Charles University, Prague, Czech Republic [c] Department of Chemistry, University of Arizona, Tucson, AZ, USA [d] Department of Theoretical Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, Japan

To cite this Article Slanina, Z. , Uhlík, F. , Adamowicz, L. and Nagase, S.(2005) 'Computing fullerene encapsulation of non-metallic molecules: $N_2@C_{60}$ and $NH_3@C_{60}$', Molecular Simulation, 31: 12, 801 — 806
To link to this Article: DOI: 10.1080/08927020500283966
URL: http://dx.doi.org/10.1080/08927020500283966

Molecular Simulation, Vol. 31, No. 12, 15 October 2005, 801–806

Computing fullerene encapsulation of non-metallic molecules: $N_2@C_{60}$ and $NH_3@C_{60}$

Z. SLANINA†‡*, F. UHLÍK¶, L. ADAMOWICZ§ and S. NAGASE†

†Department of Theoretical Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan
‡Institute of Chemistry, Academia Sinica, Taipei 11529, TaivanROC
¶School of Science, Charles University, 128 43 Prague, 2, Czech Republic
§Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041, USA

(Received July 2005; in final form July 2005)

Some endohedral fullerenes have been considered as possible candidate species for molecular memories. Recently, the encapsulation inside the fullerene cages has been extended from atoms to small molecules, for example the nitrogen molecule was placed inside the fullerene cage. The observed $N_2@C_{60}$ endohedral is computed in the paper together with $NH_3@C_{60}$, which was not yet observed. The computations are based on structural optimizations using density-functional theory (DFT) methods. In the optimized structures, the analytical harmonic vibrational analysis was carried out and the encapsulation energetics were evaluated using the second order Møller-Plesset (MP2) perturbation treatment. The lowest-energy structure has the N_2 unit oriented towards a pair of parallel pentagons so that the complex exhibits D_{5d} symmetry. At the MP2 level, the encapsulation of N_2 into C_{60} brings a potential energy gain of -9.3 kcal/mol while that for NH_3 is -5.2 kcal/mol. The entropy term is also evaluated, yielding the standard Gibbs-energy change at room temperature for the encapsulation of N_2 and NH_3 of -2.6 and 1.5 kcal/mol, respectively. Some computed structural and vibrational characteristics are also reported. Emerging broader landscape of future applications of such encapsulates in nanoscience and nantechnology is discussed.

Keywords: Endohedral fullerenes; Bonding and stability; Gibbs-energy evaluations; Molecular encapsulation; Carbon-based nanoscience

1. Introduction

$N_2@C_{60}$ and $N_2@C_{70}$ were first prepared by heating under high pressure by Peres *et al.* [1]. Out of two thousand C_{60} molecules only one was observed to incorporate N_2. The nitrogen molecule containing endohedrals were present even after several-hours of heating at 500 K. $N_2@C_{60}$ was also reported [2,3] in the chromatographic separation after the nitrogen-ion implantation into C_{60}. This ion bombardment is primarily used for the $N@C_{60}$ production [4,5] with very low yields ($Li@C_{60}$ was also prepared by the ion bombardment method [6]). Still, $N@C_{60}$ and its derivatives were studied vigorously [7–11]. Other non-metallic endohedrals are represented by complexes of fullerenes with rare gas atoms, in particular with He [12–16]. Very recently, molecular hydrogen [17] and also a water molecule [18] were placed inside open-cage fullerenes. This paper presents computations on $N_2@C_{60}$ and $NH_3@C_{60}$ in order to judge their stability and compare with other available endohedral data [19–23], especially for $N@C_{60}$.

2. Computations

The computations started with a search for stationary points by geometry optimizations using density-functional theory (DFT) methods. The standard 3-21G basis set was used at this stage and applied in two different DFT approaches. One of them employs Becke's [24] three parameter exchange functional with the non-local Lee-Yang-Parr [25] correlation functional (B3LYP) with the above basis set, i.e. the B3LYP/3-21G treatment. The other approach uses Perdew and Wang's [26] exchange and correlation functionals known as PW91. The geometry optimizations were carried out using the analytical energy gradient. In the optimized stationary points, the analytical harmonic vibrational analysis was carried out in order to check their physical nature by the number of imaginary vibrational frequencies. The ultrafine grid in numerical integrations of the DFT functional and the tight SCF convergency criterion were used. The reported computations have been carried out with the Gaussian program packages [27,28].

