

Vibrational Spectra of  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$  in the Rotor-stator and Polymer PhasesG. Klupp,<sup>\*,†</sup> F. Borondics,<sup>†</sup> É. Kováts,<sup>†</sup> Á. Pekker,<sup>†</sup> G. Bényei,<sup>‡</sup> I. Jalsovszky,<sup>‡</sup> R. Hackl,<sup>§</sup> S. Pekker,<sup>†</sup> and K. Kamarás<sup>\*,†</sup>

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$C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$  are prototypes of rotor-stator cocrystals. We present infrared and Raman spectra of these materials and show how the rotor-stator nature is reflected in their vibrational properties. We measured the vibrational spectra of the polymer phases poly( $C_{60}C_8H_8$ ) and poly( $C_{70}C_8H_8$ ) resulting from a solid-state reaction occurring on heating. On the basis of the spectra, we propose a connection pattern for the fullerene in poly( $C_{60}C_8H_8$ ), where the symmetry of the  $C_{60}$  molecule is  $D_{2h}$ . On illuminating the  $C_{60}\cdot C_8H_8$  cocrystal with green or blue light, a photochemical reaction was observed leading to a product similar to that of the thermal polymerization.

## 1. Introduction

Fullerenes and cubane have recently been shown to form so-called rotor-stator cocrystals.<sup>1</sup> These cocrystals are different from both orientationally ordered and plastic crystals, as one of their constituents (the fullerene) is rotating and the other one (the cubane) is fixed in a well-defined orientation. In the case of  $C_{60}\cdot C_8H_8$ , rotating  $C_{60}$  molecules form a face centered cubic lattice and static cubane molecules, occupying interstitial octahedral sites, serve as bearings between them.  $C_{70}\cdot C_8H_8$  crystallizes in a face-centered cubic structure above 375 K.<sup>2</sup> At room temperature, the rotation of  $C_{70}$  is somewhat restricted, which leads to a tetragonal distortion; the  $C_{70}$  molecule is able to rotate around its main axis which, in turn, precesses around the crystallographic  $c$  axis. The formation of these structures is driven by the molecular recognition between the concave surface of the cubane and the round surface of the fullerenes.<sup>1,3</sup>

On heating, the fullerene–cubane compounds undergo a topochemical reaction.<sup>1</sup> As the reaction product is insoluble in common solvents, it is most likely a copolymer of the fullerene with cubane.<sup>4</sup> X-ray diffraction patterns of the annealed samples, measured at room temperature, show a large emerging amorphous part and weakening reflections compatible with fcc structure. Compared with the original monomer phase, the shift of these reflections indicates lattice expansion, and their intensity quickly vanishes at high angles. Because of the parallel appearance of the amorphous contribution and disappearance of crystallinity, we can assume that the amorphous phase retains the local cubic order. Another observation which makes this assumption reasonable is that the morphology of the crystals does not change on heating.<sup>1</sup>

In this paper, we present a detailed vibrational (infrared and Raman) characterization of the monomer and polymer phases of  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$ . In the monomer phases, we can

confirm the rotor-stator nature of the materials. Based on the spectra of the polymer phases, we deduce the symmetry of the majority of the fullerene units as  $D_{2h}$ , similar to the linear cycloaddition polymers. This conclusion is consistent with a substantial presence of linear segments in the copolymer.

We published the infrared spectra of the monomer and polymer phases of  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$  earlier as Supplementary Information to ref 1. A thorough study of the polymerization of poly( $C_{60}C_8H_8$ ) at high temperature and high pressure has been performed by Iwasiewicz-Wabnig et al.,<sup>5</sup> using X-ray diffraction and Raman spectroscopy. Our results, obtained at ambient pressure on annealing, are complementary to that study, except that we observe a photopolymerization reaction on illumination with green or blue light, which accounts for the laser wavelength dependence of the Raman spectra.

## 2. Experimental Methods

Cubane was prepared following the method of Eaton and Cole.<sup>6</sup> Cubane and the fullerenes  $C_{60}$  and  $C_{70}$  were coprecipitated from toluene by adding isopropyl alcohol or by evaporating the solvent to form  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$ .<sup>1</sup>

The resulting black powder was pressed into KBr pellets for infrared (IR) measurements. The spectra were recorded by a Bruker IFS28 and a Bruker IFS 66v/S spectrometer. Depending on the width of the lines to be observed, the resolution was set between 2 and  $0.25\text{ cm}^{-1}$ . Temperature-dependent measurements were conducted in a flow cryostat cooled by liquid nitrogen or helium with the temperature adjustable between 20 and 600 K. The KBr pellet technique has the disadvantage that the index of refraction of the samples is generally in mismatch with that of the medium; therefore, the lineshapes become asymmetric (Christiansen effect). However, the alternative of using organic oils as Nujol was discarded because we wanted to identify as many new infrared lines as possible, without disturbing absorption from the medium.

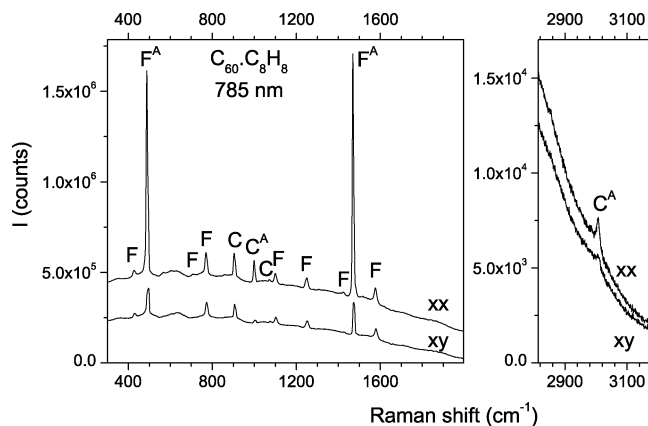
Raman microscopy data were acquired in backscattering geometry on powder samples either under ambient conditions or in an evacuated glass capillary. Spectra were taken with three

