Magnetism and Astronomical Infrared Spectrum of Fullerene C$_{60}$ and Void Induced Graphene Molecules

Norio Ota$^1$, Aigen Li$^2$, Laszlo Nemes$^3$ and Masaaki Otsuka$^4$

$^1$Graduate school of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba-City Ibaraki, 305-8571, Japan
$^2$Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA,
$^3$Research Center for Natural Sciences, Ötvös Lóránd Research Network, Budapest 1519, Hungary
$^4$Okayama Observatory, Kyoto University, Asakuchi Okayama, 719-0232, Japan.

Fullerene C$_{60}$ shows astronomical four infrared bands (IR) of carbon rich planetary nebulae. However, there remain many unidentified bands. Our previous paper revealed that single void-defect induced graphene molecule reproduce many astronomical bands. In this paper, we investigated a series of multiple void induced graphene molecules. We tried spin dependent DFT calculation. Model molecules are C$_{23}$ (one carbon pentagon ring among hexagon network), C$_{22}$ (two), and C$_{21}$ (three). Those were all magnetic molecules with spin-state of $Sz=2/2$, $2/2$ and $4/2$ respectively. Calculated IR was compared with astronomical observation. The largest astronomical band at 18.9 micrometer was found in C$_{23}$. Second largest band at 17.4 micrometer appeared both in C$_{22}$ and C$_{21}$. Other major bands from 6 to 10 micrometer were reproduced well by a combination of C$_{23}$, C$_{22}$ and C$_{21}$. Similarly, larger size graphene molecules of C$_{53}$, C$_{52}$ and C$_{51}$ were also magnetic and reproduced astronomical bands as well. Weighting sum IR of those molecules could successfully trace astronomical 12 bands from 6 to 20 micrometer. A series of multiple void induced graphene would be major component of astronomical carbon. Fullerene C$_{60}$ would be one of them.

Key words: graphene, fullerene C$_{60}$, spin state, DFT, infrared spectrum

1. Introduction

It is well known that fullerene C$_{60}$ shows astronomical infrared bands (IR). In 2010, Cami et al. reported the presence of C$_{60}$ in astrophysical environments by the detection of a set of four bands at 7.0, 8.45, 17.3 and 18.9 $\mu$m. Many studies are following it. Typical astronomical objects are the Galactic planetary nebulae Tc1 and the Small Magellanic Cloud nebulae Lin49. Observed spectra were 12 bands, which were compared with experiment and theory. There remain many unidentified bands not explained by C$_{60}$. It is also well known that graphene is a raw material for synthesizing fullerene. Otsuka et al. suggested the presence of small graphene in space. Graphene was experimentally synthesized by Geim and Novoselov.

Our recent study on graphene molecule by the density functional theory (DFT) shows that single void-defect on carbon hexagon network brings highly polarized spin configuration and structure change, and finally brings drastic change of molecular vibrational IR. Such result was understood based on pure carbon magnetism. Model molecules were C$_{23}$ and C$_{53}$, which has one carbon pentagon ring among hexagons. It was firstly revealed that calculated IR shows good coincidence with astronomically observed one. Also, calculation show rough coincidence with the laser induced carbon plasma experiment.

Those molecules were magnetic with spin-state of $Sz=2/2$. Calculated IR of C$_{23}$ and C$_{53}$ could reproduce astronomically observed one of carbon rich nebulae Tc1 and Lin49. However again, there remain some unidentified bands, especially second largest band at 17.4 $\mu$m. We should do advanced study on nano-carbon candidates.

Here is an interesting idea that we should study multiple void induced graphene molecules, because fullerene C$_{60}$ has 12 carbon pentagon rings combined with 20 hexagons. Such multiple pentagon rings could be induced from multiple voids on graphene sheet. In 2013, Tielens opened such concept under the name of top-down-process in his review article. In this study, we investigate a series of multiple void induced graphene molecules focusing on spin-state and molecular vibrational IR. Results will be compared with astronomical observation and laboratory experiment. This paper is a joint study by different research field, which would develop a new science field named as like the Astro-magnetism.

