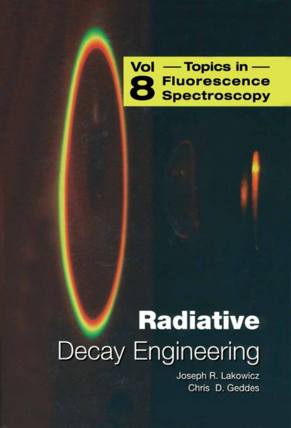

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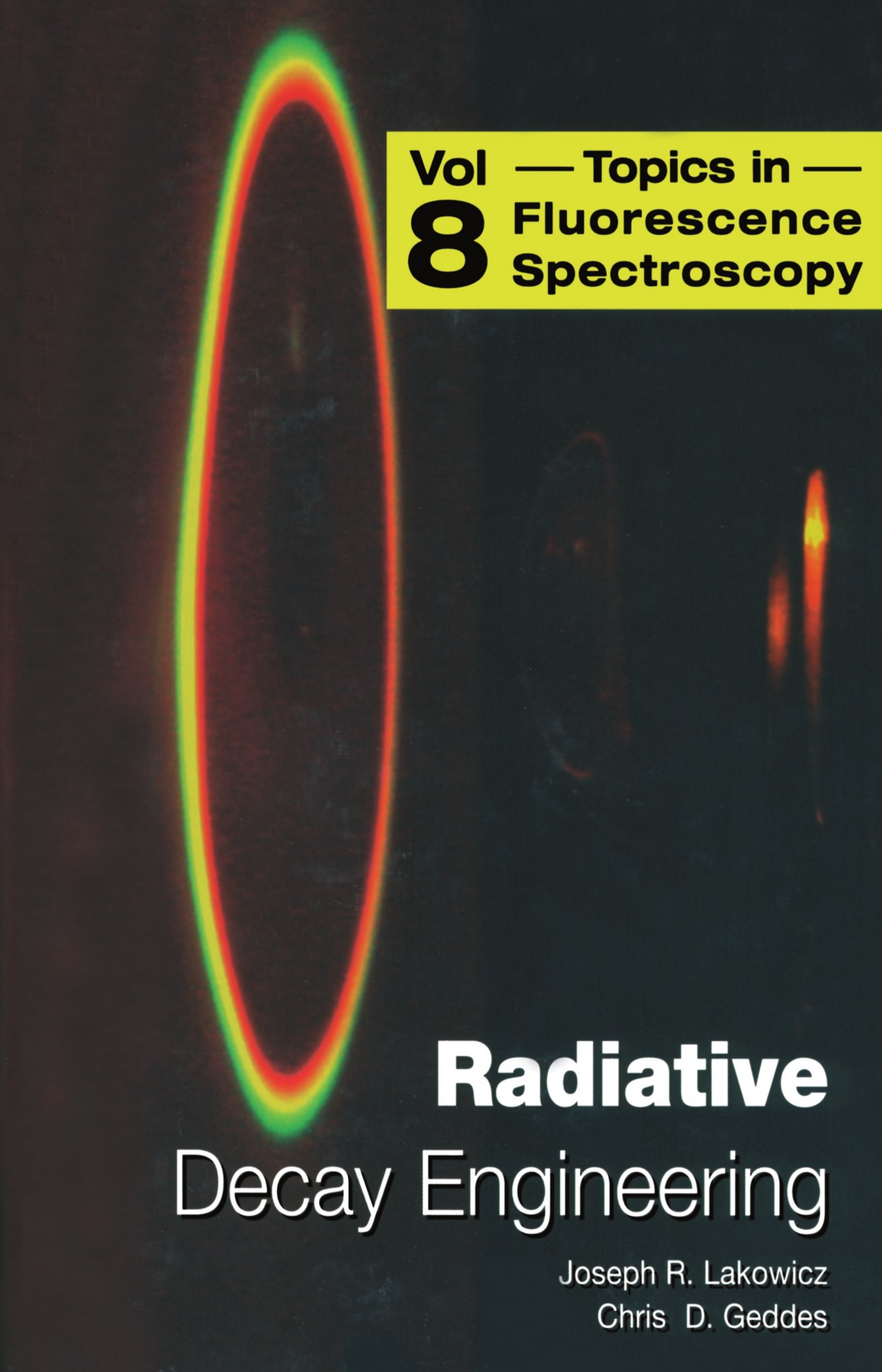

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Edited by JOSEPH R. LAKOWICZ and CHRIS D. GEDDES

Volume 1: Techniques
Volume 2: Principles
Volume 3: Biochemical Applications
Volume 4: Probe Design and Chemical Sensing
Volume 5: Nonlinear and Two-Photon-Induced Fluorescence
Volume 6: Protein Fluorescence
Volume 7: DNA Technology
Volume 8: Radiative Decay Engineering

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Edited by

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Preface

Spatial control of photonic mode density is changing the practice of fluorescence spectroscopy. This laboratory has been active in fluorescence spectroscopy for nearly 30 years. During that time we have investigated many phenomena in fluorescence, including quenching, energy transfer and anisotropy, to name a few. Until recently we relied completely on the free-space emission properties of fluorophores observed in transparent media. The free-space quantities in fluorescence are determined by the values of the radiative and non-radiative properties of excited fluorophores. The observed changes in fluorescence intensities, lifetimes, etc. are due almost completely to changes in the non-radiative decay rates such as quenching. The rate of radiative decay is determined by the extinction coefficient or oscillator strength of the transition. This rate is essentially constant in most media.

In about 2000 we began to examine the effects of silver metallic particles on fluorescence. Examination of the literature revealed that proximity to silver particles could have dramatic effects on fluorescence quantum yields and lifetimes. Such changes are typically due to changes in the non-radiative decay rates. In contrast, the metal particles changed the radiative decay rate (Γ). These changes occur due to modifications of the photonic mode density (PMD) near the particle in Γ. This was the first time in 30 years that we saw an opportunity to modify this fundamental rate. Numerous opportunities became apparent as we considered the effects of PMD, including increased quantum yields, increased photostability and changes in resonance energy transfer. Additionally, we saw the opportunity to obtain directional rather than isotropic emission based on local changes in the PMD. We described these phenomena as radiative decay engineering (RDE) because we could engineer changes in the emission based on the fluorophore-metal particle geometries.

During these three years our enthusiasm for RDE has continually increased. Many of the early predictions have been confirmed experimentally. As one example we recently observed directional emission based on fluorophores located near a thin metal film, a phenomenon we call surface plasmon coupled emission (SPCE). We see numerous applications for RDE in biotechnology, clinical assays and analytical chemistry. The technology needed to implement RDE is straightforward and easily adapted by most laboratories. The procedures for making noble metal particles and surfaces are simple and inexpensive. The surface chemistry is well developed, and the noble metals are easily tolerated by biochemistry systems.

While implementation of RDE is relatively simple, understanding the principles of RDE is difficult. The concepts are widely distributed in the optics and chemical physics literature, often described in terms difficult to understand by biophysical scientists. In this volume we have presented chapters from the experts who have studied metal particle optics and fluorophore-metal interactions. We believe this collection describes the fundamental principles for the widespread use of radiative decay engineering in the biological sciences and nanotechnology.

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Center for Fluorescence Spectroscopy
Baltimore, Maryland
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