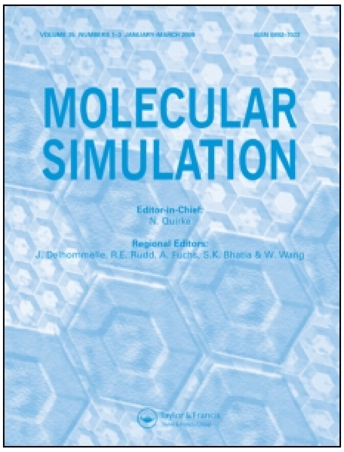

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Gibbs energy-based treatment of metallofullerenes: Ca@C_{72}, Ca@C_{74}, Ca@C_{82}, and La@C_{82}

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Gibbs energy-based treatment of metallofullerenes: $Ca@C_{72}$, $Ca@C_{74}$, $Ca@C_{82}$, and $La@C_{82}$

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The paper surveys ongoing computations on endohedral fullerene systems, combining the treatments of quantum chemistry and statistical mechanics. Relative concentrations of four isomers of $Ca@C_{72}$, six isomers of $Ca@C_{74}$, nine isomers of $Ca@C_{82}$, and four isomers of $La@C_{82}$ are evaluated using the Gibbs energy based on density-functional theory (DFT) computations. The results illustrate the enthalpy–entropy interplay in the systems produced under high temperatures. Approximations for description of the encapsulate motions are analyzed.

Keywords: Metallofullerenes; Gibbs-energy evaluations; Optimized syntheses; Bonding and stability; Carbon-based nanoscience

1. Introduction

Fullerenes and metallofullerenes have represented objects of a considerable interest [1] for both experiments as well as computations and theory. Fullerenes are commonly defined as polyhedral cages containing only carbon atoms arranged into five- and six-membered rings. More generally, *quasi*-fullerenes have also been recognized, namely as cages containing also other types of cycles like (topological) squares and heptagons. Various endohedral cage compounds have been proposed as possible candidate species for molecular memories. One approach is built on endohedral species with two possible location sites of the encapsulated atom [2], while another concept of quantum computing aims at a usage of spin states of $N@C_{60}$ [3]. At present, a still deeper knowledge of various molecular aspects of the species is needed before their tailoring to nanotechnology applications is possible.

In this report, computations on four systems related to the first approach are reported, combining the treatments of quantum chemistry and statistical mechanics. The relative concentrations of four isomers of $Ca@C_{72}$, six isomers of $Ca@C_{74}$, nine isomers of $Ca@C_{82}$, and four isomers of $La@C_{82}$ are computed using the Gibbs energy. Although these systems have been evaluated in the past, the density-functional theory (DFT) treatments have only been consistently used very recently. Moreover, the stability reasoning was previously based on mere potential-energy differences with no reference to temperature effects.

2. Computations

The computations [1] start from the structures [4–6] optimized in the past 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). Presently, the structures have been 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. As the topologies of the structures from the HF and DFT treatments are qualitatively similar, for the schemes of the structures the previous HF studies are referred to [4–6]. 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 performed with the analytical force-constant matrix. In the same B3LYP/

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3-21G ~ dz optimized geometries, a higher-level single- point energy calculation was also carried out, namely 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 are both 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:

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

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 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 which considers precision of the computed coordinates [16]. 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

It has been customary to evaluate the relative stabilities of metallofullerenes in mere terms of their separation potential energy. However, the potential energy terms themselves cannot generally decide stability order at high temperatures as the entropic part of the Gibbs energy becomes essential. Ca@C$_{72}$, Ca@C$_{74}$, 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). The stability computations [21] 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 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 figure 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.