---

*Corresponding author. Email: zdenek@ims.ac.jp

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500283966

In the optimized B3LYP/3-21G and PW91/3-21G geometries, additional single point energy calculations were carried out using the second order Møller-Plesset (MP2) perturbation treatment [29,30] with frozen core (FC) option, in which inner-shells are excluded from the correlation calculation, with the the standard 6-31G* basis set (MP2 = FC/6-31G*). The basis set superposition error (BSSE) was estimated by the Boys-Bernardi counterpoise method [31].

In addition to the interaction (dimerization or stabilization) energy, the standard entropy change upon the encapsulation was also evaluated (the 1 atm standard-state choice). The conventional rigid-rotator and harmonic-oscillator partition functions [32] were used and no frequency scaling was applied.

3. Results and discussion

The B3LYP treatment represents a prevailing choice at present for general thermochemical computations [33]. The B3LYP functional has also been the most common DFT option in the computations [34,35] of fullerenes and endohedrals. However, it was pointed out recently [36,37] that the Becke exchange functional due to its erroneous asymptotic behaviour does not produce physically acceptable description of the attraction between weakly bonded systems. It was shown [38] that the BLYP or B3LYP treatments do not produce weak energy minima in the long-range region otherwise well established by the MP2 or coupled cluster calculations. It was suggested [36–38] to use Perdew and Wang's [26] exchange and correlation functionals PW91 instead. The PW91 functional at least partly recovers the attraction [38]. Its error in the computed binding energies [38] for the hydrogen-bonded complexes was 20% in the worst case though somewhat bigger in some still weaker complexes. With respect to this finding, the DFT computations in this paper are carried out not only with the B3LYP but also with PW91 functionals.

In both the B3LYP/3-21G and PW91/3-21G treatments, the lowest-energy structure $N_2@C_{60}$ found has the N_2 unit oriented towards a pair of parallel pentagons so that the complex exhibits D_{5d} symmetry (5:5 structure, see Figure 1). Such a minimum energy structure was also found for $NH_3@C_{60}$ (Figure 2). The stationary points were reached without symmetry constraints so that some numerical inaccuracy could influence the point-group determination. In fact, the G98 symmetry finder extracts only C_i symmetry for $N_2@C_{60}$. However, application of a procedure [39] allowing for variable precision of the optimized coordinates concludes the D_{5d} symmetry while in the $NH_3@C_{60}$ we deal with C_s symmetry. Moreover, the encapsulates are to exercise motions around the equilibrium position with an averaging effect. It has been known [40] that more symmetric structures for

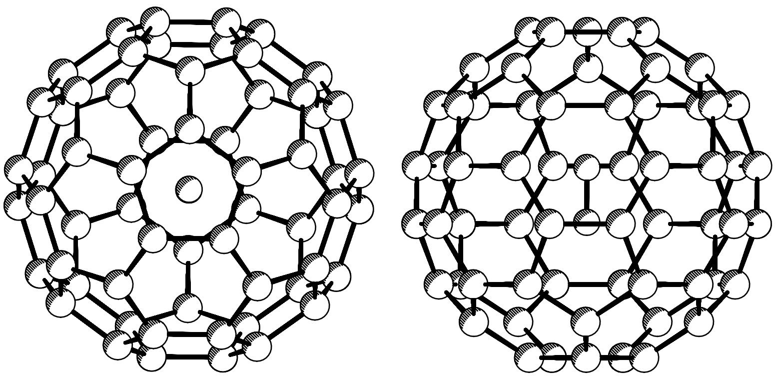

Figure 1. Two views of the PW91/3-21G optimized structure of $N_2@C_{60}$.

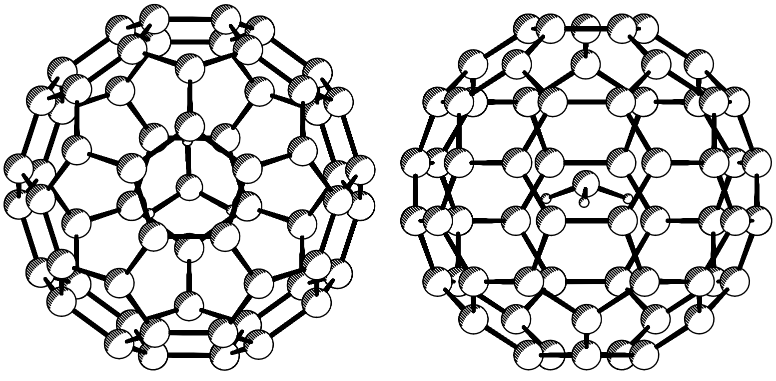

Figure 2. Two views of the B3LYP/3-21G optimized structure of $NH_3@C_{60}$.

endohedrals can in fact be saddle points and not local minima. Then, it is sometimes actually more effective to optimize their structures without symmetry constraints. In any case, the vibrational analysis is an important check for the optimized endohedral structures. The harmonic vibrational analysis confirms that the 5:5 structures are indeed local energy minima.

