Mixing of the A_1-modes in carbon nanotubes

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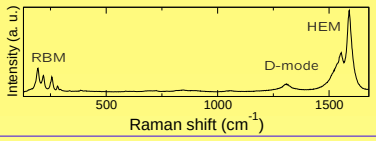
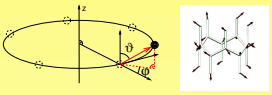
We study the mixing of the fully symmetric modes in single-walled carbon nanotubes with a variational model and *ab initio* calculations. The effects on the calculation of phonon frequencies and electron-phonon coupling matrix elements $\mathcal{M}_{e-ph}$ are analyzed. We find that neglecting the mixing leads to errors of up to 60 % for the $\mathcal{M}_{e-ph}$ and up to 50 cm^{-1} difference for the high-energy mode frequency.



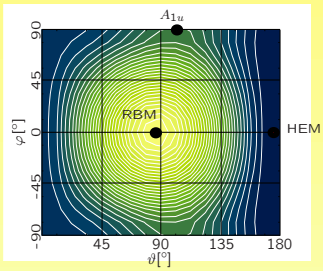
- Main features of Raman spectrum have A_1-symmetry
- *Ab initio* calculations suggest a mixing (Ref. 2)
- Observed Raman intensity is proportional to the square of the electron phonon matrix element $|\mathcal{M}_{e-ph}|^2$

Method

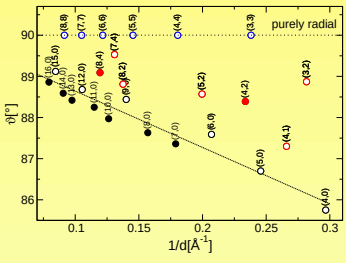


- We displace one atom freely on a sphere with fixed radius.
- We apply the fully symmetric representation A_1 to this displacement and the resulting set of displacement is added to the relaxed positions
- We calculate the total energy of the displaced system with DFT-code *SIESTA* (Ref. 3)

Eigenvectors

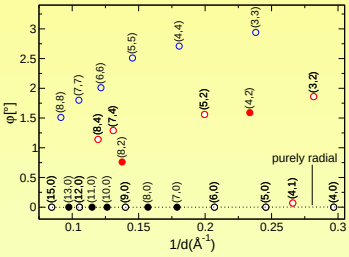


Total energy contour plot of the (5,0)-NT. Fully symmetric eigenmodes are in direction of extremal total energy.
Note the mirror symmetry at $\varphi = 0°$ corresponding to the mirror plane in zigzag $(n,0)$ NTs.



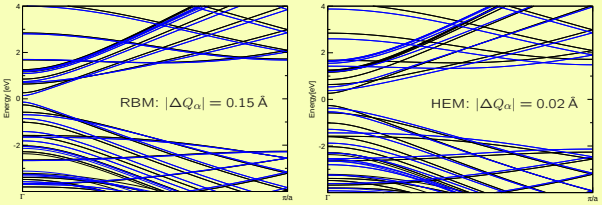
Angles ϑ, φ of the RBM.

Dashed line shows a linear fit for zigzag $(n,0)$ NTs. Metallic tubes (open symbols) are above the line, semiconducting tubes (filled symbols) are below.



The RBM of all NTs has non-radial components.
Similarly, the fully symmetric HEMs of all NTs have non-tangential components (not shown).

Electron-phonon coupling



Electronic band structure of the (16,0) nanotube in the relaxed geometry (black lines), and deformed after a displacement pattern corresponding to: (a) RBM; (b) HEM.

Deformation potential $\partial E_{\mathbf{kn}}/\partial Q_\alpha \propto \mathcal{M}_{e-ph}$ (see Ref. 4)

Ratio of the matrix elements for the non-mixed (incorrect) displacement to the mixed (correct) eigenvectors.($\mathcal{M}_i = i$th optical transition)
The mixed eigenvectors predict systematically smaller matrix elements than the simplified (non-mixed) ones for all NTs.

NT	$\mathcal{M}_1$	$\mathcal{M}_2$	$\mathcal{M}_3$	$\mathcal{M}_4$
(10,0)	1.43	1.58	1.46	1.46
(6,6)	1.36	–	–	–
(8,4)	1.34	–	1.34	–
(8,8)	1.37	1.36	1.36	–
(14,0)	1.51	1.46	1.48	–
(15,0)	1.27	1.35	1.32	1.25
(16,0)	1.45	1.51	1.47	–
(11,11)	1.31	1.36	1.37	–

The deformation potentials for the HEM are less affected:

- no detectable difference found for zigzag $(n,0)$-tubes
- for armchair (n,n)-tubes an increase of 4 to 7 % is found for the non-mixed modes

- Matrix elements of the RBM are diminished by the mixing for all NTs, irrespective of chirality.
- Relative sign of $\mathcal{M}^{\text{HEM}}$ and $\mathcal{M}^{\text{RBM}}$ depends on chirality [for armchair both matrix elements have the same sign, whereas for zigzag tubes they have opposite sign (when defined as in Ref.4)]
- but the relative orientation of the mixing is also chirality dependent (s. Figure)

Both effects lead to the observed lowering of matrix elements, independent of chirality.

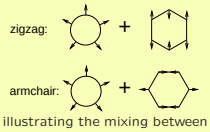
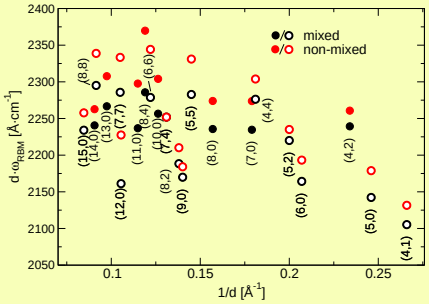


Figure illustrating the mixing between the radial and tangential components of the RBM in zigzag and armchair tubes.

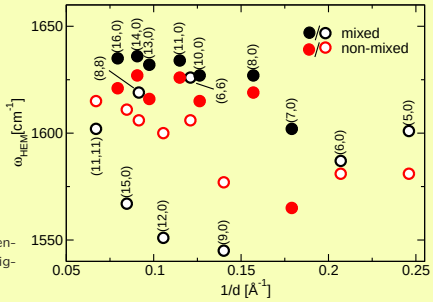
Phonon frequencies



Frequency ω_{RBM} multiplied with tube diameter d for mixed (black symbols) and non-mixed (red symbols) frozen-phonon calculation.
(metallic=open symbols, semiconducting=filled symbols)

- Non-mixed modes overestimate RBM frequencies by up to 10 cm^{-1}
- The general lowering of the metallic zigzag tubes can be recognized. (In agreement with Ref. 5)
- Linear fit $\omega_{\text{RBM}} = 2$ cm^{-1} + 2221/d cm^{-1}Å in good agreement with experiment.[6]

- Non-mixed modes underestimate the HEM frequencies by up to 50 cm^{-1}, except for most metallic zigzag tubes.



Frequency ω_{HEM} from finite-differences calculations including mixing (black symbols) and for non-mixed frozen-phonon calculation (red symbols).

Conclusion

- The RBM and the HEM have non-radial / non-tangential components.
- Neglecting the non-radial components results in errors of up to 60 % for the electron-phonon matrix element $\mathcal{M}^{\text{RBM}}_{e-ph}$
- Neglecting the non-radial/non-tangential components results in overestimated RBM frequencies and underestimated HEM frequencies.

References

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