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 H₂/Ar mixture was passed through a microwave discharge and O₂ added just upstream of an observation port. We observe emission bands at 762 nm and 1.265, 1.43, 1.51 μ m. Replacement of H₂ by D₂ caused the 1.51 μ m band to disappear, but all other bands were left unaffected. Thus the 762 nm band seems to be the O₂(${}^1\Sigma_g \rightarrow {}^3\Sigma_g$) 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, O₂(${}^1\Delta_g \rightarrow {}^3\Sigma_g^-$) and/ or HO₂(${}^2A', 001 \rightarrow {}^2A'', 000$); $\lambda = 1.43 \mu$ m, HO₂(${}^2A', 000 \rightarrow {}^2A'', 000$).

The most probable excitation mechanism is

$$\begin{array}{l} H + O_2 + M \rightarrow HO_2^* + M \qquad (4) \\ HO_2^* + O_2 \rightarrow HO_2^\dagger + O_2 \qquad (5) \\ O_2 + HO_2(^2A',001) \rightarrow O_2(^1\Delta_g) + HO_2 \\ O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) \\ (2) \end{array}$$

where HO₂* signifies some undefined excited state of HO₂, and HO₂[†] denotes the emitting states (${}^{2}A',001$; ${}^{2}A',000$; ${}^{2}A'',200$). 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 E. W. SCHLAG

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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 $F = S^V/S^H$, 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 responsivities 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