7 Fluorescence Spectroscopy of Single-Walled Carbon Nanotubes

R.B. Weisman

An overview is presented of basic and applied aspects of the fluorescent photoluminescence from single-walled carbon nanotubes (SWNT). This fluorescence was first discovered in aqueous surfactant suspensions of SWNT that had been processed for enrichment in individual, unbundled nanotubes. Spectrofluorimetric measurements of emission intensity as a function of excitation and emission wavelengths revealed a rich pattern of peaks representing distinct \((n,m)\) structural species. Careful analysis allowed each of these peaks to be assigned to a specific semiconducting \((n,m)\) species. This spectral assignment provided a large body of precise optical transition energies for a significant range of tube diameters and chiralities. Important patterns of electronic structure emerged showing the related properties of nanotubes within “families” (sharing the same \(n-m\) value) and “tribes” (sharing the same \(\text{mod}(n-m,3)\) value). The results also allowed construction of an empirical “Kataura plot,” useful for guiding experiments, that gives optical transition energies as a function of nanotube diameter for semiconducting species. In surfactant-suspended samples, optical transition energies are found to depend mildly on nanotube environment. Spectral line shapes reveal the predominant excitonic character of optical excitations in SWNT and provide information on environmental heterogeneity and on exciton dephasing rates. Nanotube fluorescence is quenched by aggregation, chemical derivatization, and by acidification in some aqueous suspensions. Fluorimetry offers a powerful method for determining the \((n,m)\) composition of mixed nanotube samples. Instrumental methods for such fluorimetric analysis are discussed and compared. Finally, the unusual near-infrared emission from SWNT can be exploited to allow selective optical detection and imaging of nanotubes in complex environments. Early results are presented showing how this approach can be used to image the locations of nanotubes inside biological cells.

7.1 Introduction

When matter is electronically excited by thermal, optical, or electrical means, it commonly relaxes through the emission of light. This luminescence process has enormous scientific value because of the detailed information that spectral positions and intensities can reveal about a sample’s electronic struc-
ture. In addition, luminescence has great practical value because it permits the sensitive qualitative and quantitative analysis of specific substances in complex mixtures. Single-walled carbon nanotubes (SWNT) represent an exciting new class of synthetic nanomaterials that hold great interest for their scientific novelty and for their potential utility in a wide range of applications [1,2]. The recent discovery of photoluminescence from SWNT offers a powerful tool for new basic and applied studies of nanotubes.

Absorption and emission of light at wavelengths from the ultraviolet to the near-infrared arise from excitations of the electrons in matter, and the wavelengths and strengths of these optical transitions reflect a sample’s detailed electronic properties. SWNT are tubular nanostructures, typically about 1 or 2 nm in diameter and hundreds or thousands of nanometers long, consisting entirely of covalently bonded carbon atoms. Each of these carbons is bound to three neighboring atoms by sigma bonds, and its remaining carbon p-electron contributes to a delocalized pi-electron system. Electronic states of this system are delocalized along the translationally periodic, quasi-infinite axis of the nanotube, but are constrained in the transverse directions by an angular periodic boundary condition reflecting the tube’s diameter and wrapping (chiral) angle.

A key feature of carbon nanotubes is the strong dependence of their electronic properties on physical tube structure [1,3]. Because SWNT are formed in a variety of discrete structures having distinct diameters and chiralities,

![Fig. 7.1. Schematic density of electronic states for a semiconducting single-walled carbon nanotube. Van Hove singularities are labeled with “v” for valence band and “c” for conduction band, along with subscripts giving the sub-band index. Vertical arrows show intense optical transitions for light polarized along the tube axis](image-url)