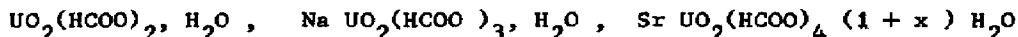


COMPARED PHOTOLUMINESCENCE AND PHOTOCHEMICAL PROPERTIES OF SOME URANYL  
FORMATES IN THE SOLID STATE

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Photochemistry of uranyl formate in the solid state has been extensively investigated in our laboratory (1). The purpose of this communication is to study the effect, on the photoluminescence and photochemical properties, of the introduction in the structure of an alkaline or alkaline-earth ion. It concerns three compounds :



the structures of which have been previously determined (2,3,4).

As for the uranyl formate, the photolysis of the two new compounds yields  $\text{U}^{+5}$  as the first intermediate and  $\text{U}^{+4}$ . Simultaneously, the formate ion evolves to  $\text{CO}_2$ .  $\text{H}_2\text{O}$  has been also detected by I.R. spectroscopy and mass spectrometry. The modifications under irradiation of the reflectance and I.R. spectra are presented.

The luminescence spectra of the uranyl ions at 298 K have been determined in the three cases. Their intensities decrease under irradiation, owing to the reduction of the uranyl ion into the non-luminescent state  $\text{U}^{+5}$ . We have shown in a laser experiment that the first excited state of uranyl ion is responsible for both luminescence and photochemistry.

The three different fluorescence quantum yields have been determined and compared. The amounts of  $\text{U}^{+5}$  and  $\text{U}^{+4}$  formed have been measured at different irradiation times. It appears that the former are so small (of the order of  $10^{-3}$ ) that they do not influence the magnitude of the latter

quantum yields . A tentative interpretation of the different rates of  $U^{+5}$  formation for the three compounds is proposed on the basis of crystal structures and electronic processes .

However, the amounts of  $U^{+4}$  formed after longer times are in the reverse order with respect to the amounts of  $U^{+5}$  formed in the initial period . This unexpected effect will be discussed .

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