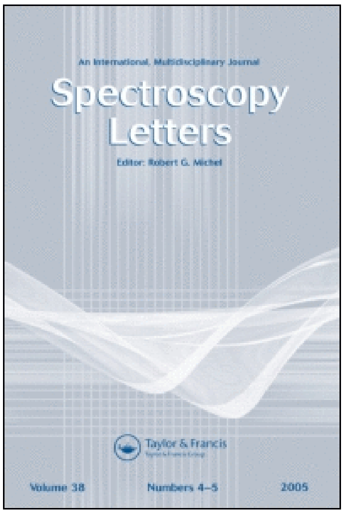

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Sergienko, V. I. , Davidovich, R. L. , Kostin, V. I. and Matstutsin, A. A.(1971) 'A Spectroscopic Study of Outer-Sphere Interaction in $M_3UO_2F_5$ Complexes', Spectroscopy Letters, 4: 1, 19 — 27
To link to this Article: DOI: 10.1080/00387017108078637
URL: http://dx.doi.org/10.1080/00387017108078637

SPECTROSCOPY LETTERS, 4(1&2), 19-27 (1971)

A SPECTROSCOPIC STUDY OF OUTER-SPHERE INTERACTION IN $M_3UO_2F_5$ COMPLEXES

KEY WORDS: IR-spectra, luminescence and ^{19}F NMR, complex uranyl fluorides

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The data available in literature on the vibration spectra of complex uranyl compounds indicate that the stretching vibration frequencies of the UO_2^{2+} group depend not only on the composition of the coordination sphere, but also on the outer surrounding of the complex anion. The outer-sphere cation, in case of uranyl complexes, acts as a competitor of the uranyl group to form bonds with ligands. At the same time, as a result of decrease in the electron density localised on the U-F bonds,the strength of these bonds becomes less.

Vdovenko et al. have shown[1] that the ν_{as} (UO_2^{2+}) frequencies found in the IR absorption spectra for $M_2UO_2Cl_4$ complexes regularly decrease with M^+ size increase. Data on cation role in uranyl complexes of other compositions, particularly in fluoride complexes, are practically absent.

The present communication cites the investigation results for the influence of outer-sphere cations on the spectral characteristics of complex uranyl fluorides with an $M_3UO_2F_5$ composition, the methods used being IR-spectroscopy, luminiscence and ^{19}F NMR.

The dependence of the asymmetric stretching vibration frequencies of the UO_2^{2+}-group in $M_3UO_2F_5$ complexes on the size of the outer-sphere cation has been scrutinized before.[2] For alkali metal cations the ν_{as} values satisfactorily correspond to a smooth curve. However, the ν_{as} (UO_2^{2+}) frequency values found in the IR-absorption spectra of $M_3UO_2F_5$

RADICAL ANIONS

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In this note we wish to report our calculations of the spin density distribution in the several hydrocarbon radical anions using the "half-electron" SCF MO [variable beta] method of Dewar[1,2]. This method calculates the energy of a system in which the unpaired electron is replaced by two "half-electrons" of the opposite spin. In this way one has the pseudo closed-shell system at equilibrium geometry and the resulting energy [E] differs from that [E_0] given by Roothaan's[3] procedure only for 1/4 J_{mm}

$$E_0 = E - 1/4\ J_{mm}$$

Term 1/4 J_{mm} represents the correction due to the spurious

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tendency of R_3NH to form H-bonds.

In the general case, the possibility of H-bond formation in complex uranyl compounds will depend both on the electron-donating properties of coordinated ligands and on the electronaccepting properties of the cation. The stability of these bonds will depend on how pronounced these properties are. It is known that fluorine, oxygen, nitrogen and chlorine atoms are capable to form the strongest H-bonds, the given order of the elements indicating a corresponding decrease in the above-mentioned ability. Taking this into account, one may expect that the role of H-bonds in outer-sphere interaction will be slight with chloride complexes. Indeed, the observed ν_{as} frequencies in the IR-spectra of $M_2UO_2Cl_4$ correlate well with the ionic radius of M^+.[1]

On the other hand, the outer-sphere interaction role of H-bonds in complex uranyl fluorides sharply increases. Hence, the values of ν_{as} frequencies found in the spectra of complexes with complex cations practically do not correlate with the cation size.

At first sight, it may seem that the cation effect in complex uranyl fluorides is of different nature for simple and complex cations. However, in reality, this is not true. Inasmuch as the cation influence is connected with the transfer of electron density from the coordinated ligands onto the cation, one may naturally expect that the thus acquired electron should occupy the lowest unfilled atomic orbital of the cation. The depth at which the orbital lies depends on the nature of the latter, and is determined by the cation-to-electron affinity. For alkali metal cations, the cation-to-electron affinity reduces with passing from Na^+ to Cs^+, and the ionic radius of these cations increases in the same series.

