

Polarization-dependent optical reflectivity in magnetically oriented carbon nanotube networks

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1 Introduction

The most striking physical property of carbon nanotubes is their one-dimensional character, resulting in highly anisotropic electrical and optical properties. However, measuring this anisotropy on macroscopic samples is not a straightforward process since typical samples consist of intertwined bundles. Orientation of these bundles and polarized optical measurements have been performed in the visible [1–3] and in the Terahertz range [4], but data are lacking at infrared-far infrared frequencies, connecting these results.

We were motivated by our earlier study in the infrared [5] to extend the investigation of optical anisotropy to a wide frequency range. To this end, we measured reflectivity of buckypapers oriented in magnetic field.

2 Experimental

Carbon nanotube networks used in this study were prepared by filtering a suspension of laser-deposited single-walled carbon nanotubes in a 25 T magnetic field [6]. Reflectivity was measured by various instruments from the far infrared through the visible with sufficient spectral overlap. After the measurement, a 2000 Å thick aluminum layer was deposited on the surface and the measured reflectance was renormalized to this background to correct for surface effects [1]. This correction is important, as seen in Fig. 1, especially in the polarization direction parallel to the tube axes.

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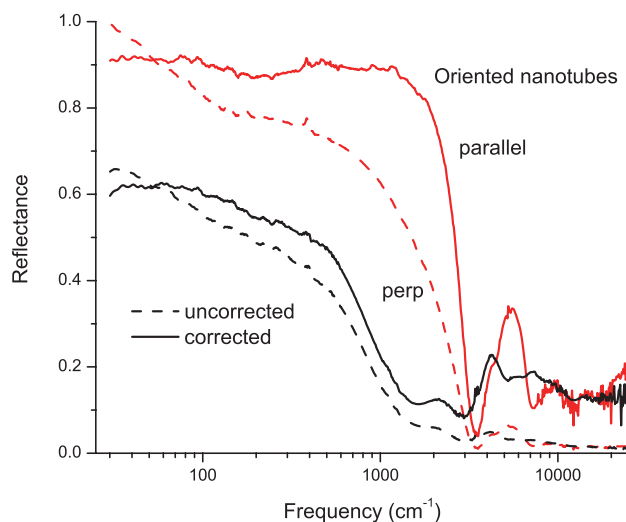


Fig. 1 (online colour at: www.pss-b.com) Reflectivity of the network in polarization parallel and perpendicular to the orientation direction, as-measured and corrected for surface scattering.

3 Results and discussion

The reflectance shows a marked anisotropy, varying smoothly with polarization angle, as depicted in Fig. 2. In Fig. 3 we included the results of a multi-oscillator (Drude–Lorentz) fit to the normalized reflectivity, with parameters shown in Table 1. In the parallel direction, we see two low-frequency oscillators, one corresponding to free-carrier (Drude) absorption and the other to small-gap tubes, and can further discern three transitions in the near-infrared and visible, corresponding to transitions between Van Hove singularities. The center frequencies are reasonably close to those derived from transmission through an unoriented film produced by the same method [7], although the intensities and widths are different.

In both polarizations, the reflectance in the infrared is high (reaching over 90% in the parallel case, suggesting that oriented nanotubes with improved surface quality could be used as far-infrared polariz-

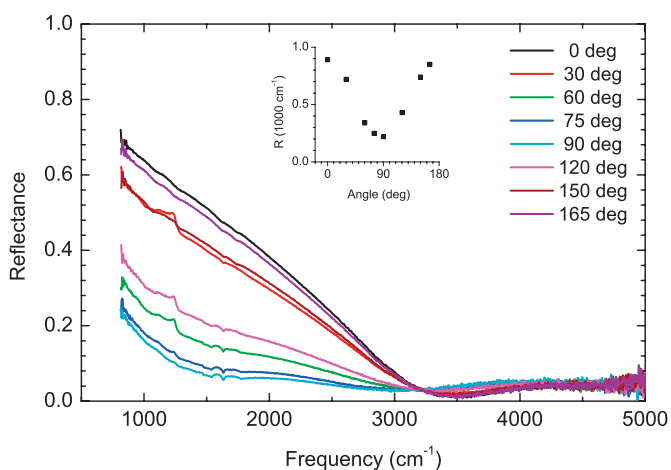


Fig. 2 (online colour at: www.pss-b.com) Polarization dependence of the mid-infrared reflectivity (uncorrected for surface scattering) of an oriented nanotube network. The inset shows the reflectivity value at 1000 cm^{-1} as a function of polarization angle measured from the parallel direction.

