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RELATIVE STABILITY EVALUATIONS FOR METALLOFULLERENES THROUGH GIBBS ENERGY TREATMENTS

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ABSTRACT

The paper surveys computations on endohedral fullerene systems, combining the treatments of quantum chemistry and statistical mechanics. The procedure is illustrated on evaluations of relative concentrations of isomers of Ca@C₇₂, Ca@C₇₄, Ca@C₈₂, La@C₈₂, and Sc₃N@C₈₀. The results point out the role of both the enthalpy and entropy terms for the systems produced under high temperatures. Approaches to description of the encapsulate motions are analyzed as well as the importance of excited electronic states.

1. INTRODUCTION

Since their discovery twenty 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 survey, relative stability computations are illustrated on four systems, combining the treatments of quantum chemistry and statistical mechanics, namely on five isomers of Ca@C₇₂, six isomers of Ca@C₇₄, nine isomers of Ca@C₈₂, four isomers of La@C₈₂, and two isomers of Sc₃N@C₈₀. While the stability reasoning has traditionally been based on mere potential-energy differences [4-6], we treat the issue in the terms of the Gibbs energy so that temperature effects can be included accordingly. The inclusion of entropy effects requires by about one order of magni-

tude 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. COMPUTATIONS

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 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], 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 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 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 $\Delta H_{0,i}^o$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula:

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

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 (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, also a modified approach to description of the encapsulate motions is considered here. It is in fact an alternative to a more rigorous solution of the nuclear problem with an anharmonic potential which is yet not accessible computationally for larger systems. The modified treatment is based on findings from observation 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@C₇₂, Ca@C₇₄, Ca@C₈₂, La@C₈₂, or Sc₃N@C₈₀ are the very first metallofullerenes to which the combined stability computations have been applied. Ca@C₇₂ was isolated earlier [18] though its observed structure is not yet available. It follows from the Ca@C₇₂ computations [4,19,21] that there are five isomers relatively low in potential energy. In fact, C₇₂ has only one [20] isolated-pentagon-rule (IPR) structure. The endohedral Ca@C₇₂ species created by putting Ca inside the sole IPR cage has been labeled [4] by (a). The other four Ca@C₇₂ isomers considered [4] are related to two non-IPR (pentagon-pentagon junction) C₇₂ cages (b) and (c), to a C₇₂ structure with one heptagon (d), while the fifth low-energy species [19] contains two heptagons (e).

The temperature development of the relative concentrations of the five isomers Ca@C₇₂ is as follows. At very low temperatures the structure lowest in the $\Delta H_{0,i}^o$ scale must be prevailing. However, already at a temperature around 200 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 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 C₇₂ IPR cage (which is statically reduced to C_1 in the Ca@C₇₂ computations). 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@C₇₂ recently so that it is clear that at least one of the two available [18,22] Ca@C₇₂

isomers has a non-IPR cage.

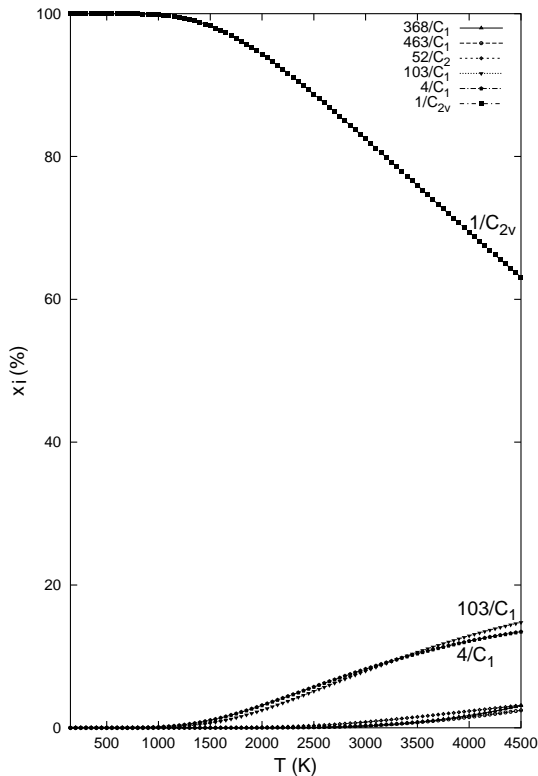


Fig. 1. Relative concentrations of the Ca@C₇₄ isomers based on the B3LYP/6-31G* energetics and the B3LYP/3-21G~dz entropy.

