

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244402721>

# Structural and electronic properties of isomers of Sc(2)@C(84)(I, II, III): (13)C NMR and IR/Raman spectroscopic studies

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · JUNE 2000

Impact Factor: 3.3 · DOI: 10.1021/jp000438l

CITATIONS

48

READS

36

10 AUTHORS, INCLUDING:



Masayasu Inaguma

Fujikura Ltd.

46 PUBLICATIONS 1,194 CITATIONS

SEE PROFILE



Chun-Ru Wang

Chinese Academy of Sciences

66 PUBLICATIONS 2,138 CITATIONS

SEE PROFILE



Martin Hulman

Danubia NanoTech Ltd. and Slovak Academy...

69 PUBLICATIONS 1,362 CITATIONS

SEE PROFILE

# Structural and Electronic Properties of Isomers of $\text{Sc}_2\text{@C}_{84}$ (I, II, III): $^{13}\text{C}$ NMR and IR/Raman Spectroscopic Studies

Masayasu Inakuma, Etsuji Yamamoto, Tsutomu Kai, Chun-Ru Wang, Tetsuo Tomiyama, and Hisanori Shinohara\*

Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

T. John S. Dennis

Department of Chemistry, Queen Mary & Westfield College, University of London, Mile End Road, London E1 4NS, United Kingdom

Martin Hulman, Matthias Krause, and Hans Kuzmany

Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

Received: February 3, 2000; In Final Form: April 4, 2000

The structures of three structural isomers of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) have been determined by  $^{13}\text{C}$  NMR and have  $C_s$ ,  $C_{2v}$ , and  $D_{2d}$  point group symmetry, respectively. By IR measurements, we have determined that the peaks below  $110\text{ cm}^{-1}$  originate from the scandium-cage vibrational modes based on temperature-dependent IR experiments. Line broadenings of the Sc-cage modes below  $110\text{ cm}^{-1}$  are quite different from those of the  $\text{C}_{84}$  (empty) cage modes in far-IR spectra. Sc-cage vibrational modes below  $300\text{ cm}^{-1}$  in Raman spectra are also identified. The force constants of the Sc-cage vibrations based on a linear three-mass-oscillator model indicate that the charge state of Sc atoms are close to  $+2$ .

## 1. Introduction

Scandium metallofullerenes are characteristic and intriguing materials as compared with other metallofullerenes because they have many structural isomers related to size of carbon cages and the number of encapsulated Sc atoms.<sup>1–36</sup> During the past 8 years, many scandium metallofullerenes have been produced and isolated. Scandium fullerenes such as  $\text{Sc@C}_{82}$ ,<sup>27–36</sup>  $\text{Sc}_2\text{@C}_{2n}$  ( $n = 74, 82, 84, 86$ ),<sup>8,11–25</sup> and  $\text{Sc}_3\text{@C}_{82}$ ,<sup>1–10</sup> have been characterized in detail by various experimental techniques via  $^{13}\text{C}$  NMR,<sup>15</sup>  $^{45}\text{Sc}$  NMR,<sup>16</sup> ESR,<sup>1–8,27–33,36</sup> HR-TEM,<sup>13</sup> UV–Vis–NIR absorption,<sup>4,5,8,11,26,30</sup> STM,<sup>8,12</sup> XPS/UPS,<sup>14,35</sup> X-ray diffraction,<sup>10,19,34</sup> and IR/Raman.<sup>17,18,20–25</sup> In these studies, the structures and electronic properties of  $\text{Sc}_2\text{@C}_{84}$  isomers, in particular, have been discussed. There also have been theoretical studies for the structural and electronic properties of the  $\text{Sc}_2\text{@C}_{84}$  isomers.<sup>37–40</sup>

The vibrations between the metal atom and the cage are one of the characteristic properties of endohedral metallofullerenes. It is well-known that there are 24 IPR (isolated pentagon rule)<sup>41</sup> satisfying structural isomers for the hollow  $\text{C}_{84}$  fullerenes.<sup>42</sup> Experimentally, two isomers,  $D_2$  (No. 22)<sup>42</sup> and  $D_{2d}$  (No. 23),<sup>42</sup> are mainly produced by arc discharge of graphite rods.<sup>43–45</sup> Recently, the two main and five minor isomers of the hollow  $\text{C}_{84}$  fullerenes were isolated and characterized by  $^{13}\text{C}$  NMR.<sup>44–46</sup> The vibrational properties of the empty  $\text{C}_{84}$  cages were studied via IR and Raman.<sup>18,23,24</sup> A theoretical study for the empty  $\text{C}_{84}$  suggests that there should be no intramolecular vibrational modes below  $200\text{ cm}^{-1}$ .<sup>47</sup> The intermolecular modes must have energy below  $50\text{ cm}^{-1}$ , which corresponds to the energy for the highest intermolecular mode in  $\text{C}_{60}$ . The new modes from

