PHOTOACOUSTIC DETERMINATION OF THE NON-RADIATIVE QUANTUM EFFICIENCY OF URANYL FORMATE MONOHYDRATE, $UO_2(HCOO)_2 \cdot H_2O$, POWDERS

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The non-radiative quantum efficiency for the $S_1^0 \rightarrow S_0^0$ transition in the uranyl formate monohydrate system was estimated from comparison between optical absorption and photoacoustic data obtained from powders of this material, by means of an extension of a method introduced by Rockley and Waugh

1. Introduction

For all materials, optical excitation leads to one or more of the following three deexcitation options [1]. (i) radiative decay accompanied by the emission of a luminescence (fluorescence or phosphorescence) photon, (ii) production of new chemical species via photochemistry, possibly accompanied by the absorption or release of heat, and (iii) non-radiative deexcitation with full conversion of the absorbed energy into heat.

Since these processes compete with one another to the extent of their relative quantum efficiencies $\eta(i)$, energy conservation considerations impose the general relation

$$\sum_i \eta(i) = 1. \tag{1}$$

This can be written explicitly as:

$$\eta(h\nu) + \eta(\text{photochem}) + \eta(\text{non-rad}) = 1, \tag{2}$$

where $\eta(h\nu)$, $\eta(\text{photochem})$, and $\eta(\text{non-rad})$ are the quantum efficiencies for luminescence, photochemistry and non-radiative transitions, respectively. In the general case where all the above processes are present during deexcitation of a physical system, the observed excited state lifetime can be defined as [2].

$$\tau = \left[\sum_i k(i) \right]^{-1}, \tag{3}$$

where τ is the relaxation time required for a given excited state population to decay to the $1/e$ of its original

value and $k(i)$ denotes the deexcitation rate via process (i). Since the lifetime $\tau(i)$ associated with deexcitation process (i) is given by

$$\tau(i) = k(i)^{-1}, \tag{4}$$

eqs. (3) and (4) may be combined to give

$$\tau^{-1} = \sum_i \tau(i)^{-1}. \tag{5}$$

It can be shown further that [2]

$$\eta(i) = \tau/\tau(i). \tag{6}$$

Measurements of the excited state population depletion rate will provide a decay curve with a time constant equal to the total relaxation time τ. The magnitude of the time-dependent decay curve is proportional to the quantum efficiency of the monitored process [3].

The photoacoustic (PAS) signal depends linearly on the quantum efficiency of non-radiative deexcitations [4]. For solids which do not exhibit luminescence or photochemistry at room temperature this efficiency is usually taken to be 100% [4,5]. In this case the non-radiative process is assumed to be instantaneous and eqs (5) and (6) give.

$$\tau = \tau(\text{non-rad}) \tag{7a}$$

and

$$\eta(\text{non-rad}) = 1. \tag{7b}$$

From this simple situation it can be seen that an accurate independent measurement of the non-radiative

lifetime τ(non-rad) associated with a physical system is possible only in the limit where τ(non-rad) is the shortest characteristic time involved in the deexcitation process. When other competing deexcitation processes are present, the PAS signal will depend on the total excited state lifetime τ which will affect both the amplitude and the phase shift [6]

If photochemical reactions are involved, the amplitude of the photoacoustic signal will also depend on the quantum efficiency η(photochem), as such reactions may contribute to the heating rate of the material either by adding heat (exothermic), or by using up heat to catalyze the reaction (endothermic) For example, the gas-phase endothermic dissociation of NO_2 at 3979 Å and below [1] exhibits a sharp drop in the PAS signal strength at this wavelength not observed in the optical spectrum

The uranyl formate monohydrate system is of interest, because it exhibits radiative and non-radiative deexcitation processes, as well as photochemistry [7]. Furthermore, it is a material for which high photochemical quantum yields have been estimated [8,9] without taking into account the non-radiative deexcitation processes. Photoacoustic data presented in this work suggest that this decay path is significant