2. Calculation Method

In calculation, we used DFT with the unrestricted B3LYP functional. We utilized the Gaussian09 software package employing an atomic orbital 6-31G basis set. Unrestricted DFT calculation was done to have the spin dependent atomic structure. The required convergence of the root-mean-square density matrix was $10^{-8}$. Based on such optimized
molecular configuration, fundamental vibrational modes were calculated, such as carbon to carbon (C-C) stretching modes, (C-C) bending modes and so on, using the same Gaussian09 \textsuperscript{33}. This calculation also gives harmonic vibrational frequency and intensity in infrared region. The standard scaling is applied to the frequencies by employing a scale factor of 0.975 for pure carbon system taken from the laboratory experimental value of 0.965 based on coronene-molecule of C\textsubscript{24}H\textsubscript{12} \textsuperscript{34}. Correction due to anharmonicity was not applied to avoid uncertain fitting parameters. To each spectral line, we assigned a Gaussian profile with a full width at half maximum of 4cm\textsuperscript{-1}. Any molecular symmetricity was not applied to compare delicate change of molecular configuration and compare small difference of total energy.

3. Fullerene C\textsubscript{60} and Graphene C\textsubscript{23}

3.1 Stable spin state

Input parameters for DFT are charge and spin parameter Sz. Charge was zero (neutral) for every case. We dealt total molecular spin S (vector). Molecule is rotatable material, easily follows to the external magnetic field of z-direction. Projected component Sz to z-direction is a good quantum number.

Result of C\textsubscript{60} is illustrated in Fig. 1. Total molecular energy of Sz=0/2 is 1.79 eV lower than that of Sz=2/2. Stable spin-state was nonmagnetic one of Sz=0/2, which is contrary to previously reported graphene molecule of C\textsubscript{23} \textsuperscript{16} with magnetic Sz=2/2. We note again here the creation step of C\textsubscript{23}. As illustrated in Fig. 2, starting molecule was C\textsubscript{24} having seven carbon hexagon rings. High-speed particle may attack one carbon atom and kick it out. Single void will be created. There occurs re-bonding between carbon atoms. Resulted molecule was C\textsubscript{23} having one pentagon ring. Initial void-defect holds 3 radical carbons and allows 6 spins. Six spins make capable spin-states of Sz=0/2, 2/2, 4/2 and 6/2. Among them, calculated energy of Sz=4/2 and 6/2 show unstable high energy. Here, we should compare Sz=0/2 and 2/2. It should be noted that molecular energy of Sz=2/2 was 0.64 eV lower (stable) than Sz=0/2. We can see up-spin major spin cloud for Sz=2/2 as illustrated on bottom right of Fig. 2 at a cutting surface of spin density 10 e/nm\textsuperscript{3}. We can see up-spin cloud (by red) at a pentagon site.

3.2 Infrared spectrum

Comparison of calculated IR with astronomically observed one is important. Both DFT targeted molecule and interstellar molecule have common condition, that is, of ultra-low material density and of low temperature. Laboratory experiment on earth cannot realize such conditions. Otsuka et al.\textsuperscript{9} opened astronomically observed bands as illustrated in Fig. 3 on top for Tc1 nebula by red and for Lin49 by blue. Laboratory gas-phase experiment for C\textsubscript{60} by Nemes et al.\textsuperscript{30} was marked by blue arrows on middle. Calculated spectrum of C\textsubscript{60} was illustrated for Sz=0/2 by green and for Sz=2/2 by light green. It should be noted that the observed spectra are seen in emission, while DFT gives absorption. A star may illuminate the molecule and excites them to give rise infrared emission. Detailed discussion was done by Li and Drain \textsuperscript{35, 36}. We regard that DFT calculated absorbed spectrum is a mirror image of emission one in case of sufficient high energy excitation.

Calculated spectrum of Sz=2/2 of C\textsubscript{60} shows so ambiguous as illustrated on bottom of Fig. 3. Whereas for stable spin-state Sz=0/2, we can see specific four bands.

In Table 1, every IR obtained by experiment, astronomical observation and DFT calculation were listed in detail. Calculated largest band of C\textsubscript{60} is 18.7 \textmu m, which is 0.1 \textmu m shorter than gas-phase laboratory experiment of 18.8 \textmu m. Whereas, astronomically observed band was 18.9 \textmu m. There remains a question that astronomical 18.9 \textmu m band would come from C\textsubscript{60} or not. Because, in our previous study, single void induced C\textsubscript{23} show a band just at 18.9 \textmu m.

\textbf{Fig. 1} Spin state of fullerene C\textsubscript{60} by DFT calculation.
In Fig. 4, sharp astronomical emission peak at 18.7 μm (marked by black arrow) is a strong atomic emission line of SIII. We are afraid that such strong atomic line may hide a band of C60.

