

Stability and vibrational spectra of toroidal isomers of C_{240}

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Abstract. To study the thermodynamic and mechanical stability of toroidal isomers of C_{240} , we use a semi-empirical tight-binding theory and calculate their electronic structure, cohesive energy and vibrational spectra within the harmonic approximation. From these, we deduce their free energy at temperatures up to 1500K. The results are also compared to the isomer with icosahedral symmetry. Finally, we discuss within this approach, their stability and abundance.

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1 Introduction

Motivated by previous predictions [1] and recent discoveries of larger fullerenes [2], we have calculated the electronic structure as well as the vibrational spectra of the 6 most symmetric isomers of C_{240} by using the tight-binding (TB) method. These isomers have the simplest nontrivial topological form after the spheroidal C_{60} and the well-known nanotubes. They have a toroidal form, and can be obtained by bending a graphite sheet along both x and y directions, or in other words, by bending and connecting the two ends of an open nanotube. In order to relax the resulting stress, one has to introduce defects such as pentagons in the outer ring and heptagons in the inner ring of the torus. The details of such constructions can be found in [3]. The considered structures are the most symmetric ones, and have a 5 fold axis perpendicular to the torus plane, and contain 10 pentagons and 10 heptagons. The 10 pentagons and heptagons are distributed above and below the equatorial plane either in phase, or shifted by $\pi/5$ with respect to each other. In order to study their stability, we calculate and compare their cohesive energy, HOMO-LUMO gap in the electronic energy levels, and their lowest vibrational frequency. This can give us information about their thermodynamic, kinetic, as well as their mechanical stability. Furthermore, we calculate their vibrational free energy as a function of temperature within the harmonic approximation, from which one can get an idea of their relative stability at higher temperatures. Previous calculations on these systems that were performed by

some of us [3] were based on classical molecular dynamics (MD) simulations (for relaxation and total energy calculation) and the Hückel approximation (for calculating the HOMO-LUMO gap). However our new approach is more consistent and improved since all the calculations are done with the same TB theory which is superior to a classical MD scheme. Furthermore, here we are mostly interested in the vibrational properties of these materials, and this has not been done in the past.

2 Method and results

The force calculation for relaxations is done by using the Tight-Binding (TB) method using the parametrization of Xu and coworkers [4]. This is an orthogonal parametrization where the Hamiltonian matrix elements have been fitted as to reproduce the ab-initio band structure of graphite (and diamond to some extent). Since one can consider all these fullerenes as closed surfaces obtained from graphitic sheets with eventually some defects, one expects that such parametrization would also work well for fullerenes. In general the LDA cohesive energy curves of graphite and diamond are reproduced very accurately with this scheme, which has also predicted successfully the atomic coordinates and bond lengths of C_{60} . It is, however, limited to structures where the hybridization between the carbon atoms is of the sp_2 or sp_3 type, and more generally when the coordination number of carbon atoms is 2, 3 or 4.

For the electronic structure calculations, however, we use the parametrization (denoted by SOSH hereafter) used by Saito et al. [6]. This non-orthogonal parametrization is obtained from a fit to the LDA band structure of graphite and can reproduce very well the occupied energy levels of C_{60} . We therefore adopt this formulation for the electronic structure calculations of the clusters.

The properties of the considered 6 isomers can be summarized in Table 1. Their geometry can be viewed in Fig. 1. The numbers in parenthesis in Table 1 are from a previous calculation [3] which is based on a classical molecular dynamics method. This method predicts the bond-lengths in C_{60} to be 1.6 Å, off by 0.2 Å from their experimental value

Table 1. Electronic properties of the 6 toroidal isomers of C_{240} along with the icosahedral C_{240} cluster. CE denotes the Cohesive Energy (the numbers in parentheses are from a previous calculation [3])

