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# Low–Lying Transition–Allowed States of Tube–Like Fullerenes $C_{60+10n}$

Yasushi Nomura, Hiroya Fujita, Susumu Narita, and Tai–ichi Shibuya

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano–ken, 386–8567, Japan

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# Low–Lying Transition–Allowed States of Tube–Like Fullerenes $C_{60+10n}$[#]

Yasushi Nomura,* Hiroya Fujita, Susumu Narita, and Tai–ichi Shibuya

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano–ken, 386–8567, Japan

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**Abstract**

**Motivation.** Several groups have theoretically shown that the HOMO–LUMO gaps of the tube–like fullerene $C_{60+10n}$ vary periodically with $n$ and take minimum values at $n = 2, 5, \ldots$. Previously we demonstrated similar periodicity for their lowest excitation energies. Here we examine the low–lying excited states from the spectroscopic viewpoint.

**Method.** SECI (or TDA) calculations are made in the semiempirical CNDO/S approximation. The geometries optimized with Gaussian 98 at the AM1 level are used.

**Results.** The excitation energy of the lowest transition–allowed state of the $C_{60+10n}$ is shown to vary periodically with $n$. In the simulated absorption spectra for $n > 3$, prominent peaks with large oscillator strengths appear at the low energy region (< 3 eV). Their peak positions also similarly vary with $n$. It is found that two SEC's of [HOMO → LUMO+1] and [HOMO–1 → LUMO] make dominant contributions to both the lowest allowed state and the excited state corresponding to the prominent peak.

**Conclusions.** The periodic $n$–dependences of the lowest transition–allowed excitation energy and of the prominent peak position are direct reflections of those of the two SEC's including HOMO and LUMO.

**Keywords.** Tube–like fullerenes; excitation energy; oscillator strength; semiempirical MO method; SECI (or TDA).

**Abbreviations and notations**

| | |
|---|---|
| CNDO/S, complete neglect of differential overlap, for spectroscopic use | MO, molecular orbital |
| HOMO, highest occupied MO | SEC, singly–excited configuration |
| LUMO, lowest unoccupied MO | SECI, singly–excited configuration interaction |
| LDM, localized density matrix | TDA, Tamm–Dancoff approximation |
| | *irreps*, irreducible representation |

## 1 INTRODUCTION

A success of synthesizing fullerene–$C_{60}$ by rational chemical methods [1] showed possibility of synthesizing higher fullerenes with any structure. Molecules $C_{60+10n}$ called tube–like fullerenes in this article are a kind of higher fullerenes and each of them consists of the bisected $C_{60}$–caps and a

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[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

* Correspondence author; E–mail: nomuray@giptc.shinshu–u.ac.jp.

single–wall cylinder.

Several groups [2–4] have shown with different computational methods that the HOMO–LUMO gaps of the $C_{60+10n}$ vary periodically with $n$ and take minimum values at $n = 2, 5, \ldots$. According to our previous calculations [4] with the semiempirical CNDO/S method [5], the HOMO's and LUMO's (and their neighboring MO's) are described in terms of the pseudo π–orbitals that are normal to the fullerene surfaces. Analyzing the pseudo π–conjugated systems with the Pauling bond order [6], we attributed the origin of the periodicity to pseudo π–conjugation separately formed on layers of the *cyclo*–pentaphenylene structure with 30 C–atoms in the central cylindrical parts [4]. In Ref. [4], we also showed that the lowest singlet excited states of the tube–like fullerenes are dominated by the HOMO → LUMO excitations and that the *n*–dependence of their energies is very similar to that of the HOMO–LUMO gaps.

We now ask: How does the periodicity of the HOMO–LUMO gap affect the spectroscopic properties of the tube–like fullerenes? In this article we make CNDO/S–TDA (or SECI) calculations on the fullerenes $C_{60+10n}$ to investigate the characters of their transition–allowed states in the low energy region.