Calculated band of C60 at 17.4 μm coincides well both with astronomical Band-B (17.4 μm) and with gas-phase laboratory experiment at 17.4 μm \(^{26}\).

In shorter wavelength region, calculated C60 show a band at 6.77 μm. It was 0.2 μm shorter than experimental bands of 6.97 μm. Cami et al. suggested that Band-L at 7.1 μm comes from C60. However, it was strange that in our previous paper \(^{16}\), graphene C23 show just 7.1 μm band. Gas phase experiment also has some difficulty. Experiment was done at temperature from 850 to 1150 K and simply extrapolated to 0 K, which has a gap of five order weak strength. Under such complicated situation, we need advanced study.

Cami et al.\(^{2}\) also suggested possibility of fullerene C70. Astronomical bands would be explained by mixing C70 and C60. However, bands of C70 were 18.7, 17.3, 15.5 and 14.8 μm. They could not explain observed major bands from 6 to 13 μm.

Fig. 2 Spin state of single void induced graphene C23.
As shown in Fig. 4, we can see many astronomical bands from Band-A to M. Our previous results are again illustrated in Fig. 4. Major band of C23 has twin peaks at 18.9 and 19.0 μm, and C53 has single peak at 18.9 μm, which are just related to observed Band-A. Second major Band-B was seen at 17.4 μm, which was reproduced well by calculated C60. However, unfortunately, C23 and C53 show weak intensity at 17.4 μm.

At shorter wavelength region from 6 to 10 μm, calculated spectrum of C60 only show two bands at positions of Band-I and M. While graphene C23 and C53 show many bands to coincide well with astronomical bands of Band-G, H, I, J, K, L and M. Moreover, C53 could reproduce further detailed bands coincide with astronomical Band-D, E, F.

4. Multiple-Void Induced Graphene Molecules

4.1 Stable spin state

Fullerene C60 has 12 carbon pentagon rings among 20 hexagons. Multiple pentagon rings could be realized from multiple voids. In this study, we assumed multiple voids for multiple carbon pentagons. We started from C24 as illustrated in Fig. 5. Single void could induce C23 with one pentagon ring marked by red circled 5. Two-voids induced C22 has two pentagons. Molecular configuration was umbrella like curved structure as shown by side view. Three voids induced C21 also show umbrella like configuration. Origin of such structure was discussed by Ota based on re-bonding between carbon atoms by mixing sp^3-orbit with sp^2. Also, Galue & Leines discussed the π-electron irregularity.

As shown in Fig. 6, possible spin states of C22 areSz =0/2, 2/2 and 4/2. Most stable state was Sz =2/2, which energy was 0.17 eV lower than Sz =4/2 and 1.06 eV lower than Sz =0/2. Spin-distribution was illustrated on right. Similarly, C21 has three pentagons. Stable spin state was Sz =4/2. In every molecule, there arises up-spin cloud (by red) at pentagon carbon atom.

Size dependence was checked. Large size molecules starting from C54 were analyzed as shown in Fig. 7. Single void induced molecule of C53 show stable spin-state of Sz =2/2. Two voids induced C52 has two carbon pentagon rings and show stable spin-state of Sz =2/2. Similarly, three voids induced C51 has three pentagons and show stable spin-state of Sz =2/2.

4.2 Infrared spectrum

In Fig. 8, calculated IR were illustrated for molecules of (C23, Sz =2/2), (C22, Sz =2/2) and (C53, Sz =2/2) compared with astronomically observed spectra of carbon rich nebulae Tc1 and Lin49.

As shown in Fig. 6, possible spin states of C22 are Sz =0/2, 2/2 and 4/2. Most stable state was Sz =2/2, which energy was 0.17 eV lower than Sz =4/2 and 1.06 eV lower than Sz =0/2. Spin-distribution was illustrated on right. Similarly, C21 has three pentagons. Stable spin state was Sz =4/2. In every molecule, there arises up-spin cloud (by red) at pentagon carbon atom.