Isomer	Gap(eV) XWCH - SOSH	CE/atom -CE(C_{60})(eV)	Group	Inner radius(Å)	Outer radius(Å)	Height(Å)
a	0.76 - 0.74(0.50)	-0.04(-0.09)	D_{5d}	3.86(4.35)	8.20(8.96)	6.55(7.46)
b	0.15 - 0.07(0.26)	+0.01(-0.05)	D_{5d}	3.42(3.78)	7.60(8.03)	7.96(8.65)
c	0.08 - 0.02(0.02)	+0.05(-0.04)	D_{5d}	3.88(4.42)	7.61(8.00)	8.08(8.42)
d	0.16 - 0.31(0.08)	-0.07(-0.10)	D_{5d}	3.36(3.69)	8.19(8.99)	6.74(7.61)
e	0.40 - 0.18(0.28)	-0.03(-0.09)	D_{5h}	3.78(4.35)	8.50(9.14)	6.57(7.52)
f	0.05 - 0.01(0.00)	+0.05(-0.04)	D_{5h}	3.79(4.42)	7.62(8.00)	7.99(8.00)
I_h	1.05 - 1.45	-0.24	I_h	-	7.34	-

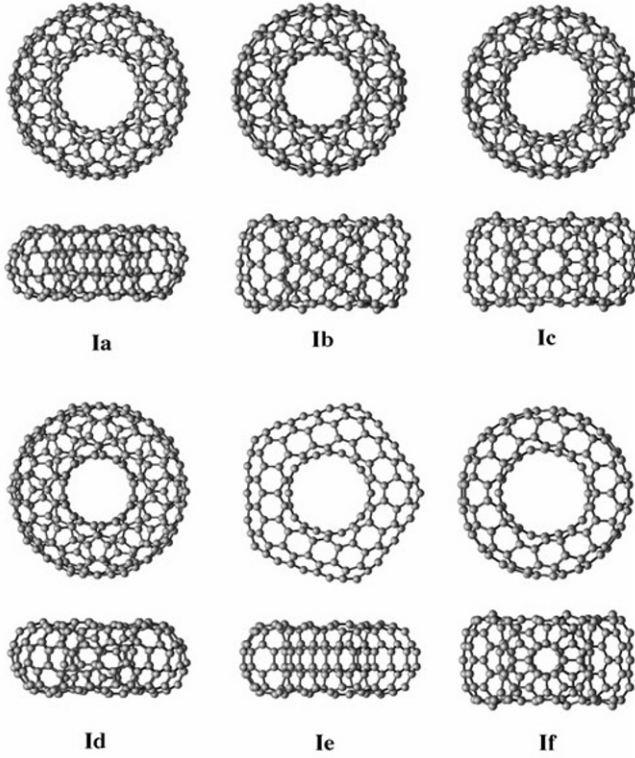


Fig. 1. Orthographic projection of the 6 isomers, topview and sideview

of 1.4 Å. Our results, however, are obtained after relaxation of the original structures with the aforementioned TB method. As one can see, the size of the relaxed structures is smaller than the previous calculation by about 15%. This large difference could induce a large change in the electronic structure of the clusters. Furthermore, the tight-binding gap energies are also more accurate than the previous calculation which uses a rather simple Hückel method.

The cohesive energies of our parametrization being from a fit to LDA calculations, are larger in absolute value than the experimental values; we therefore compare the differences in the cohesive energies with respect to C_{60} . From the above table, one can notice that 1) there is noticeable change in the coordinates and therefore the electronic structure after relaxation is quite different from before. 2) The results are qualitatively similar to those of Itoh and Ihara [3], namely that the isomers *a*, *d* and *e* are the most stable both thermodynamically (lower cohesive energy) and kinetically (largest

HOMO-LUMO gap). One can furthermore relate these properties to the geometries of the considered clusters: the most stable ones (isomers *a*, *d* and *e*) are the ones for which the height is smallest (about 6.5 Å) and the difference between the outer and inner radii highest (about 4.6 Å); in other words, the structures that have a more circular cross section (see Fig. 1). This is because there is less elastic energy stored in the latter. Furthermore, the bond distribution function for these structures is narrower (from 1.38 to 1.46 Å) with higher peaks than the ones for isomers *c* and *f* (from 1.34 to 1.5 Å) with lower peaks (more disordered in a sense!).

