W5
The Use of Photon Counting, Multichannel Scaling, and Computer Processing in the Study of Phosphorescent Decay Times

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Photon counting when combined with multichannel scaling and computer processing offers much greater precision in the determination of phosphorescent emission lifetimes than has been attained by previous data gathering methods. The present investigation utilized the advantages of APL-SV in processing data by interactive programming from a remote terminal.

Measurements made on several molecules, including pesticidal carbamates, indicate that

(1) Single exponential decay functions which adequately describe the decay over more than a few half lives are observed only rarely.

(2) The effects of other processes which are not observable by conventional methods become discernible.

A survey totalling some 370 decay curves with the techniques referred to has been made on benzene and naphthalene in glasses of 3-methylpentane, perfluoro-1, 3-dimethylcyclohexane, and 2-propanol at 77 K, in which thermal equilibration (3 min to 5 h) and excitation (30 s to 8 min) times were controlled.

In the case of benzene, a progressive increase in decay constant with each succeeding half-life period was observed in all three solvents. Glass relaxation effects were observed in 3-methyl pentane and perfluoro-1,3-dimethylcyclohexane, but were absent in 2-propanol.

Decay constants for naphthalene in perfluoro-1,3-methylcyclohexane and in 2-propanol were constant and equal over the first four half-lives. On the other hand in 3-methylpentane naphthalene exhibited a decay constant which increased over at least the first three half-lives. However, relaxation effects were not observed.

W6
Correction for the Variation of Instrument Response Function with Wavelength in Fluorescence Lifetime Studies

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The variation of the lamp decay profile and photomultiplier (PMT) response function with wavelength in single photon counting fluorescence lifetime systems is well known [1]. These instrumental variations become especially significant when one applies strict statistical and experimental criteria to the determination of short lifetimes or multi-exponential decays. There are at least four approaches which one can take to account for these effects. (1) They can be ignored altogether with concomitant loss of confidence in the decay parameters. (2) It can be assumed that the variation in the response function with wavelength of the PMT is equivalent to a small delay and the experimental data are shifted accordingly or a delay function is fitted during the deconvolution process [2, 3]. (3) The lamp decay profile can be determined by monitoring the emission of a standard fluorescent compound (whose lifetime is accurately known) at the same wavelength as that at which the emission of the experimental sample is measured [4]. The excitation wavelength is the same for both the standard and the compound studied. A deconvolution of the standard's decay profile with its decay parameters avoids wavelength effects. (4) A PMT calibration function can be determined for the experimental wavelengths which is then applied prior to the deconvolution process in order to correct for the PMT response function variation with wavelength. This calibration function is determined by measuring the emission of a scintillator with a short singlet lifetime and a broad emission spectrum which spans the excitation and emission wavelengths of the compound being studied.

The experimental and mathematical procedures for the function correction method are presented. The merits of the