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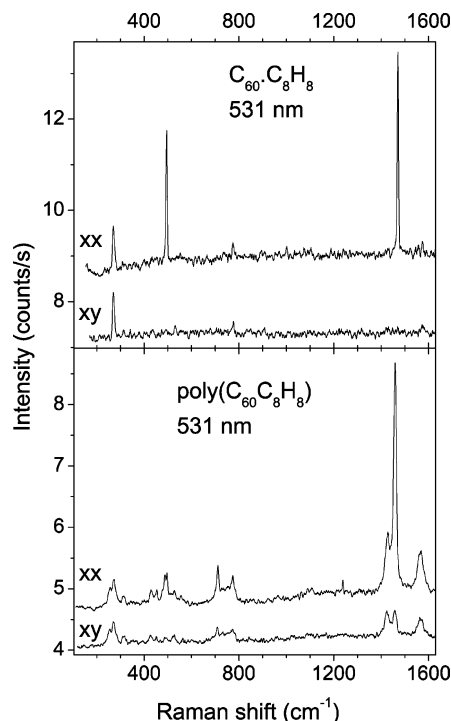
**Figure 1.** Room-temperature Raman spectra of the  $C_{60}\cdot C_8H_8$  cocrystal. The diode laser was operated at the line indicated. Spectra taken with the incident and scattered light polarizations parallel and perpendicular are labeled by *xx* and *xy*, respectively. Cubane modes<sup>7</sup> are denoted by C, and fullerene modes<sup>8</sup> are denoted by F. Totally symmetric modes are marked by superscript A.

lines (468, 531, and 676 nm) of a Kr-ion laser on a triple monochromator (Jobin-Yvon T64000). The laser power was carefully adjusted not to cause polymerization or any other type of changes in the samples. This was guaranteed with a power of 70–100  $\mu$ W focused to a spot of approximately 2  $\mu$ m diameter. The slit width was set at 300 or 400  $\mu$ m. For these small crystals (typically less than 10  $\mu$ m), the orientation of the principal axes with respect to the polarization of the incident ( $e_i$ ) and the scattered ( $e_s$ ) light could not be determined. However, in case of highly symmetric molecules, the fully symmetric  $A_g$  vibrations can easily be identified by comparing polarized ( $e_s \parallel e_i$ ) and depolarized ( $e_s \perp e_i$ ) spectra. For simplicity, we label these as *xx* and *xy*, respectively. The Raman spectra taken with the 785 nm laser line of a diode laser were collected by a Renishaw 1000 MB Raman spectrometer.

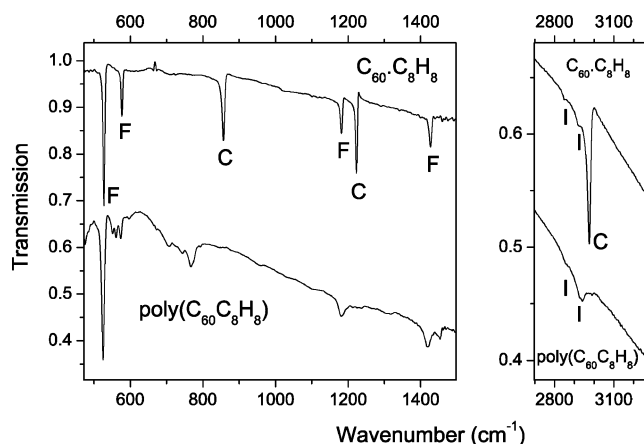
### 3. Results and Discussion

**3.1. Rotor-Stator Phases.** The Raman and infrared spectra of  $C_{60}\cdot C_8H_8$  in the rotor-stator phase are shown in Figures 1–3, and those of  $C_{70}\cdot C_8H_8$  are shown in Figures 4 and 5. The frequencies of the observed vibrational peaks of  $C_{60}\cdot C_8H_8$  are listed in Tables 1 and 2, and those of  $C_{70}\cdot C_8H_8$  are in Tables 3 and 4. We compare these frequencies to experimental data on cubane<sup>7</sup> and  $C_{60}$  (ref 8) and calculated Raman<sup>9</sup> and infrared<sup>10</sup> spectra of  $C_{70}$ , respectively. As expected for molecular cocrystals with the lattice stabilized by van der Waals interaction only, the spectra are superpositions of those of the constituents. As no crystal field splitting of the fullerene lines is observed, the infrared measurement confirms that the fullerene molecules are rotating in the crystal. The cubane lines are not split either, proving that the crystal field around the cubane has the same point group, that is,  $O_h$ , as that of the isolated molecule.<sup>1</sup> In the Raman spectrum of the rotor-stator cocrystals taken with 785 nm excitation, the fullerene lines are significantly stronger than the cubane lines, most probably because of the enhanced Raman cross section caused by the conjugated bonds, similar to what was found in fullerene clathrates.<sup>11</sup> This effect renders the cubane lines almost unnoticeable. When changing the wavelength of the exciting laser to 531 nm, all of the cubane lines are lost (Figure 2), because we approach resonant scattering in the fullerenes.<sup>12</sup>

$C_{60}$  belongs to the icosahedral ( $I_h$ ) point group and consequently shows four infrared-active vibrational modes with  $T_{1u}$

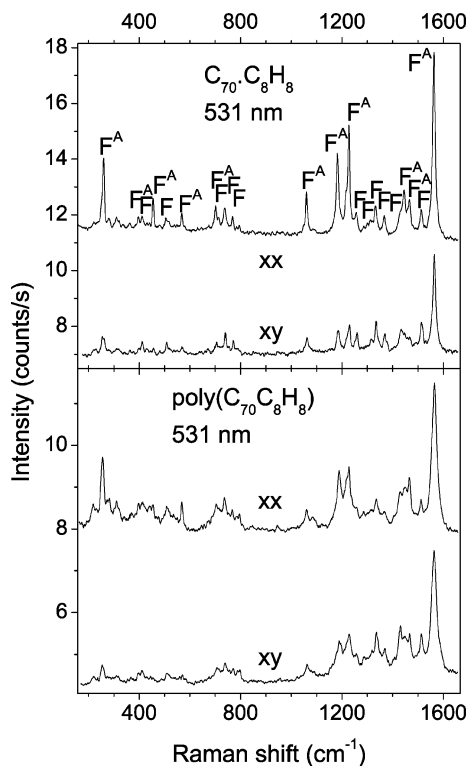


**Figure 2.** Raman spectra of  $C_{60}\cdot C_8H_8$  at room temperature before annealing (monomer) and after annealing at 470 K (polymer). The  $Kr^{+}$  laser line and the polarizations are indicated. The spectra are vertically shifted for clarity.

