Zero $m$ phonons in metal chalcogenide nanotubes

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Abstract. Phonon dispersions of single-wall MoS$_2$ and WS$_2$ nanotubes are calculated within a full symmetry implemented valence force-field model. Tubular structure is found to be characterized by two Raman active modes: by the in-phase breathing modes (in full analogy to carbon nanotubes) with frequency approaching Brillouin scattering domain (as diameter approaches nm), and by the high-energy breathing mode with sulfur shells breathing in phase, but out of phase relative to the Mo/W atoms. Likewise, the longitudinal rigid-shell mode, where sulfur shells vibrate out of phase whilst Mo/W atoms barely move, is predicted to be a fingerprint of the cylindrical configuration in infrared spectra. It is also found that twisting rigid-layer modes characterize chirality of the tubes. Finally, the large diameter limit is discussed and related to the measured Raman and infrared spectra of the layered structures.

Metal chalcogenide nanotubes [1, 2] have been synthesized soon after the discovery of the carbon ones. Raman spectroscopy [3, 4, 5, 6] proved to be one of the most efficient methods of the nanotubes’ characterization. Here we study Γ point phonons with vanishing angular momentum quantum number $m$, Raman and infrared (IR) active ones, in particular. We predict some of them to be fingerprints in Raman and IR absorption spectra of the tubular structure [7, 8].

The phonon frequency dependence on the diameter $D$ and chiral angle $\theta$ is obtained within valence-force field model [9, 10] by the full symmetry implemented numerical code POLSym [11].

A single-wall MS$_2$ (M=Mo,W) tube can be imagined as a single MS$_2$ layer with trigonal prismatic coordination rolled up into a cylinder: sulfur shells are symmetrically arranged with respect to the metal one. The chiral indices $(n_1, n_2)$ are defined in a usual way, within the metal plane. Symmetry of these nanotubes [12] are described by line groups and it yields quasi-momentum $k$ and quasi-angular momentum $m$ as the conserved quantum numbers. In addition, vertical $A/B$ and horizontal $\pm$ mirror parities are conserved in zig-zag and armchair tubes, respectively.

From the symmetry classification of the normal modes of vibration [12] it is evident that at the Γ point there are nine (six) symmetric modes in a case of the chiral (achiral) tubes.

In the chiral tubes, two acoustic modes are symmetric: the longitudinal (LA) and the twisting (TWA) one. On the other side, in the achiral tubes only one of them is symmetric as TWA changes sign upon the vertical mirror reflection ($B_0$ symmetry) in the case of the zig-zag tubes, while in the armchair ones, LA is odd with respect to the horizontal mirror reflection ($A^+_{2u}$, i.e. $A_{2u}$ symmetry).

Out of seven remaining symmetric optical phonons in the chiral tubes four are rigid-layer modes and the other three are breathing modes. Acoustic, LA and TWA modes are rigid-layer displacements with shells vibrating in-phase (longitudinally and circumferentially) with all the atoms being, at each instant, equally displaced from the equilibrium. If longitudinal rigid shell
vibrations are combined in such a way that sulfur shells move out-of-phase while metal shell remains fixed one gets symmetric optical LO mode. On the other hand, if sulfur shells move in-phase but altogether out-of-phase relative to the metal shell one gets symmetric optical LI mode. Analogously, optical symmetric rigid shell twisting modes, TWO and TWI, are obtained when sulfur shells rotate out-of-phase while metal atoms are in equilibrium positions and when sulfur shells rotate in-phase but altogether out-of-phase with respect to the rotations of the metal shell (Fig. 1).

BA and BI modes are predicted to be unique features in the single-wall MS$_2$ nanotube Raman spectra. These modes are also diameter, $D$, and chirality, $\theta$, sensitive. In a case of the MoS$_2$ NTs the dependence is as follows:

$$\omega_{BA} = \frac{664}{D} - \frac{1633}{D^2} + \frac{1215 \cos 3\theta}{D^2} + \frac{1194 \sin 3\theta}{D^2},$$

$$\omega_{BI} = 485.80 - \frac{245}{D^2} - \frac{102 \cos 3\theta}{D^2} - \frac{144 \sin 3\theta}{D^2}.$$  (1)

Taking the infinite diameter limit one gets the frequencies of the corresponding modes in the layered structure: symmetric Raman active BA and BI modes become, respectively, acoustic transversal TA and optical transversal rigid-layer TI mode with $A_{2u}$ ($A_6^0$) symmetry (thus, Raman inactive and still IR active). Hence, according to Eq. (2), TI mode has frequency of $\sim 486$ cm$^{-1}$. Such a mode has not been observed in Raman scattering measurements on a bulk 2H-MoS$_2$ crystal, but has been observed in IR absorption measurements [13], which confirms our prediction. The measured frequency was $\sim 481$ cm$^{-1}$. It should be noted that frequencies of the rigid-layer modes in the bulk are expected to be essentially the same as the frequencies of the corresponding single-layer modes due to the extremely weak inter-layer coupling.

Like the radial breathing mode in the single-wall carbon nanotubes, frequency of the BA mode shows inverse diameter dependence. However, it falls quite low: $\sim 50$ cm$^{-1}$ for the tubes with $D \approx 1$nm. Therefore, the maximal, BI mode is more convenient for the tubular structure identification by means of Raman spectroscopy.