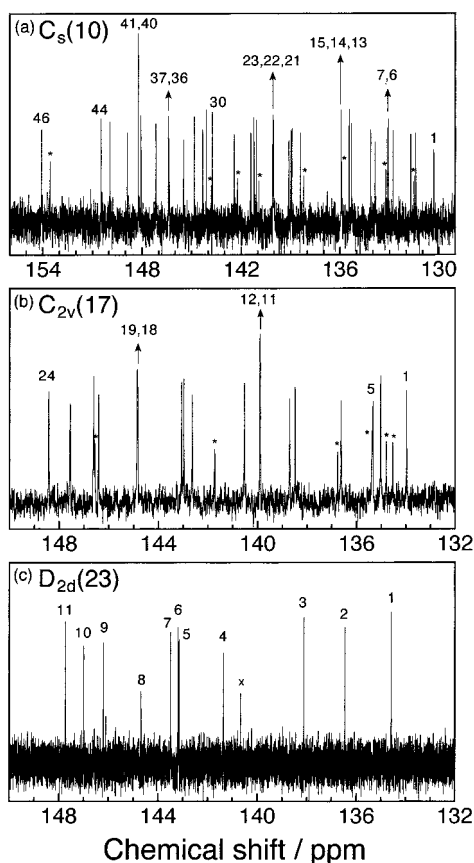
the metal-cage vibrations are, therefore, expected to fill the energy range between inter- and intramolecular modes in the metallofullerenes. They were observed for mono-metallofullerenes based on  $\text{C}_{82}$ ,<sup>48</sup> which was supported by a theoretical calculation.<sup>49</sup> The metal-cage modes were found at an energy range between  $150$  and  $190\text{ cm}^{-1}$ . For  $\text{Sc}_2\text{@C}_{84}$ , two scandium atoms might be located at characteristic positions in each  $\text{C}_{84}$  cage. To elucidate systematically the structure and metal-cage vibrations, we have observed  $^{13}\text{C}$  NMR and IR/Raman lines of three isomers of  $\text{Sc}_2\text{@C}_{84}$ .

In this study, the symmetry of three  $\text{Sc}_2\text{@C}_{84}$  isomers was determined by  $^{13}\text{C}$  NMR. We measured IR spectra between  $80$  and  $2000\text{ cm}^{-1}$  and Raman spectra between  $50$  and  $550\text{ cm}^{-1}$  of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III), which have symmetries of  $C_s$  (No. 10),  $C_{2v}$  (No. 17), and  $D_{2d}$  (No. 23), respectively. The analyses of IR and Raman measurements of these isomers clarified the vibrational properties of the cages and the metal-cage bonding. We have identified several metal-cage modes around  $100\text{ cm}^{-1}$  and around  $160\text{ cm}^{-1}$  in the IR spectra. The broadening of the metal-cage modes with varying temperature shows a behavior different from that of the carbon atoms on the cage. The temperature dependence of the line widths is discussed within the framework of a rotational diffusion model. The metal-cage modes below  $200\text{ cm}^{-1}$  in Raman spectra are also identified. The relation between the force constants of the Sc-cage vibrations and the charge state of Sc atoms is discussed on the basis of a linear three-mass-oscillator model.

## 2. Experimental Section

Sample preparation and isolation of  $\text{Sc}_2\text{@C}_{84}$  have been reported in detail previously.<sup>15</sup> Briefly, the DC arc-discharge method was used for the soot production. Scandium/graphite

\* Corresponding author. E-mail: nori@chem2.chem.nagoya-u.ac.jp.



**Figure 1.**  $^{13}\text{C}$  NMR spectra of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) in  $\text{CS}_2$  at room temperature. Peaks are half intensity lines.

composite rods (1.6 at. %, Toyo Tanso Co. Ltd.) were used for electrodes. The solution containing  $\text{Sc}_2\text{@C}_{84}$  was obtained by a Soxhlet extraction with carbon disulfide ( $\text{CS}_2$ ). Isolation of the  $\text{Sc}_2\text{@C}_{84}$  isomers was achieved by the multistage recycling HPLC method<sup>15,26</sup> using a Buckyprep column and a Bucky-clutcher column. The purity of the samples was confirmed by laser-desorption time-of-flight (LD-TOF) mass spectrometry.

$^{13}\text{C}$  NMR spectroscopic measurements of the  $\text{Sc}_2\text{@C}_{84}$  isomers were performed on a Varian Inova-600 spectrometer at 600 MHz ( $\text{CS}_2$  solution,  $\text{Cr}(\text{acac})_3$  relaxant,  $\text{C}_6\text{D}_6$  lock, at 298 K). All  $^{13}\text{C}$  NMR spectroscopic line positions were referenced with respect to that of  $\text{C}_6\text{D}_6$  at 128.00. The UV–Vis–NIR spectra of the  $\text{Sc}_2\text{@C}_{84}$  isomers were measured between 400 and 2000 nm in  $\text{CS}_2$  solution by using a Shimadzu UV-3101PC spectrophotometer.

Details of IR and Raman measurements were reported elsewhere.<sup>24</sup> Briefly, thin films of the isolated samples for IR and Raman measurements were prepared by the drop-coating technique on gold-coated silicon substrates with condensed samples in  $\text{CS}_2$ . The polycrystalline films were baked for several hours at 620 K in high vacuum ( $10^{-5}$  mbar) to remove residual solvent molecules and other impurities. The IR transmission spectra for the far-infrared region were taken at 2 and  $0.5\text{ cm}^{-1}$  resolution with both a DTGS and a liquid-helium-cooled Ge detector at temperatures from 80 to 300 K. The mid-IR transmission spectra were taken with a MCT detector at temperatures from 80 to 300 K. An Oxford cryostat with polyethylene window was used to measure the temperature dependence between 80 and 300 K. The Raman spectra were measured at  $3\text{ cm}^{-1}$  resolution by using a triple spectrometer XY 500 (Dilor) with an argon ion laser (514 nm) at temperatures from 80 to 300 K.

