

Vibrational analysis of peanut-shaped C₁₂₀ fullerenes

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Abstract. The normal modes of peanut-shaped C₁₂₀ fullerenes, which appear as stable intermediate isomers between the [2+2] dumbbell C₁₂₀ and the completely coalesced C₁₂₀ nanotube [H. Ueno, S. Ōsawa, E. Ōsawa, K. Takeuchi, Full. Sci. Technol. **6**, 319 (1998)], were investigated by semi-empirical AM1 method. It was found that the peanut-shaped C₁₂₀ isomers have a feature of infrared (IR) absorption band in the range 1300–1400 cm⁻¹, which is attributed to the in-plane atomic motions in their negative curvature region.

PACS. 31.15.Ct Semi-empirical and empirical calculations (differential overlap, Hückel, PPP methods, etc.) – 33.20.Tp Vibrational analysis – 71.20.Tx Fullerenes and related materials; intercalation compounds

1 Introduction

Polymerization of C₆₀ molecules in solid by photoirradiation, electron-beam (EB) irradiation, alkali metal doping, or high pressure at high temperature results in a new form of carbon materials [1]. It is well-known that C₆₀ molecules dimerize to form [2+2] cycloadduct C₁₂₀ or single-bonded C₁₂₀ by all the methods [2]. Recently, we found a more strongly bonded C₁₂₀ dimer than the [2+2] C₁₂₀ by EB irradiation of a C₆₀ film [3] as well as photoirradiation of a potassium-doped C₆₀ film [4]. The “coalesced” dimer was confirmed by laser desorption mass spectrometry and its structure was assigned to a peanut-shaped structure by comparison of the infrared (IR) absorption spectrum with theoretical spectra [4] of five C₁₂₀ isomers [6]. It should be noted that other groups also found the “coalesced” dimers as in aggregation following laser ablation of fullerene films [7], in collision between fullerene ions and thin films of fullerenes [8], and in fullerene–fullerene collisions [9].

Using the generalized Stone–Wales rearrangement (GSW) [5], Ōsawa *et al.* [10] presented the reaction pathway from the [2+2] dimer to the perfect C₁₂₀ nanotube *via* 22 stable intermediate isomers, which were not examined in the previous works [3,4]. In order to determine the structure of the coalesced C₁₂₀ more satisfactorily, it is necessary to examine the theoretical IR spectra of all the peanut-shaped isomers appearing in the GSW pathway.

The aim of the present work is to calculate IR vibrational modes of the peanut-shaped GSW isomers and to compare those with experimental IR spectrum by analyzing the atomic motion of IR active modes.

2 Computational method

There are 24 stable C₁₂₀ isomers in the GSW pathway including initial and final states. We designated *n*th C₁₂₀ isomer appearing in the pathway as D*n*. In this notation, [2+2] dimer (initial state) is expressed as D1, while C₁₂₀ nanotube (final state) as D24.

Because *ab initio* calculations for determining the optimized geometry and vibrational frequencies of all the C₁₂₀ isomers in the GSW pathway require enormous computational time by using a standard workstation, we adopted AM1 semi-empirical method [11] in the present work. The calculations were carried out using the Gaussian 98 program package [12] with a workstation (V-T Alpha 533, Visual Technology). The molecular charge of the C₁₂₀ isomers was set to be neutral. Because AM1 method tends to overestimate the vibrational frequency, the obtained frequencies were multiplied by 0.83 that was determined for reproducing the experimental IR frequencies of C₆₀ and [2+2] C₁₂₀ [10].

