Vibrational anatomy of C$_{90}$, C$_{96}$, and C$_{100}$ fullertubes: probing Frankenstein’s skeletal structures of fullerene head endcaps and nanotube belt midsection†

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Fullertubes are tubular fullerenes with nanotube-like middle section and fullerene-like endcaps. To understand how this intermediate form between spherical fullerenes and nanotubes is reflected in the vibrational modes, we performed comprehensive studies of IR and Raman spectra of fullertubes C$_{90}$-D$_{5h}$, C$_{96}$-D$_{3d}$, and C$_{100}$-D$_{5d}$. An excellent agreement between experimental and DFT-computed spectra enabled a detailed vibrational assignment and allowed an analysis of the localization degree of the vibrational modes in different parts of fullertubes. Projection analysis was performed to establish an exact numerical correspondence between vibrations of the belt midsection and fullerene headcaps to the modes of nanotubes and fullerene C$_{60}$-Ih. As a result, we could not only identify fullerene-like and CNT-like vibrations of fullertubes, but also trace their origin in specific vibrational modes of CNT and C$_{60}$-Ih. IR spectra were found to be dominated by vibrations of fullerene-like caps resembling IR-active modes of C$_{60}$-Ih, whereas in Raman spectra both caps and belt vibrations are found to be equally active. Unlike the resonance Raman spectra of CNTs, in which only two single-phonon bands are detected, the Raman spectra of fullertubes exhibit several CNT-like vibrations and thus provide additional information on nanotube phonons.

Introduction

The discovery of arc-discharge synthesis of fullerenes\(^ \dagger \) brought new attention to carbonaceous materials leading soon to refocusing on carbon nanotubes (CNTs) and later on graphene. Fullerene and CNT research went hand-in-hand from the start, as both feature curved C-sp\(^ 2 \) network, and it was natural to think about CNTs as of strongly elongated, tubular fullerenes. Although ideal CNT is infinitely long, real nanotubes must have an end, and a seamless termination of the tubes can be achieved with fullerene-like caps. This imaginary is also supported from the fullerene side. By the Euler’s theorem, all classical fullerenes have 12 pentagons, and the growth of fullerenes size inevitably means increase of the number of hexagons. The latter can be arranged in many ways, from quasi-spherical structures with uniform distribution of pentagons to tubular fullerenes with curved caps and CNT-like belts. Spherical fullerenes tend to be more thermodynamically stable, and high-resolution trapped ion mobility spectrometry suggested spherical shapes of large fullerenes, such as C$_{110}$-C$_{150}$.\(^ \dagger \) Nevertheless, tubular fullerenes are also well documented. C$_{70}$-D$_{3h}$ can be considered as the first tubular fullerene, and its structure can be obtained from that of C$_{60}$-Ih by insertion of a belt of 10 carbon atoms between two C$_{30}$ hemispheres and rotation of one of the hemispheres by 36\( ^\circ \). Consequent addition of C$_{10}$ fragments into the belt and 36\( ^\circ \) rotation of one cap creates a family of C$_{60}$-I$_{10n}$ tubular fullerenes with alternating D$_{3h}$ and D$_{5d}$ symmetry and a growing (5, 5) CNT fragment. The next after C$_{70}$-D$_{3h}$ is C$_{80}$-D$_{5d}(1)$ isolated in 2000,\(^ \dagger \) the minor isomer of C$_{80}$ seconds to the main C$_{80}$-D$_{2}$,\(^ \dagger \) Then follows C$_{90}$-D$_{5h}(1)$, first characterized in 2010 in a pristine form\(^ \dagger \) as well as chlorofullerenes C$_{90}$Cl$_{10,12}$.\(^ \dagger \) These works proved formation of C$_{90}$-D$_{5h}(1)$ in the arc-discharge process despite the low relative stability of this isomer. Likewise, computational studies of C$_{100}$ isomers showed that the tubular structure C$_{100}$-D$_{5d}(1)$ is not among the most stable ones.\(^ \dagger \) However, this isomer was captured as a chloride C$_{100}$Cl$_{12}$,\(^ \dagger \) and a molecular structure of the non-derivatized C$_{100}$-D$_{5d}(1)$ was recently proved by single-crystal X-ray diffraction of its co-
crystal with decapryrrocorannulene. Another structurally characterized tubular fullerene is C_{96}-D_{3d}(1). In this molecule, the caps are not resembling C_{60} hemispheres and have hexagon in the base, while the belt is a fragment of a zigzag (9,0) CNT.

The number of possible fullerene isomers grows dramatically with the fullerene size, and the separation of multiple similar isomeric structures turns into a complex and tedious procedure. Fortuitously, the studies of tubular fullerenes, aka fullertubes, gained the new boost with the discovery of the isolation route based on their reduced chemical reactivity.

While fullerenes usually readily react with amino-alcohols, tubular fullerenes appeared to be significantly less reactive, which allowed their facile separation from other fullerenes. The main fullertubes obtained this way are C_{60}-D_{5h}, C_{96}-D_{3d}, and C_{100}-D_{5d} (Fig. 1), but a possibility to isolate even larger tubular fullerenes was demonstrated in ref. 10, opening the way to their systematic exploration. C_{96}-D_{3d} was found to be an efficient O₂-reduction electrocatalyst in the recent study.

The increasing availability of such tubular structures, which can be seen as intermediates between spherical fullerenes and 1D nanotubes, raises a question of whether fullertubes exhibit the properties of fullerenes, CNTs, or should be treated as a unique phenomenon. On the other hand, the systematic study of fullertubes may help to pinpoint a transition between discrete molecular properties to periodic 1D behavior. There is hardly a universal answer to this question because different properties have different degree of locality. For instance, the low chemical reactivity of fullertubes with amino-alcohols and selective chlorination of cap regions seems to indicate that belt regions may be similar in their reactivity to CNTs. On the hand, the study of the electronic properties of fullertubes with (5, 5) and (9, 0) CNTs fragments concluded that the convergence is far from reach in realistic fullerene sizes and requires much longer tubes.

In this work, we will address this problem from the point of view of vibrational spectroscopy as the latter played a fundamental role in the studies of nanocarbon materials, from the very first indication of C_{60} presence in the carbon soot confirmed by IR spectroscopy to resonance Raman techniques which became indispensable for CNTs and graphene. Force constants usually vanish over several bonds and therefore vibrations can be considered as more local than electronic excitations. Thus, the transition between confined and periodic properties may happen on a smaller length scale. Here we combine IR and Raman spectroscopy with DFT computations to obtain comprehensive information on vibrational modes of fullertubes C_{90}-D_{3h}, C_{96}-D_{3d}, and C_{100}-D_{5d}, and then use projection technique to establish genetic relationships between vibrations of C_{100}-D_{5d}, (5, 5) CNT and C_{60}-D_{5h}.

