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NORMAL COORDINATE ANALYSIS OF "FOOTBALLENE" C_{60}^*

Keywords: C_{60} , Footballene, Vibrational frequencies

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ABSTRACT

An approximate force field previously developed for condensed aromatics is adapted to footballene, a C_{60} molecule of icosahedral symmetry. The 46 vibrational frequencies are calculated.

For a general introduction to the interesting (hypothetical) C_{60} molecule called "footballene" it is referred to another paper in this issue [3]. In the present work the reported symmetry coordinates [3] are used to calculate the assigned vibrational frequencies of footballene.

SYMMETRICAL STRUCTURE

The normal modes of vibration of C_{60} footballene are distributed into the species of the appropriate symmetry group (I_h) according to

*Part XXII of the series CONDENSED AROMATICS, which originally was intended to be terminated with Part XX [1]. For Part XXI, see [2].

$$\Gamma_{\text{vib}}(\text{footballene}) = 2A_g(\text{Ra}, \text{p}) + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g(\text{Ra}, \text{dp}) \\ + A_u + 4T_{1u}(\text{IR}) + 5T_{2u} + 6G_u + 7H_u$$

The spectroscopic activities are given in parentheses, using the abbreviations: dp depolarized; IR infrared-active; p polarized; Ra Raman active. The fundamentals of the unmarked species are spectroscopically inactive.

It is found that the 174 modes of vibration, as a consequence of the high symmetry, give rise to only 46 vibrational frequencies, the number being lowered by virtue of the degeneracy. Furthermore, most of the frequencies are inactive in infrared and Raman. In conclusion, this preliminary analysis predicts 10 Raman active and 4 infrared-active fundamentals for footballene. These are unprecedented low numbers for a molecule with 60 atoms. The 5-atomic molecule HNO_3 , for instance (which belongs to C_s), has 9 normal vibrations, which all are active in both Raman and infrared. Graphitene is another model of C_{60} (see the references cited in [3]), which has a relatively high symmetry as belonging to D_{6h} . The symmetrical structure of its normal modes of vibration predicts 39 Raman active and 25 infrared-active fundamentals for this model. The complete distribution into symmetry species is given below.

$$\Gamma_{\text{vib}}(\text{graphitene}) \\ = 10A_{1g}(\text{Ra}, \text{p}) + 9A_{2g} + 3B_{1g} + 7B_{2g} + 9E_{1g}(\text{Ra}) + 20E_{2g}(\text{Ra}) \\ + 3A_{1u} + 6A_{2u}(\text{IR}) + 10B_{1u} + 10B_{2u} + 19E_{1u}(\text{IR}) + 10E_{2u}$$

STRUCTURAL PARAMETERS

Simple Hückel molecular analyses of footballene have been reported by several authors [4-8]. We have repeated this analysis in order to produce theoretical CC bond distances to be used in the normal coordinate analysis. The previously described [1, 9] procedure gave the results of P (bond orders) and R (bond lengths) as shown in Table 1.

Table 1. Bond orders (*P*), theoretical CC distances (*R*) and CC stretching force constants (*f*) in footballene. The symbols of valence coordinates are used to identify the CC bonds.

CC bond	<i>P</i>	<i>R</i> (Å)	<i>f</i> (mdyne/Å)
d	0.476	1.432	4.219
r	0.601	1.409	4.634

FORCE FIELD

Previous parts [1, 10, 11] of the article series entitled "Condensed Aromatics" should be consulted for details about the simple approximations of the in-plane and out-of-plane "aromatic" force fields. This force field was adapted to footballene without modifications. Firstly, the footballene molecule is a completely conjugated system; it may be considered as an aromatic "hydrocarbon" without hydrogens. Thereby the number of parameters in the force field is reduced because no valence coordinates involving hydrogen exist. Secondly, footballene is a non-benzenoid system containing five-membered rings in addition to the six-membered rings. However, the aromatic force field in question [1, 10, 11] has been successfully applied to non-benzenoid systems before, and especially those with five-membered rings, viz. fluoranthene [12] and azulene [13]. Finally, we have to assume, as an additional approximation, that our aromatic force field is applicable to non-planar conjugated systems. This assumption seems to be reasonable inasmuch as we do not pretend to calculate the frequencies with a high degree of precision. By the way, the simple Hückel molecular orbital analysis has also been applied to footballene as if it was a planar system.