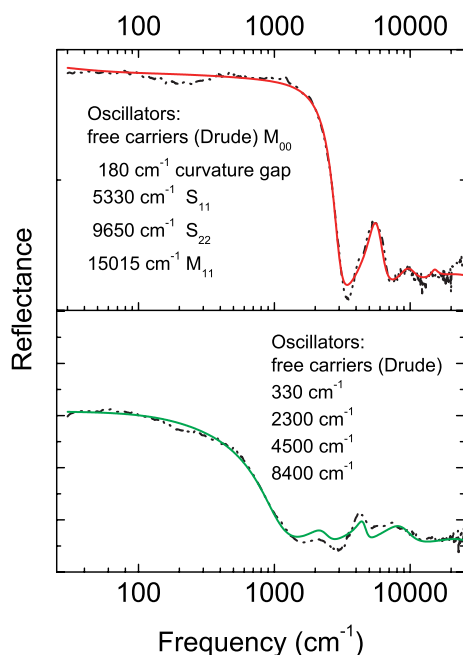


Fig. 3 (online colour at: www.pss-b.com) Drude–Lorentz oscillator fits to the parallel and perpendicular reflectance, with positions of fitted oscillators.

ers). The parallel reflectivity exhibits a plasma minimum at 3400 cm^{-1} , and the perpendicular one also shows a marked drop around 1500 cm^{-1} , although the exact minimum is more difficult to determine than in the parallel direction. We can estimate the oscillator strength below these minima by adding the square of the plasma frequencies of the low-frequency oscillators in the model in Table 1: the first two in the parallel polarization and, somewhat arbitrarily, the first two or three in the perpendicular polarization. The ratio obtained by this calculation is 6.5 and 8, respectively, in surprisingly good agreement with the ratio of the Raman intensities of the 1580 cm^{-1} peak, 7 ± 2 [6], indicating that metallic and small-gap tubes are preferentially aligned along the magnetic field.

Table 1 Parameters of fitted oscillators to the normalized reflectivity in parallel and perpendicular orientation (cm^{-1}). The background dielectric constant was taken as 1.04 and we added two high-frequency oscillators from Ref. [3].

	parallel	perpendicular
ω_{p0}	5230	423
γ_0	555	4200
ω_{p1}	5676	2617
ω_1	180	330
γ_1	368	918
ω_{p2}	6393	1700
ω_2	5330	2300
γ_2	1230	900
ω_{p3}	6284	2800
ω_3	9650	4500
γ_3	3160	800
ω_{p4}	4000	9000
ω_4	15015	8400
γ_4	2000	4500

Several transitions appear in the near-infrared and visible range (where preferentially semiconducting tubes absorb) in the perpendicular polarization as well. Because of the low reflectivity and lower polarizer efficiency the signal-to-noise ratio is higher than in the infrared and quantitative estimations cannot be made. It is, however, clear that the center frequencies are different in the two polarization directions. Distinct absorption peaks in the perpendicular direction have been predicted based on selection rules for line groups describing nanotube symmetry [8], and observed in Raman excitation profiles [9]. Different sensitivity of metallic and semiconducting tubes to orientation in magnetic field would also explain the more pronounced anisotropy in the free-carrier range. Slight doping of the material during purification (possibly diameter-dependent) can lead to loss of one-dimensional character, and simple optical resonance effects cannot be ruled out either.

4 Conclusion

We have found that the reflectivity of magnetic field-oriented carbon nanotubes is polarization-dependent over the whole spectral range. The difference is clearly distinguishable for metallic and small-gap tubes and less outspoken for semiconducting tubes. For metallic tubes, the anisotropy agrees with that found by Raman spectroscopy. It is not clear yet whether the dichroism found here reflects the peculiarities of magnetic field alignment or the intrinsic properties of individual nanotubes or nanotube bundles. To this end, further studies, especially in the high-frequency range, are necessary.

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References

- [1] J. Hwang, H. H. Gommans, A. Ugawa, H. Tashiro, R. Haggenmueller, K. I. Winey, J. E. Fischer, D. B. Tanner, and A. G. Rinzler, *Phys. Rev. B* **62**, R13310 (2000).
- [2] M. F. Islam, D. E. Milkie, C. L. Kane, A. G. Yodh, and J. M. Kikkawa, *Phys. Rev. Lett.* **93**, 037404 (2004).
- [3] Y. Murakami, E. Einarsson, T. Edamura, and S. Maruyama, *Phys. Rev. Lett.* **94**, 087402 (2005).
- [4] T.-I. Jeon, K.-J. Kim, C. Kang, I. H. Maeng, J.-H. Son, K. H. An, J. Y. Lee, and Y. H. Lee, *J. Appl. Phys.* **95**, 5736 (2004).
- [5] K. Kamarás, K. Thirunavukkuarasu, C. A. Kuntscher, M. Dressel, F. Simon, H. Kuzmany, D. A. Walters, and D. A. Moss, *Infrared Phys. Technol.* **49**, 35 (2006).
- [6] D. A. Walters, M. J. Casavant, X. C. Qin, C. B. Huffman, P. J. Boul, L. M. Ericson, E. H. Haroz, M. J. O'Connell, K. Smith, D. T. Colbert, and R. E. Smalley, *Chem. Phys. Lett.* **338**, 14 (2001).
- [7] F. Borondics, K. Kamarás, M. Nikolou, D. B. Tanner, Z. H. Chen, and A. G. Rinzler, *Phys. Rev. B* **74**, 045431 (2006).
- [8] I. Bozović, N. Bozović, and M. Damjanović, *Phys. Rev. B* **62**, 6971 (2000).
- [9] A. Jorio, M. A. Pimenta, A. G. Souza Filho, Ge. G. Samsonidze, A. K. Swan, M. S. Ünlü, B. B. Goldberg, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. Lett.* **90**, 107403 (2003).