

## W5

**The Use of Photon Counting, Multi-channel 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-methylpentane 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

four alternatives are analyzed in terms of their convenience, experimental limitations and the statistical and interpretative confidence which one requires in the decay parameters obtained from the deconvolution of the experimental data.

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### W8

#### Surface Spectroscopy and Photochemistry of Adsorbed Molecules

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From many experiments there is evidence that both spectroscopy and photochemistry can undergo drastic changes when the molecules under investigation are adsorbed on the surface of a solid [1]. For instance, the irradiation of carbon monoxide, adsorbed on a tungsten surface, by the light of a mercury resonance lamp leads to the formation of photoproducts like  $C_2O$ ,  $CO_2$ ,  $C_2O_2$  and  $C_3O_2$ . Since these reactions, according to the law of Einstein, only can proceed if photons are absorbed the absorption threshold for carbon monoxide which in the gas phase is at about 1600 Å has been shifted to longer wavelengths by the interaction with the surface. There is evidence from our previous experiments that the primary step in these photoreactions is the dissociation of CO.

Extending the pathway for chemical reactions by co-adsorption of other gases beside carbon monoxide leads to the formation of more complex compounds. In the case of carbon monoxide and methane formaldehyde has been found to be one of the major products. To ensure the formation at the surface and not in the desorbed gas we developed an absorption spectrometer in which the for-

mation can be followed *in situ*. Another advantage of the spectrometer is the capability of obtaining spectra of adsorbed molecules at coverages down to less than a monolayer. The experimental details have been described elsewhere [2].

To study the formation of formaldehyde CO and  $CH_4$  were adsorbed in equal amounts on a nickel film at 70 K. One half of the surface was irradiated by a Hg-resonance lamp and the spectrum of the photoproduct was measured as the difference in absorption between the irradiated and non-irradiated part of the surface. For identification this spectrum was compared to that of gaseous HCHO and to the spectrum of HCHO on LiF at 68 K. A very good correlation is obtained if the spectrum of the photoproduct is shifted to lower energies by  $\Delta\tilde{\nu} = 770 \text{ cm}^{-1}$ .

This bathochromic shift is explained in terms of an electric field perpendicular to the surface. The value for this field is estimated to be  $1.25 \times 10^7 \text{ V cm}^{-1}$ . In a model calculation the field strength above a surface of  $5 \times 5$  Ni-atoms is presented.

Making use of this surface field it seems to be possible to perform Stark-spectroscopy measurements on adsorbed molecules without applying an external electric field.

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### W9

#### The Condensed Phase Photochemistry of the Fluoroethylenes

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Recently, attention has been drawn to the use of the matrix-isolation technique in an effort to gain a better understanding of primary photophysical and photochemical processes [1 - 4]. In particular, the roles played by specific electronic states in the generation of specific reaction products. The application of condensed phase photolysis with monochromatic light sources has proven to be an extremely useful technique in characterizing the relative importance of atom