Vibrational Spectroscopy of Endohedral Dimetallofullerene, $La_2@C_{80}$

Masaya Moriyama, Tadatake Sato, Akira Yabe,* Kazunori Yamamoto,† Kaoru Kobayashi,†† Shigeru Nagase,*††
Takatsugu Wakahara,††† and Takeshi Akasaka*†††, ††††
National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565
†*Tokai Works, Power Reactor and Nuclear Fuel Development Corporation, Tokai, Ibaraki 319-1100*
††*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397*
†††*Graduate School of Science and Technology, Niigata University, Ikarashi, Niigata 950-2181*
††††*Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

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The first FT-IR spectra of $La_2@C_{80}$ are observed at temperatures from 353 to 83 K by dispersing the sample into the KBr pellet, which confirm that the C_{80} cage has I_h symmetry, as supported from theoretical calculations. Also discussed is the rotational motion of the C_{80} cage.

Endohedral metallofullerenes have long attracted special attention as new spherical molecules with novel properties unexpected from empty fullerenes.[1] The electronic properties and reactivities have been extensively investigated.[1,2] The structural determination and the dynamic behaviors of metal atoms are currently of primary interest.[1,3] In disclosing these points, vibrational spectroscopy is a useful tool. Thus, it has been attempted to observe and assign the vibrational modes of endohedral metallofullerenes.[4-7] For empty fullerenes, the vibrational spectra have been successfully measured on vacuum-deposited solid films.[8-10] However, preparation of the solid films consisting of dimetallofullerenes is still difficult because a considerable amount of samples is necessary. We report here the first IR study of the representative dimetallofullerene $La_2@C_{80}$,[11] which has been achieved by dispersing $La_2@C_{80}$ into a KBr pellet, together with theoretical calculations.[12]

The FT-IR spectra of $La_2@C_{80}$ measured at temperatures from 353 to 83 K are shown in Figure 1. One intense band was observed at 1384 cm^{-1} in the temperature region, which is ascribable to a carbon framework vibration. Several weak bands become appreciable at 83 K, which are at 505, 680, 1232, 1463 cm^{-1} (marked in Figure 1).[13] The intensities of all bands increased monotonically with decreasing temperature. The FT-IR spectrum of $La_2@C_{80}$ coated on the polyethylene film showed no band at wavelengths from 500 to 50 cm^{-1}. For the C_{80} fullerene, there are seven cage isomers that satisfy the isolated pentagon rule.[14] The D_2 isomer has been most abundantly produced and extracted.[15] However, it has been calculated that the I_h isomer (least stable for C_{80}) becomes the most stable upon accommodating two La atoms.[16] This I_h cage structure of $La_2@C_{80}$ has been suggested from an analysis of the ^{13}C and ^{139}La NMR spectra.[17] The simple IR spectra in Figure 1 are apparently due to the high symmetry structure.

There are 234 (3 x 80 – 6) vibrational modes for C_{80}. In I_h symmetry, these are distributed between the irreducible representation in the following way:

$$G_{vib} = A_g + 4T_{1g} + 5T_{2g} + 8G_g + 11H_g + A_u + 6T_{1u} + 7T_{2u} + 8G_u + 9H_u$$

Among these, only 6 vibrational modes are IR active which have T_{1u} symmetry. Since three valence electrons are transferred from each La to C_{80}, $La_2@C_{80}$ has an electronic structure of $(La^{3+})_2C_{80}^{6-}$.[3,17] As shown in the NMR study,[17] two La^{3+} cations rotate rapidly inside the round I_h cage of C_{80}^{6-} with small barriers.[3] Vibrational wavenumbers calculated for the C_{80}^{6-} (I_h) cage are summarized in Figure 2. As this model calculation shows, one IR absorption is relatively strong (for the vibrational mode, see Figure 3). This and the overall trends in Figure 2 agree reasonably

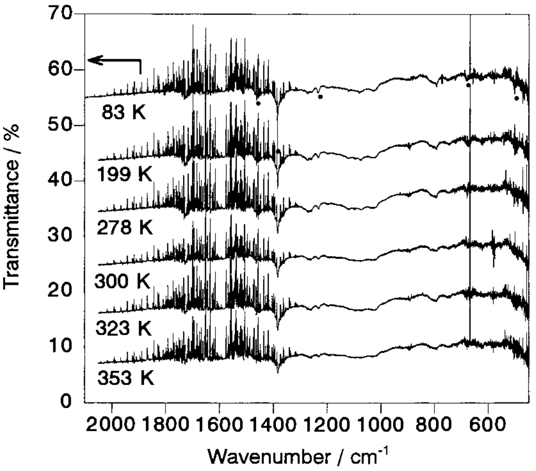

Figure 1. Infrared spectra of $La_2@C_{80}$ in KBr pellet at temperatures between 83K and 353K.

