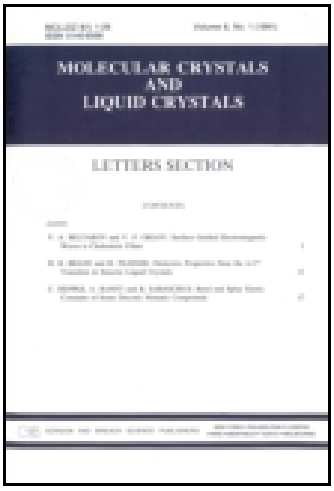

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Dynamic Behavior of Lithium-Cation in a C_{60} Fullerene Cage Elucidated by Terahertz Spectroscopy

Eunsang Kwon[a], Ken-Ichirou Komatsu[b], Kazuhiko Kawachi[b], Yasuhiko Kasama[b] & Tomoaki Endo[c]

[a] Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Sendai, Japan

[b] Idea International Co., Ltd, Sendai, Japan

[c] Sendai National College of Technology, Natori, Japan

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Dynamic Behavior of Lithium-Cation in a C_{60} Fullerene Cage Elucidated by Terahertz Spectroscopy

EUNSANG KWON,[1,*] KEN-ICHIROU KOMATSU,[2] KAZUHIKO KAWACHI,[2] YASUHIKO KASAMA,[2] AND TOMOAKI ENDO[3]

[1]Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Sendai, Japan
[2]Idea International Co., Ltd, Sendai, Japan
[3]Sendai National College of Technology, Natori, Japan

This is the first report of the dynamic behavior of lithium-cation encapsulated in a C_{60} fullerene cage with terahertz (THz) spectroscopy. The THz spectroscopy of lithium-cation showed specific bands at 4.6 and 4.9 terahertz assigned to the two reciprocating vibrational modes, respectively, in the inside space of the fullerene cage.

Keywords Endohedral metallofullerene; lithium-cation; terahertz spectroscopy; DFT calculation

1. Introduction

Metallofullerenes are expected to have novel potential applications in material science. Having the highest symmetry and the most stable fullerene cage, C_{60}, doped with alkali-metal is particularly interesting because of its superconducting properties [1], analogous to the series of the endohedral metallofullerenes (EMFs), alkali-metal@C_{60} (the '@' symbol in the formula indicates that the atom(s) are encapsulated inside the cage), has also attracted considerable attention in the field of novel material development. Among the series of the alkali-metal@C_{60}, only the isolation and characterization of lithium-cation@C_{60} have been reported recently by Aoyagi et al. [2, 3]. They demonstrated the position of this encapsulated metallic atom within the fullerene cage by single-crystal X-ray crystallography. As C_{60} fullerene has a spherical empty space inside the carbon cage, lithium-cation will sway in this nanometer scale void. Moreover, the dynamic behavior is thought to be strongly related to the functional properties of the EMFs. However, there have been no reports on the direct observation of the dynamic behavior of lithium-cation in a C_{60} fullerene cage.

In the present work, we studied the optical absorption and its theoretical interpretation of the lithium-cation@C_{60} in the terahertz (THz) region, which is thought to be strongly related to the functional properties of the EMFs.

*Address correspondence to Eunsang Kwon, Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, 6-3, Aoba Ward, Sendai 980-8578, Japan. E-mail: ekwon@m.tohoku.ac.jp