**Experimental and computational details**

The synthesis and characterization of fullertubes C_{90}-D_{3h}, C_{96}-D_{3d}, and C_{100}-D_{5d} were described in ref. 10. In brief, the fullerene-containing soot produced by arc-discharge synthesis was extracted with xylene. The fullerene mixture was then reacted with 3-amino-1-propanol. While most fullerenes react readily with 3-amino-1-propanol and form products soluble in water, fullertubes are much less reactive in these conditions and remain in the organic phase. Individual compounds were then isolated by HPLC.

For vibrational spectroscopic studies, the samples were drop-casted from toluene solution onto KBr single-crystalline substrates and dried under vacuum. IR measurements were performed at room temperature in transmission mode using a Hyperion FTIR microscope attached to Vertex 80 spectrometer (Bruker). Raman measurements were performed with T64000 spectrometer (Horiba). The samples on KBr substrates were cooled down to 78 K, and the spectra were measured with laser excitation at 532 nm (Nd:YAG laser Torus by Laser Quantum), 620 nm and 656 nm (Matisse dye laser by Sirah Lasertechnik). The spectra were also excited with 785 nm laser (BrixX diode laser by Omicron Laserage). For the latter, the samples were drop-casted on gold SERS substrates (Metrohm DropSens DRP-C220BT) and immersed in water to improve the heat transfer, and the measurements were performed at room temperature using immersion objective.

DFT calculations of fullerene molecules were performed with PBE density functional using two DFT codes. Vibrational frequencies, IR and off-resonance Raman intensities were calculated with molecular code Priroda using Λ2.
basis set\(^{23}\) with \{4,3,2,1\}/\{12s,8p,4d,2f\} contraction scheme. Vibrational calculations were also performed with periodic code VASP 5.4.4\(^{24–28}\) using recommended pseudopotentials and energy cut-offs for projector-augmented wave (PAW) scheme and 6 Å of vacuum layer to prevent interaction between periodic images. Importantly, calculations with molecular and periodic codes gave very similar vibrational frequencies, ensuring the use of balanced wavefunction description in both codes. In calculations of (5, 5) CNT, the Γ-centered sampling of the Brillouin zone along the periodic axis used 4 Monkhorst–Pack grid points per unit cell. With an accurate grid option, the tube was optimized to a mean gradient of \(10^{-5}\) eV Å\(^{-1}\). The Hessian matrix was calculated using density-functional-perturbation theory for a supercell of four primitive unit cells. Phonopy libraries\(^{27}\) and in-house python scripts were used to analyze phonon spectra and dynamic matrix operation/analysis at different \(q\)-points. Vibrational symmetry analysis was performed using DISP/SYMM package.\(^{28}\)

### Results and discussion

Fig. 2 shows UV-vis absorption spectra of C\(_{90}\)-D\(_{3h}\), C\(_{96}\)-D\(_{3d}\), and C\(_{100}\)-D\(_{5d}\) measured in toluene solution. Although (5, 5) and (9, 0) CNTs are metallic, the CNT fragments in fullertubes are obviously not long enough to develop CNT-like electronic properties and close the band gap.\(^{14}\) Thus, all studied fullertubes have considerable gaps exceeding at least 1.5–2 eV. The spectra closely resemble those reported in the literature\(^{3,10,11,15}\) thus confirming the structural identity of studied molecules.

#### Experimental vibrational spectra

Vibrational modes of fullertubes span the following irreducible representations of their point-symmetry groups:

\[
\Gamma_{\text{vib}}(\text{C}\(_{90}\)-D\(_{3h}\)) = 15A_1'(R) + 12A_2'' + 13A_2' \\
\quad + 14A_1''(IR) + 28E_1'(IR) + 26E_1''(R) \\
\quad + 28E_2'(R) + 26E_2''
\]

(1.a)

\[
\Gamma_{\text{vib}}(\text{C}\(_{96}\)-D\(_{3d}\)) = 26A_1g(R) + 22A_1u \\
\quad + 22A_2g + 26A_2u(IR) \\
\quad + 48E_2g(R) + 48E_2u(IR)
\]

(1.b)

\[
\Gamma_{\text{vib}}(\text{C}\(_{100}\)-D\(_{5d}\)) = 16A_1g(R) + 14A_1u \\
\quad + 14A_2g + 16A_2u(IR) + 30E_1g(R) \\
\quad + 30E_1u(IR) + 30E_2g(R) + 30E_2u
\]

(1.c)

where R and IR in parentheses denote Raman and IR activity, respectively. Despite rather high molecular symmetries, a large number of optically active modes are expected for all three compounds. Vibrational density of states of these molecules is thus quasi-continuous, and reliable vibrational assignment based only on computed frequencies and symmetry analysis is impossible. Therefore, we have to consider not only frequencies, but also computed IR and Raman intensities.

Experimental IR spectra of fullertubes are compared to the computed ones in Fig. 3. To benchmark the computational method, Fig. 3 also shows the spectra of well-known fullerene C\(_{70}\)-D\(_{3h}\). Based on the latter, we can conclude that the computational method gives a very good match of experimental vibrational frequencies. The difference between experiment and theory is usually less than 5 cm\(^{-1}\) and increases up to...
and theory. Using computed intensities as a guide, we could.

spectra is facilitated by a good agreement between experiment

peaks detected for each compound. The assignment of the

obtained with a combined set of spectra is very rich with 60

frequency tangential modes. Overall, the spectral information

non-resonance scattering is found for the green laser

D$_{5h}$, C$_{96}$-D$_{3d}$, and C$_{100}$-D$_{5d}$ can be found in ESI (Tables S1–

S3†). Table 1 lists the assignment of the IR spectrum of C$_{100}$-

D$_{5d}$. The spectrum of C$_{90}$-D$_{3h}$ obtained this work closely

resembles the data reported in a recent study of vibrational

spectra of C$_{90}$-D$_{3h}$ under high pressure.39

Raman spectra of C$_{90}$-D$_{3h}$, C$_{96}$-D$_{3d}$, and C$_{100}$-D$_{5d}$ are shown in

Fig. 4, 5, and 6, respectively. To obtain the most detailed

information, the spectra were excited with several laser lines.

