Phonon frequencies as computed in a frozen-phonon approximation are independent of the amplitude, unless the mode is significantly anharmonic due to e.g. an incipient structural phase transition. Anharmonic behavior is not expected for the tangential modes of undoped carbon nanotubes, since the carbon-carbon bonds are very stiff and the structure is securely situated in a stable local minimum. However, Fig. 1 demonstrates that phonons in doped carbon nanotubes can have a small but significant anharmonicity. Computed in a harmonic approximation, the frequency of the $A_{1LO}$ mode is amplitude-dependent, but only for doped tubes. Fitting the energy-displacement curve to $E(u_0) = A_0 + A_2 u_0^2 + A_4 u_0^4$ and treating the quartic term via 2nd order perturbation theory yields

$$\omega_{\text{anharm}} = \omega_{\text{harm}} + \frac{3A_4}{4A_2^2} \omega_{\text{harm}}^2 - \frac{9A_4^2}{8A_2^4} \omega_{\text{harm}}^4.$$  (1)

This correction levels out the curves at larger displacements and so produces well-defined phonon frequencies. Evaluated at the classical turning point $u_{tp}$ for the first excited state, the ratio $A_4 u_{tp}^2/A_2$ does not exceed 0.02, so the anharmonicity is weak. If the anharmonicity is large, as in the case of the $E_{2g}$ mode in MgB$_2$, one needs to go beyond the frozen-phonon approach by including phonon-phonon scattering in the whole Brillouin zone.

Why does the $A_{1LO}$ mode only acquire anharmonicity under doping? With a frozen-phonon distortion imposed, dilation of the axial bonds shifts the bands whose charge density resides predominantly along the axial bonds relative to the bands that reside mainly on off-axis bonds. When one of each type of band is slightly filled, even small phonon distortions can shift the relative band position enough to move van Hove singularities past the Fermi level, inducing rapid variations in the character of the states at the Fermi level, as shown in Fig. 2. Band motions are opposite in the ±1 (mod 3) classes.

FIG. 2: (Color online) Band structures along $\Gamma \rightarrow X$ for a (16,0) nanotube doped at 1.5 x 10^{-2} electrons per atom for stretched (left), equilibrium (center), and compressed (right) axial bonds according to the $A_{1LO}$ eigenvector. Band coloration follows Fig. 2 in the Letter. The Fermi level is zero, and the phonon amplitude corresponds to the classical turning point of the first excited state.

#### FIG. 1: The harmonic and anharmonic frequencies of the $A_{1LO}$ mode in (16,0) nanotube as a function of the magnitude of the displacement at different doping levels indicated by the curve labels. The units for frequency are cm^{-1}.

1 The cubic term is absent at first order.
3 A similar anharmonicity was previously found in undoped metallic zig-zag tubes where the mode couples strongly to continuum states around the Fermi level.