## 2 MATERIALS AND METHODS

The geometry optimization with Gaussian 98 at the AM1 level shows that the tube–like fullerenes $C_{60+10n}$ ($n = 1, \ldots, 12$) have the $C_5$–rotational axes going through the centers of the caps and symmetries $D_{5h}$ and $D_{5d}$ for odd $n$ and even $n$, respectively. Their cylindrical parts have the armchair structures, as shown in Figure 1. With these optimized geometries, CNDO/S–TDA calculations in truncated active MO–spaces around the HOMO–LUMO gaps are made to obtain the transition energies and amplitudes for the low–lying excited states. Active MO–spaces taken in our TDA calculations (Footnote 1) are as follows: showing numbers of (occupied×unoccupied) MO's, 14×14 ($n = 1$), 17×17 ($n = 2$), 17×15 ($n = 3$), 20×18 ($n = 4$), 18×16 ($n = 5$), 16×20 ($n = 6$), 17×17 ($n = 7$), 17×17 ($n = 8$), 18×18 ($n = 9$), 18×18 ($n = 10$), 18×18 ($n = 11$) and 21×18 ($n = 12$). The reliability of the TDA calculations with these truncated MO–spaces is discussed in Footnote 2.

Absorption spectra of the fullerenes are simulated through the following equation:

$$I(\omega) \propto \sum_{\ell} f_{\ell g} \exp[-(\omega_{\ell g} - \omega)^2 \big/ {\Gamma_{\ell g}}^2] \tag{1}$$

where $f_{\ell g}$ and $\omega_{\ell g}$ are the oscillator strength and the transition frequency for the optically allowed transition from the ground state ($g$) to an excited state $\ell$, respectively, and $\Gamma_{\ell g}$ is a bandwidth corresponding to the transition.

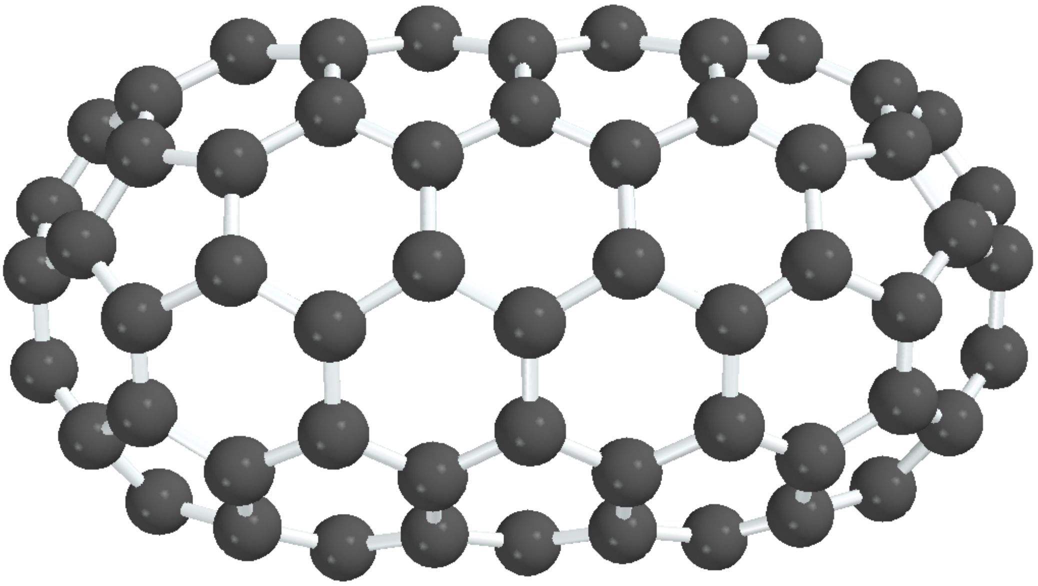

**Figure 1.** Typical structure of the tube-like fullerene. The structure of $C_{110}$ is shown, as an example.

# 3 RESULTS AND DISCUSSION

First, we consider the excitation energy $E_{\mathrm{ex}}$ of the lowest transition–allowed state of the tube–like fullerene $C_{60+10n}$, which corresponds to the longest edge of the allowed absorption. The $n$–dependence of the $E_{\mathrm{ex}}$ obtained from the present calculation is shown in Figure 2. Clearly the $E_{\mathrm{ex}}$ varies periodically with $n$, taking the minimum values at $n = 2, 5, 8, 11$.