2. Experimental [‡]. photoacoustic spectroscopy of $UO_2(HCOO)_2 \cdot H_2O$ powders

Fig 1 shows the excited-state manifold of the uranyl formate monohydrate, $UO_2(HCOO)_2 \cdot H_2O$ system [7] including the various proposed deexcitation processes (Jablonsky diagram). The system is excited upon absorption (A) of a photon of incident radiation to the level S_n^v. Subsequently, it is shown to deexcite in a multichannel manner: (i) radiatively (fluorescence (F) and phosphorescence (P)); (ii) non-radiatively (internal conversion (IC), vibrational relaxation (VR), intersystem conversion (ISC) and energy transfer (ET)), and (iii) photochemically (PC). The complexity of the deexcitation process $S_n^v \rightarrow S_0^0$ in $UO_2(HCOO)_2 \cdot H_2O$ is characteristic of many condensed-phase systems [10]. The consideration of the kinetics of the complete excited-state manifold is complicated. Previous investiga-
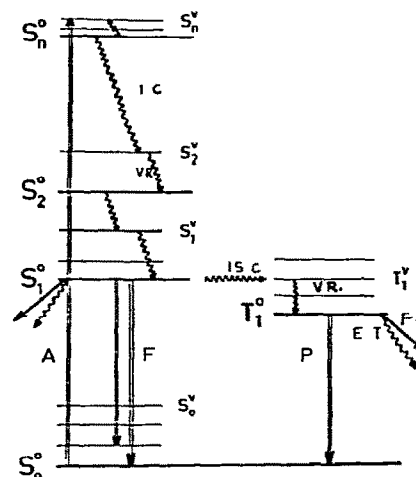
Fig 1 Jablonsky diagram of uranyl formate monohydrate, $UO_2(HCOO)_2 \cdot H_2O$. A optical absorption, I C.· internal conversion, I S.C.. intersystem conversion, F fluorescence, P: phosphorescence, V.R vibrational relaxation, E.T.. energy transfer, $\Rightarrow$· radiative transitions, $\leadsto$· non-radiative transitions, $\rightarrow$ photochemical processes (from ref [7]).

tion has indicated that the photoexcited uranyl ion rapidly loses its energy through internal conversion processes, until it arrives at the S_1^0 excited electronic state, whose lifetime is on the order of 10^{-4} s at 298 K [8].

Fig. 2 shows the photoacoustic amplitude spectrum obtained from a powdered specimen of $UO_2(HCOO)_2$ H_2O using a 1000 W xenon lamp and an Instruments S.A. H 20 holographic $1/4, f/4.2$ monochromator with a 2 nm resolution. These results show that this fluorescent material has a strong photoacoustic response at room temperature and is, therefore, a good candidate for non-radiative quantum efficiency measurements. The PAS spectrum in fig 2 is compared to an optical absorption spectrum [11] measured using an opalized silicon mull technique.

Any photoacoustic measurements on the uranyl formate monohydrate system are expected to be complicated by the change in the spectral features of the system due to the presence of the photodecomposition products. These can be produced by radiation of wavelength below 490 nm which corresponds to the energy required for the transition leading to the first electronically excited state, as determined by fluorescence [12] and by absorption [13] studies. Fig. 3 shows a series of

SIGNAL
(ARBITRARY UNITS)

——— Optical Absorption (Silicon mull)

—— PAS Amplitude

350   400   450   500

WAVELENGTH (nm)
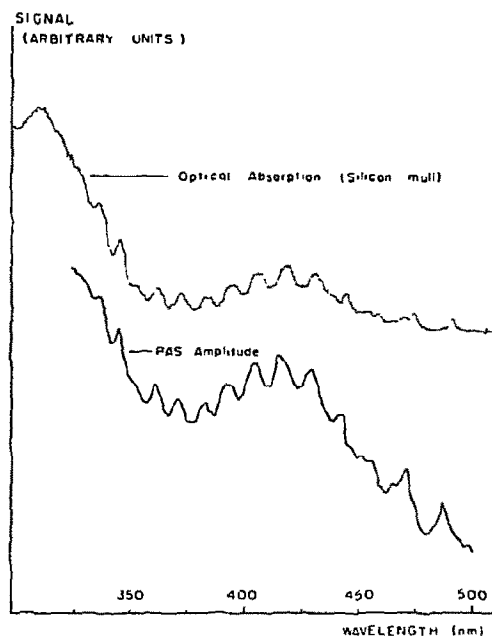
◄ Fig 2. Optical absorption spectrum (Courtesy D McClure) and photoacoustic spectrum of uranyl formate monohydrate, $UO_2(HCOO)_2 \cdot H_2O$ Modulation frequency 50 Hz, resolution 2 nm (for PAS spectrum).

