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REGULAR ARTICLE

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# Computing relative stabilities of metallofullerenes by Gibbs energy treatments

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**Abstract** The paper presents computations on endohedral fullerene systems, combining the treatments of quantum chemistry and statistical mechanics. The procedure is illustrated on evaluations of relative concentrations for five isomers of Ca@$C_{72}$, nine isomers of Ca@$C_{82}$, four isomers of La@$C_{82}$, and two isomers of $Sc_3N$@$C_{80}$. The results point out the enthalpy–entropy interplay in the systems produced under high temperatures. Approaches to description of the encapsulate motions are analyzed and a free encapsulate approximation is suggested for further use.

**Keywords** Metallofullerenes · Gibbs-energy evaluations · Cluster relative stabilities · Optimized syntheses · Fullerene-based nanoscience

## 1 Introduction

Since their discovery 20 years ago, fullerenes and metallofullerenes have been vigorously studied [1] by both experiment and theory. Fullerenes are commonly defined as polyhedral cages containing only carbon atoms arranged primarily into five- and six-membered rings though quasi-fullerenes with other types of rings (like squares or heptagons) are possible. Fullerenes and metallofullerenes are not only the objects of a pure basic research. Various endohedral cage compounds have been suggested as possible candidate species for molecular memories [2,3]. In spite of the extended research in fullerene science, fullerene/metallofullerene formation mechanisms are virtually unknown. Nevertheless, thermodynamic aspects like relative stabilities can still be computed without any knowledge of the formation mechanisms.

In this report, relative stability computations are illustrated on four systems, combining the treatments of quantum chemistry and statistical mechanics, namely on five isomers of Ca@$C_{72}$, nine isomers of Ca@$C_{82}$, four isomers of La@$C_{82}$, and two isomers of $Sc_3N$@$C_{80}$. While the stability reasoning has traditionally been based on mere potential-energy differences [4–6], we treat the issue in terms of the Gibbs energy so that temperature effects can be included accordingly. Moreover, a more realistic and reliable modification of the treatment is suggested. The inclusion of entropy effects requires by about one order of magnitude larger computational efforts compared to the traditional use of the potential–energy differences. However, once temperatures are high, as it is the case with fullerene/metallofullerene syntheses, the temperature–entropy product TS becomes substantial and cannot be ignored.

## 2 Computational details

The computations are carried using the density-functional theory (DFT), primarily with a combined basis set: 3-21G basis for C atoms and a dz basis set [7] with the effective core potential on metal (for the sake of simplicity, denoted here 3-21G∼dz). 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) are employed for the geometry optimizations with the analytical energy gradient. All the reported computations are carried out with the Gaussian program packages [10,11].

In the optimized B3LYP/3-21G∼dz geometries the harmonic vibrational analysis is performed with the analytical force-constant matrix. In the same B3LYP/3-21G∼dz

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optimized geometries a higher-level single-point energy calculation are also carried out, namely using the standard 6-31G* basis set for all atoms (if possible), or at least for the carbon atoms. The electronic excitation energies are evaluated for some cases by means of the ZINDO method [12], also known as the ZINDO/S method, a semiempirical SCF method combined with the configuration interaction technique and specifically parametrized for calculation of electronic excited states. Moreover, in other cases the electronic transitions were 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 can be 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. Equation (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 (RRHO) 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 built-in procedure [10,11] 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).

In principle, every excited electronic state could be treated as an individual isomer with its own rotational–vibrational partition function. This approach would, however, drastically increase the computational demands. Consequently, in numerical evaluations we have to follow the conventional approach in which the rotational and vibrational levels of any excited electronic state are identified with those of the respective electronic ground state. For relatively rigid fullerenes the approximation seems to be reasonable, especially if the excited electronic states are located high enough. It is, however, also possible that some excited states are low-lying and, moreover, even undergo Jahn–Teller distortions. Such cases would need a more comprehensive evaluations when computationally feasible. However, in this report the geometry optimizations and harmonic vibrational analysis are carried out for the respective electronic ground states only.