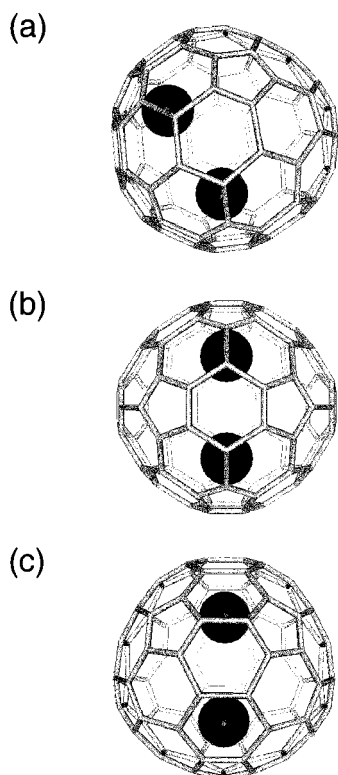
**TABLE 1:**  $^{13}\text{C}$  NMR Chemical Shifts (ppm) for Three Isomers of  $\text{Sc}_2\text{@C}_{84}$

$\text{C}_s$ (No. 10)	$\text{C}_{2v}$ (No. 17)	$\text{D}_{2d}$ (No. 23)
131.01	134.48	134.57
132.10	135.01*	136.44
132.20*	135.28*	138.11
132.42	135.54	141.36
133.51	135.81	143.14
133.76	135.86*	143.18
133.86	137.08	143.49
133.96*	137.24*	144.67*
134.59	138.99	146.19
134.85	139.20	146.99
136.03	140.38	147.73
136.16	140.41	
136.57*	141.00	
136.64	142.23*	
136.67	143.13	
138.93*	143.45	
139.13	143.55	
139.64	145.30	
139.70	145.36	
139.83	146.90	
140.75	146.56*	
140.79	147.11	
140.82	148.06	
141.65*	148.91	
141.81		
141.93		
142.13		
142.96*		
143.15		
144.46		
144.62*		
144.84		
145.06		
145.57		
146.21		
147.01		
147.14		
147.87		
148.80		
148.96		
148.96		
149.56		
150.68		
151.19		
154.29*		
154.83		

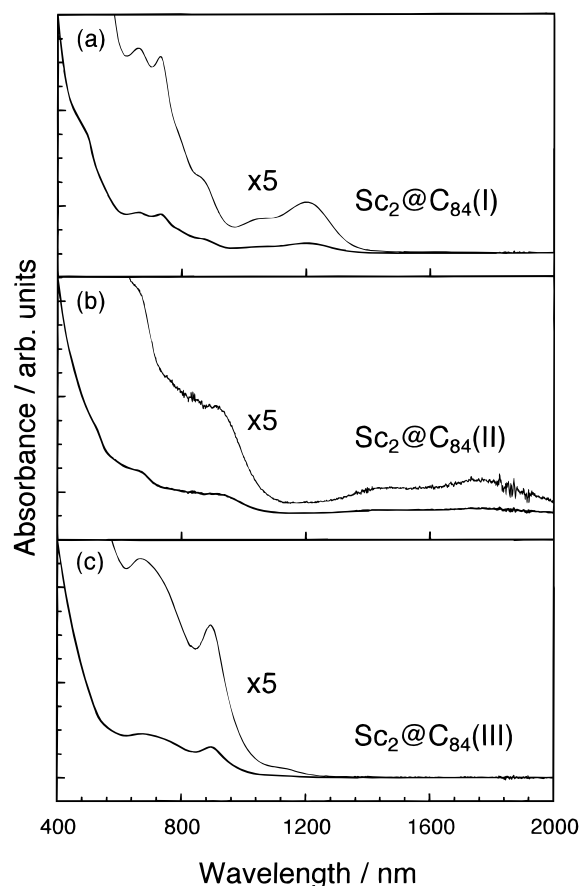
### 3. Results and Discussion

**3.1. Structures of the Three  $\text{Sc}_2\text{@C}_{84}$  Isomers.** Figure 1 shows high-resolution  $^{13}\text{C}$  NMR spectra of three isomers of  $\text{Sc}_2\text{@C}_{84}$ . All the observed NMR lines appear in the chemical shift range between 130 and 155 ppm (Table 1). The  $^{13}\text{C}$  NMR spectrum of isomer I exhibits 38 distinct lines of near-equal intensity and 8 additional lines at half the intensity (star marked lines). Isomer II shows 18 distinct lines with 6 half-intensity lines, whereas isomer III, as we already reported,<sup>15</sup> shows 10 lines and one additional line at half intensity. From these NMR patterns we can unambiguously assign the molecular symmetry of the three isomers of  $\text{Sc}_2\text{@C}_{84}$ . The molecular structures of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III), which are consistent with the present NMR results, are depicted in Figure 2a–c, respectively. The theoretical calculation<sup>38</sup> is adopted for the most probable position of Sc atoms in  $\text{Sc}_2\text{@C}_{84}$ (I). The structure of  $\text{Sc}_2\text{@C}_{84}$ (III) was already confirmed by a synchrotron X-ray diffraction study.<sup>19</sup>

The UV–Vis–NIR absorption spectra of isolated  $\text{Sc}_2\text{@C}_{84}$ -(I, II, III) in  $\text{CS}_2$  solution are presented in Figure 3a–c, respectively. The overall spectral features of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) are different from each other. Several features of  $\text{Sc}_2\text{@C}_{84}$ (I)