From Fig. 2, comparing laser wavelengths in relation to the

absorption spectra of fullerenes, we find that the 785 nm laser

should produce a non-resonant Raman scattering, whereas

other laser lines appear close to or overlap with the fullerene

absorptions and may therefore induce resonant effects.

Indeed, the computed spectra agree well with the experimental

spectra recorded with 785 nm excitation. At the same time, the

spectra measured with shorter laser wavelengths demonstrate

considerable redistribution of intensity pointing to their pre-

resonance character. A particular strong difference from the

non-resonance scattering is found for the green laser (532 nm), which strongly enhances the intensity of the high-

frequency tangential modes. Overall, the spectral information

obtained with a combined set of spectra is very rich with 60–70

peaks detected for each compound. The assignment of the

spectra is facilitated by a good agreement between experiment

and theory. Using computed intensities as a guide, we could

first identify the peaks in the off-resonance spectra with a high

degree of certainty and then continue with the remaining

peaks detected only in resonant conditions. The procedure

allowed determination of almost all fully symmetric modes

(A1′, or A1g types), which as a rule are more prominent in the

spectra, as well as a large part of E-type modes (E1′, E1g, E2g,

or E1g/E2g types, see eqn (1)). Besides, a certain number of weak

lines did not match the Raman active modes and could be ten-

Table 1  Selected IR-active vibrational modes of C$_{100}$-D$_{5d}$ with their computed frequencies, intensities, experimental assignment, and description in terms of (5, 5) CNT and C$_{60}$ modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>PAW</th>
<th>A2</th>
<th>Int,%</th>
<th>Exp</th>
<th>d$_{CNT}$</th>
<th>% CNT modes</th>
<th>d$<em>{C</em>{60}}$</th>
<th>% C$_{60}$ modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_{1u}$ (3)</td>
<td>475</td>
<td>477</td>
<td>15.1</td>
<td>480 m</td>
<td>34</td>
<td>30 A$_{1d}$(1)</td>
<td>66</td>
<td>60 F$_{1u}$(1)</td>
</tr>
<tr>
<td>E$_{1u}$ (5)</td>
<td>480</td>
<td>480</td>
<td>20.3</td>
<td>480 m</td>
<td>46</td>
<td>36 E$_{1u}$(2)</td>
<td>54</td>
<td>35 F$<em>{1u}$(2), 14 H$</em>{u}$(1)</td>
</tr>
<tr>
<td>A$_{2u}$ (4)</td>
<td>518</td>
<td>518</td>
<td>23.7</td>
<td>511 vw</td>
<td>22</td>
<td>18 A$_{2d}$(1)</td>
<td>79</td>
<td>56 F$_{1u}$(2)</td>
</tr>
<tr>
<td>E$_{1u}$ (8)</td>
<td>545</td>
<td>546</td>
<td>27.0</td>
<td>548 vs</td>
<td>24</td>
<td>18 E$_{1d}$(1)</td>
<td>75</td>
<td>65 F$_{1d}$(1)</td>
</tr>
<tr>
<td>E$_{1u}$ (9)</td>
<td>626</td>
<td>627</td>
<td>0.9</td>
<td>628 w</td>
<td>66</td>
<td>36 E$<em>{2u}$(2), 12 E$</em>{1u}$(1)</td>
<td>35</td>
<td>17 H$_{u}$(3)</td>
</tr>
<tr>
<td>E$_{1u}$ (10)</td>
<td>643</td>
<td>643</td>
<td>5.2</td>
<td>648 w</td>
<td>58</td>
<td>24 E$<em>{1u}$(4), 13 E$</em>{2u}$(2)</td>
<td>43</td>
<td>20 H$_{u}$(3)</td>
</tr>
<tr>
<td>E$_{1u}$ (11)</td>
<td>711</td>
<td>711</td>
<td>5.6</td>
<td>716 vv</td>
<td>22</td>
<td>37 E$<em>{1u}$(4), 13 E$</em>{2u}$(2)</td>
<td>78</td>
<td>30 G$<em>{u}$(2), 22 H$</em>{u}$(3), 20 H$_{u}$(4)</td>
</tr>
<tr>
<td>E$_{1u}$ (13)</td>
<td>760</td>
<td>760</td>
<td>4.5</td>
<td>761 w</td>
<td>16</td>
<td>—</td>
<td>78</td>
<td>30 G$<em>{u}$(2), 22 H$</em>{u}$(3), 20 H$_{u}$(4)</td>
</tr>
<tr>
<td>E$_{1u}$ (14)</td>
<td>772</td>
<td>772</td>
<td>11.4</td>
<td>771 vv</td>
<td>28</td>
<td>18 E$_{1d}$(1)</td>
<td>72</td>
<td>31 G$<em>{u}$(4), 28 F$</em>{1d}$(2)</td>
</tr>
<tr>
<td>E$_{1u}$ (15)</td>
<td>822</td>
<td>821</td>
<td>0.8</td>
<td>818 vv</td>
<td>88</td>
<td>88 E$_{1u}$(3)</td>
<td>11</td>
<td>10 G$_{u}$(3)</td>
</tr>
<tr>
<td>A$_{2u}$ (8)</td>
<td>1013</td>
<td>1011</td>
<td>2.7</td>
<td>1023 vv</td>
<td>32</td>
<td>28 B$_{1d}$(1)</td>
<td>69</td>
<td>66 F$_{2d}$(3)</td>
</tr>
<tr>
<td>E$_{1u}$ (18)</td>
<td>1101</td>
<td>1099</td>
<td>2.0</td>
<td>1099 vv</td>
<td>48</td>
<td>30 E$_{2u}$(3)</td>
<td>51</td>
<td>19 G$<em>{u}$(2), 10 F$</em>{1d}$(3)</td>
</tr>
<tr>
<td>A$_{2u}$ (9)</td>
<td>1155</td>
<td>1153</td>
<td>20.4</td>
<td>1156 w</td>
<td>42</td>
<td>24 B$<em>{1u}$(1), 12 A$</em>{1u}$(2)</td>
<td>43</td>
<td>41 F$_{2u}$(4)</td>
</tr>
<tr>
<td>A$_{2u}$ (10)</td>
<td>1218</td>
<td>1212</td>
<td>8.8</td>
<td>1196 vv</td>
<td>24</td>
<td>16 A$_{1u}$(2)</td>
<td>76</td>
<td>72 F$_{2u}$(4)</td>
</tr>
<tr>
<td>E$_{1u}$ (20)</td>
<td>1238</td>
<td>1235</td>
<td>4.4</td>
<td>1237 w</td>
<td>12</td>
<td>—</td>
<td>88</td>
<td>66 F$_{2u}$(3)</td>
</tr>
<tr>
<td>E$_{1u}$ (26)</td>
<td>1429</td>
<td>1428</td>
<td>100.0</td>
<td>1430 vs</td>
<td>4</td>
<td>—</td>
<td>96</td>
<td>51 F$<em>{1u}$(4), 42 G$</em>{u}$(6)</td>
</tr>
<tr>
<td>A$_{2u}$ (14)</td>
<td>1462</td>
<td>1461</td>
<td>47.4</td>
<td>1459 w</td>
<td>10</td>
<td>8 A$_{1u}$(2)</td>
<td>89</td>
<td>74 F$_{2u}$(4)</td>
</tr>
</tbody>
</table>