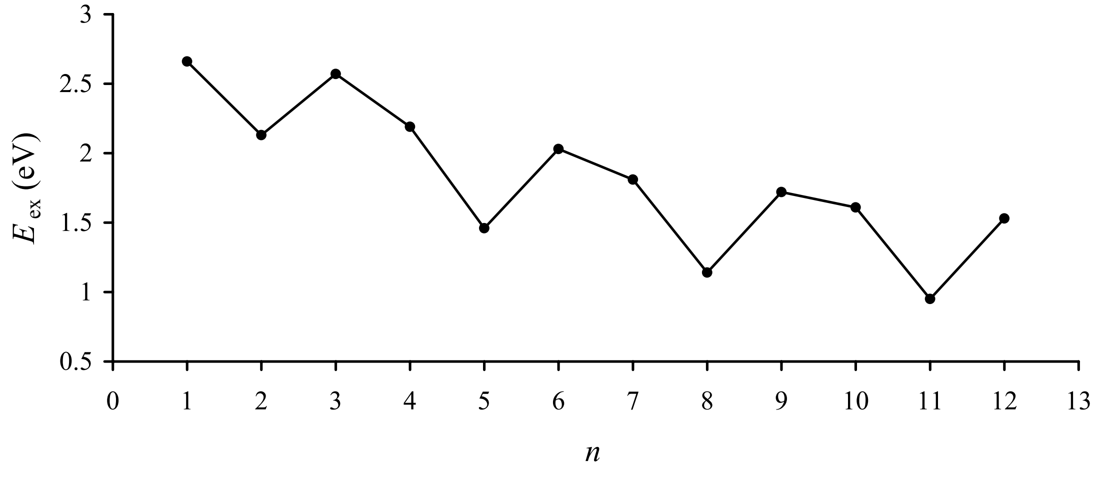

**Figure 2.** The lowest excitation energies $E_{\mathrm{ex}}$ of the tube-like fullerenes $C_{60+10n}$ vs. $n$, calculated with the CNDO/S-TDA scheme. The TDA calculations were made in truncated active MO-spaces as described in text.

Note that the lowest transition–allowed state for $n > 2$ belongs to the irreducible representations (*irreps*) $A_2''$ and $A_{2u}$ for odd $n$ and even $n$, respectively, while the lowest allowed states of $C_{70}$ and $C_{80}$ belong to the degenerate *irreps* $E_1'$ and $E_{1u}$ (see Footnote 3), respectively. Analyzing the

CNDO/S–TDA data, we notice that the states for $n > 3$ practically consist of the two singly–excited configurations (SEC's): [HOMO → LUMO+1] and [HOMO–1 → LUMO], where all the MO's belong to the one–dimensional *a*–representations (see Footnote 4). For $n = 3$, dominant SEC's are of [HOMO ($a_1''$) → LUMO+2 ($a_2'$)] and [HOMO–2 ($a_1'$) → LUMO ($a_2''$)].