The interaction hypersurface is very shallow as can be illustrated by the following data. Another optimized $N_2@C_{60}$ stationary point has the N_2 unit oriented towards a pair of parallel hexagons—a 6:6 structure. The 6:6 structure is however not a local energy minimum but a saddle point. Still, it is very close in energy to the 5:5 structure. In both the B3LYP/3-21G and PW91/3-21G approaches the 6:6 species is located less than 0.1 kcal/mol above the 5:5 structure. This feature documents that the interaction hypersurface is indeed very flat and at elevated temperatures the encapsulate unit should exhibit large-amplitude motions. In the 5:5 $N_2@C_{60}$ equilibrium structure, the closest computed N—C distance is 3.046 and 3.049 Å in the B3LYP/3-21G and PW91/3-21G method, respectively. The Mulliken partial charge on the N atoms is positive but very small, about 0.01, so that the charge transfer to the cage is negligible.

The computed interaction or stabilization energies have thermochemically the meaning of potential-energy change along the formal encapsulation processes:

$$N_2 + C_{60} = N_2@C_{60} \quad (1)$$

$$NH_3 + C_{60} = NH_3@C_{60} \quad (2)$$

Table 1 presents the MP2 = FC/6-31G* encapsulation energies before and after the BSSE correction. The value of -17.5 kcal/mol for $N_2@C_{60}$ before the BSSE correction corresponds to -7.3 kcal/mol computed [22] at the same level for $N@C_{60}$. After addition of the BSSE correction, the MP2 = FC/6-31G* stabilization for $N_2@C_{60}$ is reduced to still significant -9.28 kcal/mol while the stabilization for $NH_3@C_{60}$ is -5.23 kcal/mol. In the latter case, the stabilization can be slightly increased upon application of the MP2 = FC/6-31G(**) level: the MP2 = FC/6-31G$*$ term of -16.56 kcal/mol before BSSE changes to -17.89 kcal/mol in the MP2 = FC/6-31G(**) approach for $NH_3@C_{60}$. Effect of the functional used in the geometry optimization is negligible—for example in the $NH_3@C_{60}$ case change from the B3LYP/3-21G to PW91/3-21G geometry changes the encapsulation energy from -5.23 to just -5.25 kcal/mol. It is however likely [21] that the values will still be modified when larger basis-set computations will be possible.

Table 1. The MP2 = FC/6-31G* encapsulation energy ΔE_{pot} for $N_2@C_{60}$ and $NH_3@C_{60}$ with the 5:5 orientation†

Species	*ΔE_{pot} (kcal/mol)*	
	MP2=FC/6-31G*	*MP2=FC/6-31G* & BSEE‡*
$N_2@C_{60}$	-17.52	-9.28
$NH_3@C_{60}$	-16.56	-5.23

† See Figures 1 and 2.

‡ Estimated according to the Boys-Bernardi counterpoise method [31].

There are 180 vibrational modes in $N_2@C_{60}$. One of them is the N—N bond stretching mode [41], five are vibrations of the N_2 unit against the cage, and the remaining 174 modes are skeletal vibrations of the C_{60} cage. The N—N bond stretching frequency is only slightly affected by the encapsulation. Interestingly the N—N frequency increases in the B3LYP/3-21G approach but decreases in the PW91/3-21G treatment. The shift is large enough to be significant in observation. The changes in the N—N frequency upon encapsulation are parallel with the changes in the N—N bond distance as in the B3LYP/3-21G computations the bond is slightly compressed while in the PW91/3-21G case the bond is expanded by about 0.0003 Å. The five frequencies for the N_2-cage vibrations are low but they could be observed as it was recently possible [42,43] for $La@C_{82}$. The inter-system frequencies at the B3LYP/3-21G level are 25.4, 38.9, 83.6, 84.6, and 126.1 cm^{-1} while for the PW91/3-21G approach they read 45.9, 49.1, 55.9, 65.3, and 106.7 cm^{-1}.