$D_{5d}$ and mode compositions are given in %, contributions of less than 8–9% are omitted. Experimental intensity scale: vw < w < m < s < vs, where w = weak, m = medium, s = strong, vs = very.
tatively assigned to silent modes, as was observed earlier in Raman spectra of C_{60}^{-}\text{I}_{h} and C_{70}^{-}\text{D}_{5h}. A complete list of experimental Raman features and computed frequencies are given in ESI,\textsuperscript{†} whereas Table 2 lists all A_{1g} and selected E_{1g} and E_{2g} modes of C_{100}^{-}\text{D}_{5d}.

Projection analysis and symmetry considerations

Having established the correspondence between experimental spectral features and computed normal modes, we can proceed to the main goal of this work, the analysis of the fullertube vibrations in terms of their fullerene and CNT fragments. For the sake of convenience, the analysis will be performed for C_{100}^{-}\text{D}_{5d} as its belt region comprises two CNT periods, while two caps build up fullerene C_{60}^{-}\text{I}_{h} if the belt is removed (Fig. 1). Establishing a resemblance of vibrations of different molecules is straightforward with projection analysis used earlier by some of us for fullerene derivatives\textsuperscript{35–37} and endohedral fullerenes.\textsuperscript{38} The method is based on the fact that normal modes in mass-weighed Cartesian coordinates form an orthonormal basis, and vibrations of one molecule (C_{100}^{-}\text{D}_{5d} in this work) can be projected onto the space of vibrational eigenvectors of another molecule (C_{60}^{-}\text{I}_{h} or CNT) using scalar products:

\[ a_{\text{frag},ij} = (Q_{\text{C100}},i, Q_{\text{frag}},j), \]

where \( Q_{\text{C100}},i \) is \( i \)th vibrational mode of the fullertube C_{100}^{-}\text{D}_{5d}, \( Q_{\text{frag}},i \) is the \( j \)th mode of the fragment of interest (C_{60}^{-}\text{I}_{h} or CNT), and \( Q_{\text{C100},\text{cap}} \) vector includes only a subset of atomic displacements corresponding to this fragment. Consequently, the square \( a_{\text{frag},ij}^2 \) gives the contributions of the \( j \)th fragment mode to the \( i \)th mode of C_{100}^{-}\text{D}_{5d}, and the sum of \( a_{\text{frag},ij}^2 \) over all fragment modes amounts to the contribution of a given fragment to the \( i \)th vibrational mode of the whole C_{100}^{-}\text{D}_{5d} molecule:

\[ d_{\text{frag},i} = \sum_j a_{\text{frag},ij}^2 \]

In fact, \( d_{\text{frag},i} \) can be also obtained from vibrational eigenvectors in cartesian coordinates without the projection, and we will use that for C_{90}^{-}\text{D}_{5h} and C_{96}^{-}\text{D}_{3d}. It is also important to note that in case of a uniform distribution of a given vibration over the whole fullertube molecule, the CNT-like belt will contribute 33.3\% in C_{90}^{-}\text{D}_{5h}, 18.8\% in C_{96}^{-}\text{D}_{3d}, and 40\% in C_{100}^{-}\text{D}_{5d}. A predominant localization of the vibration on the belt region can be concluded when \( d_{\text{CNT}} \) considerably exceeds these values.

To summarize, using DFT-computed vibrational eigenvectors, we can establish exact correspondence between the vibrations of C_{100}^{-}\text{D}_{5d} caps and the modes of C_{60}^{-}\text{I}_{h}, as well as between vibrations of the C_{100}^{-}\text{D}_{5d} belt and the modes of (5, 5) CNT. When one particular fragment mode has dominant contribution \( (a_{\text{frag},ij}^2 \) is close to 1 or at least to \( d_{\text{frag},i} \)), there is a close resemblance of the corresponding vibrations of C_{100}^{-}\text{D}_{5d} and C_{60}^{-}\text{I}_{h} or CNT. When two or more fragment modes have comparable contributions, it is said that these modes are mixing. The full list of DFT-computed vibrational frequencies of C_{60}^{-}\text{I}_{h} and (5, 5) CNT can be found in ESI, Tables S4 and S5,\textsuperscript{†} For C_{60}^{-}\text{I}_{h}, Table S4\textsuperscript{†} also compares the frequencies with complete set of fundamentals, including silent modes, determined in ref. 39.
It is also useful to establish a relation between symmetry types of the vibrations as the symmetry restricts the optical activity and a possibility of the mode mixing. Since D_{5d} is a subgroup of I_h, the connection between C_{60}-I_h modes and vibrations of C_{100}-D_{5d} caps is straightforward (Table 3). All gerade (g-type) modes of C_{60}-I_h become Raman active in the D_{5d} group as they include either A_{1g}, E_{1g}, or E_{2g} representations. However, only Raman-active A_g and H_g modes of C_{60}-I_h have A_{1g} component in the D_{5d} group, and as mentioned above, the vast majority of strong Raman modes of C_{100}-D_{5d} are of A_{1g} symmetry. For ungerade modes, C_{60}-I_h has only 4 IR-active vibration of F_{1u} type, but all its degenerate u-type modes become IR active in the D_{5d} symmetry as they have either A_{2u} or E_{1u} representations. Only A_u mode of C_{60}-I_h remains silent.