In addition to the conventional RRHO treatment, a modified approach to description of the encapsulate motions is also considered here. It is in fact an alternative to a more rigorous solution of the nuclear problem with an anharmonic potential which is not yet accessible computationally for larger systems. The modified treatment is based on findings from observations and computations [1] that the encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations). One can expect that if the encapsulate is relatively free then, at sufficiently high temperatures, its behavior in different cages will bring about the same contribution to the partition functions. However, such uniform contributions would then cancel out in Eq. (1). This simplification can be called free, fluctuating, or floating encapsulate model (FEM). For practical implementation of this FEM approach, two steps are to be carried out. In addition to removal of the three lowest vibrational frequencies (belonging to the metal motions in the cage), the symmetries of the cages should be treated as the highest (topologically) possible, which reflects averaging effects of the large amplitude motions of the encapsulates known from NMR and other spectra [1]. Interestingly enough, one could also consider different binding sites for the metal in the cage as individual (near-isoenergetic) isomers though it could increase the computational demands considerably, especially for non-symmetric cages. This exhaustive approach would still be impractical at present so that we concentrate on a site expected to be the lowest-energy location. All such multiple binding sites are in the FEM approximation effectively unified by the encapsulate nearly-free internal motions.

## 3 Results and discussion

Ca@$C_{72}$, Ca@$C_{82}$, La@$C_{82}$, or $Sc_3N$@$C_{80}$ are the very first metallofullerenes to which the combined stability computations have been applied. Ca@$C_{72}$ was isolated earlier [18] though its observed structure is not yet available. It follows from the Ca@$C_{72}$ computations [4,19,20] that there are five isomers relatively low in potential energy. In fact, $C_{72}$ has only one [21] 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 four Ca@$C_{72}$ isomers considered [4] are related to two non-IPR (pentagon-pentagon junction) $C_{72}$ cages (b) and (c), to a $C_{72}$ structure with one heptagon (d), while the fifth low-energy species [19] contains two heptagons (e) as seen in Fig. 1.

The stability computations were carried out as described above with a particular feature that the electronic excitation energies were evaluated by means of TD DFT response theory at the B3LYP/3-21G∼dz level. Figure 2 presents the temperature development of the relative concentrations of the five 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 around 200 K (that has no practical meaning) the