The high symmetry of C_{60} considerably simplifies [44,45] its vibrational spectrum, for example, only four T_{1u} three-fold degenerate modes are actually active in its IR spectrum. Once the high symmetry is reduced upon introduction of an encapsulate, the symmetry selection rules will not be the same. However, in fact out of the 174 cage modes in $N_2@C_{60}$ just twelve show significant IR intensities and similarly for $NH_3@C_{60}$ (table 2). Those IR active modes are actually rooted in the original T_{1u} three-fold degenerate modes of C_{60}.

The stabilization energies from equations (1) and (2) are the potential-energy changes along the reactions. In order to get the related enthalpy change ΔH_T^o at a temperature T, the zero-point vibrational energy and heat-content functions are to be added though the change will be small. Once the corresponding entropy change ΔS_T^o is

Table 2. IR active vibrational frequencies (cm^{-1}) of $N_2@C_{60}$ and $NH_3@C_{60}$ with the 5:5 orientation.

*C_{60}** *PW91/3-21G*	*$N_2@C_{60}$* *PW91/3-21G*	*C_{60}** *B3LYP/3-21G*	*$NH_3@C_{60}$* *B3LYP/3-21G*
483.4	478.3	511.7	503.6
	478.7		503.9
	479.8		508.9
572.3	571.7	582.3	581.9
	571.8		582.4
	571.9		582.5
1157.8	1157.2	1177.4	1177.6
	1157.3		1177.8
	1157.7		1177.8
1436.1	1435.7	1453.0	1452.4
	1435.8		1452.9
	1436.8		1455.2

* All the four IR active species in the pristine C_{60} are triply degenerate T_{1u} modes (the observed [45] fundamentals of gas-phase C_{60}: 527.1, 570.3, 1169.1 and 1406.9 cm^{-1}).

Table 3. The computed standard* thermodynamic terms at room temperature for formation of $N_2@C_{60}$ and $NH_3@C_{60}$ with the 5:5 orientation (kcal/mol).

Process/term†	*Approach*‡	
$N_2 + C_{60} = N_2@C_{60}$	Rigid	Non-rigid
ΔE_{pot}	−9.28	−9.28
ΔH^o_{298}	−8.58	−8.58
ΔTS^o_{298}	−5.95	−7.01
ΔG^o_{298}	−2.64	−1.58
$NH_3 + C_{60} = NH_3@C_{60}$	Rigid	Non-rigid
ΔE_{pot}	−5.23	−5.23
ΔH^o_{298}	−3.92	−3.92
ΔTS^o_{298}	−5.46	−7.88
ΔG^o_{298}	1.53	3.96

* The standard state—ideal gas phase at 101325 Pa pressure.

† The potential energy change ΔE_{pot}, and the standard changes of enthalpy ΔH^o_{298}, entropy ΔTS^o_{298}, Gibbs energy ΔG^o_{298} at room temperature $T = 298.15$ K.

‡ Two approaches to the encapsulate motions are described in the text.

evaluated, one can deal with the thermodynamics controlling Gibbs-energy term ΔG^o_T. Using the partition functions from the DFT calculations, the $T\Delta S^o_T$ term at room temperature for $N_2@C_{60}$ and $NH_3@C_{60}$ comes as −5.95 and −5.46 kcal/mol, respectively (table 3).

Let us mention that the entropy evaluations require a due care paid to the symmetry numbers. One issue is that quantum chemistry programs rarely produce the correct symmetry number [46,47] of 60 for C_{60}. However, more important aspect deals with the averaging effect of the encapsulate motions. As the encapsulate moves nearly freely inside the cage, it will effectively recover the icosahedral symmetry of the system. There are thus two approaches to the effects of the encapsulate motions upon the symmetry number: (i) the static symmetry number derived for a rigid endohedral, or (ii) effectively icosahedral symmetry created by non-rigid, fluxional location of the encapsulate. Table 3 shows that the differences between the rigid and non-rigid approach are rather moderate at room temperature.

If the entropy values are combined with the enthalpy terms derived from the BSSE corrected MP2=FC/6-31G* stabilization energy, the ΔG^o_T standard changes for reactions (1) and (2) at room temperature read −2.64 and 1.53 kcal/mol, respectively. The latter terms represent the driving thermodynamic force for the encapsulation processes according to the presently available computational data. The value should be further checked, especially with respect [48] to the BSSE correction and basis-set finiteness in general, when computationally feasible. There are other interesting non-metal fullerene encapsulates to be studied, like $H_2O@C_{60}$ [1] or $H_2@C_{60}$ [49].

