RAMAN STUDIES OF DOPED SINGLE WALL CARBON NANOTUBE BUNDLES

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The recent discovery that single-wall carbon nanotubes (SWNT) can be produced in high yield (>70%) by a laser-assisted process [1] has opened up the possibility to study many chemical and physical properties of these interesting one dimensional (1D) wires. In a recent paper [2], we reported the Raman-active modes of small diameter pristine SWNTs, and we found good agreement between experiment and calculated frequencies for "armchair" symmetry (n,n) tubules in the range 8<n<11. In this paper, we discuss the doping-induced shifts in the SWNT Raman-active mode frequencies which serve as a clear evidence for the chemical doping of these crystalline ropes.

The chemical doping of the SWNTs was carried out in sealed quartz ampoules using vapor distilled reactants and details can be found in Ref. [3]. All the Raman spectra reported here were taken in the backscattering configuration using 514.5 nm laser excitation.

In Fig. 1, we display the T=300 K Raman spectra of pristine SWNTs and those doped with the anticipated acceptors (I_2,Br_2) and donors (K,Rb). From top to bottom, respectively, we display results for I_2-, Br_2-, pristine, Rb-, and K-doped SWNTs. As discussed previously [2], the peak at 186 cm^{-1} has been identified with the A_g symmetry radial breathing mode, and the peak at 1593 cm^{-1} has been assigned to an unresolved Raman triplet identified with tangential C-atom displacement modes. For the assignments of the weaker peaks in the spectrum for pristine SWNTs, the reader is referred to Ref. [2].

The uppermost two spectra in Fig. 1 are for SWNT bundles reacted with typical electron acceptor dopants (I_2, Br_2) which are expected to transfer electrons from the carbon π states in the tubules to the dopant molecules, creating hole carriers in the SWNT. The I_2-doping induces the smallest change in the SWNT Raman spectrum. This is perhaps not surprising, as I_2 does not intercalate into graphite. The I_2-doping of SWNT bundles is seen to slightly upshift the radial mode frequency from 186 to 188 cm^{-1} (Δ_r = + 2 cm^{-1}), and slightly downshift

the tangential mode frequencies from 1593 cm^{-1} in the pristine SWNT to 1590 cm^{-1} (Δ_t = - 3 cm^{-1}), where Δ_r and Δ_t refer to the change in the radial and tangential mode frequencies upon doping. For the case of saturated Br_2-doping, a large *upshift* Δ_r = + 74 cm^{-1} and Δ_t = + 24 cm^{-1}, which is much larger than observed for I_2- doping.

The two spectra at the bottom of Fig. 1 are for SWNTs reacted with typical electron donor dopants (K,Rb). These spectra are essentially identical, and one reaction was carried out on a sample where the nanospheres have been removed in a purification process[4]. Thus, it is apparent that no significant contribution to the Raman spectrum from carbon nanospheres is present. The low frequency radial breathing mode is not evident in the spectrum--it may have *downshifted* below our lower frequency limit (~100 cm^{-1}), or, alternatively, it may have broadened to the point it cannot be detected above the background. The asymmetric peak at ~1565 cm^{-1} observed in both alkali metal-doped SWNT bundles is identified with a Breit-Wigner-Fano (BWF) resonance[5] which usually involves an interference between Raman scattering from continuum excitations and that from a discrete phonon. The degree of coupling (1/q) determines the departure of the lineshape from a symmetric Lorentzian. The value of 1/q ~ - 0.35 we observe here for the alkali metal (M)-doped SWNT bundles is about a factor of three smaller than those observed for the broad BWF resonance in stage1 C_8M graphite intercalation compounds [5].

It is interesting to see whether doping-induced shifts in the SWNT phonon frequencies we observe are consistent with weight uptake measurements reported by Lee et al.[6]. From charge-transfer- induced changes in the E_{2g2} high frequency intralayer mode in donor or alkali metal doped (acceptor or H_2SO_4 doped) GICs, we obtain the value $\Delta\omega/\Delta f$ ~ -140 cm^{-1} (~+ 460 cm^{-1}), where "f" is the transferred charge per C-atom[7]. It should be noticed that the shift per unit transferred charge is much larger for acceptor GICs. For Br_2 , which is

