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A Photoacoustic and Fluorescent Spectroscopic Study of Uranyl Compounds

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Synopsis. The fluorescent emission spectra and fluorescent lifetimes have been measured for several available uranyl salts and natural mineral zippeite. The absolute quantum efficiency data of $UO_2SO_4 \cdot 0.5H_2O$, $H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$, and $UO_2(CH_3COO)_2 \cdot 2H_2O$ have been obtained by the simultaneous measurement of the photoacoustic and excitation spectra.

The simultaneous measurement of the intensities of the photoacoustic and fluorescent excitation signals as a function of the wavelength of the exciting light enables the determination of the absolute quantum efficiencies of fluorescence without any use of reference materials.[1] The technique was successfully applied to a series of uranyl micas: uranyl phosphate of alkali, alkaline-earth, and some other bivalent metal ions. In the present work, the simultaneous measurement of some uranyl compounds have been carried out, together with the measurement of the emission spectra and the luminescence lifetimes.

Experimental

Samples. The uranyl compounds used in the present study were all prepared according to the literature[2–5] except for a natural mineral zippeite, $3UO_2 \cdot 2SO_3 \cdot 9H_2O$.

Measurement. The fluorescent emissions were measured by means of a multi-purpose spectrometer, JASCO SS-25, using an UV light of 365 nm as the excitation source. The photoacoustic spectra and fluorescent excitation spectra were measured by means of a system, which was readily arranged by the use of the spectrometer CT-25N, a lock-in amplifier, and a sample cell designed for the simultaneous detection of photoacoustic and excitation signals.[1] The intensity of the fluorescent excitation signal was monitored at the output slit of the spectrometer adjusted at 520 ± 5 nm. A 300 w xenon lamp was used as the excitation source. The fluorescent lifetimes were measured by the multi-channel photon counting method using a microcomputer-assisted apparatus made in our laboratory, the details of the procedure will be described elsewhere.[6] All of the measurements were conducted at room temperature.

Results and Discussion

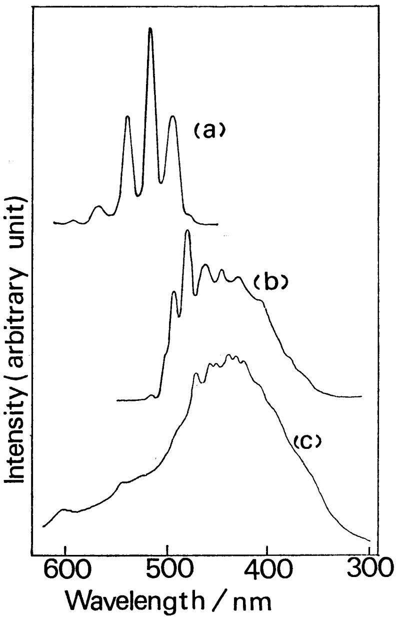

Fig. 1. Spectra of $UO_2(CH_3COO)_2 \cdot 2H_2O$.
(a) Fluorescent emission spectra, (b) fluorescent excitation spectra, (c) photoacoustic spectra (chopping frequency 80 Hz).

Figure 1 shows the fluorescent emission(a), fluorescent excitation(b), and photoacoustic(c) spectra of the powdered sample of uranyl acetate, $UO_2(CH_3COO)_2 \cdot 2H_2O$. The three kinds of spectra for the other uranyl compounds studied are very similar to those shown in Fig. 1, except for minor differences in peak positions and/or their relative intensities. Generally, the emission and excitation spectra of uranyl compounds have six and twelve peaks respectively, which can be explained as the transitions between $^1\Sigma_g^+$ and $^3\Pi_u$ states, the both split into sublevels by the symmetric stretching of the UO_2 species.[7] It should be noted that the photoacoustic spectra are very similar to the excitation spectra except for a somewhat better resolution in the latter spectra, just as was the case with the uranium-mica samples. The similarity between the two spectra shows that a definite proportional amount of the energy absorbed at a certain wavelength, λ, will always be emitted as optical energy(excitation spectra), while the remaining part of the absorbed energy will be emitted as thermal energy(photoacoustic spectra). This suggests that the de-excitation processes from the twelve excited sublevels of $^3\Pi_u$ are affected by the same transition mechanism. This seems to be closely related to the fact that the six emission peaks of $Mg(UO_2)_2(PO_4)_2 \cdot nH_2O$ have the same fluorescent lifetime.[8]

The fluorescent lifetimes and quantum efficiencies of the prepared samples are given in Table 1. The lifetimes have the same order of magnitude as those of uranium-micas reported before.[8] The mineral zippeite, $3UO_2 \cdot 2SO_3 \cdot 9H_2O$, has a lifetime by an order shorter, probably because of the trace amount of impurities.

Quantum efficiency data have been obtained for the three samples through the method of the simultaneous measurement of the photoacoustic and excitation spectra, details of which have already been reported.[1] The quantum efficiency determinations for the other compounds were not successful. There is no apparent correlation between the lifetime and the

Table 1. Fluorescent lifetime, τ; quantum efficiency, Q_f; fluorescent transition probability constant, k_f, and emission band positions, ν's, of the uranyl compounds

Samples	$\tau/10^{-4}$ s	$Q_f/\%$	$k_f \times 10^3$	ν_1[a)]	ν_2	ν_3	ν_4	ν_5	ν_6
$UO_2(NO_3)_2 \cdot 6H_2O$	7.0	—	—	474	490	512	534	560	587
$UO_2C_2O_4 \cdot 3H_2O$	3.0	—	—	476	492	512	535	561	589
$UO_2SO_4 \cdot 0.5H_2O$	3.1	77	2.5	475	491	512	535	560	588
$H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$	4.4	85	1.9	487	503	524	548	574	602
$UO_2(CH_3COO)_2 \cdot 2H_2O$	1.8	89	4.9	474	490	511	534	560	588
$UO_2(ClO_4)_2 \cdot 5H_2O$	2.5	—	—	472	488	510	533	558	586
$RbUO_2(NO_3)_3$	5.0	—	—	483	502	520 523	546	574	
$3UO_2 \cdot 2SO_3 \cdot 9H_2O$[b)] (zippeite)	0.27	—	—			—			
UO_2CO_3[c)]		—	—			—			

a) ν_1 to ν_6 correspond to the six emission bands, after Bell and Biggers.[7)] b) The emission spectrum is single and broad. c) Non-fluorescent.

quantum efficiency data. However, the fluorescent transition velocity constant, k_f, which is obtained as Q_f/τ, is correlated with the lifetime value, τ, in the sense that the larger k_f value corresponds to the smaller τ value, as may be seen in Table 1.

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