

## ABSTRACT CODE

# Spectroscopic study of sol-gel glasses doped with uranyl and uranyl complexes

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For a long time, people are interested in the properties of the uranyl ion ( $\text{UO}_2^{2+}$ ). The luminescence of uranyl compounds has already been investigated by Brewster in 1833 and allowed Stokes to formulate his famous law. In 1896, the uranyl ion played an important role in the discovery of radioactivity.

An important and interesting topic are the solvent extractions of uranyl. Uranyl forms easily complexes with simple inorganic ligands, like  $\text{NO}_3^-$  and  $\text{Cl}^-$ . These complexes play an important role concerning solvent extractions of uranyl [1-4]. Nowadays, a lot of attention is paid to the coordination properties of the uranyl ion with reference to nuclear waste disposal. The fact is, that uranyl specific ligands are able to remove uranyl selectively from waste water. People are also investigating the development of uranophilic ligands that are capable of removing uranium selectively from the human body. For this kind of ligands, the term "sequestering agents" is used [5].

The uranyl ion is a linear molecule, with an oxygen-uranium(VI) bonding of unusual strength. Consequently, the uranyl ion is a very stable unit. Furthermore, the uranyl ion is not only thermodynamically very stable, but also kinetically inert [3]. It even keeps its identity in chemically aggressive media (like in very concentrated acids). The uranyl ion has also the very important property of showing luminescence. This luminescence can occur both in solution as in the solid state [3]. When we talk about the "free uranyl ion", we indicate the ion that is obtained in a solution of a strong dissociated salt, like uranyl perchlorate. In reality, the free uranyl ion is a hydrated ion in solution [6].

The uranyl ion has a strong tendency to form coordination compounds with a wide range of ligands, both in the solid state as in solution. Uranyl can even act as a template in the formation of macrocyclic complexes [7]. Crystallographic data and infrared measurements show that uranyl exists as a well defined unit in these complexes [8]. Experimental results point out that complex formation causes changes in the spectrum. Due to complex formation, ligand-field splittings of the electronic states of uranyl are clearly observed in the spectrum. Thus, there is a relationship between the spectroscopic properties of uranyl complexes and the symmetry of the first coordination sphere of uranium in these complexes [1-4].

The uranyl ion has a  $D_{\infty h}$  symmetry. In this kind of symmetry, the filling up of the molecular orbitals leads to a symmetrical ground state,  $\Sigma_g^+$  [3]. The excited states arise from transitions from the electrons of  $\sigma_u^+$  or  $\pi_u^3$  to the non-bonding orbitals  $\delta_u$  and  $\phi_u$ . From these non-bonding orbitals, the orbital  $\delta_u$  has the lowest energy.

The absorption spectrum lies between  $20000 \text{ cm}^{-1}$  and  $30000 \text{ cm}^{-1}$  and shows a rather weak absorption with characteristic progressions (figure 1). The  $\text{UO}_2^{2+}$  unit has three fundamental vibrations: the symmetric stretching ( $\nu_s$ ), the asymmetric stretching ( $\nu_a$ ) and the bending ( $\nu_b$ ). These fundamental vibrations can be observed in the absorption spectrum. The absorption spectrum exists mainly of a number of vibrational progressions. These progressions belong to a number of electronic transitions.

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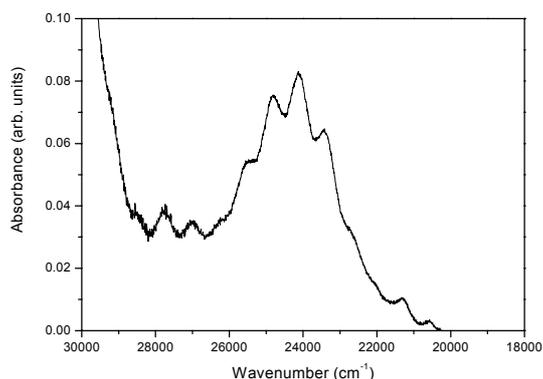


Figure 1: Absorption spectrum of the uranyl ion in a sol-gel glass at room temperature

The sol-gel technology originates in the middle of the 19<sup>th</sup> century [9]. But the general interest only came around 1930. Geffcken and Schoeder synthesized an alkoxide for the production of an oxide film in 1930 [10,11]. This technique became the first commercial application of the sol-gel process. Slowly but surely, more applications were developed. In the 90's, great progress was made in the sol-gel process. An important use of sol-gels is the synthesis of superconductors. Other new applications are the use of ceramic nuclear fuels and the development of a similar technique to prepare cement.

The sol-gel process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and condensation of tetraalkylorthosilicates, such as TMOS and TEOS [12]. Little or no heating is required in the synthesis. Moreover, the gel can be doped with molecules that are incorporated in the sol-gel glasses. Such molecules become either entrapped in or chemically bound to the growing covalent silica network. The glasses can also be transparent and thus provide a medium in which the guest molecule can be electronically excited with visible or UV light [12]. One can obtain monolith gel glass, film or fiber during different periods of sol-gel process.

A lot of research has already been done on sol-gel glasses doped with lanthanides and lanthanide complexes. Lanthanide ions have the advantage to emit narrow-band radiation with high chromatic purity. That's why many optical devices, like lasers and screens, use lanthanide ions. Furthermore, these luminescent materials containing lanthanide ions are usually found in the solid state, such as in thin films [13].

Because of the strong luminescence of the uranyl ion also sol-gel glasses doped with uranyl and uranyl complexes can be used for optical purposes.

In this work we incorporate the uranyl ion and uranyl chloride complexes in sol-gel glasses and investigate the absorption and the luminescence of uranyl in these glasses. Also the influence of the dry temperature on the spectra is discussed.

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