Interestingly, the computed entropy changes for encapsulation are quite similar to the dimerization entropy for water in gas phase [50,51]. There are no entropy data available yet for formation of other fullerene endohedrals, however, it is clear that the stabilization ΔG^o_T terms would represent a unified thermodynamic stability measure. For a complete gas-phase picture, the ΔG^o_T terms or the encapsulation equilibrium constants should be combined [52] with the typical partial pressures accessible to the fullerene cage and encapsulate under particular experimental conditions. There are however essential kinetic [53,54] and in particular catalytic [16,55–57] aspects obviously involved, too.

4. Outlook

All the above computational steps clearly represent important factors to be mastered before more practical applications of fullerene/nanotube-based computational nanoscience and nanotechnology can be launched [58–65]. At present, considerations about quantum computing focus on a usage of spin states of a nitrogen atom encapsulated in the C_{60} cage, $N@C_{60}$ [4–11,19–23,59,66]. The state of the electron spin in an external magnetic field could be read by NMR or ESR pulse. Molecular transistors based on fullerenes or nanotubes represent another interesting option for molecular electronics. Nano-memory devices could also be based on nanotubes filled with fullerenes, known as peapods. Still another option for molecular memories is suggested [58] by fullerene endohedrals allowing for two locations of the encapsulate. As long as the two locations are distinguishable, they can in principle serve for coding the information bit. The stability and distinguishability of the sites are closely related to the encapsulate motions [66–68]. This emerging picture stresses an indispensable role of computational modelling in screening and tailoring agents of nanoscience and nanotechnology.

Acknowledgements

The reported research has been supported by a Grant-in-aid for NAREGI Nanoscience Project, and for Scientific Research on Priority Area (A) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and by the Czech National Research Program "Information Society" (Czech Acad. Sci. 1ET401110505).

References

[1] T. Peres, B.P. Cao, W.D. Cui, A. Khong, R.J. Cross, M. Saunders, C. Lifshitz. Some new diatomic molecule containing endohedral fullerenes. *Int. J. Mass Spectr.*, **210**, 241 (2001).

[2] T. Suetsuna, N. Dragoe, W. Harneit, A. Weidinger, H. Shimotani, S. Ito, H. Takagi, K. Kitazawa. Separation of $N_2@C_{60}$ and $N@C_{60}$. *Chem. Eur. J.*, **8**, 5079 (2002).

[3] T. Suetsuna, N. Dragoe, W. Harneit, A. Weidinger, H. Shimotani, S. Ito, H. Takagi, K. Kitazawa. Separations of $N_2@C_{60}$ and $N@C_{60}$. (vol 8, pg 5079, 2002) *Chem. Eur. J.*, **9**, 598 (2003).

[4] T.A. Murphy, Th. Pawlik, A. Weidinger, M. Höhne, R. Alcala, J.-M. Spaeth. Observation of atomlike nitrogen in nitrogen-implanted solid C_{60}. *Phys. Rev. Lett.*, **77**, 1075 (1996).

[5] C. Knapp, K.-P. Dinse, B. Pietzak, M. Waiblinger, A. Weidinger. Fourier transform EPR study of $N@C_{60}$ in solution. *Chem. Phys. Lett.*, **272**, 433 (1997).

[6] A. Gromov, N. Krawez, A. Lassesson, D.I. Ostrovskii, E.E.B. Campbell. Optical properties of endohedral Li@C_{60}. *Curr. App. Phys.*, **2**, 51 (2002).

[7] B. Pietzak, M. Waiblinger, T.A. Murphy, A. Weidinger, M. Höhne, E. Dietel, A. Hirsch. Buckminsterfullerene C_{60}: a chemical Faraday cage for atomic nitrogen. *Chem. Phys. Lett.*, **279**, 259 (1997).

[8] E. Dietel, A. Hirsch, B. Pietzak, M. Waiblinger, K. Lips, A. Weidinger, A. Gruss, K.-P. Dinse. Atomic nitrogen encapsulated in fullerenes: Effects of cage variations. *J. Am. Chem. Soc.*, **121**, 2432 (1999).

[9] B.P. Cao, T. Peres, R.J. Cross, M. Saunders, C. Lifshitz. Do nitrogen-atom-containing endohedral fullerene undergo the shrink-wrap mechanism? *J. Phys. Chem. A*, **105**, 2142 (2001).