Thus, so far we have determined six symmetric displacements, three of them being longitudinal and three twisting. Consequently, the remaining three symmetric modes of vibration, due to the orthogonality, are radial. When all shells breath in-phase one gets radial all-breathing mode (BA). The other two symmetric breathing modes, BO and BI can be described following the pattern of LO and LI modes on the one side or TWO and TWI on the other. Only now, instead of the longitudinal and rotational rigid shell modes the radial displacements are to be combined.

In a case of the achiral tubes, the same argument can be applied to their six symmetric modes. Hence, in the armchair tubes twisting and breathing modes are symmetric while the longitudinal ones change sign upon horizontal mirror reflection. As in the zig-zag tubes there is no horizontal mirror symmetry longitudinal modes are symmetric, as well as the breathing ones. However, with respect to the vertical mirror reflection the twisting modes are odd.

Likewise the carbon nanotubes [14], symmetry allows breathing modes to have non-radial components (in the achiral tube the component perpendicular to the mirror plane is forbidden, though). However the non-radial component is here less effective, due to the larger atomic masses.

While the longitudinal and breathing modes distinguish between the cylindrical and the planar geometry, the twisting modes can help to identify the chirality. Namely, in the chiral and armchair tubes the TWO mode pertains to the symmetric part of the Raman tensor while in the zig-zag ones it contributes only to the antisymmetric part and is therefore expected to be suppressed. Further, to distinguish, between armchair (and achiral, generally) and chiral tubes, IR measurements can help as TWI mode is only in the chiral case IR active.
Figure 1. Longitudinal and twisting modes of the tube (12, 8): LO, LI and TWO, TWI from the left to the right. Sulfur atoms are in light grey while the metal atoms are in dark grey color.

Table 1. IR and Raman zero $m$ active modes. Activity is indicated in the first column: IR stands for infra-red activity while the modes corresponding to the symmetric and antisymmetric Raman tensor are denoted by $[R]$ and $\{R\}$. The next three columns single out active modes for specific tubes together with the corresponding irreducible representation and the last column refers to the layered structure with trigonal prism coordination ($\tau$-MS$_2$).

| Activity | Zig-zag NT | Chiral NT | Armchair NT | $\tau$-MS$_2$ layer |
|----------|------------|-----------|-------------|---------------------|
| IR       | L, B ($A_0$) | L, TW, B ($A_0$) | L ($A^-_0$) | BI ($A_{1u}$) |
| $[R]$    |            |           | TW, B ($A^+_0$) |                      |
| $\{R\}$ | TW ($B_0$) |            | BO ($A_{1g}$) | -                   |

Table 1 summarizes IR and Raman zero $m$ active modes in MS$_2$ tubes and single layer. Hence, it is easy to see algorithm to distinguish layered from tubular configuration and further to characterize the chirality of the tube. The algorithm [7] includes only IR, only Raman or combined Raman and IR measurements. As antisymmetric modes are expected to be suppressed we use only symmetric modes of Raman tensor.

In the case of MoS$_2$ tubes frequency of BO mode is close to the frequencies of the TWI and LI modes which lead to mixing of purely radial BO, purely circumferential TWI and purely longitudinal LI mode (Fig. 2).

The mixing decreases with diameter. In the zig-zag tubes there is no mixing of purely radial BO and purely circumferential TWI modes because of different vertical mirror parity while in the armchair tubes there is no mixing of purely radial BO and purely longitudinal LI mode due to different horizontal mirror parity. The mixing of BO and TWI in the armchair MoS$_2$ tubes is much larger than mixing of BO and LI in the zig-zag tubes. Mode BO corresponds to $A_{1g}$ layer mode with calculated frequency 421 cm$^{-1}$ (398 cm$^{-1}$) for WS$_2$ (MoS$_2$) layer. Another breathing BI mode corresponds to $A_{1u}$ layer mode with frequencies 425 cm$^{-1}$ and 485 cm$^{-1}$ for WS$_2$ and MoS$_2$ layers, respectively. As $A_{1u}$ mode has higher frequency than $A_{1g}$ mode one would expect that BI frequency is higher than BO. However, this proves to be true (within this model and relaxed configurations) only for MoS$_2$ tubes. The frequency of BI mode increases with the diameter and the frequency limits are 409 cm$^{-1}$ for WS$_2$ and 467 cm$^{-1}$ for MoS$_2$ tubes while for the smallest tubes these frequencies are 402 cm$^{-1}$ and 462 cm$^{-1}$ (for WS$_2$ and MoS$_2$ tubes, respectively). Mode BO for WS$_2$ tubes which has higher frequency than BI mode decreases with the diameter. Thus, for the smallest tube the frequency of BO mode is 434 cm$^{-1}$ while for the largest tube the frequency is 429 cm$^{-1}$. 
Figure 2. TWI and BO modes in MoS$_2$ (10, 10) tube. Dark gray dots are Mo while light gray are S. The frequency of left mode is 392 cm$^{-1}$ and of right mode is 393 cm$^{-1}$. Both modes are combinations of purely circumferential TWI and purely radial BO.

In conclusion, frequencies of Raman and IR active modes for all single-wall MS$_2$ tubes with diameters between 1 nm and 20 nm have been calculated. The established $D$ and $\theta$ dependencies of the frequencies show only slight dependence on the chiral angle. Nevertheless, a set of experimental steps in the course of determination of the tube type either by Raman or by IR experiments is proposed. It is found that the frequency diameter dependence can be used to estimate the diameter of the tube.

Finally, we found strong mixing of purely radial BI and purely twisting TWI modes in MoS$_2$ tubes which vanishes as chiral angle reaches zero. The mixing affects electron-phonon interaction and IR activity and finer analysis could provide the chiral angle characterization of the MoS$_2$ tubes.

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