Summary

Three areas of luminescence studies emerge from the selection of papers in this volume. One general area addressed by four of the papers concerns the sensitivity of luminescence phenomena to respond to small molecular perturbations such as the lumiphors' microenvironment. Another area on which two papers focus involves complementary or indirect measurements where competing phenomena such as radiational deactivation, quenching or complexation by the lumiphor provide useful information. The third area reflects the growing use of computer-assisted luminescence measurements where additional spectroscopic information can be extracted by transformation of the spectral data. These areas reflect the continuing sophisticated development of fluorescence and phosphorescence spectroscopy.

The paper by Wirth and coworkers discusses the fundamental nature of the solvation process. These solvation interactions can profoundly change both the spectroscopic characteristics as well as the chromatographic characteristics of molecular species. The difficulty in obtaining a better understanding of liquid theory has been eased by application of two-photon spectroscopy, fluorescence depolarization, and rotational diffusion studies by the authors to identify spatial properties. Using sophisticated instrumental approaches, the authors have correlated the effects of molecular shape on solvation interactions using both polar and nonpolar solvents and polycyclic aromatic hydrocarbon lumiphors. It is postulated that solvent structures composed of molecules immediately surrounding a solute molecule can be shape-selective and respond differently to molecular species based on their structure.

The results of McMorrow and Kasha on the photo-excitation steps in 3-hydroxyflavone, leading to phototautomerization in the ultra-rapid (<8 ps) regime producing an unique tautomer emission, has proven useful in detecting hydrogen-bonding impurities in solvent. Ethers, alcohols and water, and other H-bonding solvents interact with the intramolecular transfer of the hydroxyl hydrogen to the neighboring carbonyl group producing changes in the fluorescence spectrum. The use of 3-hydroxyflavone as a fluorescence probe for solvent impurities is an example of using subtle microenvironmental effects to detect $10^{-7}$ to $10^{-9}$ M water contamination.

The study by Chen and Scott concerns the use of fluorescence polarization to follow the dynamic motion of entire fluorescence-tagged proteins (global) or the more rapid motion of particular nonglobal moieties such as a dansyl
label. The results show that dansyl conjugates exhibit both a thermally activated rapid rotation and a viscosity independent rotation by steady state analysis, that rapid and slow rotations can be visualized directly by time-resolved anisotropy measurements, that some rotational freedom of subunits is possible in certain cases, and that global rotations can be obtained from steady state isothermal measurements of intrinsic protein polarization. The implication of these rapid fluctuations helps explain, for example, the action of antibodies and enzymes, how proteins undergo transitions between conformational states, and many binding phenomena.

Weinberger et al continue their definitive study of room temperature phosphorescence (RTP) in fluid solution with a discussion of four techniques: micelle-stabilized RTP, microcrystalline/colloidal RTP, cyclodextrin-induced RTP, and sensitized/quenched RTP. The analytical utility of these methods is demonstrated for several classes of chemicals including carbo- and heterocyclic aromatic hydrocarbons and drugs.

Kirkbright's paper develops the theoretical foundation for determination of absolute quantum efficiencies for both solid and liquid samples using the complementary technique of photoacoustic spectroscopy. In this technique, heat at the surface of the sample resulting from nonradiative relaxation of the excited states is measured with respect to wavelength and can give information on the quantum efficiencies of molecular species. The procedure by which this is accomplished with simple instrumentation and without reference to luminescence standard materials is described.

Seitz and coworkers developed a metal ion sensor by immobilizing a fluorogenic ligand on the tip of a bifurcated fiber optic. The ligands successfully used in this fashion included morin, quercetin, and calcein onto cellulose using cyanuric chloride as a coupling reagent.

Purcell et al demonstrate the utility of synchronous excitation fluorescence (SEF) spectroscopy as a highly sensitive and selective technique for the determination of hazardous chemicals, in particular, phenols. In conjunction with derivative spectroscopy, SEF can detect and discriminate among phenols, even isomers, in the parts per billion range.

The paper by Soglio et al involved generation of a computer library of the low-temperature luminescence spectra of approximately 60 hazardous chemicals. A feature set for each molecular species, namely, a set of only six specific features uniquely characteristic of the compound, were identified to allow rapid matching of an unknown sample spectrum to the stored standard spectrum. The six feature components used were the first four noncentral sample moments of the spectrum, the approximate normalized area under the spectral envelope, and the wavelength corresponding to the location of the maximum intensity. The feature sets performed very well in a test using a cluster analysis involving over 2000 pairwise comparisons.

The broad scope covered by these papers is an indication of the many diverse fields that use luminescence techniques and of the multitude of applications for
which luminescence spectroscopy is ideally suited. The editors hope this volume will provide the background and direction to other researchers in the field to develop additional novel uses of light-induced phenomena to form the basis of subsequent publications in this series.

_L. J. Cline Love_

Seton Hall University, Department of Chemistry, South Orange, NJ, 07079; symposium co-chairman and co-editor.

_DeLyle Eastwood_

U.S. Army Corps of Engineers, Missouri River Division Laboratory, 420 S. 18th St., Omaha, NE 68102; symposium co-chairman and co-editor.