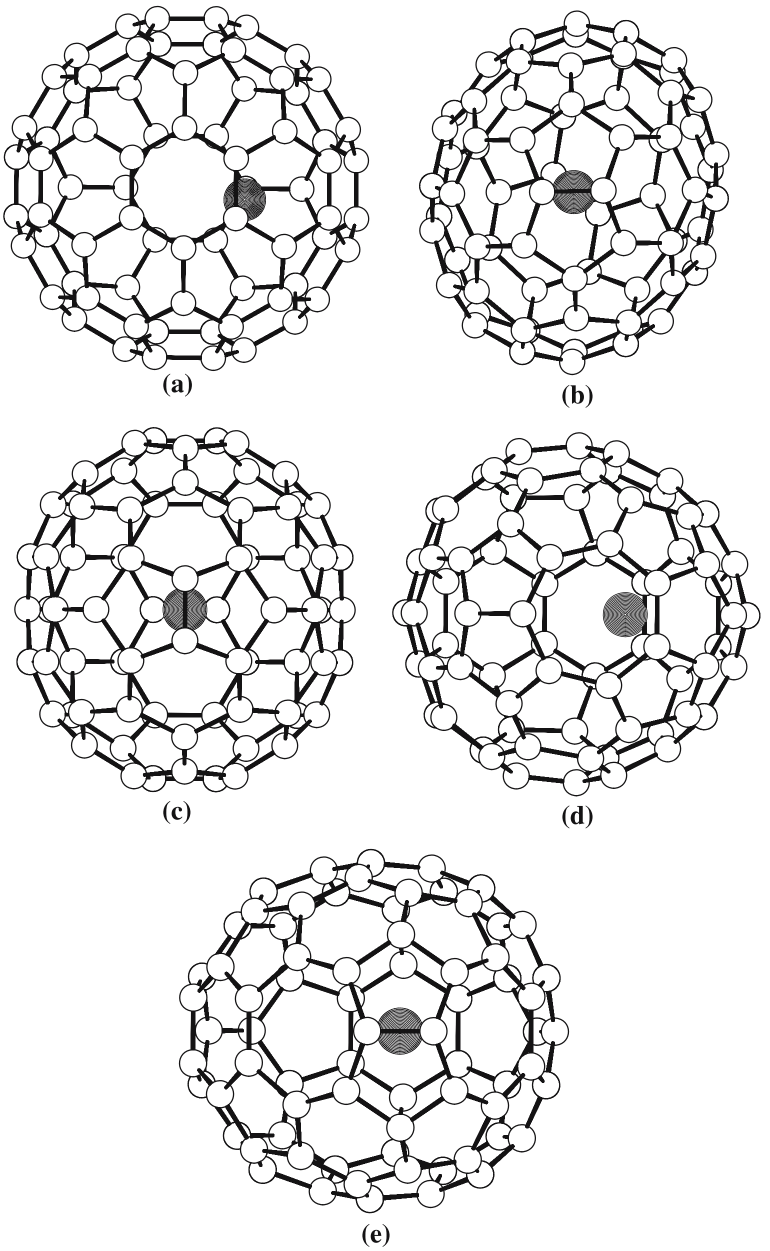


**Fig. 1** B3LYP/3-21G∼dz optimized structures of Ca@$C_{72}$ isomers: **a** IPR, **b** 5/5 pair, **c** 5/5 pair, **d** seven-membered ring, **e** two seven-membered rings

relative concentrations of the (c) and (b) structures are interchanged and beyond the point the (b) structure is somewhat more populated in a physically relevant temperature interval. The RRHO and FEM treatments differ in behavior of the IPR-satisfying (a) structure as the FEM treatment effectively recovers the $D_{6d}$ symmetry of the empty $C_{72}$ IPR cage (which is statically reduced to $C_1$ in the Ca@$C_{72}$ computations, see Fig. 1). While in the FEM approach there are only two significant species, the RRHO procedure could allow for three. Achiba et al. [22] isolated a second isomer of Ca@$C_{72}$ recently so that it is clear that at least one of the two available [18,22] Ca@$C_{72}$ isomers has a non-IPR cage. As just two isomers of Ca@$C_{72}$ are presently known, it can be concluded that the FEM treatment is actually in a better agreement with the observations. Let us mention that the situation is however quite different in Ca@$C_{74}$. Although its structure was not elucidated in the first observation [18], it was suggested that the only available IPR $C_{74}$ cage [20,23] is actually employed. This presumption was very recently confirmed by Achiba et al. [24].

The second illustrative system, Ca@$C_{82}$, exhibits the richest observed isomerism among the Ca endohedrals [25–28]. Shinohara et al. [25] isolated four isomers of Ca@$C_{82}$ and labeled the isomers by (I), (II), (III), and (IV). Dennis and