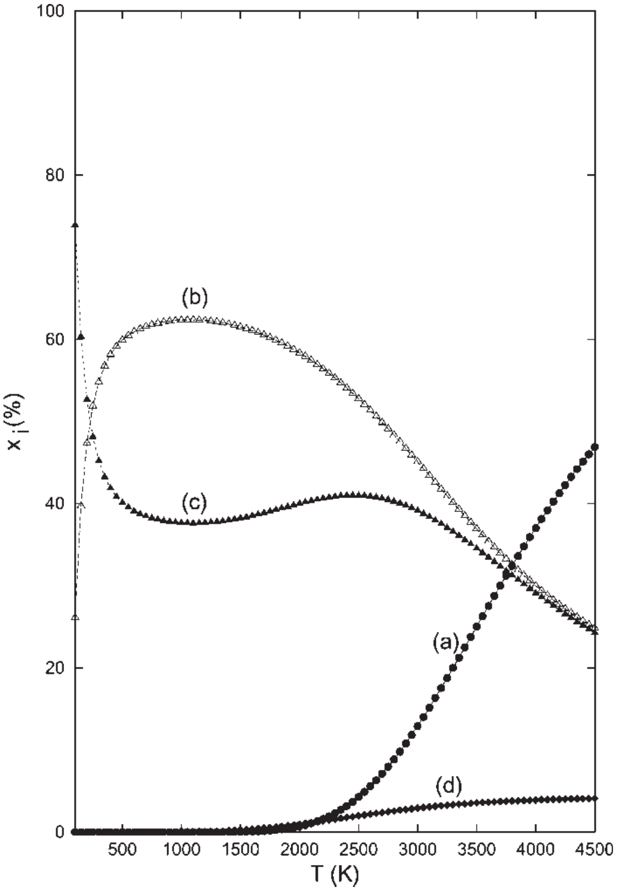

Figure 1. Relative concentrations of the Ca@C$_{72}$ isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G ~ dz entropy.

Interestingly enough, the concentration order at high temperatures for Ca@C_{72} is quite similar to that previously computed [22] for Mg@C_{72}.

Conditions are, however, quite different in the system that could be understood as the next in a row, Ca@C_{74}. Although its structure was not extracted from the first observation [18], it was suggested that the only available IPR C74 cage is actually employed. This presumption was very recently confirmed by Achiba *et al.* [23]. Our computations treat a set of six Ca@C_{74} isomers. The set consists of the isomers considered previously [18,19] to which some cages are added that exhibited non-negligible populations in evaluations of the pristine C_{74} [24]. In the evaluations, the cages were labeled by code numbers also used here (combined with the symmetry of the complexes): $1/C_{2v}$, $4/C_1$, $52/C_2$, $103/C_1$, $368/C_1$, and $463/C_1$. In fact, the $1/C_{2v}$ endohedral represents the species derived from the sole [20] C_{74} IPR structure. The previously computed encapsulates [19] derived from two non-IPR C_{74} cages are now labeled by $4/C_1$ and $103/C_1$. A pair of connected pentagons is also present in the $52/C_2$ structure. The remaining two species, $368/C_1$ and $463/C_1$, exhibit, in addition to the fused pentagon/pentagon pair, also one heptagon.

The IPR related $1/C_{2v}$ Ca@C_{74} complex is computed as the lowest in the potential energy, being followed by the $4/C_1$ and $103/C_1$ species separated by about 15 kcal/mol. The remaining three isomers ($52/C_2$, $368/C_1$, and $463/C_1$) are located relatively high in energy. Figure 2 presents the temperature development of the relative concentrations of the six Ca@C_{74} isomers at high temperatures. It turns out the $1/C_{2v}$ species has not only favorable enthalpy but also entropy term and thus, all the remaining isomers can act as minor species at best.

The third illustrative system, Ca@C_{82}, exhibits the richest 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 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 Ca@C_{82} structure–energetics relationships were also computed [5] and a qualitative agreement with the experiment found [1]. 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 [31] 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)/C_s, C_{2v}/C_s, C_2(a)/C_1, C_2(b)/C_1, C_s(b)/C_1.

