

Supporting Information for “Structural evolution of $D_{5h}(1)$ -C₉₀ under high pressure: a mediate allotrope of nanocarbon from zero-dimensional fullerene to one-dimensional nanotube”

Yan Wang[†], Mingguang Yao^{†*}, Xing Hua[†], Fei Jin^{‡*}, Zhen Yao[†], Hua Yang[‡], Ziyang Liu[‡], Qianjun Li[†], Ran Liu[†], Bo Liu[†], Linhai Jiang[†], Bingbing Liu^{†*}

[†]State Key Laboratory of Superhard Materials, Jilin University, No. 2699 Qianjin Street,
Changchun 130012, P.R. China

[‡]College of Materials Science and Engineering, China Jiliang University, No. 258 Xueyuan Street,
Hangzhou 310018, P.R. China

Corresponding Author:

* yaomg@jlu.edu.cn; 1207481234@qq.com; liubb@jlu.edu.cn

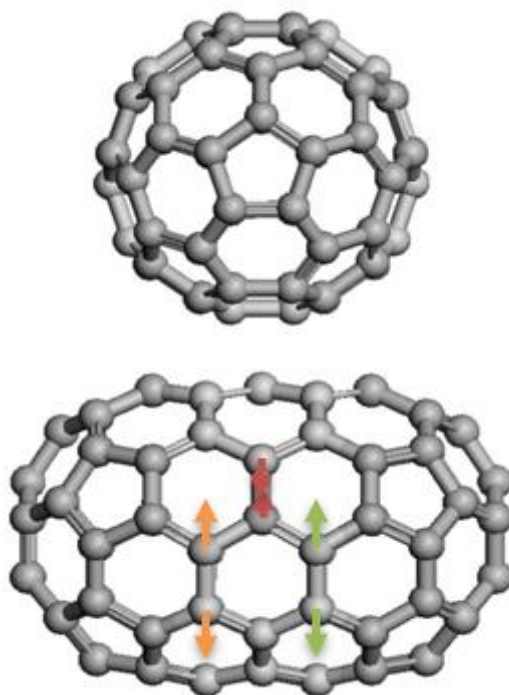


Figure S1. The stretch maps of $D_{5h}(1)$ - C_{90} from different angle of view.

Isomer pure C_{90} sample with D_{5h} symmetry has been isolated from the raw soot produced by Sm_2O_3 -doped graphite rods ^[R1]. $D_{5h}(1)$ - C_{90} has 12 pentagons and 35 hexagons on the carbon cage and can be taken as a short armchair nanotube with two half C_{60} -like caps on its two ends (sketch map see Figure S1). In order to form $D_{5h}(1)$ - C_{90} , the C_{60} was cut in half, one was rotated by 36° relative to the other, 30 carbon atoms were inserted in ^[R1]. The $D_{5h}(1)$ - C_{90} powder were treated under vacuum to remove the solvent remained in the samples.

In the high pressure Raman experiment, a small piece of $D_{5h}(1)$ - C_{90} samples and pressure transmission medium (PTM) were loaded in a hole of $\sim 100 \mu m$ diameter drilled in a preindented $40 \mu m$ steel gasket of a Mao-Bell-type diamond-anvil cell. A 4:1 methanol to ethanol mixture or liquid argon was used as PTM, which both give quite similar results. All the Raman-scattering experiments were performed by using a spectrometer (Renishaw inVia, UK) with an air-cooled charge-coupled device (CCD) detector and double-notch filtering.

High-pressure IR measurements were carried out at U2A beamline, National Synchrotron Light Source, Brookhaven National Laboratory and also have been repeated at our Laboratory. A symmetrical diamond anvil cell with a pair of type IIa diamond anvils was used with liquid argon as the PTM. $D_{5h}(1)$ - C_{90} powder samples were loaded into a $150 \mu m$ diameter gasket hole first. Then, liquid argon was cryogenically loaded and sealed in the gasket hole. The mid-IR spectra were collected in transmission mode by a Bruker Vertex 80v FTIR spectrometer and Hyperion 2000 IR microscope equipped with a nitrogen-cooled MCT detector at U2A side station.

The spectrometer was evacuated and the microscope was purged with dry nitrogen gas during the measurements. In order to measure the reference spectrum at each pressure, the aperture size was set as $25\ \mu\text{m}\times 25\ \mu\text{m}$ and the synchrotron IR beam was focused onto the argon area first then moved to the sample area. The spectra were collected from 500 to $7000\ \text{cm}^{-1}$ with a resolution of $4\ \text{cm}^{-1}$ and 2048 scans applied to all spectra. Both Raman and IR measurements are performed at room temperature and the pressure was calibrated with the ruby fluorescence technique.