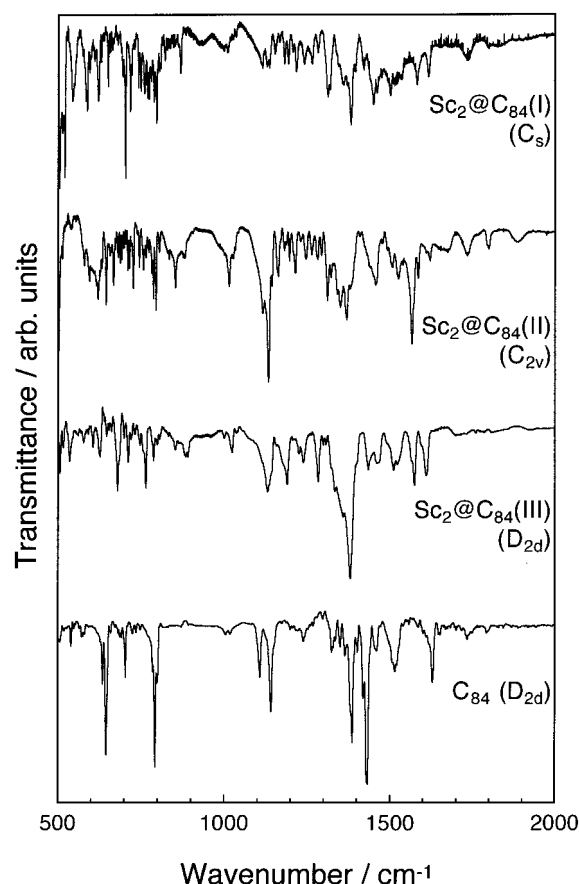


**Figure 2.** Molecular structures for  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) consistent with the  $^{13}\text{C}$  NMR results.



**Figure 3.** UV-Vis-NIR absorption spectra of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) in  $\text{CS}_2$  solution.

appear at 660, 730, 862, 1045, and 1204 nm. Characteristic features for  $\text{Sc}_2\text{@C}_{84}$ (II) are broad absorptions at 1425 and 1770



**Figure 4.** MIR spectra of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) and  $\text{C}_{84}$  at room temperature.

nm. There is no absorption below 1300 nm in the  $\text{Sc}_2\text{@C}_{84}$ (III) spectrum. The observed difference in spectral onsets of  $\text{Sc}_2\text{@C}_{84}$  isomers can be ascribed to the difference in their HOMO-LUMO gaps. The absorption onset of  $\text{Sc}_2\text{@C}_{84}$ (II) is similar to these metallofullerenes with open-shell electronic structures, such as  $\text{Sc@C}_{82}$ ,<sup>30,36</sup>  $\text{Y@C}_{82}$ ,<sup>30,50</sup> and  $\text{La@C}_{82}$ .<sup>51-53</sup> These mono-metallofullerenes also show absorption bands down to 2000 nm, indicating small HOMO-LUMO gaps. The absorption onset of  $\text{Sc}_2\text{@C}_{84}$ (II) is strongly red-shifted as compared to the absorption of isomers I and III. This is consistent with the observation that the production efficiency and stability of  $\text{Sc}_2\text{@C}_{84}$ (II) are much lower than those of isomers I and III.

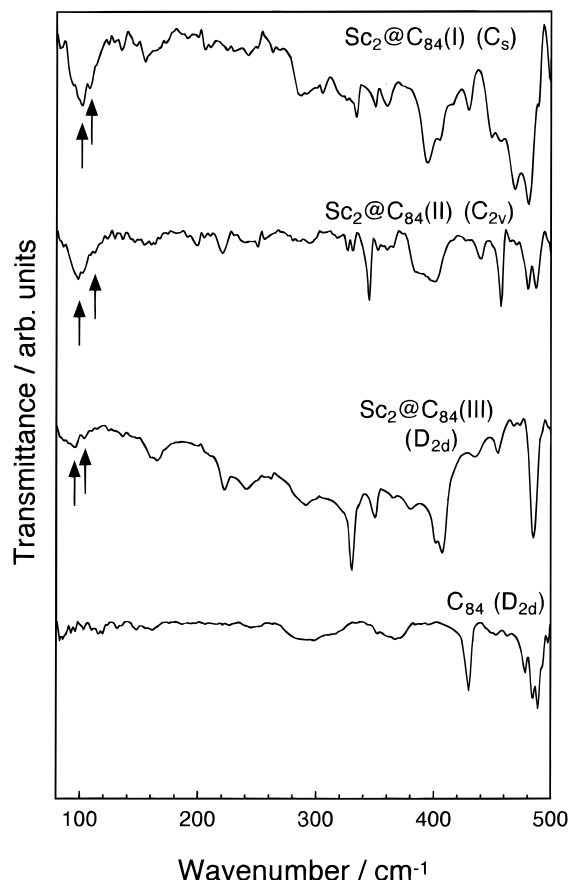
**3.2. Vibrational Properties of Three Isomers of  $\text{Sc}_2\text{@C}_{84}$ .** The molecule of  $\text{Sc}_2\text{@C}_{84}$  isomers has 252 vibrational degrees of freedom distributed on the irreducible representations of the symmetry group,

$$\text{(I): } \Gamma_{\text{vib}} = 131\text{A}'(\text{IR,Ra}) + 121\text{A}''(\text{IR,Ra})$$

$$\text{(II): } \Gamma_{\text{vib}} = 67\text{A}_1(\text{IR,Ra}) + 60\text{A}_2(\text{Ra}) + 64\text{B}_1(\text{IR,Ra}) + 61\text{B}_2(\text{IR,Ra})$$

$$\text{(III): } \Gamma_{\text{vib}} = 33\text{A}_1(\text{Ra}) + 30\text{A}_2 + 31\text{B}_1(\text{Ra}) + 32\text{B}_2(\text{IR,Ra}) + 63\text{E}(\text{IR,Ra})$$