In conclusion we end up with five parameters in the approximate force field: CC stretching force constants as given in Table 1 (and reckoned as one parameter); *f*_d for 60 stretchings and *f*_r for 30 stretchings; *f*_φ = 0.4 mdyne/Å for 180 CCC bendings, of

Table 2. Calculated vibrational frequencies (cm^{-1}) for footballene. Parenthesized values are from Ref. 14 (decimals omitted).*

Species A_g (Ra)	ν_1	1409 (1627)	Species A_u (ia)	ν_{24}	999 (1084/970)
	ν_2	388 (548)			
T_{1g} (ia)	ν_3	1281 (1464) [†]	T_{1u} (IR)	ν_{25}	1434 (1655)
	ν_4	834 (811)		ν_{26}	1119 (1374)
	ν_5	688 (567)		ν_{27}	618 (551)
				ν_{28}	472 (491)
T_{2g} (ia)	ν_6	1443 (1665)	T_{2u} (ia)	ν_{29}	1510 (1720)
	ν_7	1080 (927)		ν_{30}	1187 (1309)
	ν_8	734 (726)		ν_{31}	864 (1019)
	ν_9	525 (525)		ν_{32}	753 (627)
				ν_{33}	322 (362)
G_g (ia)	ν_{10}	1549 (1765)	G_u (ia)	ν_{34}	1537 (1765)
	ν_{11}	1384 (1590)		ν_{35}	1402 (1620)
	ν_{12}	1054 (1174)		ν_{36}	1070 (958)
	ν_{13}	917 (673)		ν_{37}	827 (756)
	ν_{14}	502 (530)		ν_{38}	684 (702)
	ν_{15}	452 (456)		ν_{39}	330 (374)
H_g (Ra)	ν_{16}	1601 (1831)	H_u (ia)	ν_{40}	1602 (1830)
	ν_{17}	1468 (1688)		ν_{41}	1380 (1579)
	ν_{18}	1221 (1399)		ν_{42}	1155 (1290)
	ν_{19}	1004 (1160)		ν_{43}	863 (770)
	ν_{20}	743 (780)		ν_{44}	652 (578)
	ν_{21}	645 (552)		ν_{45}	525 (492)
	ν_{22}	435 (428)		ν_{46}	324 (355)
	ν_{23}	218 (272)			

* Abbreviations: ia inactive; IR infrared-active; Ra Raman active.

[†] Assumed misprint [14] in species designation.

which 60 were used in the construction of symmetry coordinates, while the rest are redundant; $f_Y = 0.15$ mdyne/Å for 60 out-of-plane bendings, one for each C atom and all of them redundant coordinates; $f_T = 0.05$ mdyne/Å for 180 "boat" torsion, 60 of them having been used in the construction of symmetry coordinates; 90 torsion/torsion interaction terms of 0.02 mdyne/Å for pairs of torsional coordinates pertaining to the same CC bond.

CALCULATED VIBRATIONAL FREQUENCIES

The results of the computation of vibrational frequencies are presented in Table 2. Therein they are compared with the recently calculated frequencies by Wu et al. [14]. These investigators used an approach entirely different from ours. They did not perform the symmetrization, but diagonalized a 180×180 matrix in order to find the vibrational frequencies (+ 6 zero frequencies). In our diagonalization procedures the largest order of the matrix is 8×8 . The level of approximation in the two analyses seems to be about the same (four parameters [14] versus ours five). In general the two sets of frequencies display the same tendencies and orders of magnitude, although there is far from a quantitative agreement. Best agreements are found for the lowest frequencies. The highest frequencies exhibit differences of more than 200 cm^{-1} , those of Wu et al. [14] being consistently higher than ours.

A large-scale synthetic route to footballene is not known at present, but is eagerly awaited [15, 16]. We believe that a synthesis of C_{60} would be especially interesting in the presence of the predicted vibrational frequencies.

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