PAS spectra of the $UO_2(HCOO)_2$ H_2O, normalized by the black absorber spectrum These spectra were taken by scanning the wavelength of the incident light from 700 nm down to 250 nm. The data shown in fig 3 are the result of smoothing out the experimental data using a smoothing technique [14] in order to reduce the effect of random errors and improve the signal-to-noise ratio According to this technique each of the data points F_i was replaced by. $F_i = (F_{i-1} + F_i + F_{i+1})/3$ Spectrum 1 was taken on a previously unirradiated sample and is similar to that shown in fig 2 Spectra 2–5 were taken after irradiation at 468 nm for times equal to 30 min, 1 h, 2.5 h and 10 h respectively. Two new bands at ≈650 and 550 nm are seen to have grown during these irradiations while the individual absorption bands between 300 and 500 nm characteristic of the uranyl group have disappeared.
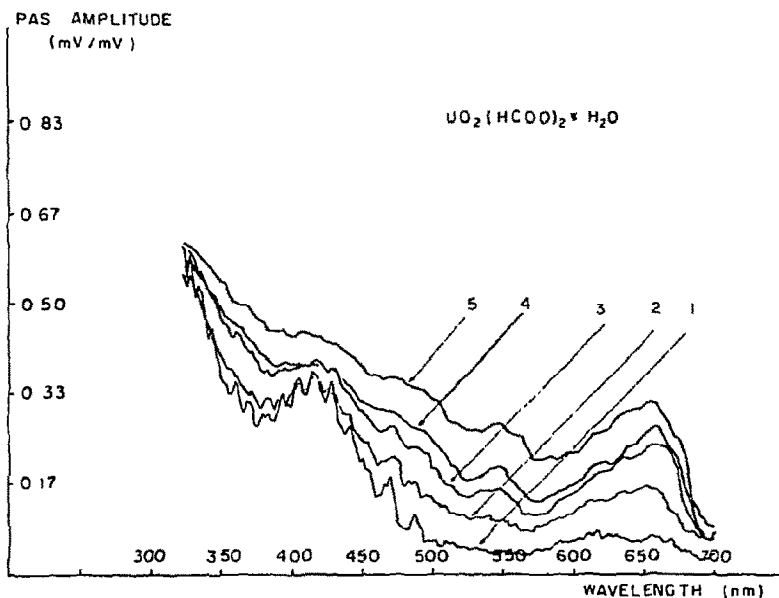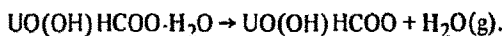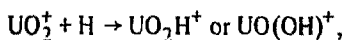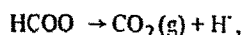
PAS AMPLITUDE
(mV / mV)

0 83

0 67

0 50

0 33

0 17

$UO_2(HCOO)_2 \cdot H_2O$

5   4   3   2   1
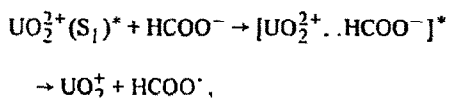
300   350   400   450   500   550   600   650   700

WAVELENGTH (nm)
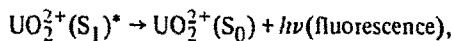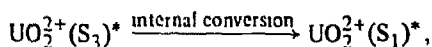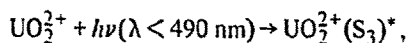
Fig. 3. Smoothed-out photoacoustic spectra of $UO_2(HCOO)_2 \cdot H_2O$. (1) unirradiated powder, (2)–(5) irradiated at 468 nm for 30 min (2), 1 h (3); 2 5 h (4); and 10 h (5) Modulation frequency 50 Hz, resolution 2 nm. Filtering time-constant of lock-in amplifier 1 s.

3. Analysis and discussion

The fluorescent quantum efficiency at 298 K has been found to be independent of the wavelength of the exciting radiation below 500 nm, and equal to 4.5×10^{-4} [8]. The overall photodecomposition reaction involves a change in the valence state of the uranium ion from U^{VI} in the monohydrate to U^{IV} in the photodecomposition product, $UO(OH)HCOO$. The decomposition reaction takes place in two stages, one of which is directly associated with the absorption of photons and the other a dark reaction. The reaction steps suggested by Sautereau [7] are.

$$UO_2^{2+} + h\nu(\lambda < 490 \text{ nm}) \rightarrow UO_2^{2+}(S_3)^*,$$

$$UO_2^{2+}(S_3)^* \xrightarrow{\text{internal conversion}} UO_2^{2+}(S_1)^*,$$

$$UO_2^{2+}(S_1)^* \rightarrow UO_2^{2+}(S_0) + h\nu(\text{fluorescence}),$$

$$UO_2^{2+}(S_1)^* + HCOO^- \rightarrow [UO_2^{2+}..HCOO^-]^*$$

$$\rightarrow UO_2^+ + HCOO^\cdot,$$

$$HCOO \rightarrow CO_2(g) + H^\cdot,$$

$$UO_2^+ + H \rightarrow UO_2H^+ \text{ or } UO(OH)^+,$$

$$UO(OH)HCOO \cdot H_2O \rightarrow UO(OH)HCOO + H_2O(g).$$

Uranium(V) appears as an intermediate product of the photodecomposition with an estimated quantum efficiency 0.83 ± 0.13 [8], or 0.96 ± 0.09 [9]. In the above quantum efficiency calculations no account was taken of the non-radiative deexcitation processes that are possible from the S_1^0 excited electronic state. The strength of the photoacoustic signal below 490 nm, fig 1, indicates that a non-zero non-radiative quantum efficiency is associated with the $S_1^0 \rightarrow S_0^0$ transition.

