Characterization of DNA-Carbon Nanotube Hybrids by their van Hove Singularities

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ABSTRACT

The optical dichroism which appears in the nanotube–DNA hybrid is studied within a phenomenological approach. Naturally non–chiral nanotubes may acquire a chiral optical response when wrapped by the DNA helix. The hybrids of the DNA and the metallic nanotubes are discussed in conjunction with the possible gap opening and the subsequent arising of a pair of van Hove singularities close to the Fermi point. Polarized light absorption experiments are proposed to find the predicted effect.

Keywords: Nanotubes, DNA, theory, optics, dichroism

In the past two decades carbon nanotubes (NT) have attracted significant interest of the physics community due to unusual mechanical and electronic properties of these macromolecules.[1] Recently, it was shown that it is possible to obtain DNA–carbon nanotube hybrids, which can be used for NT separation and selective placement.[2] There are indications that the DNA molecule forms a regular helical wrap around the NT. This opens ways for studying new physical phenomena in DNA–NT complexes, in particular, one may expect appearance of chiral effects, e.g. circular optical dichroism, in intrinsically non–chiral NTs (zigzag and armchair).

Study of NTs in photoluminescence optical experiments is complicated by the low quantum efficiency, especially when at the substrate. On the other hand, one–dimensional nature of these materials leads to a singularities in the density of states (DOS) close to the band edge — so–called, van Hove singularities. Thus, in optical experiments one observes not a continuous absorption spectrum above the absorption edge, but rather a set of discrete peaks, corresponding to transitions between different van Hove singularities.[3] There are certain selection rules associated with these transitions. In particular, in metallic tubes one cannot observe the transitions between the closest conduction and valence (metallic or zero–mass) bands: the DOS of such metallic band (with the zero effective mass) is non–singular, while the overlap of these bands at the Fermi point leads to the enhancement of non–radiative recombination mechanisms.

Recently, we studied opening of a band gap in metallic NTs due to the chiral potential,[4] which models a DNA molecule wrapped around the NT. We obtained selection rules, relating the period of the wrap and the NT indices, and estimated the size of the resulting band gaps, given by the following generic formula

$$E_g = \frac{U_0}{R} e^{-\kappa \lambda_0} \sin(\varphi), \tag{1}$$

where U_0, λ_0 are the normalized amplitude and width of the helical potential, R is the NT radius, κ and φ are determined by the symmetry of the DNA–NT hybrid.

Our calculations were supported by numerical modeling.[5] The small size of these gaps (about one hundredth of a typical semiconductor NT band gap) renders them difficult, if suitable at all, for NT characterization by usual optical setup. Such experiment would require using of microwave radiation, where achieving the radiation intensities required for observable emission is almost impossible.

However, if one uses a circularly polarized light in order to study absorption between the bands with different angular quantum number, it may be possible to detect opening of a band gap. We expect qualitative changes in the NT energy spectrum: the flat density of states transforms into a sharp van Hove singularity.

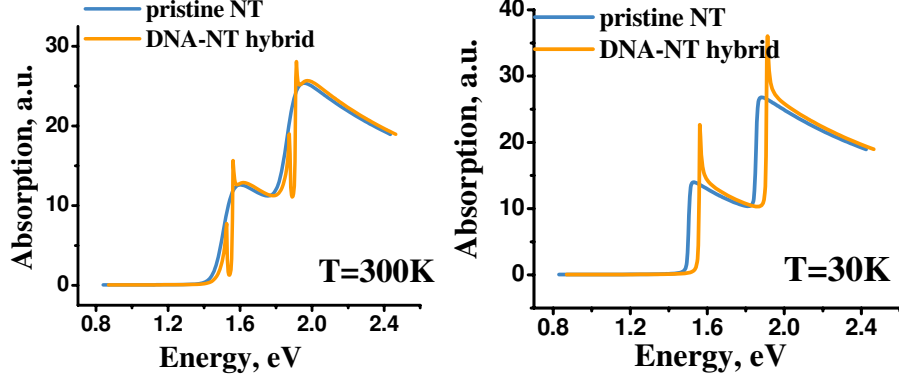Presenting author e-mail: rotkin@lehigh.edu, Telephone: 1–(610) 758–3930

Figure 1. Absorption coefficient for a pristine (9,0) NT (blue/dark in b/w) and the corresponding DNA–NT hybrid with the helix running along a zigzag direction (orange/light in b/w).