[10] K. Kobayashi, S. Nagase, K.-P. Dinse. A theoretical study of spin density distributions and isotropic hyperfine couplings of N and P atoms in N@C_{60}, P@C_{60}, N@C_{70}, N@C_{60} $(CH_2)_6$, and N@C_{60} $(SiH_2)_6$. *Chem. Phys. Lett.*, **377**, 93 (2003).

[11] T. Wakahara, Y. Matsunaga, A. Katayama, Y. Maeda, M. Kako, T. Akasaka, M. Okamura, T. Kato, Y.K. Choe, K. Kobayashi, S. Nagase, H.J. Huang, M. Atae. A comparison of the photochemical reactivity of N@C_{60} and C_{60}: photolysis with disilirane. *Chem. Commun.*, 2940 (2003).

[12] M. Saunders, H.A. Jiménez-Vázquez, R.J. Cross, R.J. Poreda. Stable Compounds of Helium and Neon: He@C_{60} and Ne@C_{60}. *Science*, **259**, 1428 (1993).

[13] M. Saunders, H.A. Jiménez-Vázquez, R.J. Cross, S. Mroczkowski, D.I. Freedberg, F.A.L. Anet. Probing the Interior of Fullerenes by 3He NMR Spectroscopy of Endohedral ^{3}He@C_{60} and ^{3}He@C_{70}. *Nature*, **367**, 256 (1994).

[14] M. Saunders, R.J. Cross, H.A. Jiménez-Vázquez, R. Shimshi, A. Khong. Noble gas atoms inside fullerenes. *Science*, **271**, 1693 (1996).

[15] R.J. Cross, M. Saunders, H. Prinzbach. Putting Helium inside Dodecahedrane. *Org. Lett.*, **1**, 1479 (1999).

[16] Y. Rubin, T. Jarrosson, G.-W. Wang, M.D. Bartberger, K.N. Houk, G. Schick, M. Saunders, R.J. Cross. Insertion of helium and molecular hydrogen through the orifice of an open fullerene. *Angew. Chem. Int. Ed.*, **40**, 1543 (2001).

[17] M. Carravetta, Y. Murata, M. Murata, I. Heinmaa, R. Stern, A. Tontcheva, A. Samoson, Y. Rubin, K. Komatsu, M.H. Levitt. Solid-state NMR spectroscopy of molecular hydrogen trapped inside an open-cage fullerene. *J. Am. Chem. Soc.*, **126**, 4092 (2004).

[18] S.-I. Iwamatsu, T. Uozaki, K. Kobayashi, S. Re, S. Nagase, S. Murata. A Bowl-Shaped Fullerene Encapsulates a Water into the Cage. *J. Am. Chem. Soc.*, **126**, 2668 (2004).

[19] C.I. Williams, M.A. Whitehead, L. Pang. Interaction and dynamics of endohedral gas molecules in fullerene C_{60} isomers and C_{70}. *J. Phys. Chem.*, **97**, 11652 (1993).

[20] J.C. Greer. The atomic nature of endohedrally encapsulated nitrogen N@C_{60} studied by density functional and Hartree-Fock methods. *Chem. Phys. Lett.*, **326**, 567 (2000).

[21] J.A. Larsson, J.C. Greer, W. Harneit, A. Weidinger. Phosphorous trapped within buckminsterfullerene. *J. Chem. Phys.*, **116**, 7849 (2002).

[22] J.M. Park, P. Tarakeshwar, K.S. Kim, T. Clark. Nature of the interaction of paramagnetic atoms (A=^{4}N, ^{4}P, ^{3}O, ^{3}S) with π systems and C_{60}: A theoretical investigation of A…C_6H_6 and endohedral fullerenes A@C_{60}. *J. Chem. Phys.*, **116**, 10684 (2002).

[23] B. Pietzak, A. Weidinger, K.-P. Dinse, A. Hirsch. Group V endohedral fullerenes: N@C_{60}, N@C_{70}, and P@C_{60}. In *Endofullerenes—A New Family of Carbon Clusters*, T. Akasaka, S. Nagase (Eds.), p. 13, Kluwer Academic Publishers, Dordrecht (2002).

[24] A.D. Becke. Density-functional thermochemistry III. The role of exact exchange. *J. Chem. Phys.*, **98**, 5648 (1993).

[25] C. Lee, W. Yang, R.G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **37**, 785 (1988).

[26] J.P. Perdew, Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, **45**, 13244 (1992).

[27] 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, J.A. Pople. *Gaussian 98, revision A.9*, Gaussian, Inc., Pittsburgh, PA (1998).

[28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03, revision C.01*, Gaussian, Inc., Wallingford, CT (2004).

