Excited Electronic States and Production Optimizations for Promising Nano-Agents

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ABSTRACT

Very high temperatures of fullerene and nanotube syntheses do allow for a significant population of excited electronic states and thus for non-negligible electronic partition functions. This unique feature can have some interesting consequences for computed fullerene/nanotube-related thermodynamics or kinetics. The excited electronic states can be evaluated by means of (limited) configuration interaction (CI) approach. At the semiempirical level, the ZINDO method developed by Zerner *et al.* represents an interesting option. The computations can also be carried out *ab initio*, using, e.g., a limited single-excitation CI approach (CI-Singles or CIS). In this paper, numerical illustrations are served with three systems: C_{78}, $Mg@C_{72}$, and C_{80}. In overall, the computations suggest that at high temperatures electronic excited states can make some significant contribution into thermodynamics. It is likely that after an extended search some isomeric system can be pointed out with especially pronounced changes in the relative isomeric concentrations upon inclusion of the electronic partition function. Metallofullerenes are more likely candidates for such enhanced effects though calculations of their vibrational and electronic spectra still represent a challenging problem. However, even pristine fullerenic isomers can show interesting effects, for example if Jahn-Teller distortions are involved.

Keywords: Carbon nanotechnology; molecular electronics; molecular electronic structure; excited states; Jahn-Teller effect.

1 INTRODUCTION

Very high temperatures of fullerene synthesis do allow for a significant population of excited electronic states and thus for non-negligible electronic partition functions. This unique feature can have some interesting consequences for computed fullerene-related thermodynamics or kinetics. The excited electronic states can be evaluated by means of (limited) configuration interaction (CI) approach. At the semiempirical level, the ZINDO method developed by Zerner *et al.* [1-4] represents the newest option. The computations can also be carried out *ab initio* [5], for larger molecules using a limited single-excitation CI approach (CI-Singles or CIS).

In this paper, numerical illustrations are discussed with C_{78}, $Mg@C_{72}$, and C_{80} isomeric systems. For example, there are five isolated-pentagon-rule (IPR) satisfying isomers for C_{78} [6-15] but only three were originally observed in experiments. Only very recently, a fourth isomer has been observed [14], too, which calls for a new evaluation of the computed isomeric relative concentrations. Similarly, relative concentrations of isomers of $Mg@C_{72}$ - a not yet isolated system belonging to an interesting class of C_{72} related species [16-20] - are studied, too. The third system, C_{80}, consists of seven IPR structures. In all three cases, the electronic partition functions are considered accordingly. The calculations supply a further interesting example of sometimes profound (nevertheless, frequently ignored) role of enthalpy-entropy interplay in stabilities of isomeric fullerenic structures, and in particular point out a possible significant role of excited electronic states.

2 COMPUTATIONS

Our previously computed C_{78} and C_{80} data are used as a starting set here. The geometry optimizations were first carried out with the semiempirical method SAM1 [21], implemented in AMPAC program package [22]. In the SAM1 optimized geometries, the harmonic vibrational analysis was carried out by a numerical differentiation of the analytical energy gradient. The C_{78} cage geometries were further on re-optimized at the *ab initio* Hartee-Fock (HF) SCF level, applying Gaussian program package [23,24], namely with the standard 3-21G basis set (HF/3-21G). Finally, the geometries have been reoptimized at the B3LYP (Becke's three parameter functional with the non-local Lee-Yang-Parr correlation functional) density-functional level with the standard 4-31G basis set (B3LYP/4-31G). The separation energetics was refined (using the fixed HF/3-21G optimized geometries) with the B3LYP density-functional treatment in the standard 6-31G* basis set (B3LYP/6-31G*//HF/3-21G - and at present the energetics is even

being re-evaluated at the B3LYP/6-311G*//B3LYP/4-31G level). The ZINDO electronic excitations energies have been evaluated in the B3LYP/4-31G optimized geometries. For C_{80} the calculations were carried out just in the SAM1 optimized geometries.