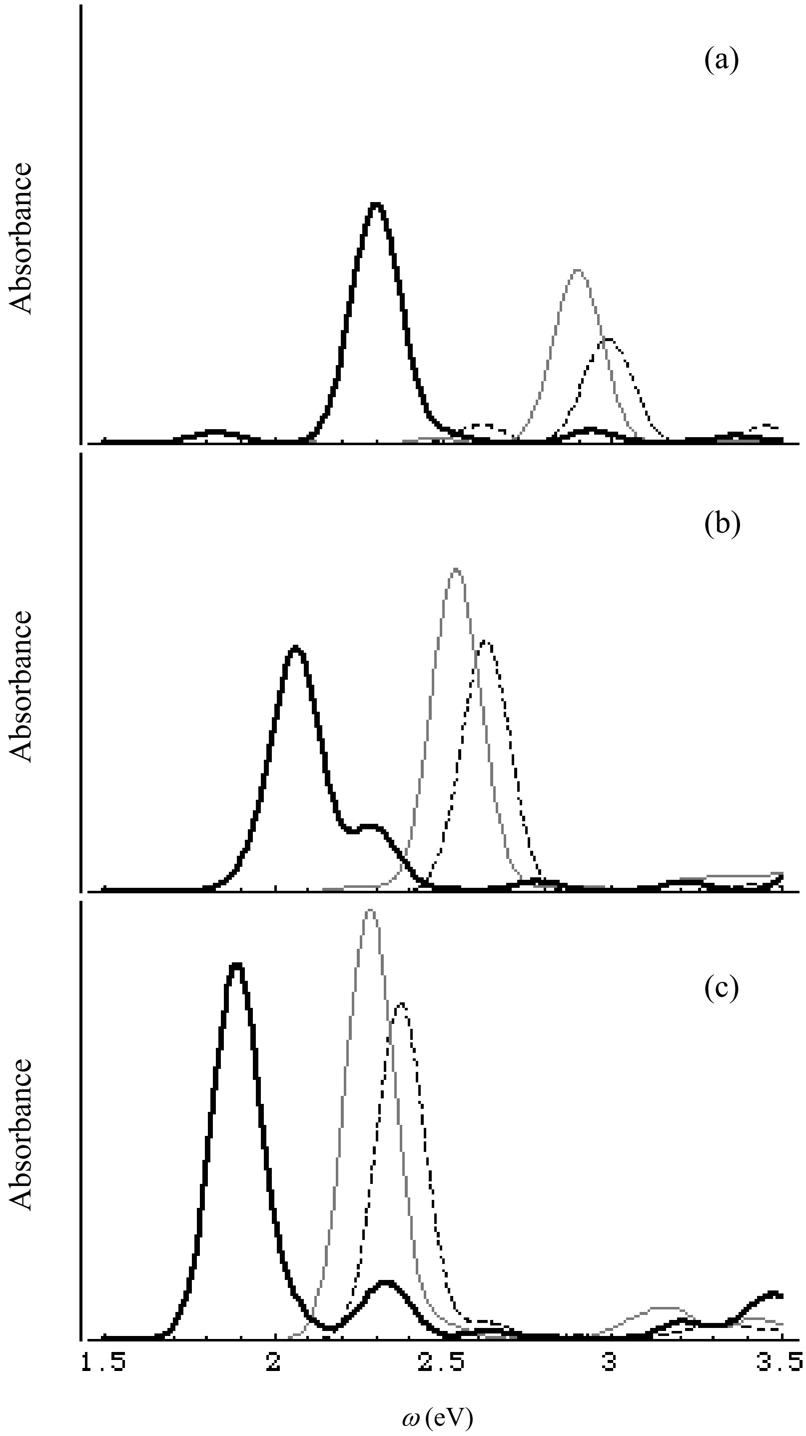

**Figure 3.** Simulated absorption spectra of $C_{60+10n}$ in the low-energy region. The vertical axis in each figure indicates the intensity relative to the largest peak of $n = 12$. (*a*) Spectra for $n = 4$ to 6; (*b*) for $n = 7$ to 9; (*c*) for $n = 10$ to 12. The broken, bold and light lines are for series $C_{70+30m}$, $C_{80+30m}$ and $C_{90+30m}$ ($m = 1$ to 3), respectively.

Next, we consider the features of the absorption spectra of the $C_{60+10n}$ for the low energy region. Simulating the absorption spectra of the $C_{60+10n}$ with $n > 3$ through Eq. (1), we notice that there are prominent peaks in the low energy region (about < 3 eV), which shift characteristically with $n$, as shown in Figures 3(a)–(c). For $C_{60+10n}$ with $n = 1$ to 3, there are no such prominent peaks in the low energy region, although the absorption spectra are not shown. The $n$–dependence of the prominent peak position is shown in Figure 4.