[29] C. Møller, M.S. Plesset. Note on an approximation treatment for many-electron systems. *Phys. Rev.*, **46**, 618 (1934).

[30] R. Krishnan, J.A. Pople. Approximate 4th-order perturbation theory of the electron correlation energy. *Int. J. Quant. Chem.*, **14**, 91 (1978).

[31] S.F. Boys, F. Bernardi. The calculation of small molecular interactions by the difference of separate total energies. Some procedures with reduced errors. *Mol. Phys.*, **19**, 553 (1970).

[32] Z. Slanina. Equilibrium isomeric mixtures: Potential energy hypersurfaces as originators of the description of the overall thermodynamics and kinetics. *Int. Rev. Phys. Chem.*, **6**, 251 (1987).

[33] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople. Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation. *J. Chem. Phys.*, **106**, 1063 (1997).

[34] J. Cioslowski. *Electronic Structure Calculations on Fullerenes and Their Derivatives*, Oxford University Press, Oxford (1995).

[35] G.E. Scuseria. Theoretical studies of fullerenes. In *Modern Electronic Structure Theory, Part I*, D.R. Yarkony (Ed.), p. 279, World Scientific, Singapore (1995).

[36] Y.K. Zhang, W. Pan, W.T. Yang. Describing van der Waals interaction in diatomic molecules with generalized gradient approximations: The role of the exchange functional. *J. Chem. Phys.*, **107**, 7921 (1997).

[37] T.A. Wesolowski, O. Parisel, Y. Ellinger, J. Weber. Comparative study of benzene…X (X=O2, N2, CO) complexes using density functional theory: The importance of an accurate exchange-correlation energy density at high reduced density gradients. *J. Phys. Chem. A*, **101**, 7818 (1997).

[38] S. Tsuzuki, H.P. Lüthi. Interaction energies of van der Waals and hydrogen bonded systems calculated using density functional theory: Assessing the PW91 model. *J. Chem. Phys.*, **114**, 3949 (2001).

[39] M.-L. Sun, Z. Slanina, S.-L. Lee, F. Uhlík, L. Adamowicz. AM1 computations on seven isolated-pentagon-rule isomers of C_{80}. *Chem. Phys. Lett.*, **246**, 66 (1995).

[40] Z. Slanina, K. Kobayashi, S. Nagase. Ca@C_{82} isomers: computed temperature dependency of relative concentrations. *J. Chem. Phys.*, **120**, 3397 (2004).

[41] K.P. Huber, G. Herzberg. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, p. 716, Van Nostrand Reinhold Company, New York (1979).

[42] S. Lebedkin, B. Renker, R. Heid, H. Schober, H. Rietschel. A spectroscopic study of M@C_{82} metallofullerenes: Raman, far-infrared, and neutron scattering results. *Appl. Phys. A*, **66**, 273 (1998).

[43] K. Kobayashi, S. Nagase. Theoretical calculations of vibrational modes in endohedral metallofullerenes: La@C_{82} and Sc_2@C_{84}. *Mol. Phys.*, **101**, 249 (2003).

[44] Z. Slanina, J.M. Rudziński, M. Togasi, E. Ōsawa. Quantum-chemically supported vibrational analysis of giant molecules: The C_{60} and C_{70} clusters. *J. Mol. Struct. (Theochem)*, **202**, 169 (1989).

[45] C.I. Frum, R. Engleman Jr, H.G. Hedderich, P.F. Bernath, L.D. Lamb, D.R. Huffman. The infrared emission spectrum of gas-phase C60 (buckmisterfullerene). *Chem. Phys. Lett.*, **176**, 504 (1991).

[46] Z. Slanina. Some aspects of mathematical chemistry of equilibrium and rate processes: Steps towards a completely non-empirical computer design of syntheses. *J. Mol. Struct. (Theochem)*, **185**, 217 (1989).

[47] Z. Slanina, F. Uhlík, J.-P. François, E. Ōsawa. Thermodynamic data bases and optical isomerism. *Croat. Chem. Acta*, **73**, 1047 (2000).

[48] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe. State-of-the-art in counterpoise theory. *Chem. Rev.*, **94**, 1873 (1994).

[49] K. Komatsu, M. Murata, Y. Murata. Encapsulation of molecular hydrogen in fullerene C_{60} by organic synthesis. *Science*, **307**, 238 (2005).

[50] Z. Slanina. Energetics, vibrations and thermodynamics of $(H_2O)_2(g)$ revised: MCY vs MCY-B potential. *Chem. Phys. Lett.*, **127**, 67 (1986).