Let us mention that the situation is however quite different in Ca@C₇₄. Although its structure was not elucidated in the first observation [18], it was suggested that the only available IPR C₇₄ cage [20,23] is actually employed. This presumption was very recently confirmed by Achiba *et al.* [24]. Our computations treat a set of six Ca@C₇₄ isomers. The set consists of the isomers considered previously [18,19] to which some cages are added that exhibited [23] non-negligible populations in evaluations of the pristine C₇₄. In the evaluations, the cages were labeled by code numbers also used here (combined with the symmetry of the complexes): 1/C_{2v}, 4/C₁, 52/C₂, 103/C₁, 368/C₁, and 463/C₁. In fact, the 1/C_{2v} endohedral represents the species derived from the sole [20] C₇₄ IPR structure. The previously computed [19] encapsulates derived from two non-IPR C₇₄ cages are now labeled by 4/C₁ and 103/C₁. A pair of connected pentagons is also present in the 52/C₂ structure. The remaining two species, 368/C₁ and 463/C₁, exhibit, in addition to the fused pentagon/pentagon pair, also one heptagon. The IPR related 1/C_{2v} Ca@C₇₄ complex is computed as the lowest in the potential energy, being followed by the 4/C₁ and 103/C₁ species separated by about 15 kcal/mol. The remaining three isomers (52/C₂,

368/C₁, and 463/C₁) are located relatively high in energy. Fig. 1 presents the temperature development of the relative concentrations of the six Ca@C₇₄ 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@C₈₂, exhibits the richest observed isomerism among the Ca endohedrals [25-28]. Shinohara *et al.* [25] isolated four isomers of Ca@C₈₂ and labeled the isomers by (I), (II), (III), and (IV). Dennis and Shinohara concluded [29] from the ¹³C NMR spectra of Ca@C₈₂(III) its symmetry as C₂. The ultraviolet photoelectron spectra measured by Hino *et al.* [30] support the finding. Very recently, Achiba *et al.* [28] measured the ¹³C NMR spectra of the all four isomers and assigned the symmetry of isomers (I), (II), (III), and (IV) as C_s, C_{3v}, C₂, and C_{2v}, respectively.

The Ca@C₈₂ 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, C₂, and C_{3v} among the nine Ca@C₈₂ structures created from the nine C₈₂ IPR cages [20], namely with the following symmetries at the HF level [5]: C_{3v}(a), C_{3v}(b), C_{2v}, C₂(a), C₂(b), C₂(c), C_s(a), C_s(b), and C_s(c). 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, C₂(a)/C₁, C₂(b)/C₁, C_s(b)/C₁.

The temperature development of the relative concentrations of the nine Ca@C₈₂ isomers was computed for both 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 fourth case deals with La@C₈₂, i.e., an electronic open-shell system. The La@C₈₂ metallofullerene is one of the very first endohedrals that was macroscopically produced [32] and solvent extracted. La@C₈₂ has attracted attention of both experiment [33-42] and computations [43-49]. Recently, structures of two its isomers were clarified [41,42] using ¹³C 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@C₈₂ and Y@C₈₂. 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). The fourth lowest La endohedral species, C₂(a), is actually already rather high in the potential energy to be

significant even after inclusion of the entropy term.

