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# Optical spectroscopic studies of uranyl chloride $UO_2Cl_2$

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**Abstract**

The first part of this work concerns essentially a qualitative energy level diagram of $UO_2Cl_2$ deduced from analysis of absorption and emission optical spectra recorded at low temperature. It describes the energy spacing of unoccupied orbitals. In the second part, the configuration coordinate model is used to explain successfully the shape of broadband transitions which are attributed to electron transfer from the last occupied orbital to orbitals showing a large 6d character.

## 1. Introduction

There has been considerable attention paid to the electronic structure of uranyl complexes [1–5] but a definitive interpretation has never been proposed. Some fundamental questions are still controversial, such as the assignment of the highest occupied molecular orbital (HOMO), although most authors seem to agree that the outermost orbital is surprisingly of $3\sigma_u$ character owing to a large destabilization of U 5f levels by relativistic core contraction [6–9]. This ungerade orbital shows more or less U 5f character depending on the effect of weakly bound secondary ligands situated in most of the complexes in or near and equatorial plane perpendicular to the main O–U–O direction. Calculated molecular orbital wave functions show evidence that both f and d orbitals participate in the uranyl bond which concerns all the valence electrons. This fact is consistent with the high stability and short length of the bond.

Since the effect of equatorial ligands is minor, the overall appearance of optical spectra of uranyl complexes at room temperature is essentially the same and is determined, in the first order, by the U–O overlapping. The secondary ligands seem to play a role through the crystal field effect in the energy ordering and spacing of the low-lying non-occupied states which are, following the calculations, U 5f non-bonding ungerade orbitals. Then, the electric dipole transitions between the HOMO ($\sigma_u$) and the lowest unoccupied orbitals are, in the first order, forbidden by the Laporte parity selection rule which is partially relaxed by the configuration interaction. For this reason, the oscillator strength associated with these transitions, which involve electron transfer from oxygen to the U 5f levels, is expected to be weak.

The primary interest of this work was a qualitative understanding of the optical spectra recorded from a $UO_2Cl_2$ single crystal and then calculation of the profile of the non-completely resolved absorption spectrum recorded at 77 K using the configuration coordinate model which takes into account the effect of the dynamic lattice.

## 2. Experimental details

Yellow–green single crystals of $UO_2Cl_2$ characterized by X-ray diffraction were grown from a saturated solution of $UCl_5$ dissolved in distilled carbon tetrachloride and contained in an incompletely sealed glass tube allowing a very weak exchange with the room atmosphere. The crystal data reported by Taylor and Wilson [10] show that the crystal is orthorhombic, space group *Pnma* ($D_{2h}{}^{16}$). The U(VI) coordination polyhedron is a pentagonal pyramid with uranyl oxygen atoms at the apices. The Cl atoms and the dual bonding O atom are in the equatorial plane forming a pentagon.

Low resolution absorption were obtained at 77 K with a Cary 17 spectrophotometer. High resolution absorption spectra were measured at 77 K and 4.2 K with a Spex model 1403 double monochromator and with a 1 meter Jobin-Yvon monochromator. Emission spectra were obtained using the above monochromators with excitation by an argon ion laser or a nitrogen laser.

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## 3. Discussion of the experimental optical spectra

The absorption spectra at 4.2 K are composed of progressions in the $UO_2^{2+}$ symmetric vibration mode separated by an interval of 748 cm$^{-1}$ (Fig. 1). Low-lying weak zero phonon transitions arise from the excitation of a $\sigma_u$ valence electron belonging to a molecular orbital constructed mainly from O 2p and U 5f and 6d atomic orbitals toward almost pure 5f empty orbitals of U(VI). These electronic transitions are accompanied by numerous vibronic side bands representing a density of states of the lattice phonons and forming an initial pattern. It consists of a series of weak and narrow bands and is reproduced steadily all over the investigated energy region with the progression frequency interval. However, at higher energy, the absorption spectrum becomes rapidly an intricate problem owing to the superposition of bands of electronic and vibronic character. Some of these different bands appear very broad and almost saturated in intensity. They should be attributed to more allowed transitions. In fact, they are very similar to the allowed f–d transitions characteristic of the $f^1$ configuration in $Ce^{3+}$ or $Pa^{4+}$ ions embedded in solid host matrices. For this reason Jørgensen's question [11] "Can the highest occupied molecular orbital of the uranyl ion be essentially 5f?" is still unanswered. In this case, the weak and narrow absorption bands in the recorded spectra can be seen as transitions between bonding 5fu orbitals and non-bonding 5f orbitals and the broad saturated features as transitions to orbitals characterized by a major d character.