The situation with the CNT is more complex and requires a deeper discussion. (5, 5) CNT is described by the T1_{10h} linear group, which is isogonal to the D_{10h} point symmetry group. In the following, we will mainly use the irreducible representations of the D_{10h} group to label vibrational modes of the (5, 5) CNT. As with any other armchair CNT, it has 8 Raman active modes (2A_{1g} + 2E_{1g} + 4E_{2g}) and 5 IR-active modes (A_{2u} + 4E_{1u}, of which A_{2u} and one E_{1u} are acoustic modes with zero frequency in Γ-point). In C_{100}, the symmetry is reduced to D_{5d}. Irreducible representations for the CNT in T_{10h}D_{10h}, D_{10h}D_{5h}, and D_{5h} groups are compared in Table 4. Furthermore, the CNT-like belt of C_{100}-D_{5d} has 40 atoms, in which 20-atomic unit cell of the (5, 5) CNT is repeated twice. For this reason, it is insufficient to consider only Γ-point modes of the CNT when comparing its vibrations to those of C_{100}-D_{5d}. Vibrations of the double-cell fragment can be formally described by two sets of the unit cell modes, one with both unit cells vibrating in phase and corresponding to Γ-point, and one with unit cells vibrating in anti-phase to each other and thus corresponding to X-point on the edge of the Brillouin zone. Fig. 7a and b shows DFT-computed dispersions of CNT phonons and variation of the composition of selected modes with k obtained by projecting k-point eigenvectors on Γ-point eigenvectors. Fig. 7 shows that both frequencies and composition of the modes can change considerably in k-space along going from Γ to X. For instance, whereas B_{1u}(1) and A_{1g}(2) modes tend to retain their shape at k ≠ 0, A_{2u}(1) mode is

### Table 2 All A_{1g} and selected E_{2g} and E_{3g} Raman-active vibrational modes of C_{100}-D_{5d} with their computed frequencies, intensities, experimental assignment, and description in terms of (5, 5) CNT and C_{60}-I_h modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>PAW</th>
<th>A2</th>
<th>Int, %</th>
<th>Exp. 785</th>
<th>Exp. 532</th>
<th>d_{CNT}</th>
<th>% CNT modes</th>
<th>d_{exp}</th>
<th>% C_{60} modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{1g}(1)</td>
<td>238</td>
<td>238</td>
<td>28.7</td>
<td>243</td>
<td>24/25</td>
<td>12</td>
<td>8 A_{1g}(1)</td>
<td>87</td>
<td>68 H_{1}(1), 9 A_{1g}(1)</td>
</tr>
<tr>
<td>A_{1g}(2)</td>
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<td>323</td>
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<td>325</td>
<td>76</td>
<td>64 A_{1g}(1), 12 B_{2u}(1)</td>
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<td>14 H_{1}(1)</td>
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<td>A_{1g}(3)</td>
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<td>26</td>
<td>18 A_{1g}(1)</td>
<td>74</td>
<td>43 A_{1g}(1)</td>
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<td>426</td>
<td>3.4</td>
<td>427</td>
<td>429</td>
<td>32</td>
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<td>65 H_{2}(1)</td>
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<td>602</td>
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<td>99</td>
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<td>44</td>
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<td>12</td>
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<td>1305</td>
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<td>1303</td>
<td>82</td>
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<td>10 H_{7}(7)</td>
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<td>—</td>
<td>1548</td>
<td>50</td>
<td>48 B_{1g}(2)</td>
<td>50</td>
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<td>1575</td>
<td>8</td>
<td>—</td>
<td>92</td>
<td>83 H_{8}(8)</td>
</tr>
</tbody>
</table>

Computed Raman intensity is for off-resonance conditions, d_{exp} and mode compositions are given in %, contributions of less than 8–9% are omitted. Experimental intensity scale: w ≤ w < w + < m < s < vs, where w – weak, m – medium, s – strong, v – very, sh – shoulder.

### Table 3 Correlation between symmetry types of vibrational modes in C_{60}-I_h and C_{100}-D_{5d} 

<table>
<thead>
<tr>
<th>C_{60}-I_h</th>
<th>C_{100}-D_{5d} caps</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 A_{1g}(R)</td>
<td>2 A_{1g}(R)</td>
</tr>
<tr>
<td>3 F_{1g}</td>
<td>3 (E_{1g}(R) + A_{2g})</td>
</tr>
<tr>
<td>4 E_{2g}</td>
<td>4 (E_{1g}(R) + A_{2g})</td>
</tr>
<tr>
<td>6 G_{1g}</td>
<td>6 (E_{1g}(R) + E_{2g}(R))</td>
</tr>
<tr>
<td>8 H_{1g}(R)</td>
<td>8 (E_{1g}(R) + E_{2g}(R) + A_{1g}(R))</td>
</tr>
</tbody>
</table>

\* R and IR in parentheses denote Raman and IR-active modes.
Table 4  Correlation between symmetry types of vibrational modes in (5, 5) CNT and C_{100}-D_{5d}^a

<table>
<thead>
<tr>
<th>(5, 5) CNT, T_{10h}</th>
<th>(5, 5) CNT, D_{14h}</th>
<th>(5, 5) CNT, D_{5d}</th>
<th>C_{100}-D_{5d}, belt</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 \sqrt{5}A_{1u} + \sqrt{5}A_{1g}</td>
<td>2 A_{1u}(R) + B_{1g}</td>
<td>3 A_{1g}</td>
<td>3 (A_{1g} + A_{2u}(IR))</td>
</tr>
<tr>
<td>2 \sqrt{5}B_{1u} + \sqrt{5}B_{1g}</td>
<td>2 A_{1g} + B_{1g}</td>
<td>3 A_{1g}</td>
<td>3 (A_{1g} + A_{1u})</td>
</tr>
<tr>
<td>2 \sqrt{5}E_{1g} + 4 \sqrt{5}E_{4g}</td>
<td>2 E_{1g}(R) + 4 E_{4g}</td>
<td>6 E_{1g}</td>
<td>6 (E_{1g}(R) + E_{1u}(IR))</td>
</tr>
<tr>
<td>4 \sqrt{5}E_{2g} + 2 \sqrt{5}E_{5g}</td>
<td>4 E_{2g}(R) + 2 E_{5g}</td>
<td>6 E_{2g}</td>
<td>6 (E_{2g}(R) + E_{2u}(IR))</td>
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<tr>
<td>2 \sqrt{5}B_{1u} + B_{1g}</td>
<td>2 B_{1u} + A_{1u}</td>
<td>3 A_{1u}</td>
<td>3 (A_{2u} + A_{1g})</td>
</tr>
<tr>
<td>2 \sqrt{5}A_{1u} + \sqrt{5}A_{1g}</td>
<td>2 B_{2u} + A_{2u}(IR)</td>
<td>3 A_{1u}</td>
<td>3 (A_{2u}(IR) + A_{1g}(R))</td>
</tr>
<tr>
<td>4 \sqrt{5}E_{1g} + 2 \sqrt{5}E_{4g}</td>
<td>4 E_{1g}(IR) + 2 E_{4g}</td>
<td>6 E_{1u}</td>
<td>6 (E_{1u}(IR) + E_{1g}(IR))</td>
</tr>
<tr>
<td>2 \sqrt{5}E_{2g} + 4 \sqrt{5}E_{3u}</td>
<td>2 E_{2g} + 4 E_{3u}</td>
<td>6 E_{2u}</td>
<td>6 (E_{2u} + E_{2g}(IR))</td>
</tr>
</tbody>
</table>