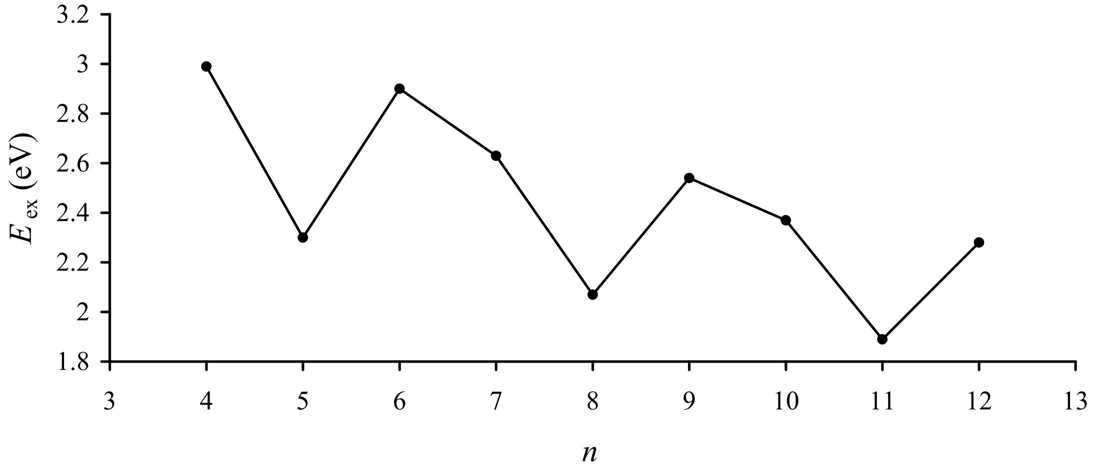

**Figure 4.** The prominent peak positions for $n = 4$ to 12 of the tube-like fullerenes $C_{60+10n}$ vs. $n$ as simulated with Eq. (1).

It is clear that the $n$–dependence of the peak position is quite similar to Figure 1. The prominent peak is red–shifted as $m$ increases in each series of $C_{70+30m}$, $C_{80+30m}$ and $C_{90+30m}$. Such shift was previously noted for $C_{90}$, $C_{120}$, $C_{150}$ and $C_{240}$ [7]. On the other hand, the $n$–dependence of its band intensity is quite different. The oscillator strength of the prominent peak increases approximately linearly to $n$: 1.47, 2.07, 2.42, 3.21, 3.36, 4.53, 4.75, 5.26 and 6.05 for $n = 4$ to 12. Hereafter, the excited state that causes the prominent peak is called the prominent state. The prominent state belongs to *irreps* $a_2''$ and $a_{2u}$ for odd $n$ and even $n$, respectively, and possesses the transition dipole moment along the molecular axis. The lowest transition–allowed states, however, generally have very small oscillator strengths (< 0.05) with no regularity in $n$–dependence.

Analyzing the CNDO/S–TDA data of the prominent states, we see that each state dominantly consists of the two SEC's: [HOMO → LUMO+1] and [HOMO–1 → LUMO]. These SEC's are also dominant components of the lowest transition–allowed states. But the phase relation between these SEC's in the prominent state is opposite to that in the lowest transition–allowed state.

Table 1 shows the excitation energies $E_{ex}(\ell)$ for the lowest transition–allowed state and $E_{ex}(p)$ for the prominent state, and the single–configuration transition energies $\Delta E_1$ for [HOMO → LUMO+1] and $\Delta E_2$ for [HOMO–1 → LUMO]. The $n$–dependences of $E_{ex}(\ell)$ and $E_{ex}(p)$ in Table 1 are periodic and their patterns are quite similar to each other. The $n$–dependences of $E_{ex}(\ell)$ and $E_{ex}(p)$ are direct reflections of those of $\Delta E_1$ and $\Delta E_2$.