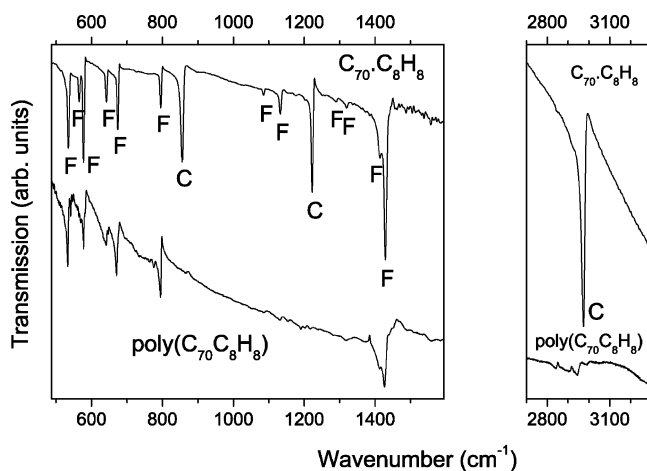


**Figure 3.** Infrared spectra of  $C_{60}\cdot C_8H_8$  before (cocrystal) and after annealing at 470 K (copolymer). C stands for cubane modes;<sup>7</sup> F stands for fullerene modes,<sup>8</sup> and I stands for impurity. The spectra are vertically shifted for clarity. The changes in the spectra show that annealing leads to the polymerization of the sample.

symmetry. Out of its 10 Raman-active modes, 2 belong to the  $A_g$ , and 8 belong to the  $H_g$  irreducible representation. We could observe all of these modes in the spectrum of  $C_{60}\cdot C_8H_8$  (the  $H_g$  (1) mode can be seen in Figure 2).  $C_{70}$  has  $D_{5h}$  symmetry and altogether 31 IR active and 53 Raman active vibrational modes. The IR modes can be decomposed as  $21 E'_1 + 10 A''_2$ , and the Raman modes can be decomposed as  $12 A'_1 + 22 E'_2 + 19 E''_1$ . Similar to the case of pristine  $C_{70}$ , not all of these modes have sufficient intensity to be easily detected.<sup>8</sup> Cubane belongs to the octahedral ( $O_h$ ) point group. Its three infrared-active  $T_{1u}$  modes are clearly visible in the spectra of the  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$  rotor-stator cocrystals. This cubane spectrum is indeed the closest to that of isolated cubane in a crystalline environment; solid cubane<sup>7</sup> shows a more complicated spectrum because of the lower site symmetry. The 8 Raman-active modes



**Figure 4.** Room-temperature Raman spectra of  $C_{70}\cdot C_8H_8$  cocrystal and copolymer. The  $Kr^+$  laser line and the polarizations are indicated. The spectra are vertically shifted for clarity. Totally symmetric modes are denoted by superscript A.<sup>9</sup> Fullerene peaks are marked by F;<sup>8</sup> no cubane peaks were found.



**Figure 5.** Infrared spectra of  $C_{70}\cdot C_8H_8$  before and after annealing at 470 K (cocrystal and copolymer phase, respectively). C: cubane peaks.<sup>7</sup> F: fullerene peaks.<sup>8</sup> The asymmetric line shape is due to the Christiansen effect.

of cubane are classified as  $2A_{1g} + 2E_g + 4T_{2g}$ . Only three out of these eight appear in the  $C_{60}\cdot C_8H_8$  spectrum taken with the 785 nm laser, and none appear in the spectra taken with the 531 nm laser, because of the aforementioned cross-section differences.

In the  $C_{60}\cdot C_8H_8$  cocrystal, the depolarization ratio  $\rho = \phi_{xy}/\phi_{xx}$  (with  $\phi_{ij}$  the oscillator strength of an excitation at either  $xy$  or  $xx$  polarization; see section 2) should be zero for the fullerene  $A_g$  modes and 3/4 for the  $H_g$  modes. The  $A_g$  modes were indeed found totally polarized, and the depolarization ratio was 0.90 for the  $H_g$  (1) and 0.71 for the  $H_g$  (4) mode (see Figure 2). In contrast, the totally symmetric modes of  $C_{70}$  should not vanish completely in the  $xy$  geometry because of its  $D_{5h}$

**TABLE 1: Raman Frequencies of the  $C_{60}\cdot C_8H_8$  Cocrystal and Poly( $C_{60}C_8H_8$ ) Copolymer, and Assignment<sup>7,8</sup> of the Cocrystal Peaks Where C Stands for Cubane and F Stands for Fullerene Peaks**

$C_{60}\cdot C_8H_8$		poly( $C_{60}C_8H_8$ )
$\nu^*$ ( $cm^{-1}$ )	assignment	$\nu^*$ ( $cm^{-1}$ )
271	F, $H_g$ (1)	255
		272
		314
428	F, $H_g$ (2)	429
		451
495	F, $A_g$ (1)	486
		524
		560
708	F, $H_g$ (3)	711
		732
		752
770	F, $H_g$ (4)	774
904	C, $E_g$	
1000	C, $A_{1g}$	
1072	C, $E_g$	
1099	F, $H_g$ (5)	
1248	F, $H_g$ (6)	
1423	F, $H_g$ (7)	1426
1469	F, $A_g$ (2)	1459
1576	F, $H_g$ (8)	1566
3008	C, $A_{1g}$	