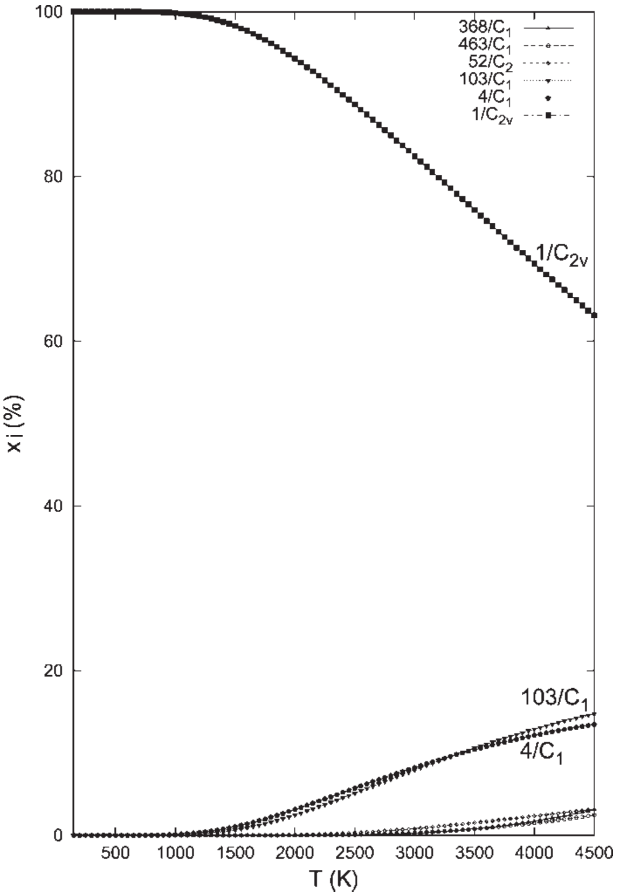

Figure 2. Relative concentrations of the Ca@C_{74} isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G ~ dz entropy.

Figure 3 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}/C 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)/C_s and C_s(b)/C_1. Although the former species is a bit more populated, their concentrations are rather close. Figure 3 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 fourth illustrative case deals with La@C_{82}, i.e. an electronic open-shell system. The La@C_{82}

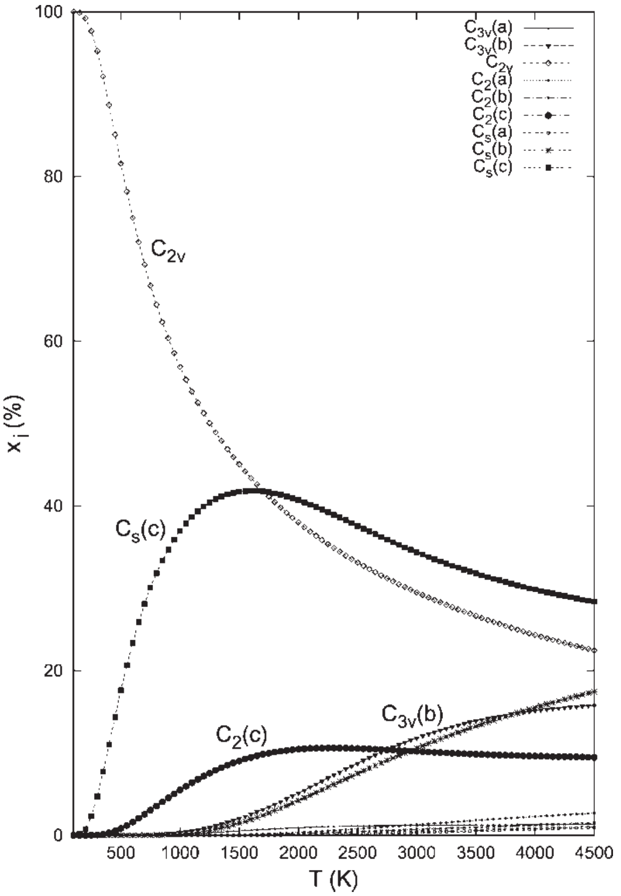

Figure 3. Relative concentrations of the Ca@C_{82} isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G~dz entropy.

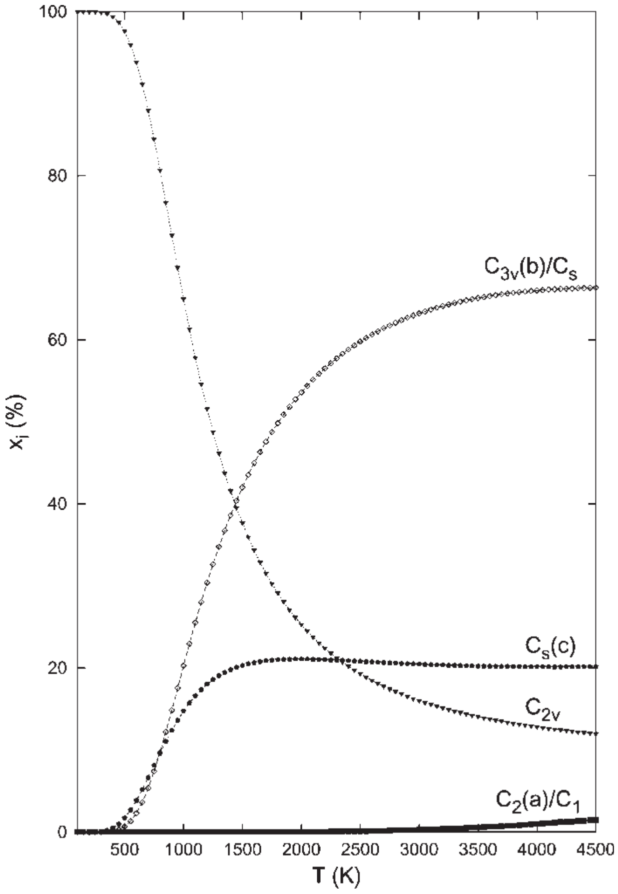

Figure 4. Relative concentrations of the La@C_{82} isomers based on the B3LYP/6-31G*~dz energetics and the B3LYP/3-21G ~ dz entropy.