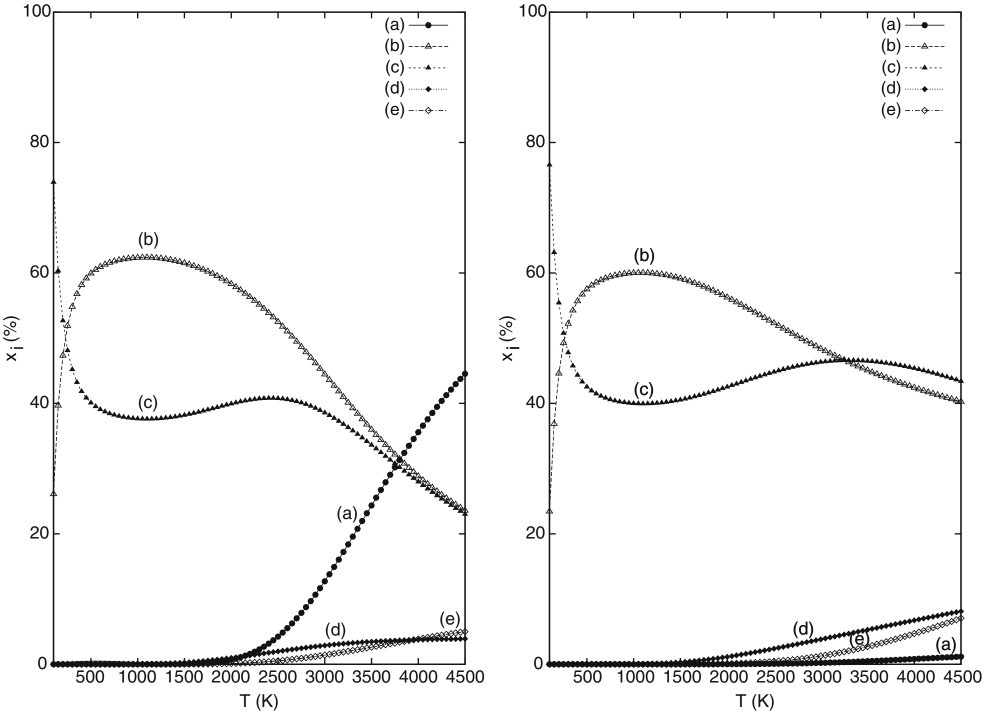


**Fig. 2** Relative concentrations of the Ca@C$_{72}$ isomers (see Fig. 1) based on the B3LYP/6-31G* energetics and the B3LYP/3-21G∼dz entropy, using the RRHO (*left*) and FEM (right) treatment