Mid-IR spectra of three isomers of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) are shown in Figure 4. The IR spectrum of  $\text{C}_{84}(\text{D}_{2d})$ , whose cage structure is identical to the cage structure of  $\text{Sc}_2\text{@C}_{84}$ (III), is also shown for comparison. The intramolecular modes of  $\text{Sc}_2\text{@C}_{84}$  appear mostly in this mid-IR region. There is a gap between 800 and 1100  $\text{cm}^{-1}$ , separating radial and tangential vibrational modes



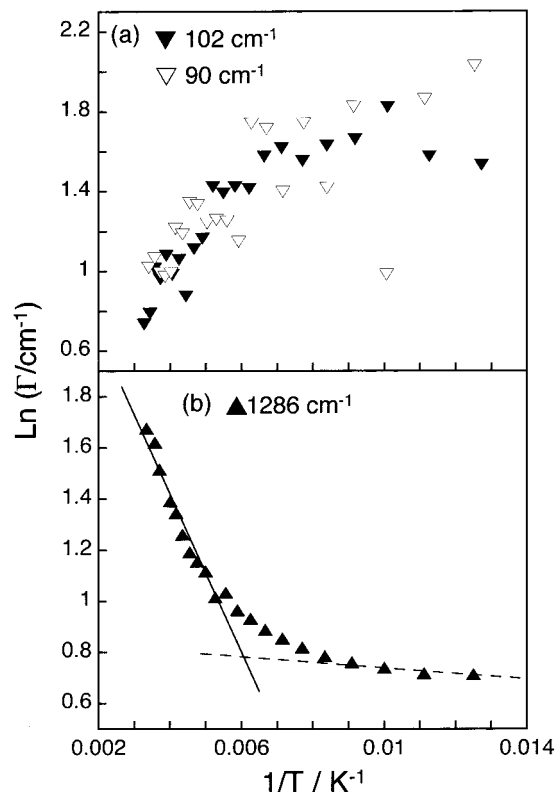
**Figure 5.** Far-IR spectra of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) and  $\text{C}_{84}$  at room temperature. The metal-cage modes are indicated by arrows.

for all the  $\text{Sc}_2\text{@C}_{84}$  isomers and  $\text{C}_{84}(\text{D}_{2d})$ . Strongly enhanced lines are observed in  $\text{Sc}_2\text{@C}_{84}(\text{III})$  compared to the  $\text{C}_{84}(\text{D}_{2d})$  spectrum in the radial part below  $800\text{ cm}^{-1}$ . Some of the lines in  $\text{Sc}_2\text{@C}_{84}(\text{III})$  are shifted with respect to  $\text{C}_{84}(\text{D}_{2d})$  because of a charge transfer from the Sc atoms to the carbon cage.<sup>24</sup>

Far-IR spectra of three isomers of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) are shown in Figure 5 together with that of  $\text{C}_{84}(\text{D}_{2d})$ . The overall peak positions are equal within a few wavenumbers, indicating that the symmetry of the cage affects the vibrational energy only weakly. The most important parts of the spectra are the broad peak around  $100\text{ cm}^{-1}$  and a weak peak around  $160\text{--}165\text{ cm}^{-1}$ . A group theoretical analysis suggests that there are three additional IR-active modes in  $\text{Sc}_2\text{@C}_{84}(\text{III})$  ( $\text{D}_{2d}$ ) as compared to  $\text{C}_{84}(\text{D}_{2d})$ . In detail we have found three distinct modes at  $98$ ,  $107$ , and  $158\text{ cm}^{-1}$ ,  $99$ ,  $110$ , and  $157\text{ cm}^{-1}$ , and  $90$ ,  $102$ , and  $166\text{ cm}^{-1}$  for isomers I–III, respectively, after deconvoluting the bands into Lorentzian lines.

From an analysis based on temperature-dependent IR experiments and from a quantum chemical calculation, the peaks below  $200\text{ cm}^{-1}$  originate from scandium-cage vibrations. The results of the temperature measurements are shown in Figure 6. An Arrhenius plot (Figure 6a) shows that the line widths of the peaks of the Sc-cage modes ( $90$ ,  $102\text{ cm}^{-1}$ ) become narrower with increasing temperature, whereas that of the intramolecular cage mode ( $1286\text{ cm}^{-1}$ ) becomes much broader (Figure 6b). The line width of the cage mode changes around  $1/T = 0.00625$  ( $T \approx 160\text{ K}$ ). The observed change can be ascribed to a phase transition of the crystal structure, as reported in the X-ray diffraction measurement of the empty  $\text{C}_{84}$ .<sup>54</sup>

The temperature dependence of the cage modes below  $1/T = 0.00625$  ( $T > 160\text{ K}$ ) may be caused by a coupling with



