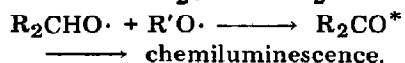
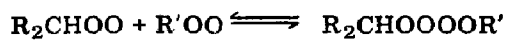


oxidation processes [2, 3] arises from a relatively efficient production of excited states from alkoxy radical disproportionations. Such alkoxy radicals can arise in low concentrations from non-Russell termination pathways of dialkyl tetroxides:



- 1 S. K. Ho and J. B. DeSousa, *J. Chem. Soc.*, 1788 (1961).
- 2 R. F. Vasil'ev, *Progress in Reaction Kinetics*, 4 (1967) 305 and references therein.
- 3 G. Lundeen and R. L. Livingston, *Photochem. Photobiol.*, 4 (1965) 1085.

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#### Major Emitting Species in Phosphorus Chemiluminescence

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The phosphorescence of phosphorus oxidation is the oldest and the best known chemiluminescing reaction, but a definitive spectroscopic study of this classic system has been lacking. In this talk we report the results of an investigation of the oxidation of  $P_4$  vapor under atmospheric conditions, with added  $H_2O$  or  $D_2O$  vapor. The visible and ultraviolet spectrum of the reaction consists of discrete band structure in the 228.8 - 272.1 nm region and a broad continuum onseting at 335 nm and extending to 800 nm and longer, upon which are superimposed a number of weak bands from 450 - 650 nm. Discrete band emissions at 228.8 - 272.1 nm belong to the  $PO \gamma$ -system transitions,  $PO(A^2\Sigma^+) \rightarrow PO(X^2\Pi)$ . Spectral changes arising from the substitution of  $D_2O$  vapor for  $H_2O$  vapor in the reaction led to the assignment of the weak bands at 450 - 650 nm to  $HPO$  (or  $DPO$ ),  $\tilde{A}(^1A'') \rightarrow \tilde{X}(^1A)$ . The main band emission in the visible region, the broad continuum which cannot be identified with any simple electronic transition, exhibits the kinetic and spectral characteristics of an excimer.

In this case the excimer is  $(PO^* \dots PO)$  and the equilibrium reaction for its formation is  $(PO^* \dots PO) \rightleftharpoons PO(^4\Pi) + PO(B^2\Pi) \rightleftharpoons PO(B^2\Sigma^+) + PO(X^2\Pi)$ . The existence of the  $(PO)_2$  excimer has been confirmed by affecting the dynamic of this equilibrium through dilution with nitrogen gas and through thermal dissociation of the excimer, resulting in the appearance of the formerly quenched (0,0) transition of the  $PO \beta$ -emission in the spectrum. Our investigation has eliminated the possibility that the visible continuum arises from either  $PO_2$  or  $HPO$ . Enough information has been extracted from temperature dependent studies to construct the approximate shapes of the potential energy surfaces of the ground ( $\Delta\bar{\nu}_g = 35 \pm 200 \text{ cm}^{-1}$ ) and the first excited states ( $\Delta\bar{\nu}_{ex} = 846 \pm 200 \text{ cm}^{-1}$ ) of the  $(PO)_2^*$  excimer.

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#### The Quantum Yield of Fluorescence of Quinine Bisulphate, Azulene and 9,10-Diphenylanthracene

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The quantum yield of fluorescence of quinine bisulphate (in 1N  $H_2SO_4$ ) has been determined by an absolute method involving the rise in temperature of a solution due to light energy absorbed but not emitted as luminescence. Quinine bisulphate (in 1N  $H_2SO_4$ ) and potassium chromate (in 0.05M KOH) were compared. A measured quantity of electrical energy ( $E_q$  and  $E_k$ , respectively) was put into the systems so that the heating (and cooling) curves were made to coincide. A 366 nm interference filter (100 Å band pass and blocking to infinity) was utilized in connection with a 500 W high-pressure mercury arc. Temperature changes were monitored with a potted glass-bead thermistor in conjunction with a Jones impedance bridge, operating in the A.C. mode, and a lock-in amplifier at 4000 Hz (100  $\mu V$  sensitivity and 300 ms time constant). At 25.00 °C the temperature coefficient was 760  $\Omega \text{ deg}^{-1}$  while solution temperature fluctuations were about 0.10  $\Omega$ , and total changes over a 500 s experiment were about 100  $\Omega$ .

Heater coils were of platinum and gold. The yield,  $\Phi_f$ , is given as

$$\Phi_f = \left( \frac{\bar{I}}{\lambda} \right) \frac{\int (dQ/d\lambda) d\lambda}{hc \int (dQ/d\lambda) d\ln\lambda} \cdot \left( 1 - \frac{E_Q}{E_K} \right)$$

where  $(dQ/d\lambda) = \text{quanta s}^{-1} \text{ nm}^{-1}$  emitted at  $\lambda$ . After correction for self-absorption, the result is  $\Phi_f = 0.561 \pm 0.039$ .

The quantum yield of fluorescence of azulene (in degassed cyclohexane) irradiated at 283 nm (100 Å band pass) was determined by comparison with quinine bisulphate. Our result is  $\Phi_f = 0.024$  for  $S_2 \leftarrow S_0$  emission. Similarly, our measured value of  $\Phi_f$  for 9,10-diphenylanthracene (in degassed cyclohexane) irradiated at 365 nm, is 0.84 at 25 °C.

## η2

### Two-Photon Doppler Free Spectroscopy of Gas Phase Molecules

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Diffuseness in the gas phase electronic spectra of complex molecules caused by the Doppler effect has been a significant limitation to investigation of the excited state. This paper describes application of the technique of counter-propagating beam two-photon absorption [1] to molecular electronic spectroscopy. Doppler free spectra have been obtained for the nitric oxide  $(A)^2\Sigma^+(v=0) \leftarrow (X)^2\Pi_{3/2}(v=0)$  transition. The measured linewidth of 250 MHz. ( $8 \times 10^{-3} \text{ cm}^{-1}$ ) at 3 Torr was instrument limited and represented about one-tenth the Doppler width.

The ungerade vibrational levels of the benzene  $^1B_{2u}$  state are being investigated at ultra-high resolution to evaluate the possibility of direct spectral manifestations of the interactions responsible for non-radiative decay in the isolated molecule. The data will also serve to evaluate the selectivity of the method for photoexcitation of single rovibronic levels in a complex spectrum. It will establish the ability to detect and identify large molecules in the gas phase and to characterize the state of vibrational and rotational excitation.

Experiments are being conducted which will test the effects of excitation coherence on radiative and radiationless decay of excited states. They rely on the ability to excite isolated molecule compound states with light of bandwidth comparable to the spectral width of the states, and to measure absorption spectra with a resolution commensurate with the product state decay time.

These experiments have been accomplished using an excitation source that combines a dye laser oscillator of the Hansch configuration [2] with an external Fabry-Perot interferometer that is piezoelectrically scanned. Output of this system is amplified and then passed through focus in a sample cell and on to a spherical mirror which returns the beam to focus in coincidence with the incoming beam. Absorption is detected by measurement of ultra-violet luminescence using a solar blind photomultiplier.

- 1 L. S. Vaslenko, V. P. Chebotaev, A. V. Shishaev, JETP Letters, 12 (1970) 113.
- 2 T. W. Hansch, Appl. Opt., 11 (1972) 898.