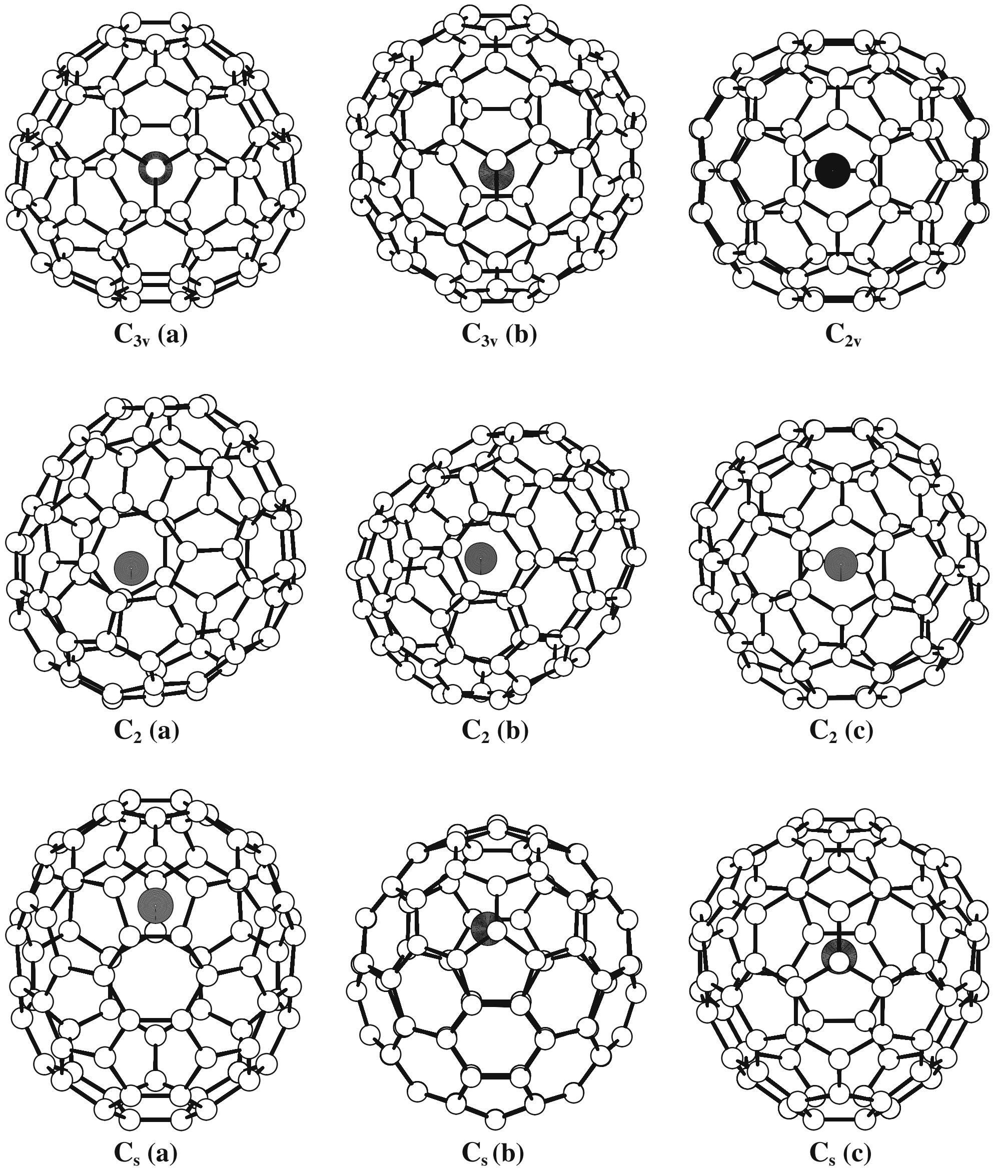
Shinohara concluded [29] from the $^{13}$C NMR spectra of Ca@C$_{82}$(III) its symmetry as $C_2$. The ultraviolet photoelectron spectra measured by Hino et al. [30] support the finding. Very recently, Achiba et al. [28] measured the $^{13}$C NMR spectra of the all four isomers and assigned the symmetry of isomers (I), (II), (III), and (IV) as $C_s$, $C_{3v}$, $C_2$, and $C_{2v}$, respectively. The observed yields [28] of the isomers were nearly equal except for the considerably less produced $C_{3v}$ species (though the HPLC chromatograms [25] could indicate somewhat larger production differences).

The Ca@C$_{82}$ isomeric system thus represents an important test example for the computations. The calculations at the HF [5] and DFT [31] level found the $C_{2v}$ structure as the lowest isomer in the potential energy. There are still three other low energy species, $C_s$, $C_2$, and $C_{3v}$ among the nine Ca@C$_{82}$ structures created from the nine C$_{82}$ IPR cages [20], namely with the following symmetries at the HF level [5]: $C_{3v}$(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) as shown in Fig. 3. However, it turns out at the B3LYP/3-21G∼dz level that some symmetries are relaxed: $C_{3v}$(b)/$C_s$, $C_{2v}$/$C_s$, $C_2$(a)/$C_1$, $C_2$(b)/$C_1$, $C_s$(b)/$C_1$.

Figure 4 presents the temperature development of the relative concentrations of the nine Ca@C$_{82}$ isomers in a wide temperature interval for the RRHO and FEM treatments. The FEM approach is in a better agreement with the available observed concentration information [25,28] as it reproduces the four isomers, placing the $C_{3v}$(b) species as the fourth most populated. In the RRHO evaluation, there is also a competing fifth structure, and the $C_{3v}$(b) cage becomes the third most populated isomer for some temperatures.