known to be a weak acceptor in a GIC (i.e., 0.2e, transferred per intercalated Br_2 unit), we find f ~ 1/19, or one free hole per 19 C-atoms in the SWNT. Weight uptake measurements by Lee et al. [6], indicate that an effective composition $C_{52}Br_2$ has been obtained under similar synthesis conditions. Thus it appears that to be consistent with this composition, significantly higher charge transfer per Br_2 is taking place in the SWNTs than in GICs. For the alkali metal dopants (K,Rb), the two contributions (i.e., charge transfer and interference (1/q)) to the BWF frequency ω_0 cannot be separated without a detailed analysis of the continuum excitations. Therefore, we cannot estimate $\Delta\omega/\Delta f$ at this time. However, the M-doped SWNT Raman spectra qualitatively indicate the bundles are highly doped, which is consistent with the large weight uptake (effective composition C_8K) observed by Lee et al. [6]. In conclusion, we have observed

clear evidence for charge transfer chemistry between both acceptor and donor reagents and SWNTs. This amphoteric behavior needs to be explored and structural information is needed to determine the distribution of the dopant in the SWNT bundles.

Acknowledgements

REFERENCES

[1] A. Thess et al., Science, 273, 483 (1996).
[2] A. M. Rao et al., Science, 275, 187 (1997).
[3] A. M. Rao et al., Nature (submitted).
[4] S. Bandow et al., Chem. Phys. Lett. (submitted).
[5] P. C. Eklund and K. R. Subbaswamy, Phys. Rev. B, 20, 5157 (1979); P. C. Eklund et al., Phys. Rev. B, 16, 3330 (1977).
[6] R. Lee et al., Nature (submitted).
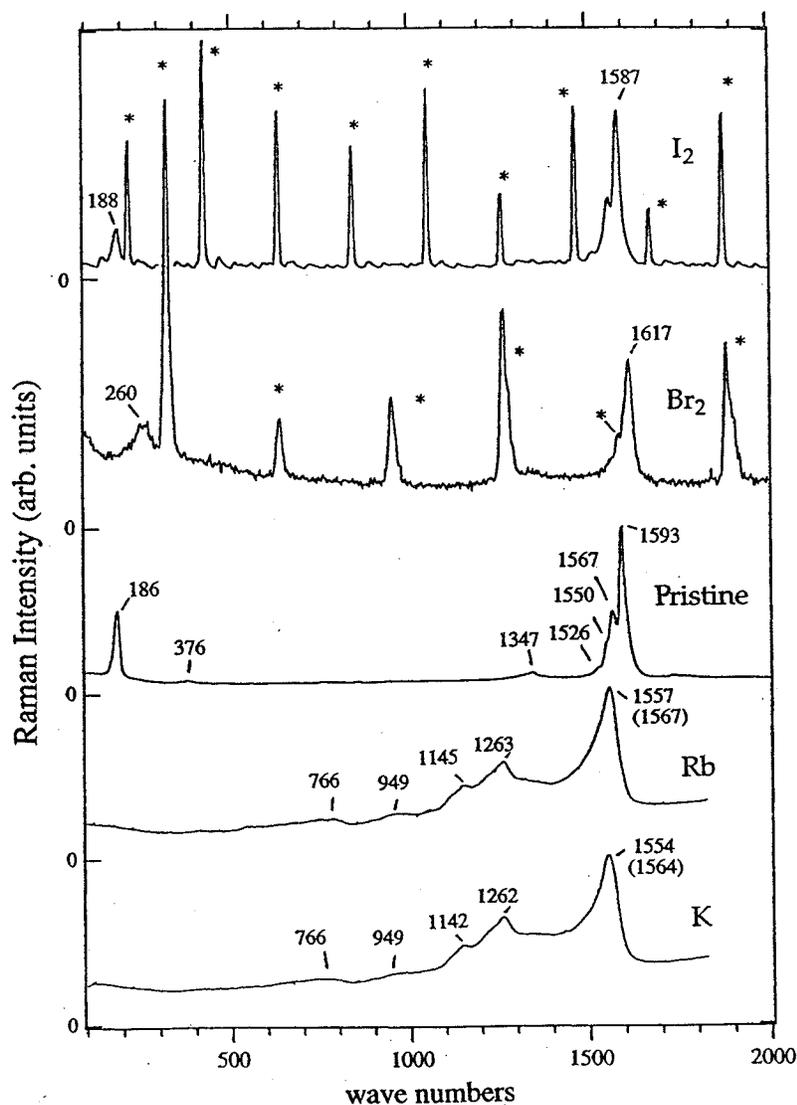[7] P. C. Eklund et al., Synth. Metals, 12, 97 (1985).

Figure 1: Raman scattering spectra for pristine SWNT bundles reacted with various donor and acceptor reagents. From top to bottom: I_2, Br_2, pristine SWNT, Rb, K. The asterisks (*) indicate the positions of peaks associated with halogen reactant. The peak frequencies indicated in parentheses for the K, Rb doped SWNTs are the renormalized phonon frequencies [2].