CALCULATED DEPENDENCE OF VIBRATIONAL BAND FREQUENCIES OF SINGLE-WALLED CARBON NANOTUBES ON DIAMETER

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We have used density functional theory (DFT) at the B3LYP/6-31G level to calculate Raman and IR spectra of the fourteen zigzag (n,0) single-walled carbon nanotubes (SWCNTs) that have n ranging from 6 to 19. In the low frequency RBM region, calculated Raman spectra indicated that there are three vibrational modes, of symmetries A_{1g}, E_{1g} and E_{2g}, whose frequencies depend strongly on nanotube diameter such as; $\omega_{RBM}(A_{1g})$ = 12.04 (cm−1 + 221.4(cm$^-$ 1.nm)/ d_t(nm) and $\omega_{BD}(E_{1g})$ = 51.9(cm$^-$ 1 + 136.8(cm^{-1}.nm)/d_t(nm); there are also two IR spectral modes (of A_{2u} and E_{1u} symmetries) found in calculated IR spectra with strong diameter dependencies; ω_{RW}(A_{2u}) = 10.4 (cm^{-1} + 192.3(cm^{-1}.nm)/d_t(nm) and ω_{CW}(E_{1u}) = 35.2(cm^{-1} + 283.7(cm^{-1}.nm)/d_t(nm). These diameter dependencies are found to agree with empirical linear fits, where such fits have been made. We have also found three Raman bands with E_{1g}, A_{1g} and E_{2g} symmetries to exist in the G-band region. For this latter case, computed spectra indicated that the frequency of the A_{1g} symmetry mode is not expected to vary much with nanotube diameter, but the frequencies of the E_{1g} and E_{2g} modes are expected to converge towards one another with increasing tube diameter. Furthermore, These calculations suggest that the curvature energy (or folding energy) of the SWCNT, in gas phase, rapidly decreases and stabilizes with increasing size of the SWCNT; a solid curve is a fit to the calculated energies using a functional form that depends inversely on nanotube diameter, $dE_{n,6} = E_{n,0} - E_{6,0}$ = -1.55 (eV) - 0.16(eV.nm)/d_t(nm) + 0.44(eV.nm)/d_t^2(nm). The calculated full natural bond orbital analysis (NBO) indicates that three of the four valence electrons of the carbon atoms in SWCNTs are sp^2-hybridized in the one-dimensional (1D) network, with 34% s and 66% $p_x y$ character, and the forth electron is 100% p_z in character. As expected, each carbon atom contributes three electrons to the sigma bonds within the surface of the CNT and has one electron left in the p_z orbitals that is delocalized over the entire surface.