**TABLE 2: Infrared Frequencies of the  $C_{60}\cdot C_8H_8$  Cocrystal and Poly( $C_{60}C_8H_8$ ) Copolymer and Assignment<sup>7,8</sup> of the Cocrystal Peaks Where C Stands for Cubane and F for Fullerene Peaks**

$C_{60}\cdot C_8H_8$		poly( $C_{60}C_8H_8$ )
$\nu^*$ ( $cm^{-1}$ )	assignment	$\nu^*$ ( $cm^{-1}$ )
527	F, $T_{1u}$ (1)	526
		551
		561
577	F, $T_{1u}$ (2)	574
		705
		723
		742
		768
857	C, $T_{1u}$	
1181	F, $T_{1u}$ (3)	1181
1224	C, $T_{1u}$	
1428	F, $T_{1u}$ (4)	1424
		1458
2976	C, $T_{1u}$	2948

symmetry. This is what is found in the  $C_{70}\cdot C_8H_8$  cocrystal. The modes that have lower depolarization ratios are labeled by A in Figure 4. These modes correspond to the ones assigned to  $A'_1$  by Sun and Kertész.<sup>9</sup>

In contrast to the fullerenes, the frequencies of the cubane principal lines in the rotor-stator crystals deviate from those of cubane in its pure solid form.<sup>7</sup> If we compare the vibrational frequencies for various environments of the cubane molecule, a clear trend can be observed. The highest vibrational frequencies occur in the gas phase.<sup>13</sup> In pure solid cubane or in solution, the lines shift to lower frequencies. Further downshift is found in  $C_{60}\cdot C_8H_8$  and finally in  $C_{70}\cdot C_8H_8$ . This trend is similar to that found in the vibrational frequencies of molecules trapped in rare gas matrices<sup>14</sup> and is caused by van der Waals interaction: the higher the polarizability of the environment, the lower the frequency. The relatively large shifts in the solids reflect the high polarizability of the fullerenes.

**3.2. Poly( $C_{60}C_8H_8$ ).** The spectra of  $C_{60}\cdot C_8H_8$  change dramatically upon annealing to 470 K either in a furnace or in a heated cryostat in the IR spectrometer (Figure 3). The Raman and IR spectra of the annealed sample are plotted in Figures 2 and 3,

**TABLE 3: Raman Frequencies of the  $C_{70}\cdot C_8H_8$  Cocrystal and Their Assignment According to Ref 9; All Peaks Are Fullerene Peaks, and the Peaks of Poly( $C_{70}C_8H_8$ ) Have Essentially the Same Center Frequencies**

$\nu^*$ (cm <sup>-1</sup> )	assignment <sup>9</sup>
259	$A_1'$
397	$A_1'$
411	$E_1''$
454	$A_1'$
507	$E_2'$
568	$A_1'$
701	$A_1'$
713	$E_1''$
737	$E_1''$
769	$E_2'$
1060	$A_1'$
1182	$A_1'$
1227	$A_1'$
1256	$E_2'$
1313	$E_1''$
1333	$E_2'$
1368	$E_1''$
1433	$E_1''$
1445	$A_1'$
1466	$A_1'$
1512	$E_1''$
1564	$A_1'$

**TABLE 4: Infrared Frequencies of the  $C_{70}\cdot C_8H_8$  Cocrystal and Poly( $C_{70}C_8H_8$ ), and the Assignment of the Former According to Ref 10; C Stands for Cubane Peaks, and F Stands for Fullerene Peaks**

$C_{70}\cdot C_8H_8$		poly( $C_{70}C_8H_8$ )
$\nu^*$ (cm <sup>-1</sup> )	assignment <sup>10</sup>	$\nu^*$ (cm <sup>-1</sup> )
535	F, $E_1'$	533
		541
565	F, $A_2''$	565
		569
578	F, $E_1'$	578
		582
642	F, $E_1'$	641
		647
674	F, $E_1'$	671
		676
		763
795	F, $E_1'$	776
		794
856	C, $T_{1u}$	
1085	F, $E_1'$	1086
1133	F, $A_2''$	1132
		1154
		1190
		1202
		1217
1202	F, $A_2''$	
1222	C, $T_{1u}$	
1291	F, $E_1''$	
1319	F, $A_2''$	
1413	F, $E_1'$	1413
1429	F, $E_1'$	1427
2974	C, $T_{1u}$	2964

and the peak positions are listed in Tables 1 and 2, respectively. Upon heating to 470 K, an irreversible reaction takes place. When annealing a few tens of mg sample in the furnace, the first changes in the IR spectra appear after 40 min:  $C_{60}$  modes split, and new modes appear. Further annealing leads to the disappearance of the original  $C_{60}$  and cubane modes and increased intensity of the new peaks. The new features of the final reaction product in the IR spectrum are the same, irrespective of whether the annealing was done in a furnace or in situ in a cryostat.

In the Raman spectrum of the annealed  $C_{60}\cdot C_8H_8$ , the  $A_g$  modes of  $C_{60}$  do not split, but the low energy, that is, radial  $H_g$  modes show at least a threefold splitting, best seen on the lone-standing  $H_g(1)$  mode. In the IR spectrum, the original  $T_{1u}$  modes of the fullerene split into at least two lines, and new peaks appear between 700 and 800 cm<sup>-1</sup>. The splitting and the new modes indicate that the  $C_{60}$  molecule is distorted. However, the number of new lines is considerably less than what would be expected if the cage opened.<sup>15</sup> In contrast, the change in the cubane lines is striking. The original lines disappear completely; only a weak IR line at 2948 cm<sup>-1</sup> indicates that there are still hydrocarbon groups in the sample. We infer from the position of this line, which corresponds to the C–H stretching in saturated hydrocarbons, that the carbon atoms involved are sp<sup>3</sup> hybridized. In the reaction, we have to account for all atoms since no mass loss was observed by thermogravimetry-mass spectrometry (TG-MS) up to 570 K.<sup>1</sup> This suggests that the cubane transforms into a different constitutional isomer and covalently bonds to  $C_{60}$ , leading to a structural distortion. The reaction product is most probably a covalently bound copolymer, as the products are insoluble in common solvents.