The Mg@C_{72} isomeric system is treated here within the previously computed data set [20]. The computations were performed with a new parametrization of the MNDO method designed by Thiel and Voityuk [25] and known as MNDO/d or MNDO with d orbitals. In fact, the MNDO/d parameters are available for Mg but not for Ca. The MNDO/d calculations were performed with the method implementation in the AMPAC program package [22]. In the MNDO/d optimized geometries, the harmonic vibrational analysis was carried out. Finally, the limited single-excitation CI approach with the standard LanL2MB basis (CIS/LanL2MB) was carried out in the MNDO/d optimized geometries, while at present is being re-computed at the CIS/LanL2DZ level.

The computed energy, structural and vibrational data are employed in the construction of isomeric partition functions, and evaluations of the relative Gibbs free energies. The rotational-vibrational-electronic partition functions q_i are of the rigid rotator and harmonic oscillator quality, and no frequency scaling is considered. Relative concentrations (mole fractions) x_i of m isomers can be expressed through the partition functions q_i and the ground-state energy $\Delta H^o_{0,i}$ by a compact formula [26]:

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

where R is the gas constant and T the absolute temperature. The geometrical symmetries of the optimized cages represent an important issue and they were determined by a new procedure which treats precision of the computed coordinates as a variable parameter [27]. Chirality contribution is also considered in Eq. (1) - for an enantiomeric pair its partition function q_i is doubled. Finally, the electronic partition function was constructed by a direct summation over twenty lowest electronic levels.

3 RESULTS AND DISCUSSION

There are just five IPR satisfying isomers of C_{78}. They are labeled 1-5 in Ref. [6] and in this order they exhibit the D_3, C_{2v}, C_{2v}, D_{3h}, and D_{3h} symmetries. Diederich *al.* [7] used modified symmetry labels: D_3, C_{2v}, C'_{2v}, D_{3h}, and D'_{3h}. In experiment, at first only two isomers were observed [7]: D_3 and C_{2v} symmetry in a ratio 1:5. However, later on, Kikuchi *et al.* [11] reported three isomers of C_{78} with the symmetries D_3, C_{2v}, and $C_{2v'}$ and in a ratio 2:2:5. Taylor *et al.* [12] also report three structures - C_{2v}, D_3, and $C_{2v'}$ with a ratio 5.2:3:1.8. NMR spectra of ^{3}He in C_{78} reported by Saunders *et al.* [13] qualitatively agree with the previous findings. Finally, Yamamoto [14] has recently reported isolation of a fourth isomer of C_{78}, namely the D'_{3h} species.

Table I. Comparison of mole fractions x_i for two selected IPR isomers[a] of C_{78}

T (K)	Appr.[b]	x_i (%)	
		$2/C_{2v}$	$3/C_{2v}$
1000	q_{el}=1	3.00	92.9
	$q_{el}(T)$	2.99	92.9
2000	q_{el}=1	12.3	74.1
	$q_{el}(T)$	11.7	74.2
3000	q_{el}=1	17.9	62.5
	$q_{el}(T)$	15.0	63.2
4000	q_{el}=1	20.9	55.6
	$q_{el}(T)$	16.2	57.0
5000	q_{el}=1	22.6	51.2
	$q_{el}(T)$	17.4	52.9

[a] IPR isomers of C_{78} are labeled [6] 1–5 and have symmetries D_3, C_{2v}, C_{2v}, D_{3h}, and D_{3h} (or D_3, C_{2v}, C'_{2v}, D_{3h}, and D'_{3h}).
[b] The upper line presents values without inclusion of the electronic excited states (q_{el}=1), the lower line with their consideration ($q_{el}(T)$).

Table I illustrates the computed equilibrium mole fractions for two C_{78} isomers, evaluated with and without the electronic partition function. At the highest temperatures the difference is in some cases about five percent points. When the electronic partition function is included, structure 5 in particular increases its presence while the relative concentration of structure 2 is reduced. In overall, the computed results agree reasonably well with the experimental findings [11,14].