R and IR in parentheses denote Raman and IR-active modes. Note that E_{1u} and A_{2u} are acoustic modes with zero frequency in Γ-point, leaving 3E_{1u} optical IR-active mode in armchair CNTs; one of the A_{2g} modes corresponds to the rotation of CNT around its axis and also has zero frequency in Γ-point.

red...
5) CNT in the following discussion. pronounced mixing, so we will stay with computed at X-point, but this resulted in a much more pro-
computed using CNT modes com-
tained in terms of C60 and CNT fragments is still quite inductive. In the IR spectrum, all strong bands have predominant contributions from C100 caps and can be traced back to IR-active F1u modes of C60. For instance, the strong peak at 1430 cm⁻¹ is assigned to the E₁u(26) mode of C100 with 51% contribution from F₁u(4) (1429 cm⁻¹ in C60). Another very strong IR peak of C100 at 548 cm⁻¹ corresponds to the E₁u(8) mode with 65% of F₁u(2) (576 cm⁻¹ in C60). Finally, the peak at 480 cm⁻¹ can be assigned to two C100 modes with close frequencies and large weights of F₁u(1) (526 cm⁻¹) and F₁u(2) C60 modes. Vibrations of the CNT-like belt have lower IR intensities. The only range where they have some prominence is around 600–850 cm⁻¹, where several weak absorptions can be seen. Particularly, a weak band at 818 cm⁻¹ is caused by the C100 vibration resembling the E₁u(3) CNT mode, which in due turn originates from the IR-active phonon of graphene detectable in graphite at 868 cm⁻¹. Further details of IR spectral assignment can be found in Table 1.

In Raman spectra, C60-like and CNT-like vibrations are represented more uniformly as can be deduced from the data in Table 2 and Fig. 9. The majority of prominent Raman features in the spectra of C100 are assigned to vibrations of A₁g symmetry type (see Table 2), and according to the symmetry analysis (Table 3), the A₁g modes with predominant localization on caps can be traced to A_g or H_g modes of C60. For instance, the Raman feature of C100 at 243 cm⁻¹ is related to the H₉(1) mode of C60 at 272 cm⁻¹, the peak at 427 cm⁻¹ corresponds to the H₉(2) mode (432 cm⁻¹), the strong peak at 1232 cm⁻¹ is related to the H₉(6) mode (1248 cm⁻¹), whereas the peak at 1575 cm⁻¹ corresponds to the H₉(8) mode (1574 cm⁻¹ in C60).

Considerable components of two A₉ modes of C60 are found in 4 modes of C100. The strongest peak in the non-resonant spectrum of C100 at 379 cm⁻¹ is assigned to A₁₃g(3), which has 26% belt and 74% cap contributions, including 43% A_g(1) mode of C60 (495 cm⁻¹). The latter is known as the fullerene breathing mode. Interestingly, the CNT part in this vibration is mainly represented by the radial breathing mode (RBM), A₁₃g(1), detected in the experimental spectrum of (5, 5) CNT at 338 cm⁻¹ (ref. 42; our DFT-computed frequency for RBM is 332 cm⁻¹). Note that the study of fullerene vibrations based on the isotropic spherical shell model demonstrated that the breathing mode frequency scales as M⁻¹/₂, where M is the fullerene mass, and this scaling works very well even for tubular fullerenes. The shift of the breathing mode frequency from 495 cm⁻¹ in C60 to 379 cm⁻¹ in C100 agrees well with this scaling. The breathing mode of C60 also contributes to the A₁₃g(6) mode of C100 at 599 cm⁻¹, in which it is mixed with H₉(4) (772 cm⁻¹).

The second totally symmetric vibration of C60, A₉g(2) (1468 cm⁻¹) known as the pentagonal pinch mode, mixes with H₉(7) (1422 cm⁻¹) in the A₁₃g(14) mode of C100. In the experimental Raman spectrum it is detected as the medium-intensity feature at 1447 cm⁻¹. Another C₁₀₀ vibration with the large

![Fig. 8 Visualization of projection matrices (|a_ij|^2 coefficients) for C₁₀₀-D₅d modes onto the spaces of (a) modes of C₆₀-Γh, and (b) modes of (5, 5) CNT in Γ-point. In (b), horizontal lines denote A₁g modes of CNT. The modes are numbered in the order of increasing frequency, counted once, giving 176 modes for C₁₀₀-Γh, and 36 modes for (5, 5) CNT.](image)

![Fig. 9 Comparison of the Raman spectra of C₁₀₀-D₅d (λ_ex = 785 nm) and C₆₀-Γh (λ_ex = 1064 nm) and the correspondence of the most intense C₁₀₀ Raman lines to the vibrational modes of C₆₀ and (5, 5) CNT. Large contributions of A_g and H_g modes of C₆₀ to C₁₀₀-D₅d vibrations are denoted with gray dashed lines, C₁₀₀-D₅d vibrations with large contribution of CNT modes are marked with cyan arrows and labels of leading CNT vibrations.](image)
weight of the pentagonal pinch mode is $A_{1g}(15)$ predicted at 1493 cm$^{-1}$. Here the cap and the belt parts contribute equally, each represented by a totally symmetric mode, $A_g(2)$ for $C_{60}$ and $A_{1g}(2)$ for CNT. However, this vibration has low predicted Raman intensity, and we cannot assign it with an acceptable degree of certainty – the only plausible experimental signal in the corresponding frequency range is a very weak and broad feature at 1482 cm$^{-1}$.