The third 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 La@C$_{82}$ 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$_{82}$. Computations indicated [6] just three IPR cages with a sufficiently low energy after La atom encapsulation: $C_{2v}$, $C_{3v}$(b), and $C_s$(c) (cf. Fig. 3). The fourth lowest La endohedral species, $C_2$(a), is actually already rather high in the potential energy to be significant even after inclusion of the entropy term.

An agreement with experiment can be found (Fig. 5) for the FEM approach in a wide temperature interval with the $C_{2v}$ species as the major isomer followed by the $C_s$(c) species. The RRHO treatment produces an unexpected stabilization of the $C_{3v}$(b) isomer that does not fit that well into the observed picture [41,42] (though it undergoes a small static $C_s$ symmetry reduction in the computations). The better predictions from the FEM approach are in agreement with the observed [40] large-amplitude motions of La in La@C$_{82}$ (i.e., the type of motion also known with smaller encapsulates [51–53]). It is however true that fullerene/metallofullerene productions are not always close [54–57] to the thermodynamic equilibrium. This factor may be pertinent to the La@C$_{82}$



**$C_{3v}$ (a)** **$C_{3v}$ (b)** **$C_{2v}$**

**$C_2$ (a)** **$C_2$ (b)** **$C_2$ (c)**

**$C_s$ (a)** **$C_s$ (b)** **$C_s$ (c)**

**Fig. 3** B3LYP/3-21G~dz optimized structures of Ca@$C_{82}$ isomers

case. Lian et al. [57] reported a Ni-catalyzed production of La@$C_{82}$ with a considerably variable isomeric ratio, indicating a possible kinetic control.

The last example deals with two known isomers of $Sc_3N$@$C_{80}$ [58–63], i.e., produced by encapsulation into the IPR $C_{80}$ cages with $I_h$ and $D_{5h}$ symmetries. The FEM approach predicts (Fig. 6) that the observed populations [61,63] of 10 and 17% for the $D_{5h}$ $Sc_3N$@$C_{80}$ species are reached at temperatures of 2,100 and 2,450 K, respectively. The RRHO treatment would already require too high temperatures to reach the observed ratios.

A more general comment is useful on the RRHO model applicability at elevated temperatures. Although all vibrations are harmonic, it should be realized that Eq. (1) actually allows for some cancellation of anharmonic effects. This feature was tested on a model set of two cyclic isomers [64] of $C_6$. At the MP2=FC/6-31G* level, the molar fraction at 2,000 K of the leading isomer was 95.2 and 96.0% in the harmonic and anharmonic [65,66] treatment, respectively. This illustrative example suggests that the cancellation of anharmonic effects can work quite well with Eq. (1) in some cases. However, Eq. (1) is still based on a presumption of the inter-isomeric thermodynamic equilibrium that cannot be verified at present.

The temperature developments reported here for metallofullerenes exhibit two features already known for more studied [67–74] hollow fullerenes: relative stability interchanges may occur with a temperature change and, in particular, the isomer lowest at the absolute zero temperature need not be the most populated species at high temperatures. The