Table II. Comparison of mole fractions x_i of two selected isomers[a] of Mg@C_{72}

T (K)	Appr.[b]	x_i (%)	
		a/C_s	**b**/C_1
1000	q_{el}=1	49.7	1.00
	$q_{el}(T)$	49.7	1.00
2000	q_{el}=1	31.2	14.2
	$q_{el}(T)$	30.8	14.8
3000	q_{el}=1	22.5	29.3
	$q_{el}(T)$	20.4	32.2
4000	q_{el}=1	17.9	39.4
	$q_{el}(T)$	14.2	44.5
5000	q_{el}=1	15.1	45.8
	$q_{el}(T)$	10.5	51.9

[a] Isomers of Mg@C_{72} are labeled [20] **a**–**d** and have symmetries C_s, C_1, C_1, and C_s.
[b] The upper line presents values without inclusion of the electronic excited states (q_{el}=1), the lower line with their consideration ($q_{el}(T)$).

The Mg@C_{72} structures considered here are closely

related to the $Ca@C_{72}$ cages [16]. In fact, C_{72} has only one isolated-pentagon-rule structure. It is however known that also non-IPR structures should be significant for both C_{72} and $Ca@C_{72}$. Four selected $Ca@C_{72}$ structures were computed [16]: the IPR structure (**a**), two non-IPR structures each with one pair of connected pentagons (**b**, **c**), and finally a structure with one heptagon (**d**). The cage labels **a**–**d** are also used here for the $Mg@C_{72}$ structures [20]. In the CIS/LanL2MB calculations of the $Mg@C_{72}$ excitation energies the **d** structure exhibits particularly low excited states. Table II reports the equilibrium mole fractions of the $Mg@C_{72}$ isomers computed with and without the electronic partition functions. The effects of the excited states are slightly larger than in the C_{78} case.

Table III. Comparison of mole fractions x_i for two selected IPR isomers[a] of C_{80}

T (K)	Appr.[b]	x_i (%)	
		$\mathbf{A}/D_2$	$\mathbf{C}/D_{5d}$
500	q_{el}=1	9.76	90.2
	$q_{el}(T)$	9.67	90.3
1000	q_{el}=1	42.6	57.1
	$q_{el}(T)$	38.3	60.4
2000	q_{el}=1	46.3	23.4
	$q_{el}(T)$	20.2	15.4
3000	q_{el}=1	15.4	5.61
	$q_{el}(T)$	4.64	2.48
4000	q_{el}=1	5.76	1.78
	$q_{el}(T)$	1.93	0.80
5000	q_{el}=1	2.86	0.80
	$q_{el}(T)$	1.10	0.38

[a] The IPR isomers of C_{80} are labeled [27] **A**–**G** and have the SAM1 optimized symmetries D_2, D_2, D_{5d}, C_{2v}, C_{2v}, C_2, and C_s.
[b] The upper line presents values without inclusion of the electronic excited states (q_{el}=1), the lower line with their consideration ($q_{el}(T)$).

C_{80} consists [27-80] of seven IPR isomers (the structures are coded **A-G** which correspond to the labels used in Ref. [27]). The **B** species has a topological symmetry I_h, but it undergoes a Jahn-Teller distortion towards lower energy and lower symmetry, D_2. The SAM1 computations predict the **C** isomer (D_{5d} symmetry) as the system ground state, being followed by the **A** species of a D_2 symmetry. At very low temperatures the ground-state structure, **C**, has to be prevailing. At a temperature of 1178 K the **A** species reaches equimolarity with the **C** species, and also other species become gradually significant. At about 2300 K the **F** species reaches equimolarity with the **C** isomer, too. These SAM1 results without inclusion of the electronic partition function are now compared in Table III with the values corrected for the ZINDO electronic excitations. Interestingly enough, the computed effects of the excited states are still larger than in the $Mg@C_{72}$ case.

In overall, the computations suggest that at high temperatures electronic excited states can make some significant contribution into thermodynamics. It is likely that after an extended search some isomeric system can be pointed out with especially pronounced changes in the relative isomeric concentrations upon inclusion of the electronic partition function. Metallofullerenes are especially interesting systems for such enhanced effects though calculations of their vibrational and electronic spectra still represent a difficult problem. However, even pristine fullerenic isomers can show interesting effects, for example if Jahn-Teller distortions are involved. The research line is closely related to rational selection and preparation of the species for fullerene-based nanochnology applications in future.

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