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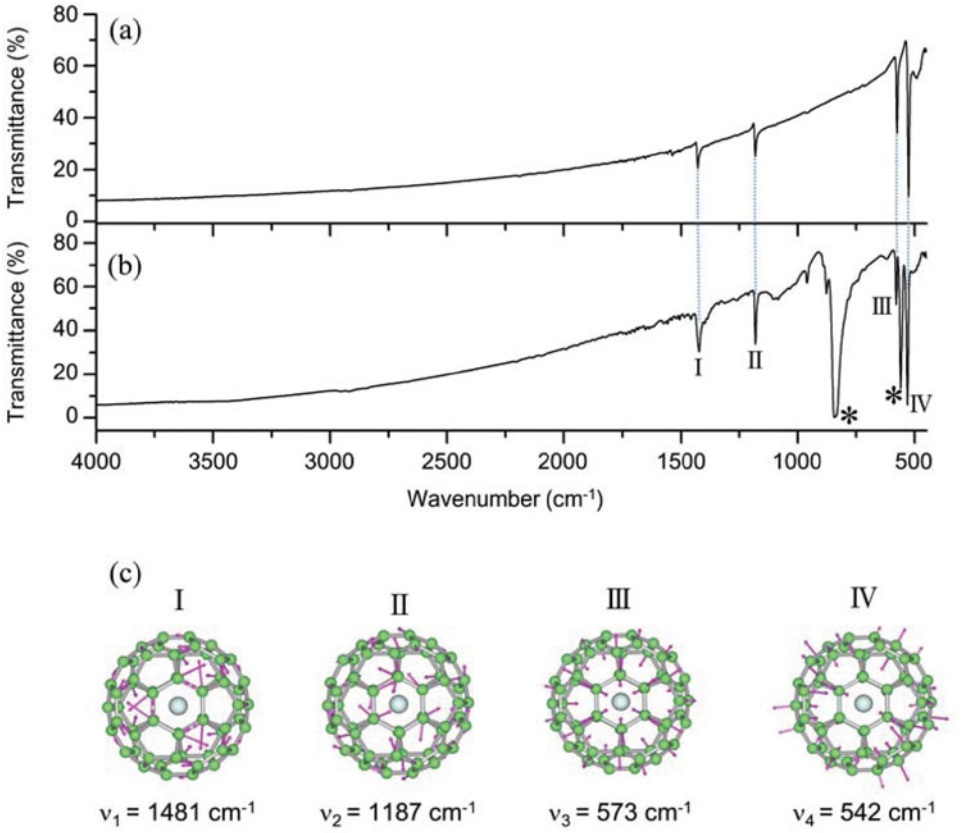

Figure 1. (a) Infra-red (IR) spectrum of C_{60} fullerene in KBr pellet (b) IR spectrum of $[Li^+@C_{60}]\bullet[PF_6]^-$ in KBr pellet (* = vibrational bands of the PF_6 anion). (c) Displacement vector diagrams and frequency of each vibrational mode for $[Li^+@C_{60}]\bullet[PF_6]^-$ calculated by the density functional theory (DFT) method with the B3LYP functional and LanL2DZ basis set (PF_6 anion has been omitted for clarity).

2. Experimental

Lithium-cation endohedral metallofullerene hexafluorophosphate salt ($[Li^+@C_{60}]\bullet[PF_6]^-$) (**1**) is commercially available from Idea International Co., Ltd., Japan [4]. Fourier transform infrared (FT-IR) spectra were recorded using FT/IR-4100 type A (JASCO, Japan) with KBr pellets formed from dry powder samples. The absorption spectra of the powder samples of $[Li^+@C_{60}]\bullet[PF_6]^-$ in the THz region were measured using a THz time-domain spectrometer (TR-1000, Otsuka Electronics Co., Ltd., Osaka, Japan), at room temperature under nitrogen atmosphere. The DFT calculations were carried out by the hybrid B3LYP functional using LanL2DZ basis set [5].

3. Results and Discussion

As shown in Fig. 1, the FT-IR spectrum of **1** exhibited four remarkable peaks similar to those found in the C_{60}. The comparison of the experimental data and the DFT calculations showed that the vibrational bands are due to the motions of the C_{60} cage and counter anion.