Indeed, the dispersion relation and the DOS of a metallic NT near the Fermi point are given by

$$E^{(0)}_\pm (k) = \pm v_F |k|, \qquad DOS^{(0)}(E) = \frac{4}{\pi \hbar v_F}. \tag{2}$$

Here, v_F is the Fermi velocity, k is the electron momentum. After opening of a gap of size 2Δ, the same quantities are given by

$$E_\pm(k) = \pm\sqrt{\Delta^2 + v_F^2 k^2}, \qquad DOS(E) = \frac{4}{\pi \hbar v_F} \frac{E}{\sqrt{E^2 - \Delta^2}}, \tag{3}$$

where DOS has an obvious singularity at the new band edge.

The absorption coefficient is calculated as

$$\alpha_\pm \propto \frac{e^2}{m_0 \omega \varepsilon} \int_{BZ} dk \, |\langle k, m_F \pm 1, \lambda | \mathbf{e} \cdot \mathbf{p} | \Psi_{\lambda'}(k) \rangle|^2 \frac{\Gamma_{scatt} f\left(E_{\lambda'}(k)\right) \left[1 - f\left(\epsilon_\lambda(k, m_F \pm 1)\right)\right]}{\left[\epsilon_\lambda(k, m_F \pm 1) - E_{\lambda'}(k) - \hbar\omega\right]^2 + \Gamma_{scatt}^2} \tag{4}$$

where ω is the frequency of the incident circularly polarized radiation; $M = \langle k, m_F \pm 1, \lambda | \mathbf{e} \cdot \mathbf{p} | \Psi_{\lambda'}(k) \rangle$ is the optical matrix element for the transition between one of the Fermi subbands with the angular quantum number m_F and the energy dispersion $E_{\lambda'}(k)$, and a subband with the angular quantum number $m_f \pm 1$ and the energy dispersion $\epsilon_\lambda(k, m_F \pm 1)$; $f(E) = \left[1 + \exp\left(\frac{E - E_F}{k_B T}\right)\right]^{-1}$ is the Fermi distribution function. The optical density of states

$$\rho(E) = \frac{1}{\pi} \frac{\Gamma_{scatt}}{E^2 + \Gamma_{scatt}^2} \tag{5}$$

is introduced to account for the broadening of the transition due to scattering effects. The full absorption coefficient is calculated by summing contributions from all possible transitions.

As we see from Eq.(4), as long as the broadening Γ_{scatt} is not too big, absorption will exhibit different behavior, depending on whether the energy denominator has a singularity or not.

As an illustration for this effect, we provide in Fig. 1 the results of calculations of the absorption coefficient for a (9,0) zigzag NT with the DNA helix running along a zigzag direction of this tube (i.e. at the angle $\pi/3$ in respect to the circumference). These graphs are calculated with the following values of the parameters involved: $\lambda_0 = 1$Å, $U_0 = 2$ eV·Å, $2\Delta = 0.33$ eV, $E_{g1} = 3.08$ eV, $E_{g2} = 3.76$ eV, $\Gamma_{scatt} = 0.0029$ eV.

In a pristine NT the absorption exhibits two steps corresponding to the absorption from the uppermost valence band, m_F, to the bands with $m = m_F \pm 1$. In a metallic NT there is no band edge at the Fermi point, and the steps occur due to the sharp Fermi distribution, and, consequently, broadened when the temperature increases.

In conclusion, the absorption of a DNA–NT hybrid, where a small gap opens as the result of breaking of the NT symmetry by the DNA wrap, exhibits sharp van Hove singularities at the energies where absorption steps occur in a pristine metallic NT. In addition, there is a slight increase in absorption threshold due to opening of the gap. Another distinct feature is the doubling of the van Hove singularity which occurs with increasing temperature. (The traces on the figure for $T = 300K$ are artificially displaced in order to reduce their overlap.) This is a phase space filling effect – due to the small size of the emerging gap, increasing temperature causes populating of the bottom of the condition band with the resulting absorption transitions between these states and higher subbands. In pristine NTs such effects are typical for high pumping intensity, and constitute part of nonlinear optics studies,[6] whereas our effect would be linear in the incident field.

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