On the CNT side, several totally symmetric modes of $C_{100}$-$D_{3d}$ with considerable Raman activity can be pointed out. The vibration resembling the CNT RBM mode is found at 325 cm$^{-1}$, not far from the actual RBM mode frequency in the $(5, 5)$ CNT at 338 cm$^{-1}$ (ref. 42). The relative intensity of this vibration in $C_{100}$ is rather low in pre-resonant conditions, when the spectra are excited with 620 nm or 532 nm lasers. Quite interesting is the $A_{1g}(5)$ mode of $C_{100}$ at 551 cm$^{-1}$, which resembles the radial $B_{2g}(2)$ CNT mode predicted at 625 cm$^{-1}$. Its intensity is strongly enhanced under 620 nm excitation so that it becomes the strongest feature in the spectrum. $A_{1g}(10)$ at 1195 cm$^{-1}$ is another medium-intensity Raman feature of $C_{100}$ largely originating from ungerade CNT vibration, this time $B_{2g}(2)$ predicted at 1319 cm$^{-1}$. This CNT mode, mixed with $B_{1g}(1)$ (predicted at 1377 cm$^{-1}$), also contributes to the second strongest non-resonant Raman feature of $C_{100}$, $A_{1g}(12)$ at 1301 cm$^{-1}$. In fact, the latter can be described as the Kekule vibration of the belt hexagon. Note that Kekule vibrations are usually rather strong in Raman spectra of aromatic compounds.

Only a handful of $E_{2g}$ and $E_{2u}$ modes of $C_{100}$ have considerable Raman intensity. Those of them with enhanced cap contribution can be traced back to $H_g$ modes of $C_{60}$, similar to $A_{1g}$ vibrations discussed above (Table 2). A specific example of the belt-localized mode worth highlighting here is the lowest-frequency $E_{2g}(1)$ vibration at 144 cm$^{-1}$ with the strong non-resonance Raman intensity. It shows considerable temperature dependence and is shifted to 154 cm$^{-1}$ at 78 K. This mode is traced back to the squashing CNT vibration, also of $E_{2g}(1)$ type, predicted at 69 cm$^{-1}$ in the $(5, 5)$ CNT. Note that in the aforementioned treatment of fullerene vibrations as that of an elastic sphere, this vibration can be identified as the component of the 5-fold degenerate quadrupolar mode. Other components are cap-based vibrations at 220–245 cm$^{-1}$ with a large weight of the $H_g(1)$ $C_{60}$ mode. Ref. 44 showed that the average frequency of the quadrupolar mode also scales with the fullerene mass roughly as $M^{-1/2}$, whereas the splitting degree in non-spherical fullerenes was found to be a function of the cage form, being the largest for elongated molecular shapes.

Another CNT-like vibration of $C_{100}$ of E-type, $E_{1g}(28)$ at 1508 cm$^{-1}$, corresponds to the $E_{1g}(2)$ mode of the CNT with longitudinal oscillations of carbon atoms along the tube axis. This is one of the CNT modes, whose origin comes from the Raman-active phonon of graphene at 1582 cm$^{-1}$ known as the G-band, but it is not active in the CNT spectrum of the $(5, 5)$ CNT. 

It is quite remarkable that the Raman spectra of $C_{100}$ have several pronounced features of CNT-like vibrations. Vibrational studies of CNTs usually rely on strong resonance enhancement in Raman spectra when the laser matches transition between van-Hove singularities. In such resonance spectra, only two single-phonon bands are observed, the lower-frequency RBM mode and the high-energy G-band, which in CNTs includes several modes originated from the graphene optical phonon at 1582 cm$^{-1}$. In armchair $(n, n)$ CNTs, three modes of this type are Raman active, $E_{2g}(4) + A_{1g}(2) + E_{1g}(2)$. However, unlike chiral CNTs, demonstrating the G-band splitting into $G^*$ and $G^-$ components with longitudinal and circumferential motions of carbon atoms, armchair CNTs exhibit only one narrow $G^*$-band in resonance Raman spectra, presumably due to the $A_{1g}(2)$ mode with circumferential atomic displacements.

In the $(5, 5)$ CNT, such $G^*$ feature was detected at 1573 cm$^{-1}$, whereas the RBM mode is found at 338 cm$^{-1}$ (ref. 42). While the resonance enhancement is extremely useful for CNTs as it enables the measurement of tiny sample amounts, down to a single nanotube, it also imposes a limitation on the information obtained from such spectra as it only attests to enhanced modes. Other IR and Raman active vibration usually remain obscure, and even though some studies focusing on such vibration were reported, their assignment is rather unspecified because bulk samples of individual CNTs were not available.

The situation is quite different for fullertubes. As they have no van-Hove singularities and therefore specific resonance conditions typical for CNTs are absent, there is no physical reason for the belt vibrations resembling $A_{1g}$ modes of CNT to show enhanced Raman intensity. Indeed, the RBM-like vibration of $C_{100}$ has considerable relative intensity only in non-resonance conditions and becomes weaker when the spectra are excited at 656, 620, or 532 nm (Fig. 6), while the fullertube vibration derived from the $G^*$-$A_{1g}(2)$ CNT mode is so weak that we cannot reliably identify it in our spectra. It may certainly be that these vibrations show higher intensity at shorter excitation wavelengths, as the $(5, 5)$ CNT has its $E_{11}^M$ transition at 412 nm, but such a short wavelength laser is not available to us at this moment. On the other hand, we have found several other belt-localized vibrations of $C_{100}$, which can be traced to CNT vibrations that cannot be observed in the spectra of CNT itself.

**Vibrational spectra of $C_{90}$-$D_{3h}$ and $C_{90C}$-$D_{3d}$**

As $C_{90}$-$D_{3h}$ also has the belt derived from the $(5, 5)$ CNT and two $C_{60}$-like caps, albeit rotated at a different angle than in $C_{100C}$-$D_{3d}$, vibrational features of $C_{90}$-$D_{3h}$ and $C_{90C}$-$D_{3d}$ are rather similar. The strongest IR bands in $C_{90}$-$D_{3h}$ are found near 500–600 cm$^{-1}$, as in many other fullerenes. Among the CNT-like vibrations, the most prominent is the band at 815 cm$^{-1}$ with rather high IR intensity. It has 72% belt contribution and can be assigned to the IR-active phonon of graphene ($868$ cm$^{-1}$ in graphite). Similar vibration in $C_{100C}$-$D_{3d}$ is found at 818 cm$^{-1}$, but with a much lower intensity. In Raman spectra, the prominent peaks with strong CNT contribution are found at 165 cm$^{-1}$ (CNT squashing mode), 338 cm$^{-1}$ (RBM), 1216 cm$^{-1}$ and 1329 cm$^{-1}$ (Kekule vibration).
Compared to \( \text{C}_{100^{-}}D_{5d} \), CNT squashing and RBM modes in \( \text{C}_{90^{-}}D_{3h} \) are upshifted by 21 and 13 cm\(^{-1} \), respectively. High-intensity fullerene-like vibrations in \( \text{C}_{90^{-}}D_{3h} \) occur at 234/257 cm\(^{-1} \) (fullerene squashing mode, \( \text{H}_5(1) \)), 397 cm\(^{-1} \) (breathing mode), and 1446/1484 cm\(^{-1} \) (both with a significant contribution of pentagonal pinch mode).