**Figure 6.** Arrhenius plot for the peak line width of the cage and the metal-cage modes.

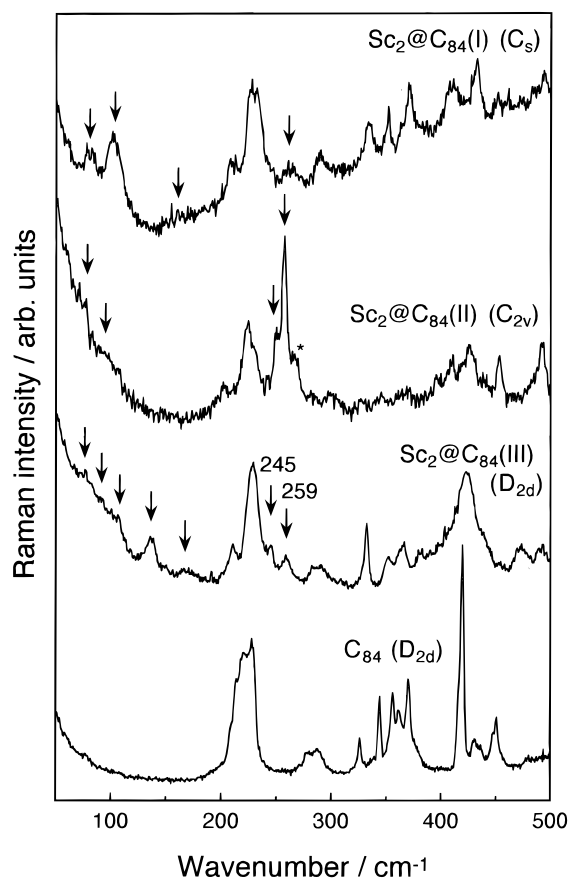
a thermally activated rotational motion of the molecules. Assuming that  $\tau$  is a characteristic correlation time for a molecular reorientation, the line width  $\Gamma$  is expressed as  $\Gamma = \tau^{-1} = \exp(-E_a/k_B T)$  in the rotational diffusion model, where  $E_a$  is an activation energy for the reorientation.<sup>18,21</sup> We have obtained the activation energy of  $\text{Sc}_2\text{@C}_{84}(\text{III})$  for the reorientation ( $26.1\text{ meV}$ ) by fitting the slope below  $1/T = 0.00625$  ( $T > 160\text{ K}$ ) (Figure 6b). The temperature independence of the line widths at lower temperatures suggests a suppression of molecular rotations.

**3.3. Electron Transfers and the Charge State of the  $\text{Sc}_2\text{@C}_{84}$  Isomers.** We have also identified the metal-cage vibrational modes below  $300\text{ cm}^{-1}$  in Raman spectra of the  $\text{Sc}_2\text{@C}_{84}$  isomers, which are shown by arrows in Figure 7. In the  $\text{Sc}_2\text{@C}_{84}(\text{III})$  spectrum, there are at least 9 additional lines with respect to the empty case, which is more than expected from the degrees of freedom originating from encaged Sc atoms.<sup>24</sup> A detailed analysis of the metal-cage vibrational modes shows that the crystal fields affect and split these vibrational modes.<sup>24</sup>

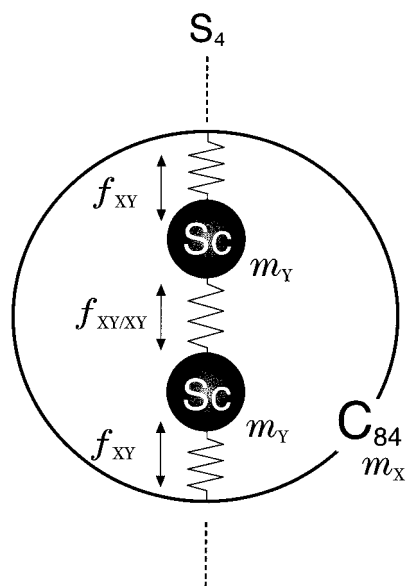
The metal-cage vibration of several mono-metallofullerenes has been discussed within the framework of the charge state and the weight of the metal atom.<sup>48,55,56</sup> We can also derive the information on the charge state of the current discandium metallofullerenes based on a similar analysis. For example, the highest metal-cage modes observed at  $245$  and  $259\text{ cm}^{-1}$  are strong in Raman and weak in IR spectra. These modes are thus assigned to symmetric stretching modes of the two scandium atoms along the  $S_4$  axis of the  $\text{C}_{84}(\text{D}_{2d})$  cage.<sup>57</sup>

The force constant of the metal-cage vibrations can be derived on the basis of a linear three-mass-oscillator model, as we described previously (Figure 8).<sup>24</sup> The obtained force constant  $f_{\text{XY}}(\text{Sc-C}_{84})$ ,  $1.19\text{ N/cm}$ , is similar to those of  $\text{Tm@C}_{82}$  and  $\text{Eu@C}_{74}$ <sup>25,48,58</sup> in which the encapsulated atom has a +2





**Figure 7.** Raman spectra of  $\text{Sc}_2\text{@C}_{84}$ (I, II, III) and  $\text{C}_{84}$  at room temperature. The metal-cage modes are indicated by arrows. \* marked lines are from a  $\text{C}_{60}$  contamination.