Pristine cubane also isomerizes at 470 K,<sup>16</sup> the same temperature where the polymerization appears in  $C_{60}\cdot C_8H_8$ . Hence, a straightforward assumption is that the first step of the copolymerization reaction must be the decomposition of cubane. Pristine cubane can decompose into several products, for example, cyclooctatetraene, bicyclooctatriene, styrene, and dihydropentalene.<sup>16</sup> As the first three form known adducts with  $C_{60}$ ,<sup>17</sup> which we could not detect by either IR spectroscopy or HPLC,<sup>4</sup> we can exclude these as being the connecting units between the fullerenes.

In principle both fullerene–fullerene and fullerene– $C_8H_8$  bonds can be realized in the polymer.  $C_8H_8$ – $C_8H_8$  bonds can be excluded, as the  $C_8H_8$  molecules are well-separated by the fullerene molecules. We can also exclude the possibility of covalent fullerene–fullerene bonding because of the following experimental observations. There are two known bond types between fullerene molecules in fullerene homopolymers. In neutral polymers, the [2 + 2] cycloaddition leads to a cyclobutane-type ring with two single bonds between the buckyballs.<sup>18,19</sup> A Raman peak at approximately 950 cm<sup>-1</sup> is associated with this bond.<sup>20</sup> This peak is absent in the spectrum of poly( $C_{60}C_8H_8$ ). The other possible bond type is one single bond between two fullerene molecules.<sup>21</sup> This bond leads to the appearance of a characteristic IR peak between 800 and 850 cm<sup>-1</sup>. As this peak is also absent, we can rule out the fullerene–fullerene direct bond. There is still another observation which confirms this assumption. In fullerene polymers<sup>22,23</sup> and in the dimer-oxide  $C_{120}O$ ,<sup>23,24</sup> interball vibrational peaks appear in the Raman spectrum between 100 and 140 cm<sup>-1</sup>. We measured the Raman spectrum down to 20 cm<sup>-1</sup> but did not find any peaks below the split  $H_g(1)$  mode. The reason for the absence of the interfullerene bonding comes from structural considerations. The large interfullerene distance observed by X-ray diffraction<sup>1</sup> does not allow the  $C_{60}$  molecules to approach each other close enough for a reaction to occur between them.

In the following, we try to establish the connection pattern of the fullerene unit based on the infrared and Raman spectra. Since the IR and Raman spectra retain mutual exclusion (no lines are observed to appear simultaneously in both), the inversion center of the  $C_{60}$  balls must be preserved. This means that the possible point groups of the 60 molecules are:  $I_h$ ,  $T_h$ ,  $S_6$ ,  $D_{5d}$ ,  $D_{3d}$ ,  $D_{2h}$ ,  $C_{2h}$ , or  $C_i$ . In Table 5, we show the evolution and splitting of the Raman active  $A_g$  and  $H_g$  and the IR active

**TABLE 5: Correlation Tables for the  $A_g$ ,  $H_g$ , and  $T_{1u}$  Representations of  $I_h$ , for the Subgroups of  $I_h$  Containing Inversion Where R Denotes Raman and IR Denotes Infrared Active Modes**

$I_h$	$A_g$ (R)	$H_g$ (R)	$T_{1u}$ (IR)
$T_h$	$A_g$ (R)	$T_g$ (R) + $E_g$ (R)	$T_u$ (IR)
$S_6$	$A_g$ (R)	$A_g$ (R) + $2 E_g$ (R)	$A_u$ (IR) + $E_u$ (IR)
$D_{5d}$	$A_{1g}$ (R)	$A_{1g}$ (R) + $E_{1g}$ (R) + $E_{2g}$ (R)	$A_{2u}$ (IR) + $E_{1u}$ (IR)
$D_{3d}$	$A_{1g}$ (R)	$A_{1g}$ (R) + $2 E_g$ (R)	$A_{2u}$ (IR) + $E_u$ (IR)
$D_{2h}$	$A_g$ (R)	$2 A_g$ (R) + $B_{1g}$ (R) + $B_{2g}$ (R) + $B_{3g}$ (R)	$B_{1u}$ (IR) + $B_{2u}$ (IR) + $B_{3u}$ (IR)
$C_{2h}$	$A_g$ (R)	$3 A_g$ (R) + $2 B_g$ (R)	$A_u$ (IR) + $2 B_u$ (IR)
$C_i$	$A_g$ (R)	$5 A_g$ (R)	$3 A_u$ (IR)

$T_{1u}$  modes caused by symmetry reduction from  $I_h$  to these point groups (correlation table). The  $C_{2h}$  and  $C_i$  point groups can be ruled out because the expected number of additionally activated peaks<sup>25,26</sup> is too high to be reconciled with the observed data. A  $D_{2h}$  distortion could in principle be positively identified as it leads to a threefold splitting of the  $T_{1u}$  modes, in contrast to the others; unfortunately, in this case, our fits were not sufficiently robust to distinguish between a three- or twofold splitting.  $I_h$  or  $T_h$  symmetry would not cause splittings; therefore, these cannot be the only point groups appearing; there must be units of reduced symmetry even if the connection pattern of the fullerene units is not uniform throughout the whole polymer.

To draw the possible structures with the appropriate point groups, we recall our assumption based on structural data<sup>1,5</sup> that the local arrangement of the molecules does not change significantly on polymerization; thus, the fullerenes must still be surrounded octahedrally by cubanes. In addition, on polymerization, the inversion center of the  $C_{60}$  molecule can be retained only if it is connected to an even number of  $C_8H_8$  molecules. The connection patterns selected by this condition from the set of possible point groups are depicted in Figure 6. This subset contains  $T_h$ ,  $S_6$ ,  $D_{3d}$ , and  $D_{2h}$ .

