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First-principles calculations of the radial breathing mode of single-wall carbon nanotubes

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The radial breathing mode is a promising candidate for the analysis of conformational and electronic properties of carbon nanotubes. The paper presents calculations based on the local density approximation to determine the radial breathing mode (RBM) frequency of various zigzag and armchair tubes with radii between 3.5 and 8.1 Å. The frequencies are derived from both frozen phonon calculations for nanotubes and from the elastic constants of the flat graphene sheet. The RBM frequency of the (10,10) armchair tube is found to be 175 cm^{-1} and 174 cm^{-1} for the two techniques, respectively. These values are in very good agreement with one of the strongest components in the structured Raman band of the radial breathing modes observed at 177 cm^{-1}. Since the RBM frequency turns out to scale with $1/R$ the calculations also allow one to evaluate the frequency of this mode for tubes with arbitrary chirality.

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The discovery of carbon nanotubes (see, e.g., Ref. 1) attracted great interest and inspired many theoretical and experimental investigations. Unfortunately, early experiments were faced with the difficulty that samples consisted of various multiwall tubes making an assignment of observed features to specific species rather difficult. Nowadays the preparation of single wall carbon nanotubes (SWCNT) is possible,[2] however the interpretation of, e.g., spectroscopic measurements is still not straightforward because usually tubes of various diameter and chirality exist in the sample. As a result even the thermodynamically most stable tubes have not yet been identified. Therefore, a reliable method to characterize the tubes would be of great value.

On the basis of x-ray analysis it was claimed originally that the majority of the SWCNT's have a diameter of 1.38 nm, corresponding to (10,10) tubes.[2,3] In addition, based on the competition between folding, edge, and cap energies, recent calculations also suggested that this species is the energetically most favorable form, although other tubes with similar diameter seem to have rather similar stability.[5] The energetical competition between different tubes is also confirmed by the fact that many different armchair, zigzag, and even chiral tubes are found by means of scanning probe microscopy and Raman spectroscopy.[6–11]

A particular promising tool for the identification and probing of carbon nanotubes is Raman spectroscopy. SWCNT's have 15 or 16 Raman active vibrational modes; the exact number depends on the symmetry of the tube but is independent of its diameter.[4] However, only four Raman bands are strongly resonance enhanced.[8–11] Three of them are located around 1600 cm^{-1} and correspond to the characteristic A, E_1, and E_2 modes of the graphene sheet. The fourth strong band at around 200 cm^{-1} is caused by the radial breathing mode (RBM), where all atoms move in phase perpendicular to the tube axis changing the radius of the tube.

We focus on the RBM because it is unique to nanotubes, without any counterpart in graphene sheets. The phonon modes and the RBM mode in particular have already received some attention in theoretical work. Jishi *et al.* used Born von Kármán force constants to predict the vibrational frequencies of carbon nanotubes.[4] Interaction up to fourth nearest-neighbor was considered, and the force constants were optimized to fit the experimental phonon dispersion of a flat graphene sheet.[4] Within the force constant model, it is easy to show that the RBM frequencies ν are inverse proportional to the radius R of the tube, $\nu = A/R$.[4] This makes the mode an ideal candidate for the identification of the diameter of nanotubes by means of, e.g., Raman spectroscopy.

Subsequently, the previously mentioned empirical force constants or slightly modified versions were used extensively for the calculation of phonon dispersion relations and for the interpretation and prediction of Raman spectra.[8,12,13] Unfortunately calculations relying on these empirical force constants have several shortcomings. First, the electron-energy-loss spectroscopy (EELS) measurements to which the force constants were fitted were performed on graphite; the phonon modes of an isolated graphene sheet are different to those of bulk graphite. Second, for the acoustic modes around $q \rightarrow 0$, only very few experimental data are available leading to uncertainties particularly for the prediction of the RBM mode (see below). Indeed, the calculated RBM frequencies of (10,10) tubes (156 cm^{-1} in Ref. 4, 165 cm^{-1} in Refs. 8, 12, and 13) do not agree well with the frequency of maximum intensity in the Raman spectrum (around 177 cm^{-1}). This indicates that either the theoretical values

TABLE I. Calculated radii (R), folding energies (E), and frequencies (ν) of the RBM for (n,n) armchair tubes.

n	8	9	10	11	12
R (Å)	5.4	6.1	6.7	7.4	8.1
E (meV)	69	54	45	36	29
ν (cm^{-1})	219	195	175	159	146

are inaccurate, or the assignment of the observed Raman frequencies to the RBM is incorrect, or that (10,10) tubes are in fact not dominant.