It is well-known that zigzag type tubes are usually semi-conducting whereas armchair types are metallic. The isomer *a*'s inner and outer tubes are both of zigzag type; that could explain why it has the largest gap among the 6 considered isomers. In Table 1 we have included both gaps obtained from the orthogonal parametrization of Xu et al. [4] and the non-orthogonal one of Saito et al. [6]. The two results agree qualitatively well. In this case, however, we think that SOSH's parametrization is more reliable since it yields a gap of 2 eV for C_{60} compared to the experimental and ab-initio GW value of 2.15 eV [7] and Xu's of 1.6 eV; and generally, when compared to ab-initio calculations, one finds similar level spacings. It is, furthermore, because of the non-orthogonality, more transferable.

We next turn our attention to the vibrational spectra of these isomers. The first and second derivatives of the TB Hamiltonian can be calculated analytically. We can therefore construct and diagonalize the dynamical matrix of these clusters, and find their vibrational frequencies within the harmonic approximation. From the eigenvectors, one can also get the polarization of each vibrational mode. The vibrational frequencies of C_{60} have also been calculated by this method, and we obtained results in quite good agreement with experiments given the large uncertainty on ab-initio LDA-based calculations. The calculated lowest modes of the 6 isomers are displayed in Table 2. It was found that generally there were one one-fold and two two-fold degenerate modes between 50 and 100 cm^{-1} , separated from the rest of the spectrum. In the case of isomers *c* and *f*, because of the lower symmetry, these break into 5 single modes, the lowest of which goes to zero and makes the molecule extremely soft and unstable. This softness must be related to the electronic property, since the two isomers with this extra-soft vibrational mode have also zero gap i.e. are kinetically unstable. Presumably, for a small specific displacement (along the soft

Table 2. Lowest vibrational frequencies (in cm^{-1}) of the 6 isomers compared to the icosahedral structure and C_{60} . The isomers c and f do not have 2 fold degenerate states due to a lowering of their symmetry

Isomer	first	degeneracy	second	degeneracy	third	degeneracy
a	57	2	65	1	82	2
b	50	1	70	2	79	2
c	7	1	52-54	(2)	74-75	(2)
d	59	1	75	2	89	2
e	53	2	65	1	80	2
f	0	1	50-50	(2)	75-75	(2)
I_h	110	5	137	3	140	4
C_{60}	237	5	318	4	327	3

mode) the HOMO and LUMO are interchanged, and there is no net change in the total energy, hence the softness: One can assume that the HOMO and LUMO levels are mostly affected by an infinitesimal displacement. For systems with a gap, such displacement usually decreases the gap because that would increase the energy. However for systems with zero (or almost zero) gap, again since we are already at the minimum of the energy, the displacement can not increase the gap, so it can only interchange the HOMO and LUMO levels. That would not cost any energy, hence the softness.

The free energy function including the entropy contribution, can also give us an idea about the relative stability of different clusters at high temperatures; since, after all, they are created at high temperatures. The shape of the isomers being similar, their rotational free energies would differ by a very small amount; the main contribution to the free energy coming first from the electrons, and next from the vibrations of the carbon atoms. The total free energy is given by: $F_{elec} + F_{vib} + F_{rot}$ where

$$F_{elec} = 2 \sum_i \left\{ n_i E_i - \frac{1}{\beta} [n_i \log n_i + (1 - n_i) \log(1 - n_i)] \right\}, \quad (1)$$

i refers to the electronic eigenstates of energy E_i , n_i is the Fermi-Dirac distribution function of level i , and $\beta = 1/k_B T$. The vibrational free energy within the harmonic approximation can also be calculated from the following formula in which ω_i is the phonon frequency of the i^{th} mode.

$$F_{vib} = \frac{1}{\beta} \sum_i \log \left[2 \sinh \left(\frac{\beta \omega_i}{2} \right) \right]. \quad (2)$$

Likewise the rotational free energy is given by:

$$F_{rot} = -\frac{1}{\beta} \sum_{i=1}^3 \log[f(y_i)], \quad (3)$$

where $y_i = \frac{\beta \hbar^2}{2I_i}$, I_1, I_2 and I_3 are the three principal moments of inertia of the cluster, and the function f is defined by:

$$f(y) = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)y}. \quad (4)$$

The isomers, being of the same mass, have the same translational free energy. We must add that this free energy is calculated for an isomer of *given geometry*, and therefore