metallofullerene is one of the very first endohedrals that was macroscopically produced [32] and solvent extracted. La@C_{82} has attracted the attention of both experimentation [33–42] and computations [43–49]. Recently, the structures of two 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 contrast to Ca@C_{82} with four known isomers. Computations at *ab initio* HF and DFT levels [6] pointed out 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 experiments.

An agreement with experiments can be reached (figure 4) for temperatures roughly from 1000 to 1300 K when the C_{2v} species is the major isomer followed by an isomer that actually 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.

The C_{3v}/C_s species deserves further comment. It corresponds to the Ca@C_{82} C_{3v}(b)/C_s isomer. In fact, the C_{3v}(b) structure actually undergoes [20] a similar symmetry reduction already for its empty form, C_{82}. Interestingly enough, it is not a Jahn–Teller distortion as the HMO topological HOMO–LUMO gap [20] is non-zero (albeit relatively small). There is just one C atom on the topological C_3 axis (figure 5) and the three topologically equivalent bonds to its three neighboring C atoms are at the B3LYP/3-21G level split into two classes—bond lengths 1.421 and 1.436 Å. If the C_{3v} symmetry is forced to the empty C_{82} cage, a saddle point results that is just 2.2 kcal/mol higher than the C_s local minimum at the B3LYP/3-21G level (in Ca@C_{82} the barrier is reduced further). The difference in the C—C bonds in the C_{3v}(b)/C_s La@C_{82} species at the B3LYP/3-21G ~ dz level is 0.007 Å and in LaC_{82}^- 0.009 Å. The ^{13}C NMR spectra in the case of La@C_{82} were measured [41,42] for LaC_{82}^-. Then, the structural differentiation translates in the ^{13}C NMR spectrum computed for the C_{3v}(b)/C_s LaC_{82}^- at the (restricted) B3LYP/6-31G* ~ dz//B3LYP/3-21G ~ dz level into a difference of chemical shifts of 1.8 ppm. Such differences should be seen in the measured high-resolution NMR spectra so that the whole pattern could look like that of a C_s species as long as motions of the La atom are negligible, i.e. at very low temperatures. However, at

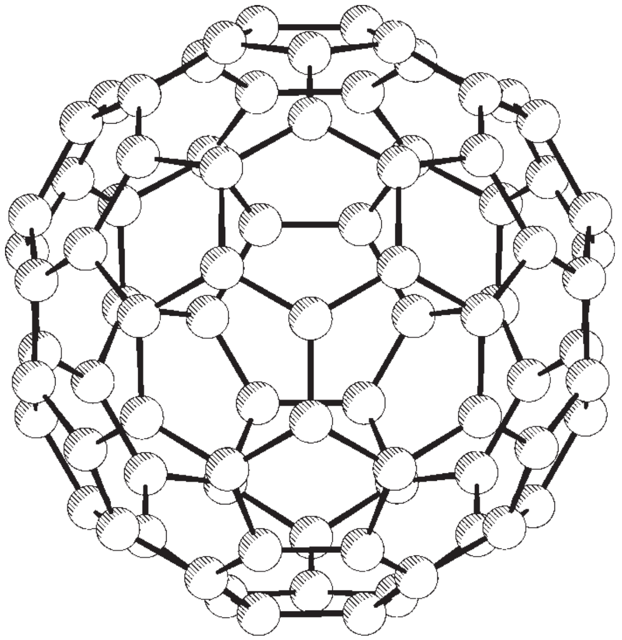

Figure 5. B3LYP/3-21G optimized structure of the empty C_{3v}(b)/C_s isomer of C_{82} viewed along the topological C_3 axis.