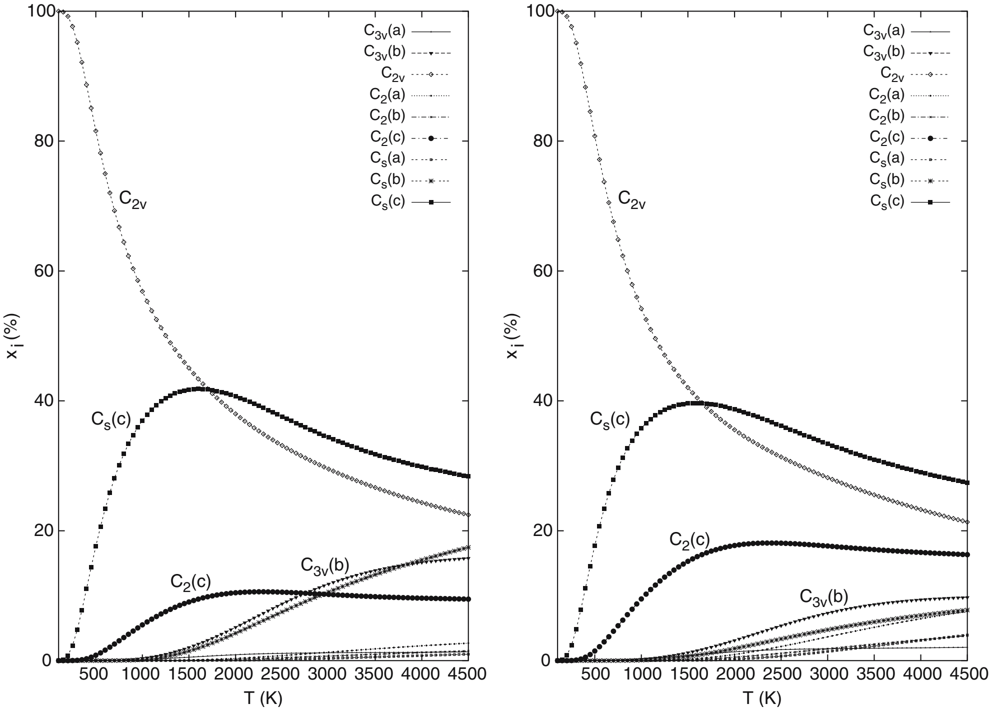


**Fig. 4** Relative concentrations of the Ca@$C_{82}$ isomers (see Fig. 3) based on the B3LYP/6-31G* energetics and the B3LYP/3-21G∼dz & ZINDO entropy, using the RRHO (*left*) and FEM (*right*) treatment

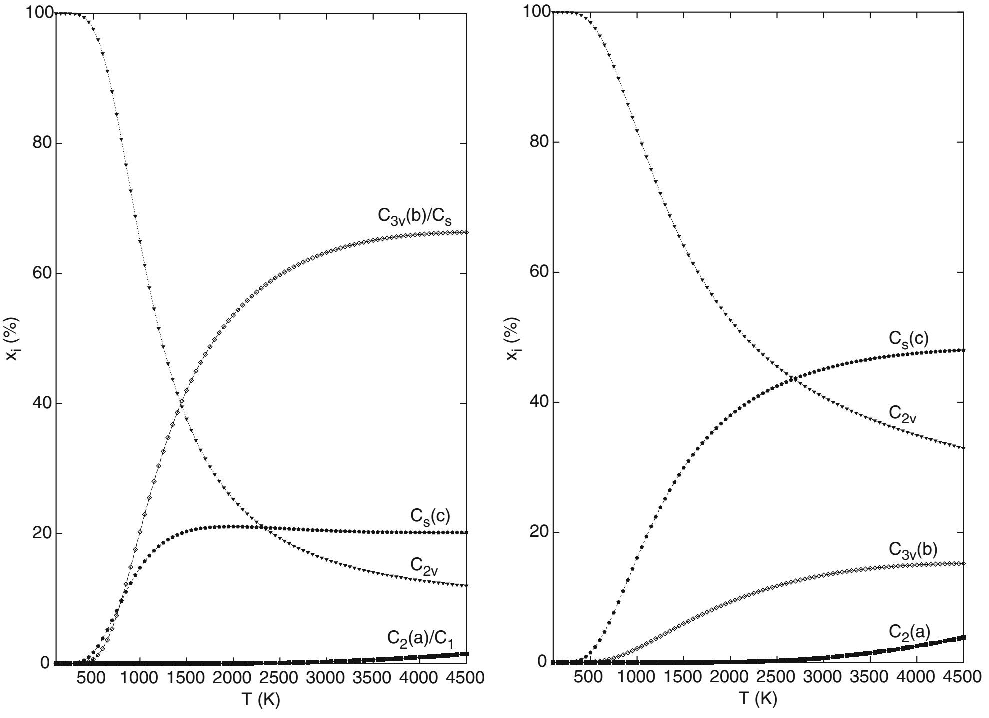


**Fig. 5** Relative concentrations of the La@$C_{82}$ isomers (cf. Fig. 3) based on the B3LYP/6-31G*∼dz energetics and the B3LYP/3-21G∼dz entropy, using the RRHO (*left*) and FEM (*right*) treatment

systematically better predictions from the FEM treatment should further be tested on the available observed metallofullerene data. However, as with empty fullerenes, the relevant temperature interval for metallofullerene formation is also not well established. Very recently, Cross and Saunders [75] pyrolyzed fullerenes subliming them into a stream of