In order to obtain more reliable theoretical values for the frequency of the RBM a careful theoretical investigation is therefore required. To do that, we have carried out first-principles local density approximation (LDA) calculations for achiral tubes with a diameter between 7 and 16 Å. Armchair tubes from (8,8) to (12,12) and zigzag tubes with $n = 9$, 10, 15, 17, and 20 have been considered. Chiral tubes have not been taken into account because for the diameters of interest the number of carbon atoms in the unit cell is too large ($N > 1000$).

We used the Vienna *ab initio* simulation package (VASP) which was developed among others by one of the authors (G.K.).[14,15] In VASP the solution of the generalized self-consistent Kohn-Sham equations is calculated using an efficient matrix-diagonalization routine based on a sequential band-by-band residual minimization method and a Pulay-like charge density mixing. For details, see Ref. 15 and references therein. The electron-ion interaction is described by ultrasoft Vanderbilt-type pseudopotentials (Ref. 16) allowing for a low cut-off energy in the plane-wave expansion of the valence states. The cut-off energy was set to 290 eV in the present work. VASP allows for a conjugate gradient (CG) or quasi-Newton optimization of the geometry using analytical forces and the stress tensor. The program has already been used extensively for the investigation of the stability of carbon phases.[17] The phonon dispersion relations of diamond and graphite have been determined with an overall accuracy of approximately 1%, indicating the reliability of the employed pseudopotential for the prediction of vibrational frequencies.[18]

LDA-based calculations were carried out to evaluate the RBM frequency of selected tubes with a frozen phonon approach and using the elastic constants of the graphene sheet. For the frozen phonon calculations, the starting geometries were obtained by simply wrapping up a graphene sheet according to (n,m) with a carbon-carbon distance of $a_{\mathrm{C-C}} = 1.4$ Å. The number of carbon atoms is $4n$ for both (n,n)-armchair and $(n,0)$-zigzag tubes. Although VASP always employs three-dimensional (3D) periodic boundary conditions, our calculations relate to infinitely long isolated tubes. This was achieved by arranging the tubes in a tetragonal lattice with lattice parameters of 20 Å in the directions perpendicular to the tube axis. The resulting vacuum region is large enough so that there is almost no interaction between the tubes but sufficiently small to keep the number of plane waves at a reasonable level (typically around 10 000 plane waves). Only parallel to the tube axis (z direction) the periodicity was maintained. To calculate the total energy and the forces accurately, several k points were used in the z direction. For the evaluation of the folding energies (see below) four k points corresponding to (1/16, 3/16, 5/16, and 7/16) $\times 2\pi/z$ were used, whereas the optimized geometries and the RBM frequencies were obtained with only two k points corresponding to (1/8 and 3/8)$\times 2\pi/z$. To ensure that this setup is sufficiently accurate several tests were carried out as elaborated below.

Before calculating the RBM frequencies a two-step geometry optimization was carried out. First, all degrees of freedom—including the length of the cell in the direction of the tube axis—were allowed to relax. This first procedure exhibits a rather slow convergence because when changing the unit cell the effective plane-wave cutoff changes as well. The well known systematic error in the diagonal components of the stress tensor due to the finite size of the basis set was corrected by subtracting a constant value from the diagonal components of the stress tensor. The required correction was estimated from the difference of the stress in z direction between the 290 eV basis set and a 500 eV basis set. After 10–20 CG relaxation steps in which the z-lattice vector was allowed to change, the final optimized geometry was obtained in a second relaxation—now with fixed unit cell parameters. For the relaxed geometry the Cartesian components of the forces on individual atoms were always less than 0.03 eV/Å but typically less than 0.01 eV/Å. We found that the carbon-carbon bond lengths are not uniform in the tubes. In armchair tubes they are 1.401 Å and 1.417 Å, the shorter bond is perpendicular to the tube axis. In zigzag tubes they are 1.408 Å and 1.413 Å; the shorter is parallel to the tube axis. The final tube radii obtained with our geometry optimization are summarized—together with other results—in Tables I and II for armchair and zigzag tubes, respectively.

From our calculations, we can easily derive the tube folding energies, which are defined as the energy difference per carbon atom between the tubes and a graphene sheet. For a graphene sheet we obtained a cohesive energy of -10.130 eV (with respect to a nonspin-polarized C atom). Tables I and II show the calculated folding energies of the considered armchair and zigzag tubes. The folding energy

TABLE II. Calculated radii (R), folding energies (E), and frequencies (ν) of the RBM for $(n,0)$ zigzag tubes. Values in parentheses have been derived assuming a $1/R$ scaling behavior of the RBM frequency (see text).

n	9	10	15	16	17	18	19	20
R (Å)	3.5	3.9	5.8	(6.2)	6.6	(7.0)	(7.4)	7.8
E (meV)	159	128	57		45			32
ν (cm^{-1})	329	298	200	(188)	178	(167)	(158)	150

per carbon atom is expected to increase inverse proportional to the square of the nanotube radius.[19] This is in fact the case, but the constant of proportionality is about 10% smaller in the present work than in Ref. 19.

