

$$R(\alpha) = R_0 \left\{ 1 + r \frac{[3\cos^2\alpha - (1+F+G-2FG)]}{(1+F)(1+G)} \right\}$$

where $R(\alpha)$ is the recorded signal, and R_0 is the signal that would be recorded for an equivalent but depolarized sample (i.e. $r = 0$) and thus is directly proportional to the total intensity emitted by the sample.

For a given α ; r , F , G , and R_0 can be obtained by placing polarizers in the excitation and emission beams and taking four orthogonal readings $R_V^V(\alpha)$, $R_V^H(\alpha)$, $R_H^V(\alpha)$ and $R_H^H(\alpha)$ where superscripts refer to the mode of the excitation polarizer and subscripts refer to the orientation of the emission polarizer. V refers to vertical and H to horizontal where the plane of the instrument is in the horizontal (see Ref. 1 for procedure).

If a measure of R_0 only is desired, it has been found that if a polarizer is placed in the emission beam at an angle of $54\frac{3}{4}^\circ$ ($\cos^{-1}\sqrt{1/3}$) from the vertical, and if the emission is viewed at 45° to the direction of propagation of the exciting light, the reading obtained is

$$R_{54.75(45^\circ)} = \frac{1}{3} R_0 \left(\frac{G+2}{G+1} \right)$$

Thus this reading is independent not only of the state of polarization of the exciting light (i.e. F) but also the degree of emission anisotropy r , and is also directly proportional to R_0 .

These equations have been verified experimentally with data obtained from a sample which has a high degree of emission anisotropy (Nile Blue A perchlorate in glycerol). A recently designed goniospectrofluorimeter was used and will be described.

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G4

Excited State Relaxation: Laser Pumped Fluorescence Studies

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We describe recent measurements of fluorescence with simultaneous wavelength

and time resolution of emission. The laser source is a mode-locked, cavity dumped dye laser pumped by an Ar^+ laser. The tunable visible light is converted to ultraviolet with non-linear optical crystals and the output pulse train consists of subnanosecond pulses separated by 200 ns or longer intervals. The method of time-correlated photon counting allows high sensitivity in studies of single vibronic (and even rovibronic) excitation of fluorescence, fluorescence quenching, and excited state vibrational relaxation. Results will be presented for a variety of molecules including ketones and aza-aromatics.

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G7

Energy Transfer From Single Vibronic Levels of Benzene ($^1B_{2u}$) and Fluorobenzene (1B_1)

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Electronic and vibrational energy transfer from specific vibronic levels of the first excited singlet states of benzene and fluorobenzene to a variety of acceptor molecules has been investigated. The excited states, prepared with a narrow band excitation source at low pressures (< 0.3 Torr), are monitored by both individual fluorescence transitions and total fluorescence from the donor molecule. The energy transfer from these states can be separated into effective collision cross sections for electronic (σ_e^2) and vibrational (σ_v^2) energy transfer.

Examination of quenching by molecules capable of both electronic and vibrational energy removal from vibronic states of benzene and those capable of only vibrational energy removal indicate that σ_v^2 is comparable for the series of molecules acetone, acetone- d_6 , isopropyl alcohol, methylether and propane. Further σ_v^2 is found to be linearly dependent on excess vibrational energy (ϵ_v) in the excited electronic state. As ϵ_v varies from 0 to 2300 cm^{-1} , σ_v^2 varies from 4 \AA^2 to 47 \AA^2 . Previous estimates [1] of σ_e^2 have been verified and indicate that

electronic energy transfer from benzene to acetone is only slightly dependent upon vibrational energy content and vibrational mode for the vibronic states studied ($0, 6^1, 6^{11}, 6^{12}$). The cross sections are approximately 50% of gas kinetic values.

In the case of fluorobenzene, energy transfer from the vibrationless state has been studied for a variety of carbonyl acceptor molecules. Both σ_e^2 and σ_v^2 values are larger than in the case of benzene, the former approaching hard-sphere gas kinetic values. For the series of molecules acetone, 2-pentanone, and 2-heptanone the electronic cross section increases from 21 \AA^2 to 41 \AA^2 while the vibrational cross section increases from 10 \AA^2 to 15 \AA^2 for the same series. The values observed for σ_e^2 imply that nearly all collisions are effective even though the change in molecular size is restricted to the aliphatic side chain. Based on previous studies [2] regarding singlet-singlet electronic energy transfer between benzene and carbonyl compounds, the present results are consistent with the notion that collisions occur over a sufficient time period that an encounter by the aromatic donor at the opposite end of the aliphatic chain from the carbonyl group may eventually result in energy transfer. This would presumably follow appropriate conformational changes which place the carbonyl moiety in close association to the aromatic ring. Results of these studies will be discussed in the light of previous work [2] which indicated that steric effects could be observed in singlet-singlet electronic energy transfer in the gas phase.

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G8

Phosphorescent Benzene: Triplet Sublevel Origins of Decays

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Theory predicts that the radiative emission from the lowest triplet state (phosphorescence) should originate almost entirely from the (nearly degenerate) upper pair of levels. However different kinds of experi-

ments yield rather disparate figures for the sublevel origin of the emission: ~70% from the upper pair from polarization of emission measurements [1, 2] and ~100% from microwave induced delayed phosphorescence results [3].

A third experiment, involving precise intensity and lifetime measurements over the 2 - 30 K range in various solvents has found, for example, a longer lifetime (by 1.8%) at 2.15 K, as compared to 4.13 K. Since spin lattice relaxation times are still short enough at these temperatures, we can confirm the ~100% figure for radiative decay. For the first time, the origin of the non-radiative decay has also been determined: it is similar to the radiative decay's origin.

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G10

Photophysics of Bound and Dissociative Guest Molecular States in Rare Gas Lattices

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Host rigid cage effects have been observed in the photodissociation of matrix isolated ICl and alkyl iodide molecules. In ICl, excitation as much as 6000 cm^{-1} above the $B O^+$ dissociation barrier produces vibrationally relaxed B fluorescence, with near unity quantum yield and a risetime $< 10 \text{ ns}$. A differential matrix shift between the B and C states produces five bound B vibrational levels in Ne and Ar lattices, while only four exist in the gas phase. Excitation spectra in the B dissociative region do not show possible vibrational structure due to constrictive cage forces. Excitation of alkyl and perfluoroalkyl iodides in their ultraviolet dissociative continua produces a near infrared (700 - 1100 nm) spectral progression in the ground state C-I stretching frequency. This fluorescence apparently originates from a bound state in which the alkyl radical and excited I ($^2P_{1/2}$) atom are held together by constrictive cage forces. Photoselection