Three types of fullerene- $C_8H_8$  connections appear in the possible structures. In the first case (patterns  $a$ ,  $b$ , and  $d$  in the second column of Figure 6), the  $C_8H_8$ -fullerene connection involves two adjacent carbon atoms on the double bond of the  $C_{60}$  molecule connecting two hexagons, just as in the case of the high-pressure high-temperature (HPHT)  $C_{60}$  polymers.<sup>19</sup> The difference is that while in those polymers a cyclobutane ring is formed on polymerization; here, both a four-center (cyclobutane) and a three-center (cyclopropane) ring is possible. The second type of fullerene- $C_8H_8$  connection (patterns  $c$  and  $e$  in the third column of Figure 6.) is formed again by two atoms of  $C_{60}$ , but these lie on pentagon-hexagon bonds. It has been shown that such a connection pattern can only exist if the ball is opened.<sup>27</sup> As an opening was excluded on the basis of IR results, patterns  $c$  and  $e$  can be eliminated. The last type of connection between a fullerene and a  $C_8H_8$  is a single bond (patterns  $f$ ,  $g$ , and  $h$  in the fourth column of Figure 6).

Next, we subject these remaining structures to closer scrutiny. Pattern  $a$  was observed in the linear orthorhombic  $C_{60}$  polymer, and  $b$  was observed in the two-dimensional tetragonal polymer.<sup>19</sup> In these polymers and in the  $C_{60}$  dimer, an empirical relation holds between the shift of the  $A_g$  (2) mode and the number of bonds on a single  $C_{60}$  ball: the shift is  $5 \text{ cm}^{-1}$  for every cycloaddition connection (i.e., two adjacent single bonds).<sup>20</sup> The softening occurs because the bonds formed in the polymerization reaction originate from the  $\pi$  bonds of the fullerene. The shift of  $10 \text{ cm}^{-1}$  in poly( $C_{60}C_8H_8$ ) fits perfectly to pattern  $a$ . As the half width of the measured peak is  $7 \text{ cm}^{-1}$ , it is highly unlikely that pattern  $b$  or pristine  $C_{60}$  are present in poly( $C_{60}C_8H_8$ ).

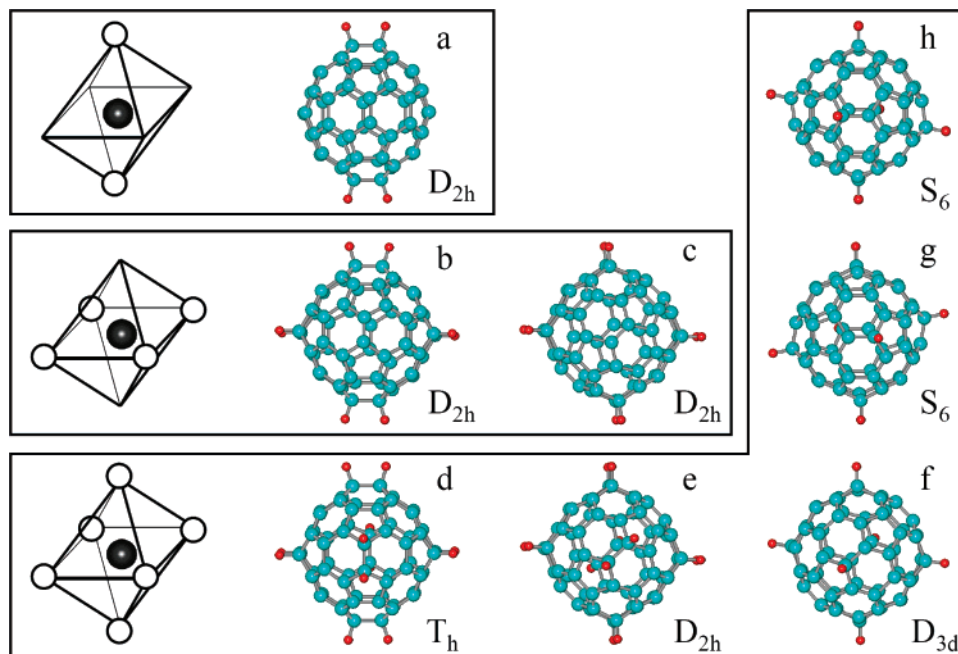
We can rule out that each fullerene is connected to six cubanes. In this case, because of the stoichiometry, the  $C_8H_8$  molecule should also show sixfold coordination, which would lead to a steric tension with six of the eight C atoms of the hydrocarbon bound to a  $C_{60}$  molecule. Therefore, structures  $d$ ,  $f$ ,  $g$ , and  $h$  would automatically imply structure  $a$  to be present as well.

According to our knowledge, no fullerene compounds with the connection patterns  $d$ ,  $f$ ,  $g$ , and  $h$  have been thoroughly investigated by vibrational spectroscopy so far. A similar well-known structure only appears in the case of pattern  $d$ : the two-dimensional rhombohedral  $C_{60}$  polymer<sup>19</sup> has six pairs of  $\sigma$  bonds on hexagon-hexagon bonds of the  $C_{60}$  molecule, although arranged in a different way. The rhombohedral polymer shows the  $A_g$  (2) peak at  $1406 \text{ cm}^{-1}$  (ref 28). We can expect a shift of similar magnitude in the case of pattern  $d$ , but a peak with such a shift was not observed. Another argument which confirms the absence of pattern  $d$  comes from the polarization dependence of the Raman spectrum. If poly( $C_{60}C_8H_8$ ) contained only fullerenes with  $T_h$  symmetry, then the spectrum should show totally polarized modes, which is not the case. If, on the other hand, it contained fullerenes with different connection patterns and pattern  $d$  were one of these, then the peaks should shift or at least change their shape as we change the polarization. As this was not observed either, we can again come to the conclusion that pattern  $d$  is not present in poly( $C_{60}C_8H_8$ ).