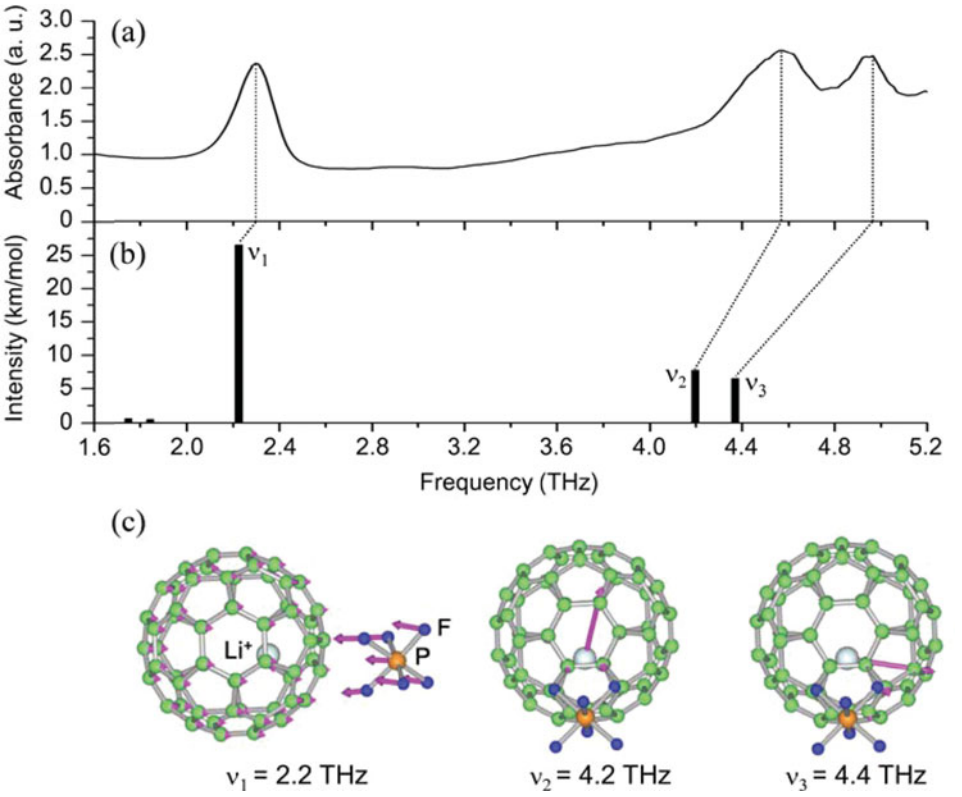

Figure 2. (a) Terahertz absorption spectrum of $[Li^+@C_{60}]\bullet[PF_6]^-$ in the frequency region 1.6 to 5.2 THz. (b) Terahertz vibrational absorption bands of $[Li^+@C_{60}]\bullet[PF_6]^-$ calculated using the DFT method at the B3LYP/LanL2DZ level of theory. (c) The calculated vibrational modes at 2.2, 4.2 and 4.4 terahertz, respectively.

Thus, vibration modes strongly coupled to the lithium-cation were not observed in the near to middle infrared region.

The absorption spectra using THz time-domain spectroscopy of **1** revealed distinct absorption bands at 2.3, 4.6, 4.9 THz, respectively (Fig. 2). A theoretical calculation was performed to identify the origin of the vibrational modes observed in the spectra of **1**. Density functional theory calculations showed that the vibration modes for the endohedral lithium-cation at 4.2, 4.4 THz and for the cation-anion pair at 2.2 THz were in excellent agreement with the experimentally observed values. The intensity of the vibrational bands at 4.2 and 4.4 THz was almost the same as those bands assigned to the two reciprocating vibrational modes in the inside space of the fullerene cage.

As described above, we demonstrated the first direct observation of the dynamic behavior of lithium-cation in a C_{60} fullerene cage. The movement of lithium-cation in a C_{60} fullerene cage is influenced by the terahertz radiation. This information would enable us to control the properties of EMFs. Further research relating to the dynamic behavior of lithium-cation in a C_{60} fullerene cage is in progress.

4. Conclusions

The dynamic behavior of lithium-cation in a C_{60} fullerene cage was investigated using THz spectroscopy and DFT calculations. The THz spectroscopy of endohedral lithium-cation showed bands at 4.6 and 4.9 terahertz assigned to the two reciprocating vibrational modes, respectively. In combination with DFT calculations, we provide insight into their vibrational properties.

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