The frequency of the radial breathing mode was finally calculated by a frozen phonon method: the tube radius was increased and decreased by 1 and 2%, and the total energy was calculated for each configuration. From a quadratic fit the harmonic force constant and—taking into account the mass of the unit cell—the RBM frequency were obtained. To make the results more robust with respect to nonperfect relaxation we allowed for a shift of the minimum of the energy away from zero. However the shift was usually smaller than 0.1% of the tube radius, indicating that our structural relaxation was rather accurate. Tables I and II show the calculated frequencies of the radial breathing mode of the selected armchair and zigzag tubes.

To check our results we have performed several test calculations. First, the RBM frequencies were recalculated for the (10,10) and (17,0) tubes with four k points. This changed the RBM frequency by less than 0.5% confirming that two k points are in fact sufficient for an accurate prediction of the frequency. Second, we evaluated the radial breathing mode of the C_{60} molecule using a similar procedure as outlined above. The calculated result was $494\ \mathrm{cm}^{-1}$ which is in excellent agreement with the experimental value of $493\ \mathrm{cm}^{-1}$.[21] Finally, we have already pointed out at the beginning that a force constant approach based on the same LDA code and the same pseudopotentials as in the present work yielded phonon frequencies with an average accuracy of 1% for graphite and diamond.[18] Considering all these points, we are confident that the error of the calculated phonon frequencies is less than 1%.

The obtained RBM frequencies are almost perfectly inverse proportional to the radius of the tube as shown in Fig. 1. A fit to A/R yields $A=1180$ for armchair and $A=1160$ for zigzag tubes (in $\mathrm{cm}^{-1}\times\text{Å}$). With the proportionality constant we can predict the RBM frequency of nanotubes not considered in the first-principles calculations, and the resulting values for (16,0), (18,0), and (19,0) zigzag tubes are given in Table II. To check the linearity between the inverse of the tube radius and the RBM frequency we also fitted our results to the relation $\omega\propto 1/R^{\kappa}$.[13] We found $\kappa=1.003\pm0.007$ and $\kappa=0.982\pm0.007$ for the armchair and zigzag tubes, respectively. However, within the estimated error bars our values are equally consistent with $\kappa=1$. Furthermore, an exact $1/R$ dependence is to be expected if the force constants of graphene were directly transferable to nanotubes.[4]

Interestingly, our calculation reveals that the proportionality constant A is almost the same for armchair and zigzag tubes. This may be surprising at first glance. There is, however, a simple explanation for it. The RBM corresponds to a stretching of the graphene sheet in the [110] (armchair tubes) or [100] (zigzag tubes) direction. For such a stretching, the energy change can be derived from elastic theory. Because the elastic properties of hexagonal systems are isotrope in the hexagonal plane (see, e.g., Ref. 20) the elastic constant that describes the stretching of a graphene sheet is the same for any direction in the hexagonal plane. Therefore, if the elastic constants of the graphene sheet were directly transferable to the nanotubes, the proportionality constant would be the same for all tubes and the RBM frequency would depend only on the radius of the tube. Our calculation indicates that this is exactly the case. As an additional check for this deduction we have calculated the elastic stretching constant of the flat graphene sheet by distorting the graphene sheet either in the [100] or in the [110] direction. Both distortions lead practically to the same elastic constant of $C=30.3\ \mathrm{eV}/\text{Å}^2$. With this value, we obtain a proportionality constant of $A=1170\ \mathrm{cm}^{-1}\times\text{Å}$ for the $1/R$ law to calculate the RBM of tubes with any helicity (zigzag, armchair, or even chiral). Obviously this value agrees very well with the values derived directly from the frozen phonon approach, indicating that the elastic constants change indeed only little when the graphene sheet is rolled up to form a nanotube.

