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## Optical properties of ammonium uranyl fluoride characterized by photoluminescence and photoacoustic spectroscopy



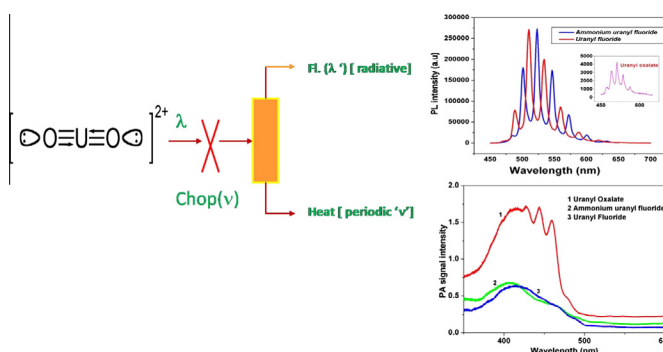
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### HIGHLIGHTS

- PL and PAS spectrum of ammonium uranyl fluoride is being reported for the first time.
- PL lifetime data indicates the presence of two different uranyl environments.
- At 77 K enhancement in PL intensity and lifetime value is observed.
- $E_{act}$  at which  $^3\Pi$  and  $^1\Sigma$  potential surfaces will cross is calculated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

PL and PAS studies were performed on uranyl compounds viz. uranium oxalate, uranium fluoride and ammonium uranyl fluoride. PL and PAS spectrum of ammonium uranyl fluoride is being reported for the first time. Ammonium uranyl fluoride is blue shifted with respect to uranyl fluoride, as a result of ammonium bonding. The vibronic separations were determined in the excited state and the ground state using excitation/PAS spectra and emission spectra respectively. Fluorescence decay data could be fitted only with biexponential decay in all of these compounds indicating the presence of two different environments in these compounds. Low temperature luminescence leads to enhancement in emission intensity and lifetime value. The temperature dependence studies of average fluorescence lifetimes of ammonium uranyl are described in this paper. Based on this studies activation energy value for ammonium uranyl fluoride at which  $^3\Pi$  and  $^1\Sigma$  potential surfaces will cross is calculated.

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### Introduction

Complexes of uranium in which the metal exhibits different oxidation states (III–VI) are still of great interest. One of the reasons for this is the special role of uranium as a source of nuclear energy. Therefore, its use as a fissionable element has considerably changed the amount and scope of research on uranium complexes. Spectroscopic investigations until now have addressed mainly complexes of U(VI), which is the most common oxygenated form

i.e.  $UO_2^{2+}$ , called uranyl and retains its identity in most chemical reactions. A peculiarity of uranyl ion is the inclusion of three atoms (2 atoms of oxygen and 1 atom of uranium). Therefore, it can easily be observed by spectroscopy using its characteristic intra-molecular vibrations (two stretching ( $\nu_1$  and  $\nu_3$ ) and one doubly degenerate bending ( $\nu_2$ )). These vibrations are unique markers for the presence of uranyl ion in one compound or another. The main source of information on the uranyl complexes, including solid crystalline phases, can be gathered using electronic and vibrational spectroscopy. A change of electronic and vibrational spectra of crystals under the influence of external forces or a splitting of the spectral lines provides a variety of information on the

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dynamics of electronic photo-processes occurring in the crystals and solution complexes.

The 5f electrons in actinides and relatively more close-lying  $5f^{n-1}6d$  configurations are more strongly affected by a crystal field [1,2] than the corresponding state of lanthanides. Whenever the states arising from these configurations are excited, the relaxation is predominantly through non-radiative processes. This makes the actinide solids attractive candidates for photoacoustic spectral investigations. Luminescence spectra of uranyl compounds at room temperature typically have bands located in the visible region. As the temperature is lowered, the spectra acquire a quasi-line nature that allows the nature and symmetry of the  $UO_2^{2+}$  environment and the various manifestations of intermolecular and exciton-phonon interactions in the crystals to be analyzed. Uranyl salts are known to exhibit distinctive spectral characteristics that have been attributed to effect of ligand. In solutions the effect of solvent media and metal to ligand ratio on luminescence of uranyl compounds are also reported. In general, uranyl compounds exhibit their absorption/excitation spectra in 345–500 nm ( $29,000$ – $20,000\text{ cm}^{-1}$ ) regions while emission is observed in 450–600 nm ( $22,200$ – $16,700\text{ cm}^{-1}$ ) spectral regions. Extensive studies have been reported for sulphates, chlorides, nitrates, phosphates, acetates, etc. in solution and in crystals [3,4]. A few reports also exist on uranyl oxalate and fluoride in solution. Fluorescent emission and electronic absorption spectra of powdered uranyl oxalate at liquid air and liquid nitrogen temperature is also reported [5,6].