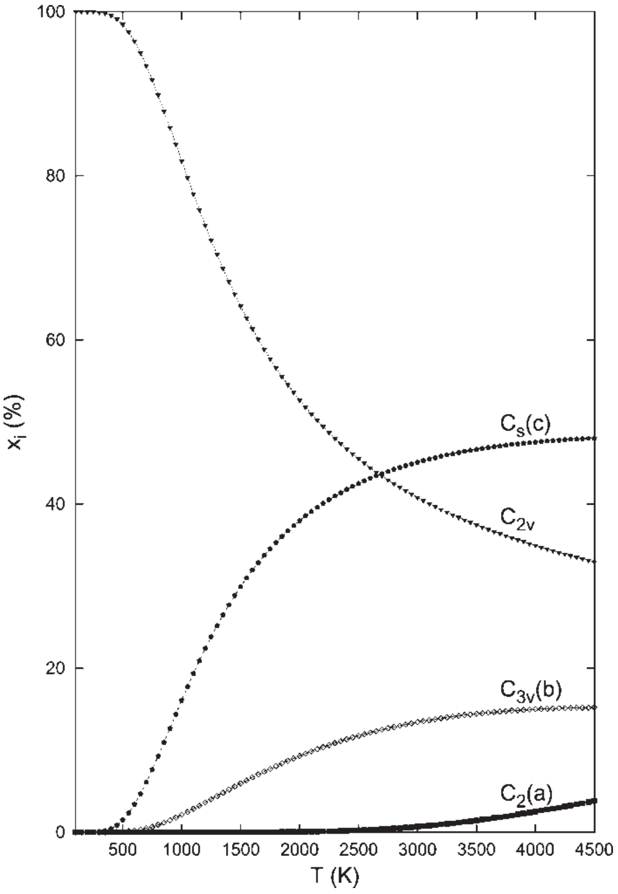

Figure 6. Relative concentrations of the La@C_{82} isomers derived within the FEM approach.

moderate temperatures the spectrum would be simplified towards the C_{3v} pattern owing to an averaging effect of large amplitude motions [40] of the encapsulated La atom. It should also be noted that the computed [42] ionization potential and electron affinity of the C_s(c) isomer correlate better with the measured oxidation and reduction potential than the terms computed for the C_{3v}(b)/C_s species. Moreover, though an inclusion of solvent effects could influence the computed values, the C_{3v}(b)/C_s structure shows a distinctly higher electron affinity. This feature suggests a higher reactivity as a possible reason for a suppression of the C_{3v}(b)/C_s isomer in condensed phase. Thus, a plausible scenario could be that while in the equilibrium gas phase the C_s(c) isomer is only the third most populated, it can then become the second in condensed phase owing to higher reactivity of the C_{3v}(b)/C_s species, which prevents its isolation.

An alternative approach to description of the encapsulate motions would be represented by solution of the nuclear problem with an anharmonic potential which is yet not accessible computationally for larger systems. However, 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 [51–53]. The contributions would than cancel out in equation (1). This simplification can be called free, fluctuating, or floating encapsulate model (FEM). In the FEM model, in addition to the removal of the three lowest vibrational frequencies, the symmetries of the cages should be treated as the highest possible, considering the averaging effect of the large amplitude motions of the encapsulate. Figure 6 shows the results for the La@C_{82} isomeric system evaluated now within the FEM approach. In fact, the results are actually closer to the observed facts.

There is still another aspect to be considered. The fullerene and metallofullerene production is not always close [54–57] to the inter-isomeric equilibrium. This factor may be pertinent to the La@C_{82} 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 at least in some arrangements. Consequently, it would, at least in principle, be possible that the C_{3v}(b) La@C_{82} species is actually suppressed by some specific kinetic factors already in the gas phase.

The presence of a metal considerably affects the stability picture, frequently leading to a complete change of proportions. Still, the temperature developments reported here for metallofullerenes exhibit two features already known [58–60] for the isomeric hollow fullerenes: relative stability interchanges may occur in a wide temperature region and, in particular, the isomer lowest at the absolute zero temperature need not be the most populated species at high temperatures. The interchanges come from a complex interplay of rotational, vibrational, electronic, symmetry, chirality, and energy terms. By now, the isomerism of metallofullerenes based on the cage isomerism have been studied. However, as isomerism based on different metal locations in a given cage is also possible [61], a further expansion of the treatment is envisaged. As the interconversion barriers can be low and flat, an anharmonic treatment would then represent a more adequate option, too.

Note added in proof

Achiba *et al*. [62] isolated a second isomer of $Ca@C_{72}$ so that it is clear that at least one of the two available $Ca@C_{72}$ isomers [18,62] has a non-IPR cage.

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