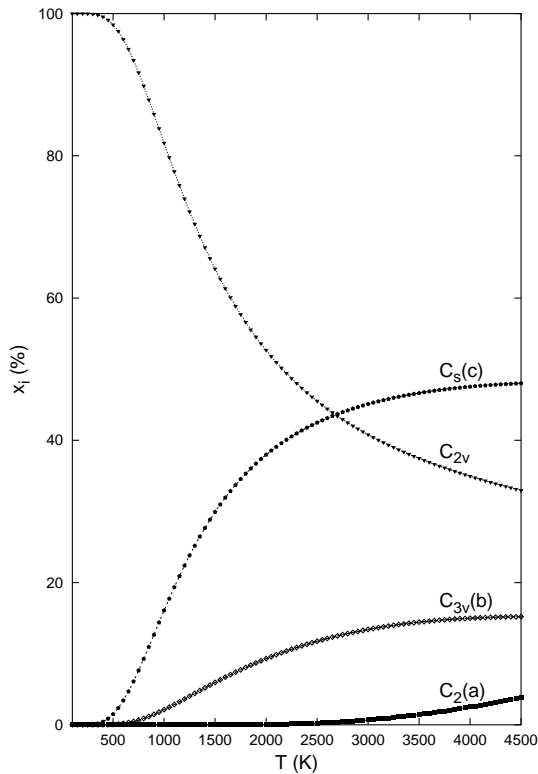


Fig. 2. Relative concentrations of the La@C_{82} isomers based on the B3LYP/6-31G* \sim dz energetics and the B3LYP/3-21G \sim dz entropy, using the FEM treatment.

An agreement with experiment can be found (Fig. 2) 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]. 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 other encapsulates [51-53]). It is however true that fullerene/metallofullerene productions are not always close [54-57] to the thermodynamic equilibrium - Lian *et al.* [57] reported a Ni-catalyzed production of La@C_{82} with a variable isomeric ratio.

The last example deals with two known isomers of $\text{Sc}_3\text{N@C}_{80}$ [58-63], i.e., produced by encapsulation into the IPR C_{80} cages with I_h and D_{5h} symmetries. The FEM approach predicts that the observed populations [61,63] of 10 and 17 % for the D_{5h} $\text{Sc}_3\text{N@C}_{80}$ species are reached at temperatures of 2100 and 2450 K, respectively.

A more general comment could be of interest regarding 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 2000 K of the leading isomer was 95.2 and 96.0 % in the harmonic and anharmonic [65,66] treatment, respectively.

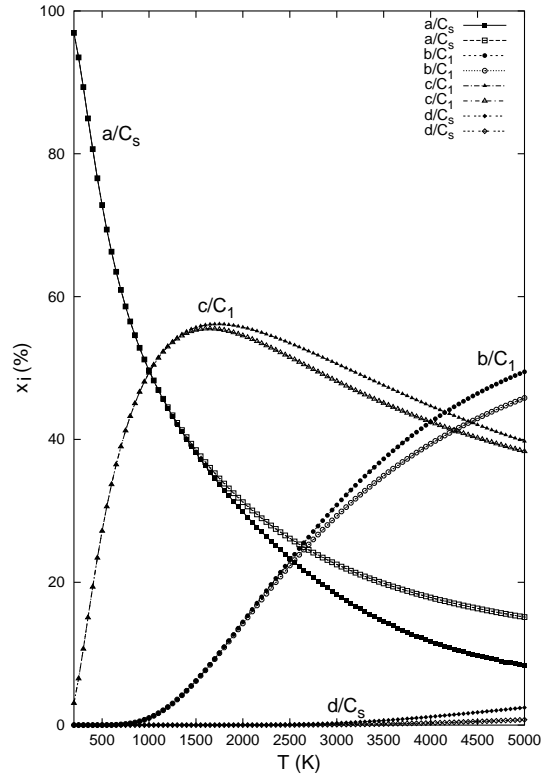


Fig. 3. Mole fractions x_i of four isomers of Mg@C_{72} - the CIS/LanL2DZ electronic partition function q_{el} (the full and empty symbols refer to the calculations with and without q_{el} , respectively).

In addition to the vibrational partition function, electronic excitations can also be significant at higher temperatures. Fig. 3 presents the equilibrium mole fractions of the Mg@C_{72} isomers computed with and without the electronic partition functions so that the effects of excited states can be seen. The Mg@C_{72} structures are closely related to the Ca@C_{72} cages (a)-(d). It can be expected that in some systems the effects can actually become crucial.

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