Emission spectra (Fig. 2), in which a higher energy progression mode (875 cm$^{-1}$) is also observed, show three prominent components of which the first (1) is assigned to the pure electronic transition at 20549 cm$^{-1}$ and the other features (2 and 3) are attributed to vibronic transitions.

Following these conclusions, a schematic orbital energy diagram for $UO_2Cl_2$ is proposed in Fig. 3.

## 4. Profile simulation of the absorption spectrum

Unlike the d elements, the actinide ions usually present a weak electron–phonon coupling. However, it is well known that for the interconfiguration and charge transfer transitions, the vibrations of the matrix play an important role in the absorption and luminescence mechanism. For example, in these cases, in a one-electron transition picture, a change in the bonding properties occurs after excitation. Then both the optical bandshape and the energy difference between the absorption and emission bands (Stokes shift) depend strongly on the coupling of the phonons with the electronic levels involved in the observed transition. One of the simplest models to describe an optical transition taking into account the lattice vibrations is the single-configuration-coordinate model, where the ground and the excited states are represented by two parabolas displaced along one normal vibrational coordinate [12]. The method most widely used to interpret the optical spectroscopic data is the well known Frank–Condon analysis based on calculations of the vibrational overlap integrals as a function of this displacement [13].

Usually, the electronic spectrum is not sufficiently resolved to observe the vibronic progressions, which makes the interpretation quite difficult. However, in our case, Fig. 4 shows a rather well resolved absorption feature; so, it is possible to calculate the profile of this

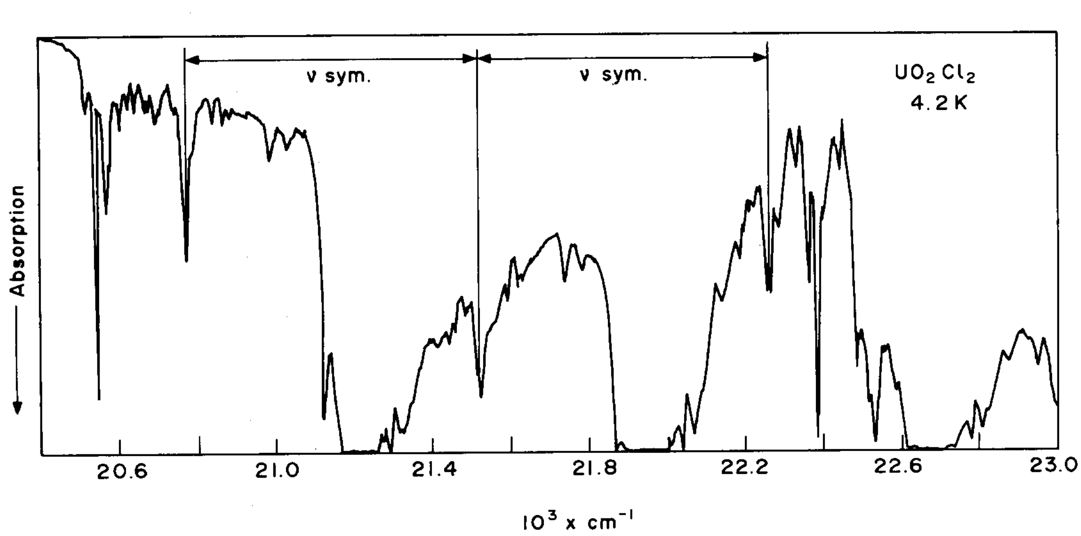

Fig. 1. Absorption spectrum recorded at 4.2 K in the 20500–23000 cm$^{-1}$ energy region.