**Figure 8.** Three mass oscillator model for the metal-cage vibration of a  $\text{Sc}_2\text{@C}_{84}$ (III) molecule. The scandium ions of mass  $m_Y$  are bonded to the rigid  $\text{C}_{84}$  cage of mass  $m_X$  by a valence force constant  $f_{XY}$ .  $f_{XY/XY}$  is a coupling constant of both oscillators.

oxidation state (Table 2). The obtained force constant  $f_{XY}(\text{Sc}-\text{C}_{84})$ , therefore, strongly suggests that the charge state of Sc atoms is close to +2, which is consistent with the previous reports based on synchrotron X-ray diffraction,<sup>19</sup> UPS,<sup>14</sup> and theoretical calculations.<sup>37–39</sup> Detailed analyses for the low energy vibrations of the other two isomers of  $\text{Sc}_2\text{@C}_{84}$  (I, II) will be reported elsewhere.<sup>25</sup>

**TABLE 2: Force Constants for the Metal-Cage Mode of Metallofullerenes**

substance	wavenumber ( $\text{cm}^{-1}$ )	force constant ( $\text{N cm}^{-1}$ )
$\text{Sc}_2\text{@C}_{84}$ (III)	245, 259	1.19
$\text{Tm@C}_{82}$ (A)	118 <sup>a</sup>	1.18
$\text{Eu@C}_{74}$	123 <sup>a</sup>	1.16
$\text{Y@C}_{82}$	179, <sup>a</sup> 183 <sup>b</sup>	1.50, 1.61
$\text{La@C}_{82}$	160, <sup>a</sup> 163 <sup>b</sup>	1.88, 1.90
$\text{Gd@C}_{82}$	151, <sup>a</sup> 155 <sup>b</sup>	1.80, 1.91
$\text{Ce@C}_{82}$	162 <sup>b</sup>	1.89

<sup>a</sup> Data are taken from refs 25, 55, and 56. <sup>b</sup> Data are taken from ref 48.

**Acknowledgment.** We thank K. Kuroki and T. Kuriyama for experimental help. M.I. thanks the Japan Society for the Promotion of Science for a Research Fellowship for Young Scientists. H.S. thanks JSPS for Future Program on New Carbon Nano-Materials for the financial support of the present study. H.K. also thanks financial support from the Fonds zur Foerderung der Wissenschaftlichen Forschung in Austria (P11943).

## References and Notes

- (1) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y. *Nature* **1992**, 357, 52.
- (2) Yannoni, C. S.; Hoinkis, M.; de Vries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, 256, 1191.
- (3) van Loosdrecht, P. H. M.; Johnson, R. D.; de Vries, M. S.; Kiang, C.-H.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Stevenson, S. *Phys. Rev. Lett.* **1994**, 73, 3415.
- (4) Shinohara, H.; Inakuma, M.; Hayashi, N.; Sato, H.; Saito, Y.; Kato, T.; Bandow, S. *J. Phys. Chem.* **1994**, 98, 8597.
- (5) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Sun, Z.; Kiang, C.-H.; Salem, J. R.; de Vries, M. S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, 66, 2680.
- (6) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, 366, 123.
- (7) Kato, T.; Bandow, S.; Inakuma, M.; Shinohara, H. *J. Phys. Chem.* **1995**, 99, 856.
- (8) Shinohara, H.; Tansho, M.; Inakuma, M.; Saito, Y.; Sato, H.; Hayashi, N.; Kato, T.; Hashizume, T.; Sakurai, T. *Surf. Rev. Lett.* **1996**, 3, 799.
- (9) Anderson, M. R.; Dorn, H. C.; Stevenson, S.; Burbank, P. M.; Gibson, J. R. *J. Am. Chem. Soc.* **1997**, 119, 437.
- (10) Takata, M.; Nishibori, E.; Sakata, M.; Inakuma, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* **1999**, 83, 2214.
- (11) Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkohchi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, 97, 4259.
- (12) Shinohara, H.; Hayashi, N.; Sato, H.; Saito, Y.; Wang, X.-D.; Hashizume, T.; Sakurai, T. *J. Phys. Chem.* **1993**, 97, 13438.
- (13) Beyers, R.; Kiang, C.-H.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Harich, K.; Stevenson, S. *Nature* **1994**, 370, 196.
- (14) Takahashi, T.; Ito, A.; Inakuma, M.; Shinohara, H. *Phys. Rev. B* **1995**, 52, 13812.
- (15) Yamamoto, E.; Tansho, M.; Tomiyama, T.; Shinohara, H.; Kawahara, H.; Kobayashi, Y. *J. Am. Chem. Soc.* **1996**, 118, 2293.
- (16) Miyake, Y.; Suzuki, S.; Kojima, Y.; Kikuchi, K.; Kobayashi, K.; Nagase, S.; Kainosho, M.; Achiba, Y.; Maniwa, Y.; Fisher, K. *J. Phys. Chem.* **1996**, 100, 9579.
- (17) Grannan, S. M.; Birmingham, J. T.; Richards, P. L.; Bethune, D. S.; de Vries, M. S.; van Loosdrecht, P. H. M.; Dorn, H. C.; Burbank, P.; Bailey, J.; Stevenson, S. *Chem. Phys. Lett.* **1997**, 264, 359.
- (18) Hulman, M.; Pichler, T.; Kuzmany, H.; Zerbetto, F.; Yamamoto, E.; Shinohara, H. N. *J. Mol. Struct.* **1997**, 408/409, 359.
- (19) Takata, M.; Nishibori, E.; Umeda, B.; Sakata, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* **1997**, 78, 3330.
- (20) Hulman, M.; Inakuma, M.; Shinohara, H.; Kuzmany, H. In *Electronic Properties of Novel Materials—Progress in Molecular Nanostructures*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; AIP: New York, 1998; p 379.
- (21) Hulman, M.; Krause, M.; Inakuma, M.; Dennis, J.; Shinohara, H.; Kuzmany, H. In *Electronic Properties of Novel Materials—Science and Technology of Molecular Nanostructures*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; AIP: New York, 1999; p 90.
- (22) Hulman, M.; Inakuma, M.; Shinohara, H.; Kuzmany, H. *Synth. Met.* **1999**, 103, 2565.

