Anomalous pressure behavior of tangential modes in single-wall carbon nanotubes

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Using molecular-dynamics simulations and the force-constant model, we have studied the Raman-active tangential modes (TMs) of a (10,0) single-wall carbon nanotube under hydrostatic pressure. With increasing pressure, the atomic motions in the three TMs present obvious diversities. The pressure derivative of E_{1g} , A_{1g} , and E_{2g} mode frequencies shows an increased value ($d\omega_{E_{1g}}/dP > 0$), a constant value ($d\omega_{A_{1g}}/dP \sim 0$), and a negative value ($d\omega_{E_{2g}}/dP < 0$) above 5.3 GPa, respectively. The intrinsic characteristics of TMs consumedly help us understand the essence of the experimental *T* band of CNT. The anomalous pressure behavior of the TM frequencies may originate from the tube symmetry alteration from D_{10h} to D_{2h} then to C_{2h} .

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In the case of carbon nanotubes (CNTs) at high pressure, their vibrational spectra probed by Raman spectroscopy have been found particularly fruitful both as a characterizational tool and a testing ground for the theoretical predictions.^{1,2} In particular, Raman-active vibrational modes, such as radial breathing mode (RBM) and tangential modes (TMs), have attracted considerable attention,^{2–15} because they are not only strongly resonance enhanced but also sensitive to the structural deformation of CNTs. The reduction in intensity and the broadening of R and T bands with increasing hydrostatic pressure have been observed in some investigations both for single-wall carbon nanotube (SWNT) bundles²⁻¹¹ and individual SWNTs.¹⁴ Several Raman studies reported a disappearance of the R band as well as a decreased pressure derivative (but still $d\omega/dP > 0$) of the T band near 2 GPa.³⁻⁷ and the latter was interpreted as the sign of a subtle structure transition. Moreover, Amer et al.⁸ have observed a plateau $(d\omega/dP \sim 0)$ of the T band under increasing pressure and have ruled out significant deformation of bundles below 10 GPa. On the other hand, softening $(d\omega/dP < 0)$ of certain TMs between 10 and 16 GPa has been observed by Teredesai et al.,^{10,11} which may, although, be related to the solidification of the pressure-transmitting medium (PTM) at 10 GPa.^{3,8} Clearly, a change in the pressure derivative $(d\omega_T/dP)$ of the T band occurs under increasing pressure, but the exact nature of this change has proved controversial. Most authors seem to favor a change to the hexagonal,^{4,5} oval⁶ cross-section deformation or tube collapse,¹⁴ while others propose an "adsorptionlike" molecular ordering of the PTM around tubes.^{8,9} However, in fact, differences in sample composition (e.g., diameters and chiralities), inevitably intertube interaction in the bundles, and variances in experimental conditions, especially in terms of the PTM and the laser excitation power, may mask or smear the nature of the TM change with pressure.³ Therefore, the intrinsic characteristics of TMs for an isolated SWNT under hydrostatic pressure should be traced out, and it may consumedly help us understand the essence of TMs of CNT. With regard to TMs, corresponding to the characteristic A, E_1 , and E_2 modes located around 1600 cm⁻¹, they are experimentally difficult to distinguish from one another because of their similar frequencies.¹⁶ Therefore, the experimentally observed T band

is, in fact, composed of three Raman-active TMs, and the peak position is naturally used to refer to the T band.

Here, we will mainly focus on the effect of hydrostatic pressure on the TMs, e.g., A_{1g} , E_{1g} , and E_{2g} modes, of a (10,0) SWNT. Our theoretical calculations were performed using a constant-pressure molecular-dynamics (MD) simulation,¹⁷ in which the interactions between carbon atoms are obtained by empirical Tersoff-Brenner potential.¹⁸ The simulation time step is 1 fs and the residual force per atom is 0.01 eV/Å in the structural optimization. The TMs including A_{1g} , E_{1g} , and E_{2g} modes were calculated by combining the above MD results with the force-constant model.^{15,19} The present scheme has been carefully checked and a detailed RBM study of isolated SWNTs under pressure has been published.¹⁵ In this work, the anomalous pressure behavior of TMs is clearly observed, i.e., three TMs manifest distinct characteristics from one another above 5.3 GPa. For example, E_{1g} , A_{1g} , and E_{2g} mode frequencies show an increased value $(d\omega/dP > 0)$, a constant value $(d\omega/dP \sim 0)$, and a negative value $(d\omega/dP < 0)$ above 5.3 GPa, respectively. Moreover, a linear blueshift and a decreased pressure derivative under increasing pressure observed by Lebedkin et al.¹⁴ may be rationalized in terms of Lorentzian fitting of a sum of three calculated TMs to the experimental T band.

