VIBRATIONAL STRUCTURE OF THE Cs[UO₂(NO₃)₃]
FLUORESCENCE SPECTRUM*

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Vibrational structure of the fluorescence spectrum of the solid Cs[UO₂(NO₃)₃] was
evaluated. The lines of the various progressions were selected by computer and the essential
lines were assigned by using room temperature IR and R frequencies of the ground state.

The vibrational structure of the electronic spectra of polyatomic com-
pounds cannot usually be explored because a number of vibrations (fundamental,
harmonics and combinations) are coupled to the electronic jumps. In
general the spacings between the adjacent bands are smaller than the halfband
width (HBW); thus, we are able to measure only the envelope of the overlapped
bands. The number of vibrations is significantly increased in the solid state
because the lattice vibrations and their overtones and combinations can also
appear in the electronic spectra.

The theoretical discussion is also very difficult if the atomic numbers
of any component atoms are high or if various bond strengths are present
in the molecule.

Uranyl compounds in the solid state have all these unfavourable proper-
ties. In spite of all these facts uranyl compounds have favourable spectro-
scopic significance because:

(i) The “central atom” is a triatomic linear system O=U=O in which
the oxygens are strongly bonded. The real bond order is 3 rather than 2.
(ii) The U atom perpendicular to the O—U—O axis in the equatorial
plane has a strong coordinative capacity, however, the 6 coordinated M—L
metal-ligand bonds are not so strong as the bonds inside the ligands. Because
of the perpendicular positions, in the first approximation the ligand bonds are
independent of the uranyl U—O bonds. The interaction of the equatorial and
axial bonds can be seen from the vibrational spectra: The stronger the M—L
bonds the lower the frequency of the uranyl stretching vibrations.
(iii) The longest wavelength electronic transition can be assigned unambi-
guously to the uranyl ion. Therefore mainly the normal vibrations of the
3-atomic system combine with the electronic jump.

* Dedicated to Prof. R. GÁSPÁR on his 60th birthday

(iv) The excited electronic state of uranyl shows an intensive radiative energy degradation.

(v) The strong spin-orbit interaction owing to the high atomic number of U cancels the spin selection rule. Thus the probability of the $T_1 \leftrightarrow S_0$ direct electronic transition is significant in absorption and luminescence alike (we therefore use the “singlet-triplet fluorescence” terminology) [1].

![Fig. 1. Space structure of the UO$_2$(NO$_3$) anion. The blackened arcs represent the couplings of the bidentate ligands (in the present case $\text{O} - N = \text{O}$)](image)

In the present work the fluorescence spectrum was chosen as a means of discussing the vibronic structure from two points of view.

(a) The fluorescence spectrum contains only a single electronic transition $T_{1,1} \rightarrow S_0$. (The first index of $T$ is the number of the state, the second one refers to the component of the triplet.) The triplet — probably under the influence of the ligand field — splits into 3 components. These components are near to each other and their potential surfaces overlap. We usually utilize the inequality of the transition probability $\varepsilon_{T_{1,3}} \gg \varepsilon_{T_{1,2}} \gg \varepsilon_{T_{1,1}}$ at the excitation (the energy sequence: $E_{T_{1,3}} > E_{T_{1,2}} > E_{T_{1,1}}$) because the Kasha rule is quantitatively valid. Intersystem crossing is also impossible since the emitting level is the lowest triplet. The quantum efficiency is considerably less than 1. Presumably the axial intermolecular interactions of the uranyl ion are responsible for the nonradiative energy loss.

(b) In the fluorescence spectrum the normal vibrations of the ground state combine with the electronic jump. The numerical value of these vibrations can be measured by infrared (1R, FIR) or Raman techniques. (In absorption the excited state vibrations are present: these are of lower frequencies than the ground state vibrations because in the electronic excited state the U—O — axial — interatomic distances are longer.)

An important fact is that the ligand vibrations are also capable of combining with the uranyl electronic jumps. The arrangement of the ligands (or their coupling atoms) around the uranyl ion in the case of a coordination...