- (23) Krause, M.; Hulman, M.; Kuzmany, H.; Dennis, T. J. S.; Inakuma, M.; Shinohara, H. In *Electronic Properties of Novel Materials—Science and Technology of Molecular Nanostructures*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; AIP: New York, 1999; p 136.
- (24) Krause, M.; Hulman, M.; Kuzmany, H.; Dennis, T. J. S.; Inakuma, M.; Shinohara, H. *J. Chem. Phys.* **1999**, *111*, 7976.
- (25) Krause, M.; Hulman, M.; Kuzmany, H.; Kuran, P.; Dunsch, L.; Dennis, T. J. S.; Inakuma, M.; Shinohara, H. *J. Mol. Struct.*, in press.
- (26) Wang, C.-R.; Inakuma, M.; Shinohara, H. *Chem. Phys. Lett.* **1999**, *300*, 379.
- (27) Suzuki, S.; Kawata, S.; Shiromaru, H.; Yamauchi, K.; Kikuchi, K.; Kato, T.; Achiba, Y. *J. Phys. Chem.* **1992**, *96*, 7159.
- (28) Kato, T.; Suzuki, S.; Kikuchi, K.; Achiba, Y. *J. Phys. Chem.* **1993**, *97*, 13426.
- (29) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Haynes, J.; Kiang, C.-H.; Salem, J. R.; de Vries, M. S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, *66*, 2675.
- (30) Inakuma, M.; Ohno, M.; Shinohara, H. In *"Fullerenes" Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; ECS: New Jersey, 1995; Vol. 2, p 330.
- (31) Rübsam, M.; Schweitzer, P.; Dinse, K.-P. *Chem. Phys. Lett.* **1996**, *263*, 540.
- (32) Knorr, S.; Grupp, A.; Mehring, M.; Kirbach, U.; Bartl, A.; Dunsch, L. *Appl. Phys. A* **1998**, *66*, 257.
- (33) Seifert, G.; Bartl, A.; Dunsch, L.; Ayuela, A.; Rockenbauer, A. *Appl. Phys. A* **1998**, *66*, 265.
- (34) Nishibori, E.; Takata, M.; Sakata, M.; Inakuma, M.; Shinohara, H. *Chem. Phys. Lett.* **1998**, *298*, 79.
- (35) Hino, S.; Umishita, K.; Iwasaki, K.; Miyamae, T.; Inakuma, M.; Shinohara, H. *Chem. Phys. Lett.* **1999**, *300*, 145.
- (36) Inakuma, M.; Shinohara, H. *J. Phys. Chem. B*, submitted.
- (37) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *231*, 319.
- (38) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1997**, *276*, 55.
- (39) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131.
- (40) Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **1999**, *302*, 312.
- (41) Fowler, P. W.; Batten, R. C.; Manolopoulos, D. E. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3103.
- (42) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Clarendon: Oxford, U.K., 1995.
- (43) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142.
- (44) Dennis, T. J. S.; Kai, T.; Tomiyama, T.; Shinohara, H. *J. Chem. Soc., Chem. Commun.* **1998**, 619.
- (45) Dennis, T. J. S.; Kai, T.; Asato, K.; Tomiyama, T.; Shinohara, H.; Yoshida, T.; Kobayashi, Y.; Ishiwatari, H.; Miyake, Y.; Kikuchi, K.; Achiba, Y. *J. Phys. Chem. A* **1999**, *103*, 8747.
- (46) Tagmatarchis, N.; Avent, A. G.; Prassides, K.; Dennis, T. J. S.; Shinohara, H. *Chem. Commun.* **1999**, 1023.
- (47) Nishikawa, T.; Kinoshita, T.; Nanbu, S.; Aoyagi, M. *THEOCHEM* **1999**, *461–462*, 453.
- (48) Lebedkin, S.; Renker, B.; Heid, R.; Schober, H.; Rietschel, H. *Appl. Phys. A* **1998**, *66*, 273.
- (49) Andreoni, W.; Curioni, A. *Appl. Phys. A* **1998**, *66*, 299.
- (50) Kikuchi, K.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.* **1994**, *116*, 9367.
- (51) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67.
- (52) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T. *J. Phys. Chem.* **1994**, *98*, 2008.
- (53) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T.; Suzuki, T.; Maruyama, Y. *J. Phys. Chem.* **1994**, *98*, 12831.
- (54) Margadonna, S.; Brown, C. M.; Dennis, T. J. S.; Lappas, A.; Pattison, P.; Prassides, K.; Shinohara, H. *Chem. Mater.* **1998**, *10*, 1742.
- (55) Dunsch, L.; Kuran, P.; Krause, M. In *"Fullerenes" Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; ECS: New Jersey, 1998; Vol. 6, p 1031.
- (56) Krause, M.; Kuran, P.; Kirbach, U.; Dunsch, L. *Carbon* **1999**, *37*, 113.
- (57) The identification of the scandium-cage vibrations at 245 and 259 cm<sup>-1</sup> has been questioned by most recent results from Y<sub>2</sub>@C<sub>84</sub> (D<sub>2d</sub>), which exhibits an almost identical pattern in this spectral region, although the yttrium atom is 2 times heavier than scandium.
- (58) Kuran, P.; Krause, M.; Bartl, A.; Dunsch, L. *Chem. Phys. Lett.* **1998**, *292*, 580.