3 Results and discussion

One of the features that characterize the progress of the GSW pathway is the population of polygonal carbon rings

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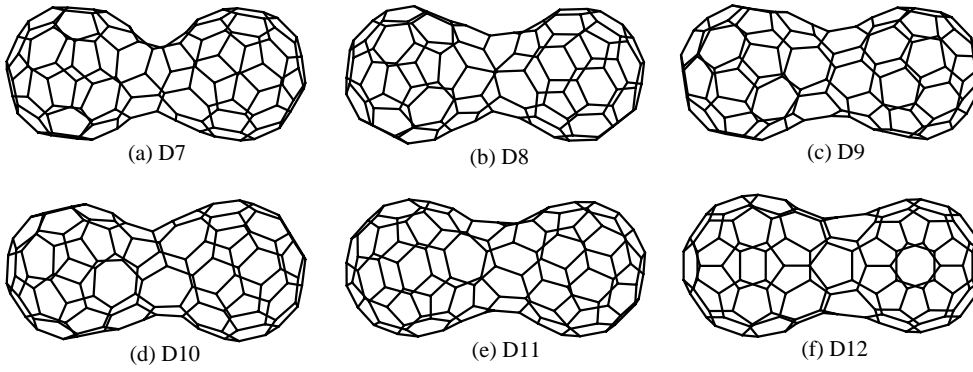


Fig. 1. The optimized structure of stable peanut-shaped C_{120} isomers appearing in the GSW pathway: (a) D7, (b) D8, (c) D9, (d) D10, (e) D11 and (f) D12.

of the C_{120} isomers. As the coalescence reaction proceeds, the large polygonal rings, *i.e.*, heptagons, octagons, nonagons, \dots , in the C_{120} cage decreased. Ōsawa *et al.* characterized [10] the calculated IR spectra of the intermediate C_{120} isomers in the GSW pathway with the population of the polygonal carbon rings as follows: (1) there are four absorption regions in the IR spectrum of the initial state D1, *i.e.*, I (near 500 cm^{-1}), II ($700\text{--}800\text{ cm}^{-1}$), III ($1100\text{--}1200\text{ cm}^{-1}$) and IV ($1400\text{--}1500\text{ cm}^{-1}$), (2) when decagonal ring disappeared in D7, new absorptions appeared around 1300 cm^{-1} between the regions III and IV, (3) these vibrations become more intense and increase in number when nonagonal ring vanished in D9, and (4) when the rearrangement proceeds to form D12 in which the octagonal ring disappeared, the regions III and IV merge into one, and after this, the spectra does not show any noticeable change, although the final state D24 (nanotube) shows markedly simple spectrum with only a few absorptions in I, III and IV regions.

On the basis of the molecular structures and the above property of the IR spectra, here we focus on the intermediate isomers D7–D12 as a peanut-shaped dimer. Figures 1a–1f show their optimized structures. The calculated IR absorption spectra of these isomers are shown in upper side in Figures 2a–2f. In the IR spectra, the absorption peaks were expressed using Lorentzian functions with a width of 4 cm^{-1} . The IR spectra in Figures 2 were almost same as those reported by Ōsawa *et al.*

The structural feature of the peanut-shaped C_{120} is to have a negative curvature region containing larger polygonal carbon rings than hexagon at the center of the molecule. In the present work, we estimated the contribution of the vibrations arising from the “waisted” region to the whole atomic motion of IR active modes of the C_{120} isomers. There is an ambiguity in definition of the “waisted” region in the structure of the peanut-shaped isomers. Here we defined the region as follows: (1) the center of mass was placed as the origin, (2) the molecular principal moment axis was set to be coincide with the z -axis, (3) the space from $z = -0.4z_{\min}$ to $z = 0.4z_{\max}$ Å was defined as the “waisted” region.