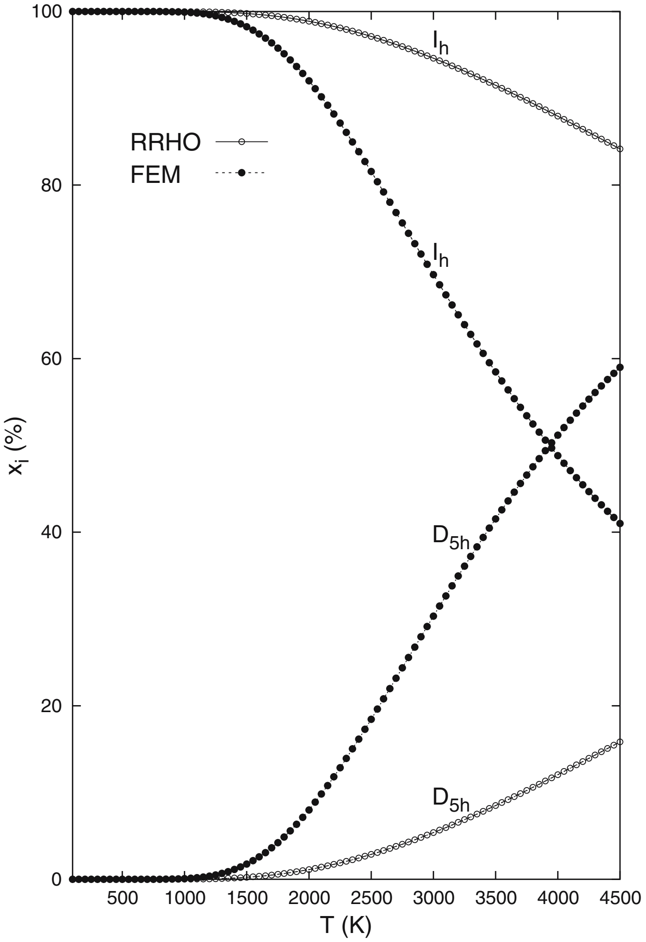


**Fig. 6** Relative concentrations of the $Sc_3N@C_{80}$ isomers based on the B3LYP/6-31G*∼dz energetics and the B3LYP/3-21G∼dz entropy, using the RRHO and FEM (*the full circles*) treatment

flowing argon gas and then passing them through an oven heated above 1,300 K. Decomposition including isomerization appears for $C_{78}$ around 1,320 K while decomposition of $C_{76}$ needs some 1,380 K. Decomposition could not be recorder for $C_{60}$ even at 1,470 K, the upper limit of the apparatus. This observation could indicate that a lower temperature limit for viable fullerene changes is 1,300–1,500 K though the experiment dealt with empty fullerenes only. In combustion synthesis of fullerenes studied by Takehara et al. [76], temperatures varied in a wide range from 1,000 to 2,500 K. Maruyama and Yamaguchi [77,78] in molecular dynamics simulations needed for cage structures temperatures from 2,500 to 3,000 K. In the case of metallofullerenes, kinetic barriers could however be reduced [79] by metal catalysis. In overall, at present, one could still expect a plausible temperature interval for fullerene synthesis possibly from 1,500 to 2,500 K, or perhaps even 3,000 K, i.e., temperatures guessed in the past [80] for significant carbon-cluster equilibrium populations.

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