**Table 1.** Excitation energies $E_{ex}(\ell)$ and $E_{ex}(p)$, and transition energies $\Delta E_1$ and $\Delta E_2$ of $C_{60+10n}$ ( $n = 4 - 12$ ).

| $n$ | $E_{ex}(\ell)$ (eV) | $E_{ex}(p)$ (eV) | $\Delta E_1$ (eV) | $\Delta E_2$ (eV) |
|---|---|---|---|---|
| 4 | 2.19 | 2.99 | 4.79 | 4.69 |
| 5 | 1.46 | 2.30 | 3.78 | 3.76 |
| 6 | 2.03 | 2.90 | 4.35 | 4.55 |
| 7 | 1.81 | 2.63 | 4.12 | 4.15 |
| 8 | 1.14 | 2.07 | 3.35 | 3.31 |
| 9 | 1.72 | 2.54 | 3.86 | 4.00 |
| 10 | 1.61 | 2.37 | 3.72 | 3.77 |
| 11 | 0.95 | 1.89 | 3.05 | 2.98 |
| 12 | 1.53 | 2.28 | 3.55 | 3.64 |

We have shown the periodic $n$–dependences of several excitation energies for the tube–like fullerene $C_{60+10n}$, which may be generally called the capped (5,5) armchair nanotube. For $C_{60+10n}$ with sufficiently large $n$, however, the periodic variations practically vanish and the energies converge to limiting values expected for an infinite–length (5,5) nanotube. According to the $n$–dependence of the HOMO–LUMO gap evaluated by Cioslowski *et al*. [3], the periodic variation practically vanishes for $n$ larger than about 20. In Ref. 3, they also pointed out that the periodic behavior constituted a signature of metallic character at the bulk limit with periodic boundary conditions [8].

Several groups theoretically estimated the electronic properties of various types of nanotubes [2–4,9–12], and showed that the HOMO–LUMO gaps of the uncapped armchair nanotubes vary periodically with $n$ [2,12]. We have confirmed such a periodicity by making CNDO/S calculations on the uncapped (5,5) nanotubes. We have attributed the origin of the periodicity to pseudo $\pi$–conjugation separately formed on layers of the *cyclo*–pentaphenylene structure in the central cylindrical parts [4]. For the armchair nanotubes, the *cyclo*–pentaphenylene structures exist in their cylindrical parts. On the other hand, for the zigzag nanotubes with no *cyclo*–pentaphenylene structures, the HOMO–LUMO gaps monotonously decrease with $n$ [3].

## 4 CONCLUSIONS

CNDO/S–TDA calculations were made on the tube–like fullerenes $C_{60+10n}$ (n = 1, 2, …, 12), each consisting of a pair of the bisected caps of $C_{60}$ and a single–wall cylinder. A periodic $n$–dependence was found in their excitation energies of the lowest transition–allowed states. For larger $C_{60+10n}$ ($n > 3$), these states practically consist of the two SEC's: [HOMO → LUMO+1] and [HOMO–1 → LUMO]. These SEC's also make dominant contributions to the prominent states that lead to the prominent peaks in the low energy region (about < 3 eV). The $n$–dependence of the excitation energy of the prominent state, or the position of the prominent peak, is quite similar to that of the lowest transition–allowed state. These $n$–dependences are direct reflections of those of the SEC's.

It has been also shown that the oscillator strength of the prominent state with the transition dipole moment along the molecular axis increases almost linearly to $n$. This implies that the integrated intensity of the prominent peak in the low energy region is approximately proportional to the length of the molecular axis.

### Acknowledgment

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### Footnote 1. Tamm–Dancoff approximation (TDA)

The equation of motion (EOM) method [13] is a useful method to study the electronic transition properties of molecules. TDA is the lowest–order approximation of the EOM: The Hatree–Fock ground state is assumed for the electronic ground state and the single electron excitations form the excited states of the molecule. TDA is therefore identical with the singly–excited configuration interaction (SECI) method.

### Footnote 2. SECI calculations with truncated active MO–spaces

As mentioned in text, two energetically close SEC's of [HOMO → LUMO+1] and [HOMO–1 → LUMO] are dominant components of both the lowest transition–allowed states and the prominent states of $C_{60+10n}$ with $n > 3$. Other SEC's have energies far from the two SEC's and make only minor contributions to these excited states. Therefore, the present calculations with truncated MO–spaces as described in Section 2 are supposed to be reasonable to examine the properties of these excited states. Actually, calculating the excitation energies and the oscillator strengths of the excited states with larger MO–spaces for $C_{60+10n}$ with $n = 1$ to 6, we have confirmed that the differences are small.