Since the Raman and IR spectrum of $\text{D}_{5\text{h}}(1)\text{-C}_{90}$ have not been reported before, theoretical calculations were performed to investigate and assign the vibration modes of $\text{D}_{5\text{h}}(1)\text{-C}_{90}$. The molecular geometries were optimized using Density Functional Theory (DFT) method with B3LYP hybrid functional 6-311g(d) basis set^[R2]. Both the frequency and intensity of each vibrational mode were calculated. All calculations were performed by using Gaussian 09 package^[R3]. The Gauss View program was used to propose an initial geometry of investigated molecules and for visual inspection of the vibration modes.

In order to validate the structure of $\text{D}_{5\text{h}}(1)\text{-C}_{90}$ under high pressure, we have carried out classical molecular dynamics simulations using the universal force field implemented in the Material Studio package. This force field includes van der Waals, bond stretch, bond angle bend, inversion and torsion terms. Taking into account the interaction between adjacent $\text{D}_{5\text{h}}(1)\text{-C}_{90}$ molecules, we used the Lennard-Jones 12-6 potential to describe the van der Waals interaction between molecules^[R4]. For the simulation, we construct a $2\times 3\times 2$ super cell model according to the experimentally determined crystalline parameters, which contains 48 $\text{D}_{5\text{h}}(1)\text{-C}_{90}$ molecules in a box with periodical boundary conditions in all three directions. After that we performed the molecular dynamics in the microcanonical ensemble (constant number of particles, pressure, and temperature) during 20 ps (time step=1 fs). To compare with the experimental results, the simulations have been done in the pressure range from 0 GPa to 14 GPa. And the temperature is set as room temperature (298 K) to ensure the authenticity of the simulation.

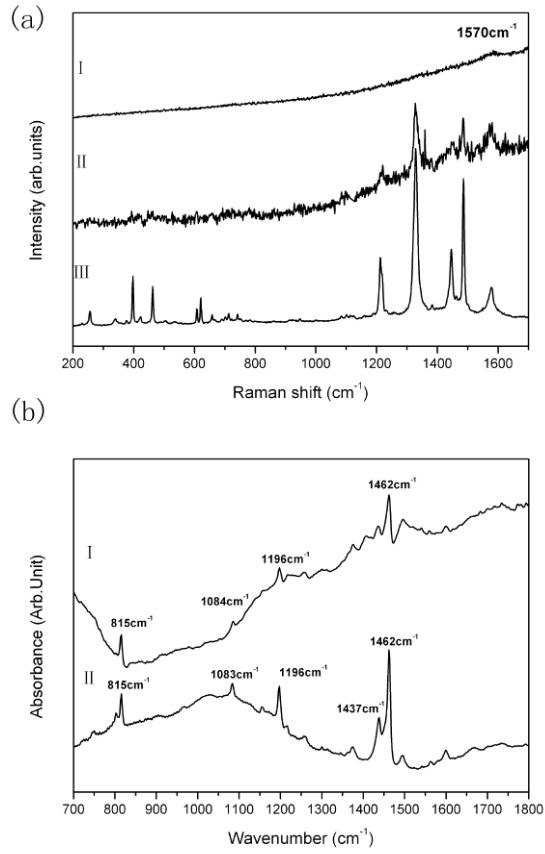


Figure S2. (a) Raman spectra of the $D_{5h}(1)-C_{90}$ decompressed from 35.1 GPa (I), 24 GPa (II) and ambient pressure (III). (b) IR spectra of the $D_{5h}(1)-C_{90}$ decompressed from 25 GPa (I) and ambient pressure (II).

Table S1. The pressure coefficient for the selected four Raman peaks at the transition pressures of 2.5 GPa and 6.6 GPa, respectively.

Raman peaks	Pressure coefficient($\text{cm}^{-1} \text{GPa}^{-1}$)			
	2.5 GPa		6.6 GPa	
1213 cm^{-1}	<1.88 GPa	>1.88 GPa	<5.81 GPa	>5.81 GPa
	9.25	8.16	7.08	18.45
1445 cm^{-1}	<1.88 GPa	>1.88 GPa	<6.66 GPa	>6.66 GPa
	5.85	5.52	5.56	5.42
1485 cm^{-1}	<2.96 GPa	>2.96 GPa	<6.66 GPa	>6.66 GPa
	5.22	5.03	5.70	5.14
1576 cm^{-1}	<1.88 GPa	>1.88 GPa	<6.66 GPa	>6.66 GPa
	5.04	4.62	3.81	5.11

Table S2. The pressure coefficient for the selected five IR peaks at the transition pressures of 2.5 GPa and 6.6 GPa, respectively.