In general externally excited solid can relax to thermal equilibrium by emission of either photons (radiative processes) or phonons (nonradiative processes). Highly sophisticated spectroscopic techniques to detect and analyze emitted photons have been well established. Since photoacoustic (PA) signals are produced only by the absorbed light actually converted to heat in the sample, PA spectroscopy is applicable to the study of nonradioactive processes. In PA spectroscopy, the sample to be studied is placed inside a closed cell containing gas and a sensitive microphone, which is then illuminated with modulated monochromatic light. The signal from the microphone which is related to nonradiative processes following light absorption is applied to an amplifier, whose output is recorded as a function of wavelength (or photon energy) of the incident light. One of the principal advantages of PA spectroscopy is that it enables one to obtain not only signal intensity spectra similar to optical absorption but also signal phase spectra on any type of solid or semisolid material, whether it be crystalline powder, amorphous, etc. This method prevails over other technique because of its applicability for studying highly absorbing, layered, highly scattering samples, which otherwise are difficult to study using ordinary transmission and reflection methods [7,8].

A large number of reports are available in the literature regarding the absorption data of uranium in various oxidation states. Gruen and Fred [9] in one of their earliest works have given a detailed account of the absorption spectra of tetravalent uranium ions in different fluoride matrices. Conway [10] has reported on absorption spectrum of  $UF_4$  in calcium fluoride matrix and energy levels of uranium (V). Carnall and Crosswhite [11] and Hodul [12] in their respective papers have also showed the absorption and PAS spectra of tetravalent uranium ions in different fluoride matrices. Uranium in +4 oxidation state strongly absorbs in the region 600–650 nm. Similarly, pentavalent uranium absorption in  $\alpha$  and  $\beta$   $UF_5$  has also been reported in the literature by Hecht et al. [13] where the absorption maxima is observed in the near-IR region at 900–1100 nm. Kimura et al. [14] have studied speciation of uranium in aqueous solutions and in precipitates by photoacoustic spectroscopy. Schrepp et al. [15] has used PAS technique for detection of U(IV) and U(VI) in aqueous solution.

Present studies were carried out on  $(NH_4)_3UO_2F_5$  in solid using spectroscopic techniques such as fluorescence and photo-acoustic spectroscopy. In particular, photo acoustic spectroscopy (PAS) is a powerful tool for absorption studies in powder samples. Further, PAS is a complementary technique to fluorescence, since signal in PAS is produced due to non-radiative relaxation process occurring in the system. Spectroscopic data obtained in the present studies was used to obtain the vibrational characteristics of  $UO_2^{2+}$  ions. The luminescence and photoacoustic properties of ammonium uranyl fluoride are also compared with uranyl oxalate and uranyl fluoride to see the effect of ligand. To understand the changes that take place at low temperature; luminescence experiments (emission and life time spectroscopy) were also carried at liquid nitrogen temperature for ammonium uranyl fluoride.

## Experimental

### Sample preparation

All the chemicals used were of AR grade. Ammonium uranyl fluoride samples were prepared via solution route as discussed below.  $U_3O_8$  is used as a starting material. Initially uranyl nitrate solutions are prepared by dissolving  $U_3O_8$  in 8 M nitric acid. Ammonium uranyl fluoride precipitate was obtained by slow addition of concentrated solution of uranyl nitrate to an excess concentrated  $NH_4F$  solution under ice bath. A mass of greenish yellow powdery crystal is precipitated immediately. From XRD, it has been confirmed that the compound formed does not contain water of hydration and the formula of the compound is  $(NH_4)_3UO_2F_5$ . Uranyl fluoride precipitates are obtained with the addition of hydrofluoric acid solution into these pure uranyl nitrate solution. Uranyl oxalate precipitate is obtained by adding saturated oxalic acid to heating concentrated solution of uranyl nitrate.

### Instrumental details

For the PAS investigations, a home built PAS spectrometer was used [16]. Photo-acoustic spectra were recorded in the 350–700 nm regions using a 250 W tungsten–halogen lamp source and a 0.25 m monochromator using a lock in detection at 33 Hz.

Rosencwaig and Gersho in their classical work have given a detailed description and theoretical background for the photoacoustic effects with solids [17]. Photoacoustic signal is obtained by detecting the heat generated through non-radiative transitions by the sample after absorbing a periodically varying incident light.

The PA signal ( $P$ ) can be written as  $P = kA_{\text{abs}}\gamma$  (1)

Here  $A_{\text{abs}}$  is the absorbance of the sample,  $\gamma$  the probability of non-radiative transitions after excitation, and  $k$  a coefficient which is a characteristic of sample and the spectrometer.

PL studies were done on the samples as a complimentary technique for PAS. This was carried out on an Edinburgh time resolved fluorescence spectrometer provided with CD-920 controller and microsecond Xe flash lamp.

X-ray diffraction (XRD) measurements carried out on a STOE X-ray diffractometer using a Ni filter and graphite monochromator. The diffraction patterns were obtained using monochromatic  $Cu\ K\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ), keeping the scan rate at  $0.035^\circ/\text{min}$  in the scattering angle range ( $2\theta$ ) of  $10$ – $60^\circ$ . The XRD patterns obtained were then compared with the standard ICDD files and was found to match with PDF No. 73-0774. The PL emission and life-time (decay time) data were recorded on an Edinburgh CD-920 unit equipped with Xe flash lamp as the excitation source. The acquisition and analysis of the data were done by F-900 software provided by Edinburgh Analytical Instruments, UK. Life time stud-

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