The optimized structures of a (10.0) SWNT under different pressures are shown in Fig. 1(a). Clearly, the pressure induces mechanically cross-section shape transition from a circle to a convex oval then to a nonconvex oval shape. For a (10,0) SWNT, TMs located around 1600 cm⁻¹ correspond to the characteristic A_{1g} , E_{1g} , and E_{2g} modes, which are all out-of-phase motions. In Figs. 1(b)-1(d), apparently, in circumferential $(E_{2\varrho}, A_{1\varrho})$ and axial $(E_{1\varrho})$ TMs, two of the three nearest-neighbor atoms move in opposite directions, perpendicular and along to the tube axis, respectively. Note that E_{2g} and A_{1g} modes have the same C-C bond stretching motions as well as C-C-C bond bending motions, but differ in the relative phase of their C-atom displacements in the unit cell. These motions being tangential to the nanotube surface are particularly sensitive to the nanotube strain. Therefore, with the pressure elevated, the motions of three TMs present obvious diversities in terms of C-atom displacements and its amplitudes as shown in Figs. 1(b)-1(d) and 2. Specifically,



FIG. 1. (Color online) (a) The cross-section shape elevation of (10,0) SWNT at some selected pressures (5.3, 5.5, 5.8, 6.1, and 6.8 GPa, respectively), and corresponding symmetry group is attached. [(b)–(d)] The atomic motions of E_{1g} , A_{1g} , and E_{2g} modes at symmetry transition pressures of 5.3, 5.5, and 6.1 GPa, respectively.



FIG. 2. The calculated amplitudes of half a unit cell atoms arranged in a line for (10,0) SWNT at some selected pressure (5.3, 5.5, 5.8, 6.1, and 6.8 GPa from top to bottom panels, respectively).



FIG. 3. (Color online) (a) The energy as well as the length of the long and short axes as a function of pressure for (10,0) SWNT. [(b)-(d)] The calculated frequencies vs pressure of E_{2g} , E_{1g} , and A_{1g} mode, respectively, and the pressure derivatives mentioned alongside.

there are distinct changes in the amplitudes at some special points corresponding to the long axis and the short axis of an oval shape in the deformed tube. Microscopic dependence of these motions on the structural deformation will be discussed in detail later.

Furthermore, E_{2g} , E_{1g} , and A_{1g} mode frequencies of a (10,0) SWNT under different hydrostatic pressures are calculated and plotted in Figs. 3(b)–3(d), respectively. In order to clearly illustrate a dependence of TM frequency transition on the structural deformation, the length of an oval shape long and short axes as well as calculated energy as a function of applied pressure are also plotted in Fig. 3(a). The important result here is that at 5.5 GPa, a pressure-induced structural transition occurs corresponding to circle-to-oval shape changes; nevertheless, at 5.3 GPa the long and short axes have been unequal to each other, which may indicate a start in structural transition in elevated pressure runs. Interestingly, such a subtle structural change at 5.3 GPa affects the E_{2g} mode greatly in contrast to E_{1g} and A_{1g} modes, and an obvious softening occurs in the range of 5.3–5.5 GPa, as

shown in Fig. 3(b). We think that the softening of the E_{2g} mode may originate from the symmetry alteration of (10,0) SWNT from D_{10h} to D_{2h} point group, as shown in Fig. 1(a).

Microscopically, the structural transition is driven by the competition between compression and bending of a tube under pressure.²⁰ Below 5.3 GPa, a circular tube shrinks by reducing its radius, which mainly costs compressive strain energy. So, the tube at 5.3 GPa still holds D_{10h} symmetry like that of the original tube without any pressure. Above 5.3 GPa, because it is easier to bend than to compress a tube, the tube begins to greatly cost bending strain energy to increase curvature. At a critical pressure (5.5 GPa), the tube transforms from an analogous circle to an anisotropic oval shape. Then the symmetry lowers, with only three twofold rotational axes, to D_{2h} point group according to careful analysis of the new structural data. As the tube continues to shrink, it no longer compresses (maintaining its perimeter) but only bends (reducing its overall curvature), and then must adopt a shape to minimize bending energy. This eventually leads to another shape transition from a convex oval to a nonconvex oval shape at 6.1 GPa. Meanwhile, the tube symmetry continues to lower, absent inversion centers, down to C_{2h} group, as shown in Fig. 1(a). It should be noted that as the applied pressure elevates up to 7.0 GPa, the length of the short axis approaches nearly 3.35 Å, which means that an additional van der Waals (vdW) interaction may lead to the collapse of the tube,²¹ and then the TMs of the SWNTs may not be exhibited. Here, therefore, we only focus on the TM characteristics of the (10,0) SWNT subject to compression up to 6.8 GPa without regarding the vdW interaction.