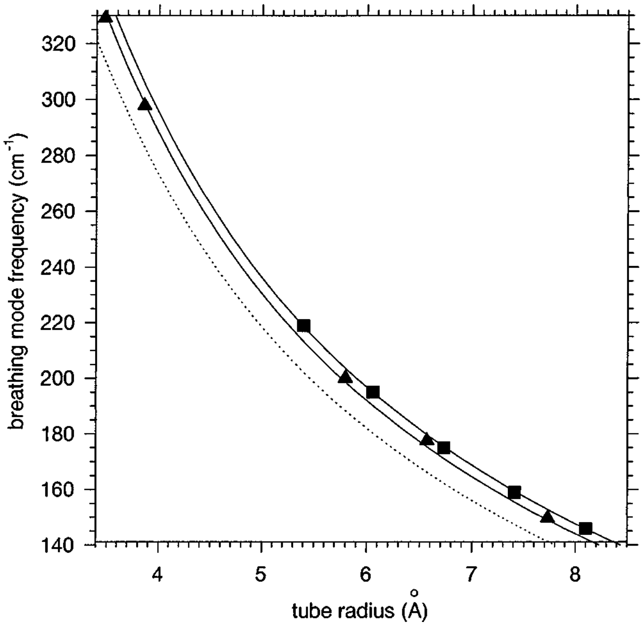

FIG. 1. Frequency of the RBM of various SWCNT's for armchair (squares) and zigzag (triangles) tubes. There is a small difference between the fits for the two kinds of tubes (solid lines). For comparison, the $1/R$ behavior calculated in Ref. 4 is shown by the dotted line.

On the basis of a force constant method Jishi *et al.* were also able to evaluate the RBM frequency.[4] The two approaches are insofar related as the elastic constants can be obtained from a properly weighted sum of the interatomic force constants corresponding to the $q\rightarrow0$ slope of the acoustic phonons of a graphene sheet. Using the results of Jishi *et al.* the elastic constant is $26.1\ \mathrm{eV}/\text{Å}^2$ which is significantly lower than the value obtained by us. On the reasons discussed above the larger value obtained from the LDA calculations is expected to be more reliable.

We are now prepared to compare our results with the experimentally determined Raman frequencies.[11] Table III shows the calculated frequencies together with 14 experimentally observed components of the RBM of SWCNT's measured for a tube material prepared by a two-step laser evaporation process.[2] The underlined numbers refer to the lines with the strongest response. As it can be seen, each calculated value (except one) matches one of the observed frequencies within 1–2 wave numbers. In one case there are two types of tubes, namely (10,10) and (17,0), corresponding

TABLE III. Vibrational frequencies used to fit the experimentally observed Raman lines of the radial breathing mode of single wall carbon nanotubes (Ref. 11) in comparison to calculated results.

Observed lines	147	156	162	167	172	177	182	185	190	195	199	206	211	230
Calculated for	146		159			175				195			219	
armchair (n,n)	(12)		(11)			(10)				(9)			(8)	
Calculated for		158		167		178		187			200		214	231
zigzag $(n,0)$		(19)		(18)		(17)		(16)			(15)		(14)	(13)
chiral tubes					172		182		190			206		

to the same strong Raman component at 177 cm^{-1}. From an analysis of the Raman excitation profile in the 1.6–2.7 eV region, this overlap could be disentangled confirming that two tubes contribute to the same Raman line.[11] The concentration of the (10,10) tubes was found to be much larger than that of the (17,0) tubes.

The remaining four rather weak components observed in the experiment cannot be attributed either to an armchair or to a zigzag tube. This might indicate that chiral tubes were also present in the sample. The results of the LDA calculation allow one to estimate the radius of the corresponding chiral tubes by using the $1/R$ law with a proportionality constant of $A = 1170\ \mathrm{cm}^{-1} \times \text{Å}$.

In conclusion, we have demonstrated that elaborated LDA calculations for single wall nanotubes reveal values for the RBM frequency that can be assigned unambiguously to observed experimental Raman frequencies. The RBM of the (10,10) tube was found to be at 175 cm^{-1}, in very good agreement with one of the strongest lines observed in the Raman spectra. In combination with Raman measurements, the results show that tubes with a radius between 5.8 and 8.0 Å are favorable, with the tube radius strongly peaked around 6–7 Å.

In addition, we have shown that simple LDA calculations of the elastic constants of a flat graphene sheet allow one to predict the RBM of nanotubes with very good accuracy. This calculation seems to be particularly promising, because it shows unambiguously that the elastic constants and the closely related force constants of a flat graphene sheet can be transferred to carbon nanotubes without modifications. It should be stressed that these constants can be calculated reliably from first principle,[18] avoiding uncertainties in their determination from experiments. In the future, methods combining force constants determined from first-principles methods with simple folding techniques might become a reliable tool for the prediction of elastic and vibrational properties of carbon nanotubes.

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