IR peaks	Pressure coefficient($\text{cm}^{-1} \text{GPa}^{-1}$)			
	2.5 GPa		6.6GPa	
815 cm^{-1}	<3.54 GPa	>3.54 GPa	<6.13 GPa	>6.13 GPa
	-1.98	-0.45	-0.75	-0.45
1083 cm^{-1}	<2.91 GPa	>2.91 GPa	<6.13 GPa	>6.13 GPa
	4.28	4.23	3.87	4.45
1196 cm^{-1}	<2.91 GPa	>2.91 GPa	<5.55 GPa	>5.55 GPa
	4.43	2.96	3.15	2.73
1437 cm^{-1}	<2.91 GPa	>2.91 GPa	<6.74 GPa	>6.74 GPa
	6.51	1.47	3.61	1.39
1462 cm^{-1}	<1.60 GPa	>1.60 GPa	<6.74 GPa	>6.74 GPa
	5.14	4.27	6.86	4.18

Table S3. The assignments, pressure coefficient and the pressure at which the mode disappear for the selected four Raman bands are compared with their slope of Pressure dependent frequencies.

Raman vibration modes	Band assignment	Pressure coefficient ($\text{cm}^{-1} \text{GPa}^{-1}$)	Pressure at which the mode disappear
1213 $\text{cm}^{-1} A_1'$	hexagon: stretching vibration	8.23	6.6 GPa
1445 $\text{cm}^{-1} E_1'$	Pentagon: stretching vibration	5.57	11.2 Gpa
1485 $\text{cm}^{-1} A_1'$	bending vibration	5.34	11.2 Gpa
1576 $\text{cm}^{-1} E_1''$	hexagon: stretching vibration	4.13	13.9 Gpa

Table S4. Selected five IR bands assignment are compared with their slope of Pressure dependent frequencies.

IR vibration modes	Band assignment	Pressure coefficient ($\text{cm}^{-1} \text{GPa}^{-1}$)	Pressure at which the mode disappear
815 $\text{cm}^{-1} E_1'$	hexagon: stretching vibration	-0.49	25.0 GPa
1083 $\text{cm}^{-1} A_2''$	hexagon: stretching vibration	4.20	7.6 GPa
1196 $\text{cm}^{-1} A_2''+E_1'$	hexagon: stretching vibration	3.05	9.0 Gpa
1437 $\text{cm}^{-1} E_1'$	pentagon: bending vibration	1.82	20.1 GPa
1462 $\text{cm}^{-1} A_2''+E_1'$	Pentagon: stretching vibration	5.36	2.91 GPa

vibration	Frequency of vibration mode (cm^{-1})		
	calculation	experiment	
		IR	Raman
radial breathing	153		170
radial breathing	247		256
radial breathing	393		397
radial breathing	459		462

radial breathing	606		608
radial breathing	620		621
stretching of hexagonal carbon rings	1080	1083	
stretching of hexagonal carbon rings	1208	1196	
stretching of hexagonal carbon rings	1213		1213
stretching of hexagonal carbon rings	1312		1328
bending of hexagonal carbon rings	1442	1437	
stretching of pentagonal carbon rings	1447		1445
stretching of pentagonal carbon rings	1476	1462	
stretching of hexagonal carbon rings	1480		1485
stretching of hexagonal carbon rings	1571		1576

Table S5. IR and Raman frequencies measured from experiment and calculated by theoretical simulations and their assignments to the corresponding Vibration modes of $D_{5h}(1)$ - C_{90} .

REFERENCES

- [R1] Yang H, Beavers C M, Wang Z, Jiang A, Liu Z, Jin H, Mercado B Q, Olmstead M M and Balch A L 2010 *Angew. Chemie Int. Ed.* **49** 886–90
- [R2] Schettino V, Pagliai M, Ciabini L and Cardini G 2001 *J. Phys. Chem. A* **105** 11192–6
- [R3] Frisch, M. J.; et al. Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT, **2008**
- [R4] Braga S F and Galvão D S 2007 *J. Comput. Chem.* **28** 1724–34