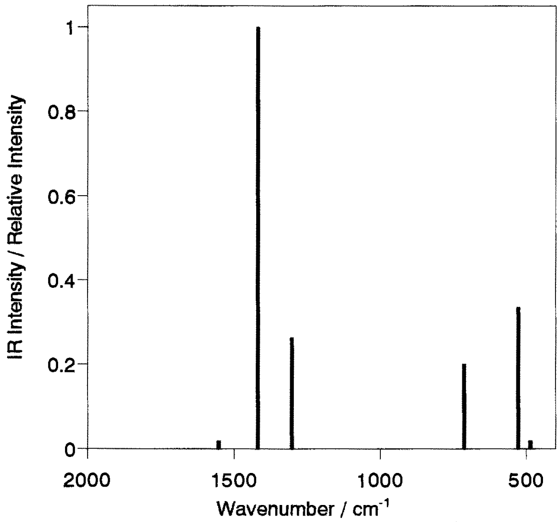

Figure 2. Infrared spectrum calculated for $C_{80}^{6-}(I_h)$. Because of the absence of two La atoms, the intense band shifts by ca. 40 cm^{-1} smaller than that of $La_2@C_{80}$.

well with the observed IR spectra.

Upon decreasing the temperature to 83 K, the band at 1384 cm^{-1} becomes sharp and strong but shifts little (see Figure 1). This result indicates that there is little structural change in carbon network in the temperature region. The change in the lineshape of IR bands is relevant to the rotational state of the fullerene cage as described later. The most stable endohedral structure of La$_2$@C$_{80}$ optimized with the I$_h$ cage has D$_{2h}$ symmetry[3,16] in which two La atoms are ca. 2.6 Å apart from cage carbons and located equivalently along a C$_2$ axis with a La- La distance of 3.743 Å. Vibrational calculations for this D$_{2h}$ structure show that two vibrational modes at 66 (b$_{2u}$) and 72 (b$_{1u}$) cm^{-1} are IR active which are associated with the vibrations of two La atoms: these correspond to the vibrations of the La-La unit in two directions perpendicular to the La-locating C$_2$ axis. We were unable to observe these small wavenumbers at very low temperatures in the present study. However, it is noteworthy that the band observed at 1384 cm^{-1} is in good agreement with the intense one at 1317 cm^{-1} (corresponding to the vibrational mode in Figure 3) calculated for the static D$_{2h}$ structure of La$_2$@C$_{80}$.

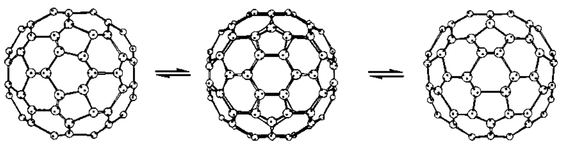

Figure 3. The vibrational mode with a strong intensity.

For empty fullerenes, the temperature dependence in the lineshape of vibrational bands has been explained by a picture of freely rotating molecules in the solid state[8]; the slope of temperature dependence curve of linewidth has been drastically changed at the temperature corresponding to phase transition between rotational diffusion state and ordered state. The similar tendency has been observed in the IR study on a cast film of Sc$_2$@C$_{84}$.[7] Figure 4 shows the temperature dependence of the linewidth of the band at 1384 cm^{-1}. The linewidth monotonically narrowed from ca. 14 cm^{-1} to 1.5 cm^{-1} with a decrease in the temperature from 353 K to 83 K. In this temperature region, the change in the dynamics of La atoms observed around 258 K by the ^{139}La NMR measurement[17] was not observed. This result indicates that the vibration and/or rotation of the C$_{80}^{6-}$ cage is unsusceptible to the circular motion of La atoms. Moreover, the behavior corresponding to the phase transition reported for empty fullerenes[8] was not observed for La$_2$@C$_{80}$ during the temperature changes. Since the observed linewidths (1.5 - 14 cm^{-1}) are larger than those (0.5 - 2.0 cm^{-1}) of C$_{60}$ in the ordered state,[8] La$_2$@C$_{80}$ should be in the rotational diffusion state. For this observation, the following possible interpretations can be considered; i) there is a repulsive electrostatic-interaction between La$_2$@C$_{80}$ molecules which disturbs their aggregation and ii) La$_2$@C$_{80}$ can not form the ordered state because of its dispersion in the KBr pellet. The observed temperature dependence, therefore, may be explained by the vibration-rotation coupling.

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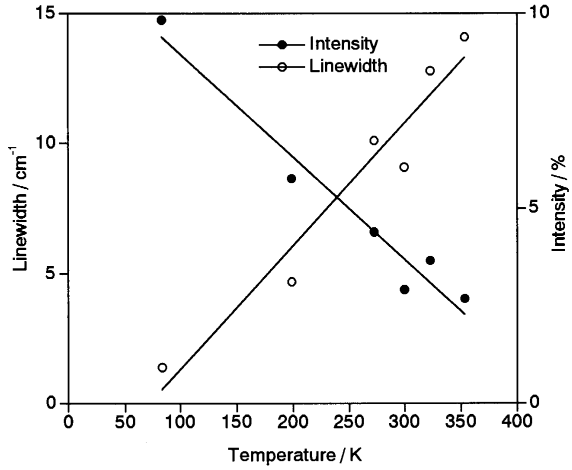

Figure 4. Temprature dependence of intensity and linewidth for the 1384 cm^{-1} band of La$_2$@C$_{80}$

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