The contribution of the “waisted” regional atomic motion to mode m is defined from the square sum of the vector elements of the normal coordinate \mathbf{q}_m among the

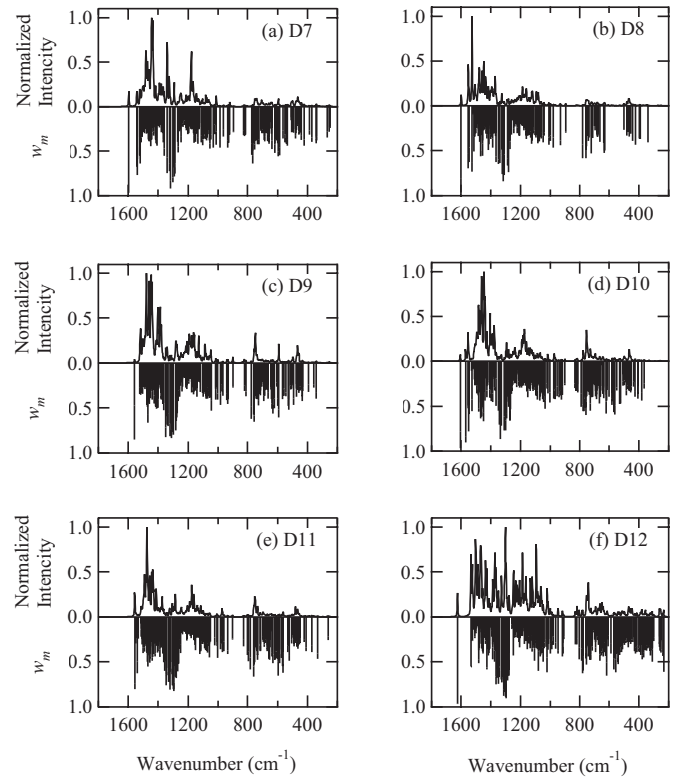


Fig. 2. Calculated IR absorption spectra (upper half) and w_m (lower half) of the peanut-shaped C_{120} isomers in the GSW pathway: (a) D7, (b) D8, (c) D9, (d) D10, (e) D11 and (f) D12.

atoms in the region

$$w_m = \sum_{i \in \text{waisted region}} q_m^2(x_i) + q_m^2(y_i) + q_m^2(z_i). \quad (1)$$

Because \mathbf{q}_m is normalized, $0 \leq w_m \leq 1$. The lower side of Figures 2a–2f shows the calculated w_m for C_{120} isomers D7–D12. It was found that w_m are relatively large in the range $1300\text{--}1400\text{ cm}^{-1}$. This region corresponds to that in which Ōsawa *et al.* utilized to characterize the IR spectra in the GSW pathway [10]. As they pointed out [10], the number of IR absorption peaks in this region increases as the GSW reaction proceeds (D7–D11, Figs. 2), and their intensities become large in

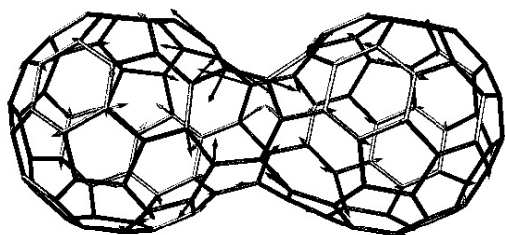


Fig. 3. Atomic motion of the mode at 1319 cm⁻¹ for the D7 isomer ($w_m = 0.85$).

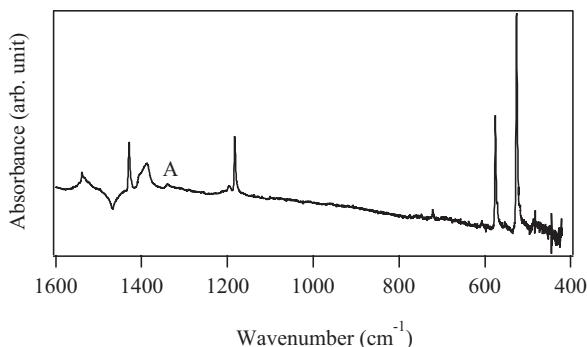


Fig. 4. The experimental IR spectrum of an EB irradiated C₆₀ film on a CsI substrate [3].

comparison with those of D1–D6 in the early stage of the GSW pathway (not shown). Although there are absorptions in the range 1300–1400 cm⁻¹ in and after D12, it is difficult to specify them because the range merged into the neighboring regions III and IV [see, *e.g.*, Fig. 2f]. From the above result, the IR peaks appearing in the range 1300–1400 cm⁻¹ are unique modes due to the C₁₂₀ peanuts in the GSW pathway (D7–D11). Figure 3 shows the atomic motion of the IR mode at 1319 cm⁻¹ for the D7 isomer ($w_m = 0.85$). Large atomic displacements are clearly shown in the “waisted” region.