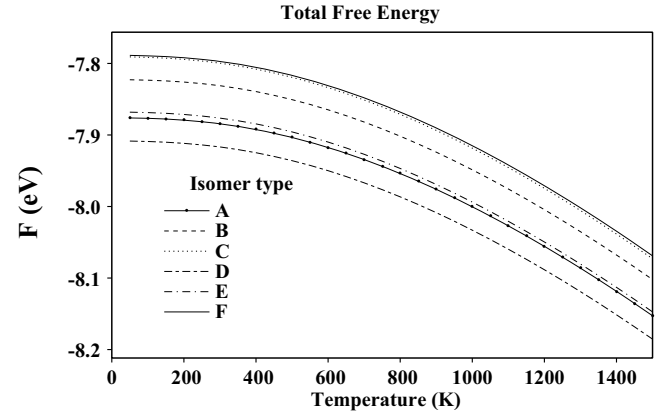


Fig. 2. comparison of the total (electronic, vibrational and rotational) free energy per atom of the 6 isomers. Almost all the decrease in the energy at high temperature is due to the vibrational (harmonic) entropy

does not include any configurational entropy. For that purpose, one should confine oneself to a class of definite shape (like torus in our case), and compute all possible isomers of C_{240} that have this shape. We suspect that other isomers would have higher total energies and their entropy can not make up for it, except maybe at high temperatures where such tori become mechanically unstable anyways, as can be seen from our vibrational analysis. To illustrate this, one can consider the typical energy difference between two isomers; it can be of the order of 20 eV (per cluster) or more, however the entropic contribution which is always of the order of $k_B T$ can hardly exceed this energy even at temperatures of the order of a few thousand Kelvin! In our analysis, we therefore confine ourselves only to these lowest energy symmetrical isomers for which, the degeneracy is the same (the symmetry group is either D_{5h} or D_{5d}), thus the configurational entropy contribution in F would be the same.

It turns out from our calculations, that the phonon free energies and the rotational free energies are almost identical for all isomers. Therefore the total free energy is dictated mostly by the zero temperature total energies. One must, however, notice that the contribution of the entropy of the phonons is as large as the cohesive energies (at about 10,000 K), and must be included in any finite temperature calculation. The electronic entropy and the rotational free energies are very small corrections of the order of 0.01 eV per atom. The graph of the total free energy is displayed in Fig. 2.

3 Conclusions

Several isomers of C_{240} were considered in this work. We can deduce from our tight-binding calculations their electronic properties and stability. The calculation of their vibrational frequencies give us further information about their mechanical properties, their softness for example and the polarization of the corresponding mode. We find that the isomer a is the most stable one kinetically (largest gap) whereas isomer d is energetically and thermodynamically the most stable isomer. The isomer e also displays similar properties. For isomers a, b, d and e , the lowest frequency

mode is of the same order (50 cm^{-1}), which means that they are equally soft. Compared to C_{60} , this frequency is lower by a factor of 4. The isomers c and f have zero gap and also zero frequency for their lowest mode, which means they are electronically and mechanically unstable in their isolated cluster form. The icosahedral C_{240} in comparison, was found to be much more stable than the considered isomers by 0.24 eV per atom. It has furthermore a gap of 1.5 eV and an electronic structure very similar to C_{60} . As a general rule of thumb, we can deduce from this study that isomers with more circular cross sections are more stable because the elastic energy stored in them is less. Furthermore, the kinetic and mechanical stabilities seem to be related to each other (zero gap \leftrightarrow ultra soft vibrational mode).

Inclusion of finite temperature effects did not modify the relative stability of the isomers at least at low temperatures ($T \leq 1500 \text{ K}$) and within the harmonic approximation. We believe it would be rather hard to make such toroidal clusters experimentally, since they are much softer (by at least a factor of 16, since the elastic moduli are proportional to the square of the phonon frequencies) than C_{60} for example. Larger rings would have a better chance for mechanical stability if their cross section is more circular with a larger radius. This way, there would be less stress stored in them. The latter may be produced in an appropriate environment (by making a “mold” for them for example).

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