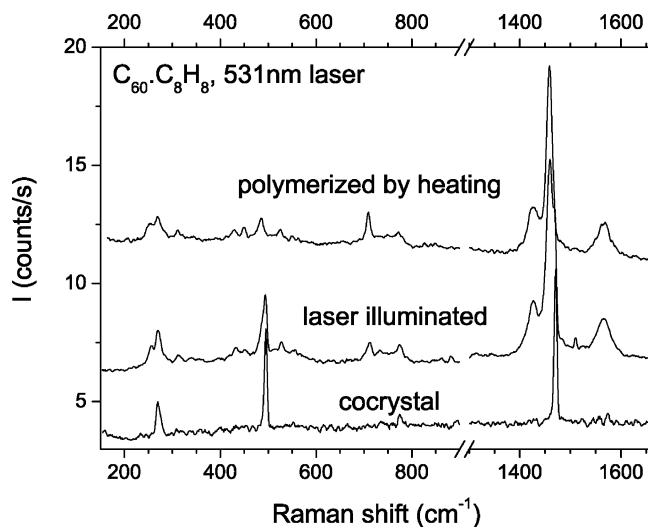
Up to this point, we derived that poly( $C_{60}C_8H_8$ ) definitely contains fullerene units with connection pattern  $a$ , but the possibility of patterns  $f$ ,  $g$ ,  $h$ , or all three cannot be unambiguously excluded. If more connection patterns are present, then many newly activated modes should appear, which would lead to a very rich spectrum, like, for example, that of the  $C_{60}$  photopolymer.<sup>29</sup> This is in contradiction to the observed spectra. The presence of sixfold, besides twofold, coordinated  $C_{60}$  would also mean that in the frequency region of the  $A_g$ ,  $H_g$ , and  $T_{1u}$  modes we would have to see at least 2, 8, and 5 modes, respectively. Instead, we only see somewhat broader peaks as usual. The only remaining possibility would be that all of the Raman and infrared modes of the sixfold coordinated  $C_{60}$  units behave in a very similar way to those of the units with pattern  $a$ , which would lead to unobservable splitting. This is very unlikely since the fullerene- $C_8H_8$  bonds in the two cases are different. Thus, on the basis of our infrared and Raman measurements, we propose that poly( $C_{60}C_8H_8$ ) consists of  $C_8H_8$  molecules and fullerene molecules connected according to pattern  $a$ .

The twofold coordination of the fullerene unit means that the  $C_8H_8$  unit also has a coordination number of two leading to a structure consisting of chains. We cannot derive a definite assignment as to the structure of the cubane isomer connecting two fullerenes. One possible product, dihydropentalene, would lead to linear chains, but there are possibilities to introduce a  $90^\circ$  turn as well. The simultaneous appearance of the two would introduce disorder in all directions, leading to the cubic and amorphous crystal structure in accordance with X-ray diffraction.<sup>1</sup> The variety in the connecting cubane isomers would also explain the broadening of the vibrational lines.

We can also relate the above conclusions to the structural data on  $C_{60}C_8H_8$  polymerized at various temperatures and pressures.<sup>5</sup> Iwasiewicz-Wabnig et al. found two different polymer structures depending on polymerization temperature and pressure: a pseudo-cubic and a pseudo-orthorhombic one. They concluded from Raman spectroscopy that the two do not differ significantly from the molecular level, but the pseudo-



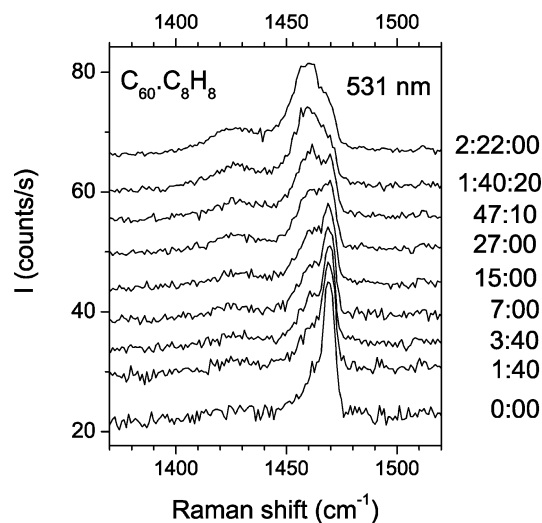
**Figure 6.** Possible connection patterns of the fullerene in poly( $C_{60}C_8H_8$ ). The first column shows the arrangement of  $C_8H_8$  molecules (white spheres) which connect to a  $C_{60}$  ball (gray sphere). In the next columns, the carbon atoms of fullerene origin are colored blue, and those of cubane origin are red. We assumed in this scheme that the connection is four-centered, including two atoms of cubane origin. The point group of the fullerene unit is indicated.



**Figure 7.** Raman spectrum of poly( $C_{60}C_8H_8$ ) after photochemical reaction compared with the spectrum of the cocrystal and the spectrum of the copolymer obtained by annealing.

orthorhombic form is more ordered since its formation occurs at pressures where the rotation of the fullerene balls is sterically hindered. This leads us to believe that the  $D_{2h}$  symmetry, compatible with the orthorhombic crystal structure, is intrinsic to the polymer, and the pseudo-cubic allotrope results from a disordered arrangement of these molecular units.