Figure 4 shows the IR absorption spectrum of an EB irradiated C₆₀ film [3]. The sharp peaks at 527, 576, 1183 and 1429 cm⁻¹ are considered to those of C₆₀. The feature of this spectrum is the broad peak around 1395 cm⁻¹. Although AM1 cannot reproduce the IR intensities of fullerene well, the large peaks in the range 1400–1500 cm⁻¹ in the calculated spectra of D7–D11 (Figs. 2) may correspond to this broad peak. The IR absorption peaks originating from the “waisted” region seem to correspond to the broad IR band marked by “A” (1300–1400 cm⁻¹) in Figure 4. Their intensities are weak but become an indicator for characterizing the peanut-shaped C₁₂₀ isomers.

For the IR modes due to the “waisted” region (1300–1400 cm⁻¹), we re-examined the IR spectra of the three peanut-shaped C₁₂₀ isomers that were previously calculated by a different computational method [13]. Figures 5a, 5b and 5c show the structure of the three C₁₂₀, P55, P56 and P66 (not GSW intermediate isomers), respectively. Figures 6a–6c show their calculated IR spectra and w_m . It was found that the number of the IR modes arising from the “waisted” region is few and their IR inten-

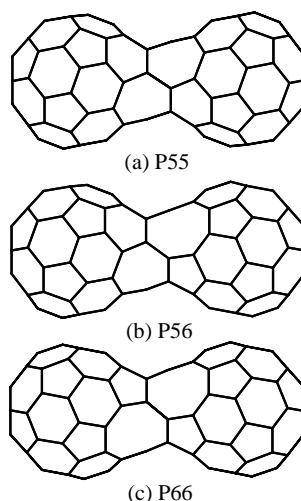


Fig. 5. Structures of the peanut-shaped C₁₂₀: (a) P55, (b) P56 and (c) P66.

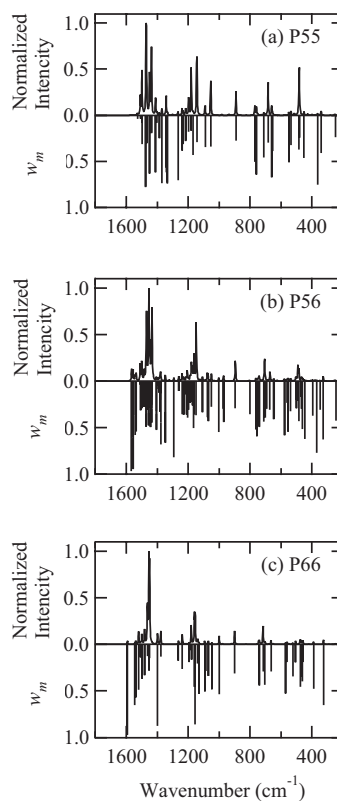


Fig. 6. Calculated normalized IR absorption spectra (upper part) and $w_m d$ (lower part) of the peanut-shaped C₁₂₀ isomers: (a) P55, (b) P56 and (c) P66.

sities are weak in the range 1300–1400 cm⁻¹. It is likely that the GSW isomers are preferable to explain the experimental IR results in comparison with the three isomers (P55, P56, and P66) (Fig. 1).

4 Conclusion

The IR spectra of all the stable peanut-shaped C₁₂₀ isomers appearing in the GSW pathway were obtained using the AM1 semi-empirical calculations and compared to that of an EB irradiated C₆₀ film. It was found that IR absorption band observed in the range 1300–1400 cm⁻¹ is

attributed to the atomic motions in the “waisted” region of peanut-shaped C_{120} shown in Figure 1.

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