A rough estimate of the non-radiative quantum efficiency, $\eta(\text{non-rad})$ of the $S_1^0 \rightarrow S_0^0$ transition in the uranyl formate monohydrate system may be given by an extension of the method presented by Rockley and Waugh [15]. These authors used the $S_n \rightarrow S_1$ transition probability as an internal standard for comparison with the $S_1 \rightarrow S_0$ radiationless transition probability, both probabilities being measured by photoacoustic spectroscopy. Assuming a rapid non-radiative decay of the S_n^0 level of $UO_2(HCOO)_2 \cdot H_2O$ to the lowest excited

state, S_1^0, with an efficiency close to 100% [7], for every photon of energy $E(S_n^0)$ the fraction of the energy corresponding to $[E(S_n^0) - E(S_1^0)]/E(S_n^0)$ will immediately appear as heat coming from the sample. The measured PAS signal is proportional to the total heat emitted by the sample. If the proportionality constant is k, then the PAS signal, p_n, from excitation into S_n and S_m states, respectively, can be described by the equations.

$$p_n = k\{E(S_n) - E(S_1)$$

$$+ E(S_1)[1 - \eta(h\nu) - \eta(\text{photochem})]\} \qquad (8)$$

and

$$p_m = k\{E(S_m) - E(S_1)$$

$$+ E(S_1)[1 - \eta(h\nu) - \eta(\text{photochem})]\}, \qquad (9)$$

where eq (2) was used. Defining $H \equiv \eta(h\nu) + \eta(\text{photochem})$ and dividing eq. (8) by eq. (9) gives:

$$p_n/p_m = [E(S_n) - HE(S_1)]/[E(S_m) - HE(S_1)]. \qquad (10)$$

Eq. (10) can be written as

$$p_n/p_m = [E(S_n) - E(S_1)H]/[\alpha E(S_n) - E(S_1)H](11)$$

where $\alpha \equiv E(S_m)/E(S_n)$. Eq. (11) gives

$$H = (R\alpha - 1)/\gamma(R - 1), \qquad (12)$$

where $R \equiv p_n/p_m$ and $\gamma \equiv E(S_1)/E(S_n)$. The optical absorption spectrum of $UO_2(HCOO)_2 \cdot H_2O$ in fig. 2 shows that at two wavelengths, 374 and 444 nm, the sample has equal optical densities. Therefore, the same fraction of incident photons is absorbed at each wavelength. At the same wavelengths the normalized PAS signal intensities give. $R = p_{374}/p_{444} = 1.34$ and $\alpha = E(S_{444})/E(S_{374}) = 0.84$. The first excited state is at 492.5 nm according to Sautereau [7], so that $\gamma = E(S_{492.5})/E(S_{374}) = 0.76$. Using these values in eq. (12), it is seen that:

$$H = 0.52.$$

This result indicates that the quantum efficiency for the $S_1^0 \rightarrow S_0^0$ non-radiative transition is ≈ 0.48. No previous estimates of $\eta(\text{non-rad})$ for $UO_2(HCOO)_2 \cdot H_2O$ have appeared in the literature, however, the high value found here is consistent with the strong photoacoustic signal observed from this material. Assuming that the lifetime of the S_1 excited electronic state is on the or-

der of 10^{-4} s at 298 K [8], eq. (6) gives:

$$\tau_{S_1^0 \to S_0^0} \text{ (non-rad)} \approx 2 \times 10^{-4} \text{ s.}$$

The bands centered around 550 nm and 650 nm, which grow after irradiation of $UO_2(HCOO)_2$ H_2O below 500 nm, have been identified by Heidt and Moon [16] as due to the presence of U^{IV} as a photolysis product. Fig. 3 shows that the individual absorption bands below 495 nm associated with the uranyl complex disappear gradually after repeated irradiations This, however, is not the case with optical transmission data [11]. The different behavior under the PAS probe may be associated with an increasing thickness of a photoproduct surface layer with total irradiation time. At these wavelengths the photoproducts may absorb light differently from the unreacted material, whose frequency domain PAS signal, attenuates exponentially with increasing thickness of the protoproduct overlayer [6]. This photoproduct growth would result in depletion of the spectral features of the substrate from the PAS spectrum for overlayer thicknesses larger than a few thermal diffusion lengths and would be accompanied by enhancement of the spectral characteristics of the photoproduct layer.

Acknowledgement

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