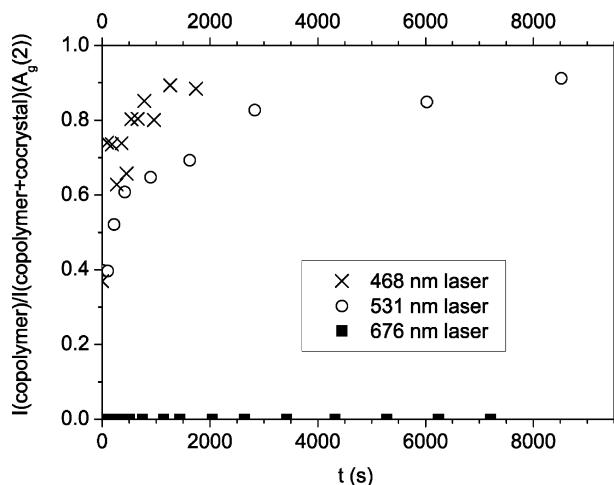
**3.3. Photochemical Reaction in  $C_{60}C_8H_8$ .** We observed a reaction between the constituents on illumination at room temperature similar to that taking place on heating. After already 100 s of laser illumination in the Raman microscope at both 531 and 468 nm, the intensity of the Raman peak at  $1469\text{ cm}^{-1}$  decreases, and a new line at  $1459\text{ cm}^{-1}$  appears. The Raman spectrum obtained after about an hour of illumination by the 531 nm laser is depicted in Figure 7. The new features in the spectrum coincide with those of the polymer produced by annealing. However, as we will see later, the polymerization



**Figure 8.** Change of the Raman spectrum of  $C_{60}C_8H_8$  on illumination by the 531 nm laser. The time (in hours:minutes:seconds) of the illumination is indicated on the right-hand side.

here is not triggered by laser-induced heating. Unfortunately, we do not observe any cubane vibrations when exciting with the laser lines at 531 and 468 nm, so we do not know whether cubane isomerizes the same way as in the thermal polymerization process; we can only deduce that the connection pattern of the fullerene is identical.

The gradual evolution of the new spectral pattern around the  $A_g(2)$  mode during illumination is illustrated in Figure 8. We fitted the spectra with three Lorentzians: one for the  $A_g(2)$  mode of the monomer, one for the  $A_g(2)$  mode of the polymer, and one for the  $H_g(7)$  mode of the polymer. From the obtained integrated intensity values, the intensity of the polymer  $A_g(2)$  peak normalized to the total intensity of the two  $A_g(2)$  peaks was calculated. We repeated the procedure for three exciting laser wavelengths: 531, 468, and 676 nm (see Figure 9). We found that longer wavelength laser lines (676 nm or 785 nm)



**Figure 9.** Fractional intensity of the poly( $C_{60}C_8H_8$ )  $A_g(2)$  peak as a function of illumination time for three different lasers.

did not induce the reaction; therefore, the effect of laser heating can be excluded. The wavelength dependence is analogous to that in  $C_{60}$ , where photopolymerization takes place on illumination.<sup>22</sup> On the basis of these analogies, we classify the reaction as photocopolymerization with excitation of  $C_{60}$  as the first step. (We note that the photochemical reaction is also the reason why the accumulation time for the spectrum of the  $C_{60}\cdot C_8H_8$  cocrystal taken at 531 nm (Figure 2) had to be shorter than for that taken at 785 nm (Figure 1), which accounts for the poorer statistics of the former spectrum.)

**3.4. Poly( $C_{70}C_8H_8$ ).** In  $C_{70}\cdot C_8H_8$ , a similar irreversible change as in  $C_{60}\cdot C_8H_8$  takes place on heating to 470 K. We show the Raman and IR spectra of the reaction product in Figures 4 and 5 and list the center frequencies of the peaks in Tables 3 and 4, along with the assignments of  $C_{70}$  modes by Stratmann et al.<sup>10</sup> The reaction leads to the disappearance of the cubane peaks from both the IR and the Raman spectra, and a new peak appears at  $2946\text{ cm}^{-1}$  in the IR spectrum. At the same time, the IR lines of the fullerene split, but the splitting is much less than that in the  $C_{60}$  analogue. The Raman lines only broaden, probably due to unresolved splitting.

We found that below  $800\text{ cm}^{-1}$  the splitting is twofold in the case of doubly degenerate  $E'_1$  modes. Above  $800\text{ cm}^{-1}$ , no clear splitting can be seen, but the lines become somewhat smeared out. From the apparent twofold splitting of the low-frequency  $E'_1$  modes, the loss of the fivefold axis can be concluded, corresponding to the point group of  $C_{70}$  being  $C_{2v}$  or one of its subgroups.

The changes in the IR spectra of  $C_{70}\cdot C_8H_8$  on annealing reveal a reaction in which the cubane structure changes completely. The resulting hydrocarbon bonds to  $C_{70}$ , whose cage distorts, but remains intact. As the reaction product is insoluble in common solvents,<sup>1</sup> it must indeed be a polymer. At this stage of the research, we cannot say anything more about the structure of this polymer, which is partly due to the scarcity of sound spectroscopic results on  $C_{70}$  derivatives and partly due to the more complicated structure of  $C_{70}$ .

#### 4. Conclusions

The IR and Raman spectra of  $C_{60}\cdot C_8H_8$  and  $C_{70}\cdot C_8H_8$  were measured both in their rotor-stator and in their polymer phases. The rotor-stator nature of the cocrystals directly manifests itself in the spectra being simple superpositions of those of the constituents. Hence, van der Waals forces are the exclusive interaction between the static cubane and the rotating fullerene

molecules. The slightly lower frequency of the cubane lines can be explained on the basis of the highly polarizable environment of the cubane molecules in these structures.

In the IR and Raman spectra of the polymer phases, the fullerene lines are split and new lines appear, corresponding to a symmetry lowering of the fullerene molecules while their cage remains intact. As the cubane lines change dramatically during the polymerization, we conclude that the cubane isomerizes to another constitutional isomer, which binds to the fullerenes. According to the vibrational spectra, no  $C_{60}\text{--}C_{60}$  bonding occurs. The comparison of structural and spectroscopic results allows us to identify linear chains connected via the apical cubane as the most probable polymerization pattern in poly( $C_{60}C_8H_8$ ), with possibly another cubane isomer introducing occasional  $90^\circ$  turns in the chains.

Finally, we found a photochemical reaction in  $C_{60}\cdot C_8H_8$  under illumination with green or blue light. The symmetry of the fullerene molecules in the product turns out to be the same as that in the thermopolymer.

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