Size dependence was checked. Large size molecules starting from C54 were analyzed as shown in Fig. 7. Single void induced molecule of C53 show stable spin-state of Sz =2/2. Two voids induced C52 has two carbon pentagon rings and show stable spin-state of Sz =2/2. Similarly, three voids induced C51 has three pentagons and show stable spin-state of Sz =2/2.
At middle wavelength region, Bands D, E, and F were reproduced by C₄₄ family. Also at shorter region, Bands from H to M were reproduced well. While calculated band at 6.2 μm was not shown by observation. We are afraid of the sensitivity at 6.2 μm, because detection range of Spitzer/IRS spectra was 6 to 9 μm.

Fig. 5 Creation of multi-void induced C₂₄ family.

| Number of Carbon Rings | Spin State Energy | Spin-configuration | Stable spin state, Spin-configuration |
|------------------------|-------------------|--------------------|--------------------------------------|
| C₂₄                    | S=0/2             | No spin-distribution | C₂₅ S=0/2                            |
|                        | S=2/2             |                    | C₂₃ S=2/2                            |
|                        | S=0/2             |                    | C₂₂ S=0/2                            |
|                        | S=2/2             |                    | C₂₁ S=0/2                            |

Fig. 6 Stable spin state of graphene C₂₄ family.

Fig. 7 Stable spin state of larger size graphene C₅₄ family.

Fig. 8 Calculated IR of (C₂₃, Sₓ =2/2), (C₂₂, Sₓ =2/2) and (C₂₁, Sₓ =4/2) compared with observation. Band B was well reproduced by C₂₂ and C₂₁.
5. Weighting Sum IR

As discussed in a previous section, C_{60} was difficult to reproduce full bands of astronomical bands as shown on panel (C) in Fig. 10. A series of multiple void induced graphene has a capability to reproduce full bands. We tried a weighting sum spectrum by C_{23}, C_{22}, C_{53}, and C_{52}. It was demonstrated on panel (D). Observed major bands of Band-A and B were well reproduced. Also detailed bands of Band-C, D, E, F, were reproduced well. Shorter wavelength bands of Band-G, I, K, L and M were well reproduced again. In panel (E), we add spectrum of C_{60} to above weighting sum of graphene. It looks that major part of (E) was similar with (D). There is not any significant difference. Major contribution of astronomically observed spectrum may come from graphene. Fullerene C_{60} would contribute a part of them.

6. Laser Induced Carbon Plasma Experiment

As an analogy of astronomical creation of carbon dust, the laser induced carbon plasma experiment (LICP) was done. High power laser irradiates bulk graphite to create carbon plasma and finally creates nano-carbon. In third column of Table 1, IR by LICP was noted. In Fig. 11, we can see rough coincidence of LICP spectrum with calculated weighting sum IR of C_{23}, C_{22}, C_{53} and C_{52}. While as marked on middle, there was little coincidence with gas-phase experimental two bands of C_{60}.
7. Conclusion

A series of multiple void induced graphene molecules were studied by DFT calculation comparing with astronomical observation and laboratory experiments. Fullerenes $C_{60}$ gives astronomically observed IR. We could obtain four bands by calculation. However, there remain many unidentified astronomical bands. Single void-defect induced graphene molecule reproduced well many bands. However, there remain major astronomical band at 17.4 μm. A series of multiple-void induced graphene molecules were studied. Model graphene were $C_{23}$ (one void induced one pentagon ring), $C_{22}$ (two), $C_{21}$ (three). Stable spin state was $S_z = 2/2$, $S_z = 2/2$ and $S_z = 4/2$ respectively. The largest band at 18.9 μm was found in $C_{23}$. Second largest band at 17.4 μm was seen both in $C_{22}$ and $C_{21}$. Similarly, large size graphene $C_{26}$, $C_{52}$ $C_{51}$ could also reproduce astronomical bands as well. Weighing sum IR by $C_{23}$, $C_{22}$, $C_{53}$ and $C_{52}$ could successfully trace observed 12 bands from 6 to 20 μm. Laboratory experiment of laser induced carbon plasma suggested rough coincidence of spectrum with a weighing sum IR by $C_{23}$, $C_{22}$, $C_{53}$ and $C_{52}$. A series of multiple void induced graphene molecules would be a major component of astronomical carbon dust. Fullerenes $C_{60}$ would be a part of them.

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Note on abbreviation of astronomical journals, ApJ: The Astrophysical Journal, ApJL: The Astrophysical Journal Letters A&A: Astronomy and Astrophysics MNRAS: Monthly Notices of the Royal Astronomical Society PNAS: Proceedings of the National Academy of Sciences

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