### Footnote 3. Lowest transition–allowed states of $C_{70}$ and $C_{80}$

According to the results of our CNDO/S–TDA calculation for $C_{70}$, the SEC of [the highest occupied (HO) $a_2''$–MO → the lowest unoccupied (LU) $e_1''$–MO shell] was the major component of the lowest transition–allowed state belonging to $E_1'$. Shumway and Satpathy theoretically analyzed the absorption spectrum of $C_{70}$ with a simple tight–binding model [14]. Their assignment of the lowest allowed transition is coincident with our result. However, the energetic order of their MO's were different from ours, that is, the (LU) $e_1''$–MO shell was our LUMO but it was their LUMO+1.

For $C_{80}$, the SEC of [HO $a_{2g}$–MO → LU $e_{1u}$–MO shell] was the major component of the lowest transition–allowed state belonging to $E_{1u}$.

### Footnote 4. Two dominant SEC's

By inspection of the properties of the HOMO and the LUMO, the tube–like fullerenes $C_{60+10n}$ are classified into three series of $C_{70+30m}$, $C_{80+30m}$ and $C_{90+30m}$ [4]. Here we consider two SEC's that make major contributions to both the lowest transition–allowed state and the prominent state of the $C_{60+10n}$ with $n > 3$. The two SEC's for $C_{70+30m}$ with $D_{5d}$ symmetry are [HO $a_{2u}$–MO → LU $a_{1g}$–MO] and [HO $a_{2g}$–MO → LU $a_{1u}$–MO]. Similarly, for $C_{80+30m}$ with $D_{5d}$ symmetry they are [HO $a_{2g}$–MO → LU $a_{1u}$–MO] and [HO $a_{2u}$–MO → LU $a_{1g}$–MO], and for $C_{90+30m}$ with $D_{5d}$ they are [HO $a_{1u}$–MO → LU $a_{2g}$–MO] and [HO $a_{1g}$–MO → LU $a_{2u}$–MO]. In the case of the $D_{5h}$ symmetry, $a_{1g}$, $a_{2g}$, $a_{1u}$ and $a_{2u}$ should be replaced by $a_1'$, $a_2'$, $a_1''$, and $a_2''$, respectively.

For $C_{70+30m}$ ($m = 1, 2, 3$) with $D_{5d}$ ($D_{5h}$) symmetry, the HO $a_{2g}$ ($a_2'$)–MO and the LU $a_{1g}$ ($a_1'$)–MO are energetically very close to the HO $a_{2u}$ ($a_2''$)–MO and the LU $a_{1u}$ ($a_1''$)–MO, respectively. Therefore, the energetic order of the HO $a_{2u}$ ($a_2''$)–MO and the HO $a_{2g}$ ($a_2'$)–MO and that of the LU $a_{1u}$ ($a_1''$)–MO and the LU $a_{1g}$ ($a_1'$)–MO are very sensitive to the molecular geometries used in the calculation and to the computational methods.

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## Biographies

**Yasushi Nomura** is assistant professor of chemistry at the Faculty of Textile Science and Technology, Shinshu University. He obtained a Ph.D. degree in chemistry from Tohoku University. His research field is quantum chemistry.

**Hiroya Fujita** is graduate student of chemistry at the Faculty of Textile Science and Technology, Shinshu University.

**Susumu Narita** is associate professor of chemistry at the Faculty of Textile Science and Technology, Shinshu University. He obtained a Ph.D. degree in chemistry from Tokyo University of Education. His research field is computational chemistry.

**Tai–ichi Shibuya** is professor of chemistry at the Faculty of Textile Science and Technology, Shinshu University. He obtained a Ph.D. degree in physical chemistry from Yale University. His major research field is quantum chemistry.