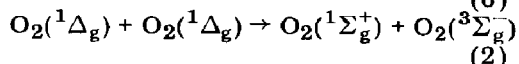
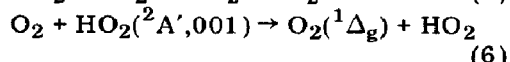
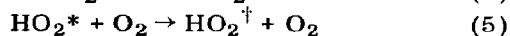
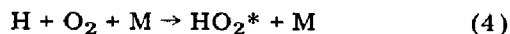


Energy transfer from $O_2(^1\Delta_g)$ to HO_2 has been reported previously [5]. We now present evidence for the reverse transfer. An H_2/Ar mixture was passed through a microwave discharge and O_2 added just upstream of an observation port. We observe emission bands at 762 nm and 1.265, 1.43, 1.51 μm . Replacement of H_2 by D_2 caused the 1.51 μm band to disappear, but all other bands were left unaffected. Thus the 762 nm band seems to be the $O_2(^1\Sigma_g^- \rightarrow ^3\Sigma_g^-)$ emission rather than the (possible) $9 \rightarrow 4$ vibrational transition in OH. The other bands are tentatively assigned to the following transitions: $\lambda = 1.265 \mu m$, $O_2(^1\Delta_g \rightarrow ^3\Sigma_g^-)$ and/or $HO_2(^2A', 001 \rightarrow ^2A'', 000)$; $\lambda = 1.43 \mu m$, $HO_2(^2A', 000 \rightarrow ^2A'', 000)$; $\lambda = 1.51 \mu m$, $HO_2(^2A'', 200 \rightarrow ^2A'', 000)$.

The most probable excitation mechanism is



where HO_2^* signifies some undefined excited state of HO_2 , and HO_2^\dagger denotes the emitting states ($^2A', 001$; $^2A', 000$; $^2A'', 200$). However, other excitation processes are not excluded, and further experiments are in progress to elucidate the mechanism.

More detailed information on the HO_2 system is published in Chem. Physics Letts., 32 (1975) 586; a description of the NO_2 system will appear in J. Chem. Soc. Faraday Trans.

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G1

High Resolution Lifetimes in Excited States

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We will discuss recent results with naphthalene showing the additional information which can be obtained with high resolution laser experiments. We have demonstrated that it is possible to obtain lifetimes of isolated vibronic states at pressures below 1 Torr with a resolution in the picometer range. For this purpose a tunable high resolution laser is doubled into the U.V. It is shown that a single shot suffices for the entire decay curve hence obviating averaging techniques for these experiments. Isotope effects at high resolution will also be discussed. It will be shown that it is now also possible to populate isolated states in the low pressure limit by two-photon absorption. This allows new states to be reached which have hitherto not even been assigned.

G3

Polarization Effects on Fluorescence Measurements

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Polarization effects on fluorescence measurements are a function of four independent variables, The first is $F \equiv S^V/S^H$, the polarization ratio of the exciting light flux S which reaches the sample. The second is r , the emission anisotropy of the sample, which is the polarization "response" of the sample to plane polarized exciting light. The third is $G \equiv T_V/T_H$, the emission detection system, which is the ratio of the sensitivities of the emission detection system to vertically and horizontally polarized light. The fourth is α , the viewing angle, which is the angle between the direction of the propagation of the exciting light and the direction from which the emission is being detected.

The equation which defines the overall relative error which can be obtained due to polarization effects is

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

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 $R_V^V(\alpha)$, $R_V^H(\alpha)$, $R_H^H(\alpha)$ and $R_H^V(\alpha)$ 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.

This work has benefited from support of the Petroleum Research Fund, the Research Corporation, the National Science Foundation and The Alfred P. Sloan Foundation.

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