[51] Z. Slanina. A comparative study of the water-dimer gas-phase thermodynamics in the BJH- and MCYL-type flexible potentials. *Chem. Phys.*, **150**, 321 (1991).

[52] Z. Slanina. Entropy-controlled reactions: An interesting textbook error. *J. Chem. Educ.*, **68**, 474 (1991).

[53] T.R. Walsh, D.J. Wales. Relaxation dynamics of C60. *J. Chem. Phys.*, **109**, 6691 (1998).

[54] K. Kobayashi, S. Nagase. Structures and electronic properties of endohedral Metallofullerenes; Theory and Experiment. In *Endofullerenes—A New Family of Carbon Clusters*, T. Akasaka, S. Nagase (Eds.), p. 99, Kluwer Academic Publishers, Dordrecht (2002).

[55] B.R. Eggen, M.I. Heggie, G. Jungnickel, C.D. Latham, R. Jones, P.R. Briddon. Autocatalysis during fullerene growth. *Science*, **272**, 87 (1996).

[56] S. Patchkovskii, W. Thiel. How does helium get into buckminsterfullerene? *J. Am. Chem. Soc.*, **118**, 7164 (1996).

[57] S. Patchkovskii, W. Thiel. Radical impurity mechanisms for helium incorporation into buckminsterfullerene. *Helv. Chim. Acta*, **80**, 495 (1997).

[58] J.K. Gimzewski. Scanning tunneling and local probe studies of fullerenes. In *The Chemical Physics of Fullerenes 10 (and 5) Years Later*, W. Andreoni (Ed.), p. 117, Kluwer Academic Publishers, Dordrecht (1996).

[59] W. Harneit, M. Waiblinger, C. Meyer, K. Lips, A. Weidinger. Concept for quantum computing with N@C_{60}. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, K.M. Kadish, P.V. Kamat, D. Guldi (Eds.), Fullerenes for the New MillenniumVol. 11, p. 358, Electrochemical Society, Pennington (2001).

[60] A. Ardavan, M. Austwick, S.C. Benjamin, G.A.D. Briggs, T.J.S. Dennis, A. Ferguson, D.G. Hasko, M. Kanai, A.N. Khlobystov, B.W. Lovett, G.W. Morley, R.A. Oliver, D.G. Pettifor, K. Porfyrakis, J.H. Reina, J.H. Rice, J.D. Smith, R.A. Taylor, D.A. Williams, C. Adelmann, H. Mariette, R.J. Hamers. Nanoscale solid-state quantum computing. *Phil. Trans. Roy. Soc. London A*, **361**, 1473 (2003).

[61] K.E. Drexler, R.E. Smalley. Nanotechnology. Drexler and Smalley make the case for and against ‘molecular assemblers’. *Chem. Engn. News*, **81**(48), 37 (2003).

[62] M.S. Dresselhaus, Y.M. Lin, O. Rabin, A. Jorio, A.G. Souza, M.A. Pimenta, R. Saito, G.G. Samsonidze, G. Dresselhaus. Nanowires and nanotubes. *Mater. Sci. Engn. C*, **23**, 129 (2003).

[63] N. Tagmatarchis, M. Prato. Fullerene-based materials: Structure and properties. *Struct. Bond.*, **109**, 1 (2004).

[64] Z. Slanina, K. Kobayashi, S. Nagase. Isomeric fullerenes and endofullerenes: stability computations on promising nanoscience agents. In *Handbook of Theoretical and Computational Nanotechnology*, M. Rieth, W. Schommers (Eds.), American Scientific Publishers, Stevenson Ranch, CA (2005).

[65] R.K. Gupta, I. Dwivedy. International patenting activity in the field of carbon nanotubes. *Curr. Appl. Phys.*, **5**, 163 (2005).

[66] F. Uhlík, Z. Slanina, E. Ōsawa. Thermodynamic properties of N@C_{60}. In *Electronic Properties of Novel Materilas—Molecular Nanostructures*, H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), p. 183, AIP, Melville, New York (2000).

[67] F. Uhlík, Z. Slanina, E. Ōsawa. Thermodynamic properties of He@C_{60}. *Fullerene Sci. Technol.*, **8**, 453 (2000).

[68] F. Uhlík, Z. Slanina, E. Ōsawa. Thermodynamic properties of He inside fullerenes and nanotubes. *Mol. Mater.*, **13**, 231 (2000).