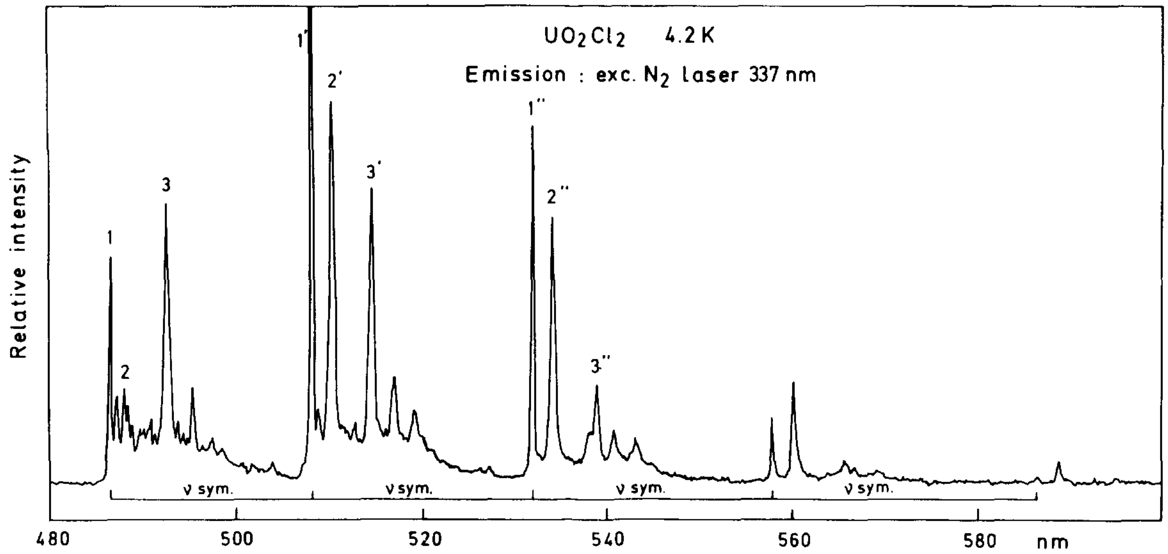

Fig. 2. Emission spectrum recorded at 4.2 K in the 480–600 nm region showing progressions separated by an interval of 875 $cm^{-1}$.

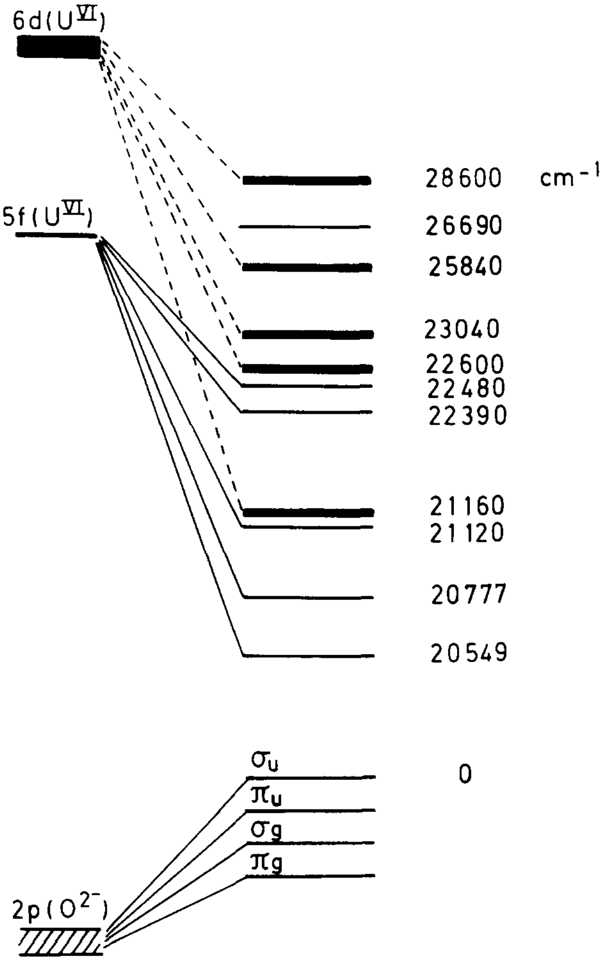

Fig. 3. Schematic energy level diagram in $UO_2Cl_2$.

spectrum and to determine parameters used for the configurational coordinate diagram such as the Huang–Rhys parameter.

In this work we used the time-dependent theory of electronic spectroscopy because of its calculational simplicity and powerful physical picture. This theory, already well described elsewhere [14–16], calculates the absorption and/or emission intensity between two potential energy surfaces. The most important point is the propagation of the initial vibrational gaussian wavepacket $\Phi$, after a vertical transition according to the Franck–Condon principle, on the potential energy curve of the excited state which is displaced relative to that of the ground state. This wavepacket is, in general, not a stationary state and evolves according to the time-dependent Schrödinger equation. Then, the absorption spectrum $I(\omega)$ is given by the Fourier transform of the overlap of the initial wavepacket and the time-dependent wavepacket $\Phi(t)$. This is determined by solving numerically the time-dependent Schrödinger equation using the split operator technique of Feit *et al.* [17]:

$$I(\omega) = C\omega \int \exp(i\omega t) < \Phi|\Phi(t) > dt$$

where $C$ is a constant and $I(\omega)$ the absorption cross-section at frequency $\omega$. Thus, in order to calculate the absorption profile it is necessary to define the nature and the vibrational frequency $\omega$ associated with the potential curve of the excited state.