In \( \text{C}_{96^{-}}D_{3d} \), the belt has only one unit cell of the (9, 0) CNT with 18 carbon atoms, and thus the contribution of the belt to vibrations is on average rather low. Yet, several Raman modes with enhanced contribution still can be pointed out. The squashing mode with 43\% of the belt involvement is found at 158 cm\(^{-1} \). Vibration with a pronounced RBM character occurs at 353 cm\(^{-1} \). We are not aware of vibrational spectroscopic studies of isolated (9, 0) CNTs, but when identified as internal tubes in double-walled and triple-walled CNTs, their RBM mode was found at 324–325 cm\(^{-1} \) (ref. 54 and 55). The strongest non-resonance Raman line at 1327 cm\(^{-1} \) also has noteworthy belt contribution of 40\%. Finally, the highest-frequency vibration at 1599 cm\(^{-1} \) may have a considerable belt contribution resembling \( \text{A}_{1g}(2) \) mode with longitudinal displacement of carbon atoms. The assignment is however rather ambiguous since another vibration of \( \text{C}_{96^{-}}D_{3d} \) with only 2\% of the belt has a similar DFT-predicted frequency. In the IR spectrum, the strong belt participation is found for the mode at 829 cm\(^{-1} \). The rest of IR bands are caused by fullerene-like vibrations. In Raman spectra, the prominent fullerene modes are the squashing modes at 229 and 243 cm\(^{-1} \) as well as the radial breathing mode at 392 cm\(^{-1} \). Assignment of other lines is less straightforward since the caps are not resembling of \( \text{C}_{60} \) shape, and we cannot use projection analysis here.

Variation of the low-frequency Raman modes in the \( \text{C}_{90^{-}}\text{C}_{96^{-}}\text{C}_{100} \) series can be also rationalized with the elastic shell model\(^{34,44} \) already discussed above in application to \( \text{C}_{100} \). The radial breathing mode frequency in the series decreases systematically from 397 cm\(^{-1} \) (\( \text{C}_{90^{-}}D_{3h} \)) to 392 cm\(^{-1} \) (\( \text{C}_{96^{-}}D_{3d} \)) to 379 cm\(^{-1} \) (\( \text{C}_{100^{-}}D_{3d} \)) following the mass increase. The quadrupolar mode in these fullerenes is split into 3 components, two two-fold degenerate and one totally symmetric with the highest frequency: 165/234/257 cm\(^{-1} \) (\( \text{C}_{90^{-}}D_{3h} \)), 158/229/243 cm\(^{-1} \) (\( \text{C}_{96^{-}}D_{3d} \)), and 144/223/243 cm\(^{-1} \) (\( \text{C}_{100^{-}}D_{3d} \)). The averaged frequency again decreases gradually with fullerene mass from 211 cm\(^{-1} \) in \( \text{C}_{90^{-}}D_{3h} \) to 203 cm\(^{-1} \) in \( \text{C}_{96^{-}}D_{3d} \) to 195 cm\(^{-1} \) in \( \text{C}_{100^{-}}D_{3d} \), but the degree of splitting has a different order: the largest one of 99 cm\(^{-1} \) is found in \( \text{C}_{100^{-}}D_{3d} \), followed by 92 cm\(^{-1} \) in \( \text{C}_{96^{-}}D_{3d} \) and 85 cm\(^{-1} \) in \( \text{C}_{90^{-}}D_{3h} \). This sequence is in line with the shape variation among the three, and goes from the most elongated \( \text{C}_{100^{-}}D_{3d} \) to the least tubular \( \text{C}_{90^{-}}D_{3h} \).

**Conclusions**

Detailed IR and Raman study of tubular fullerenes augmented with computational analysis allowed to address the problem of the resemblance between vibrational modes of fullertubes, nanotubes, and fullerenes. Using \( \text{C}_{100^{-}}D_{3d}(1) \) for a case study, we employed projection analysis to establish precise numerical correspondence between vibrations of fullertube belt and caps and normal modes of \( \text{[5, 5]} \) CNT and fullerene \( \text{C}_{60} \). This analysis showed that IR spectra are dominated by vibrations of the caps, which can be traced back to IR-active \( \text{F}_{1u} \) modes of \( \text{C}_{60} \). The only belt vibrations with some, although still rather low IR intensity are found near 820 cm\(^{-1} \) and can be traced back to CNT modes related to the IR-active phonon of graphene. In the Raman spectra, \( \text{C}_{60} \)-like and CNT-like vibrations are presented more uniformly. For caps-localized modes, we again observed a high degree of transferability from \( \text{C}_{60} \) as the most intense Raman features could be associated with Raman-active \( \text{A}_{g} \) and \( \text{H}_6 \) modes of \( \text{C}_{60} \). Vibrations with significant belt contributions showed more unusual pattern. Raman spectra of CNTs have strong resonance character and are dominated by two single-phonon bands, radial breathing mode and components of the G-mode. But in the Raman spectra of fullertubes, these vibrations have modest intensity. We could identify RBM-derived vibrations close to their position in CNTs, but the modes originating from the G-type CNT modes are hard to identify in fullertubes. On the other hand, we found several intense Raman features corresponding to CNT vibrations, which are not observed in the spectra of CNTs. This finding shows that fullertubes may provide additional information on CNTs, which is hard to obtain otherwise.

**Conflicts of interest**

The authors declare no conflicts of interest.

**Acknowledgements**

The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (grant PO 1602/6-1 to A. A. P.) and the National Science Foundation (grant 1856461 to S. S.). Computational facilities were partially provided by the Center for High Performance Computing at the TU Dresden. We appreciate the technical support with local computational resources in IFW Dresden by Ulrike Nitzsche.

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