Therefore, due to the pressure-induced symmetry alteration, not only the C-atom displacements [Figs. 1(b)-1(d)] and its amplitudes (Fig. 2) but also the frequencies [Figs. 3(b)-3(d) of the three TMs present obvious diversities. Specifically, interestingly enough, the frequencies exhibit anomalous pressure behavior at certain critical pressures (5.3, 5.5, and 6.1 GPa). For example, the E_{2g} mode shows obvious softening between 5.3 and 5.5 GPa, as shown in Fig. **3(b)**. Beyond 5.5 GPa, the E_{2g} mode frequency sharply shifts to higher frequencies, and then softens again slightly at 6.1 GPa; in terms of the E_{1g} mode [Fig. 3(c)], there is an increased pressure derivative between 5.5 and 6.1 GPa and then reaches a plateau, whereas the A_{1g} mode frequency [Fig. 3(d)] shows a constant value between 5.5 and 6.1 GPa, and then softens considerably. For unambiguous evidence that the anomaly is an intrinsic property of CNTs,³ the anomalous pressure behaviors of TMs, e.g., the softening or a plateau, would most likely arise from the change of phonon deformation potentials which soften the C-C intratubular bonds. It is important to note that these anomalous pressure behaviors of the three TMs are hardly observed experimentally, because these TMs are difficult to distinguish from one another due to their similar frequencies. We hope that our results will inspire to carry out subtle experimental studies to identify the different TMs, once purified aligned samples become available.

Altogether, at low pressure, the three TMs all fit to linear

equations and the fitted values of pressure derivatives, e.g., $d\omega_{E_{2a}}/dP = 5.8 \text{ cm}^{-1}/\text{GPa}, \quad d\omega_{E_{1a}}/dP = 5.0 \text{ cm}^{-1}/\text{GPa}, \text{ and}$ $d\omega_{A_1}^{23}/dP = 6.3 \text{ cm}^{-1}/\text{GPa}$, are given in Figs. 3(b)-3(d), respectively. These theoretical results approximately agree with the experimental value $(d\omega_T/dP=6.4 \text{ cm}^{-1}/\text{GPa})$ of individually dispersed SWNTs.¹⁴ Furthermore, at higher pressure, we predict that if the three TMs are Lorentzian fitted to the experimental T band identified with the peak position of a triplet of TMs $(A_{1g}, E_{1g}, E_{2g})^{22}$ the change in $d\omega_T/dP$ of the fitted T band may be consistent with experimental results.¹⁴ The intensities of A_{1g} , E_{1g} , and E_{2g} modes differently vary with increasing applied pressure¹³ even with changes of experimental conditions, e.g., the PTM and the laser excitation power. The peak position of the fitted T band is mainly based on the more intense mode. Thereafter, if the intensity of the softening mode [e.g., E_{2g} mode in Fig. 3(b)] is weak, the fitted T band may exhibit no softening but a positive value $(d\omega_T/dP > 0)$ or maybe a constant value $(d\omega_T/dP \sim 0)$ like the majority of experimental results.^{3-9,14} It would be rational that the values of $d\omega_T/dP$ are different in diverse experiments under higher pressure. In addition, it is obvious that the anomalous behaviors of three TMs are presented at three different pressures, e.g., 5.3, 5.5, or 6.1 GPa, as shown in Figs. 3(b)-3(d), which would most likely make the transition of the fitted T band uncertain. Therefore, we agree with some authors^{8,14} that the plateau or a change in the pressure derivative of the T band may not reliably be interpreted as a sign of the structural transition, whether our prediction is true or not. A theoretical Lorentzian fitting, combining the acquired frequencies with the coming calculated resonant Raman intensity, is planned for the future. Besides, in order to further understand comprehensive properties of TMs, it is desirable to extend the calculations of pressure effects on TMs in SWNTs of different radii and different sorts, and to look for the dependence of tube diameter or chirality on the pressure derivative of the TM frequency in our following work.

In summary, we investigate the intrinsic characteristic features in three TMs of an isolated (10,0) SWNT under hydrostatic pressure. The results show that the atomic motions in the three TMs present obvious diversities with increasing pressure. The most interesting finding is the anomalous pressure behavior of different TM frequencies; for example, E_{1g} , A_{1g} , and E_{2g} mode frequencies show an increased value $(d\omega/dP>0)$, a constant value $(d\omega/dP\sim0)$, and a negative value $(d\omega/dP<0)$ above 5.3 GPa, respectively. The intrinsic characteristics of TMs for an isolated SWNT under hydrostatic pressure consumedly help us understand the essence of the experimental T band of CNT. These anomalous behaviors may originate from the tube symmetry alteration from D_{10h} to D_{2h} then to C_{2h} with increasing pressure.

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