In the first approximation it is assumed, for simplicity, that each electronic level involved in the charge transfer transition is represented by a harmonic one-dimensional potential energy curve defined in terms of one oscillator strength. Moreover, the configurational coordinate is chosen to represent the O–U–O symmetric stretching mode. The phonon energy associated with this mode is 748 $cm^{-1}$, as determined from the absorption

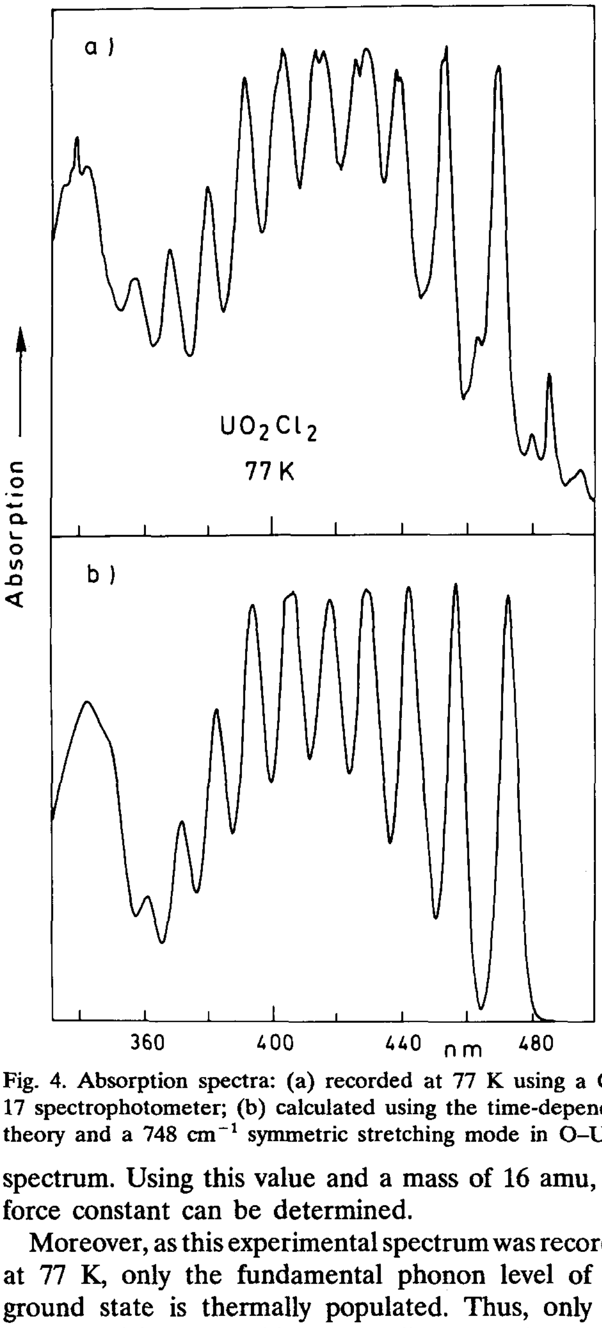

Fig. 4. Absorption spectra: (a) recorded at 77 K using a Cary 17 spectrophotometer; (b) calculated using the time-dependent theory and a 748 $cm^{-1}$ symmetric stretching mode in O–U–O.

spectrum. Using this value and a mass of 16 amu, the force constant can be determined.

Moreover, as this experimental spectrum was recorded at 77 K, only the fundamental phonon level of the ground state is thermally populated. Thus, only the spectra arising from this lowest vibrational level were calculated.

Following this hypothesis, the fitting of the experimental spectrum was carried out without taking into account the weak transition peaks. Many iterations were required to find the correct values of Stokes shift for each of the "d levels" giving the correct experimental feature. The simulation obtained (Fig. 4) is in rather good agreement with the experimental profile without the weak transitions. The values of displacement found are the following:

$$+0.081\ \text{Å} \longrightarrow 21\,160\ \text{cm}^{-1} \quad +0.081\ \text{Å} \longrightarrow 22\,480\ \text{cm}^{-1}$$
$$+0.13\ \text{Å} \longrightarrow 23\,100\ \text{cm}^{-1} \quad +0.081\ \text{Å} \longrightarrow 28\,600\ \text{cm}^{-1}$$

In this model the positive sign represents an increase in the U–O bond lengths. The differences in these values can be explained by the different orientations of each d orbital on the O–U–O axis. The change in bond length during the charge transfer should depend on which d orbital is occupied in the absorption process. Unfortunately, this optical measurement does not allow the assignment of the d orbital symmetry to the observed transitions.

## 5. Conclusion

Through this work, we conclude that some of the excited levels of $UO_2Cl_2$ in the energy range 20 000–30 000 $cm^{-1}$ have a large 6d contribution which makes transitions from a $\sigma_u$ ground state to them much more allowed. The absorption spectrum profile calculated on this basis is in good agreement with the experimentally recorded spectrum.

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