In the case of complex cations, the cation-to-electron (or -to-electron pair) affinity does not correlate with their sizes, and is determined solely by the nature of the cation itself. In the case when the cation is not a strong electron acceptor, its influence on the uranyl complex is slight, and the values of the ν_{as} frequency shall fit in with the curve plotted for cations of alkali metals. If, on the other hand, the cation contains considerably "stripped" protons, then its affinity to the electron will be great, and its influence on the spectral and geometric (possibly also magnetic) characteristics of the uranyl complex will correspondingly rise.

It should be expected that the sensitivity of uranyl complexes of various compositions to the influence of the cation will be different and will be determined by the properties of the coordinated ligands. This should be especially perceptible in complexes with complex cations, since the main path for the electron density transfer in such compounds is the H-bond, whose strength depends not only on the properties of the cation, but also on the electronegativity of the ligands. The IR absorption spectra for $Cs_2UO_2Cl_4$, $(R_3NH)_2UO_2Cl_4$, $Cs_3UO_2F_5$ and $(R_3NH)_3UO_2F_5$ complexes are rather notable in this plane. In chloride complexes, substitution in the outer sphere of the Cs^+ cation for R_3NH^+ leads[1] to an increase of ν_{as} (UO_2^{2+}) only by 1 cm^{-1}. A similar substitution in pentafluorouranylates is accompanied by a 68 cm^{-1} frequency shift in asymmetric stretching vibrations (see Table 1).

The absolute magnitude of outer-sphere interaction, expressed through a shift in the ν_{as} (UO_2^{2+}) frequency with

TABLE 1

Spectral characteristics of $M_3UO_2F_5$ complexes.

Compound	ν_o (cm^{-1})	$\nu_s(UO_2^{2+})$ (cm^{-1})	$\nu_{as}(UO_2^{2+})$ (cm^{-1})	ν_{UF} (cm^{-1})	F_{UO} (mdyn/Å)	n_{UO}	n_{UF}	$\delta_F \cdot 10^6$	$R_i(M^+)$ (Å)
$Na_3UO_2F_5$	-	821*	884	-	6.48	2.16	0.336	-	0.98
$K_3UO_2F_5$	19986	803**	865	379	6.14	2.06	0.376	450	1.33
$Rb_3UO_2F_5$	19950	798**	855	375	6.00	2.02	0.392	437	1.49
$Cs_3UO_2F_5$	19816	791**	848	359	5.87	1.98	0.408	428	1.65
$(NH_4)_3UO_2F_5$	20024	823**	887	354	6.48	2.16	0.333	480	1.43
$(R_4N)_3UO_2F_5$	-	802*	866[3]	$\left.\begin{matrix}409\\383\end{matrix}\right\}$[3]	6.11	2.05	0.380	-	≥2.00
$(R_3NH)_3UO_2F_5$	-	842*	910[3]	348[3]	6.77	2.25	0.300	-	≥2.00

* calculated in accord with Vdovenko et al.[7]; ** values obtained from luminescence spectra.

substitution of one cation for another depends on the nature of the ligands not only in the case of complex cations. For example, substitution of Na^+ for K^+ in the outer sphere of acetate uranyl complexes[4,5] is accompanied by a shift in ν_{as} by only 4 cm^{-1}; in the case of chloride complexes, the shift is equal to circa 16 cm^{-1}; and with pentafluofouranylate complexes -- the passing from $Na_3UO_2F_5$ to $K_3UO_2F_5$ leads to a decrease in ν_{as} (UO_2^{2+}) frequency by 19 cm^{-1}.

The studies conducted for long-wave IR absorption spectra of $M_3UO_2F_5$ complexes[2,3] allow us to trace the influence of the cation directly in the frequencies of the stretching vibrations of U-F bonds. It follows from Table 1 that the ν_{UF} frequencies in the series $K_3UO_2F_5$ - $Rb_3UO_2F_5$ - $Cs_3UO_2F_5$ decrease, though the nature of the ν_{as} (UO_2^{2+}) change implies an increase of ν_{UF} in the series. Apparently, this behaviour of the stretching vibration frequencies in U-F bonds of $M_3UO_2F_5$ (M - K, Rb and Cs) is connected with the increase of the cation mass forming a bond with the coordinated fluorine atoms. An analysis of the IR absorption spectra for $M_3UO_2F_5$ complexes with outer-sphere complex cations, whose interaction with the anion is achieved by way of H-bonds (hence, the cation mass does not play an essential role), shows quite a clear dependence of the ν_{UF} frequency on the degree of the cation-anion interaction. Thus, for example, the U-F bond stretching vibration frequency found in the $(R_4N)_3UO_2F_5$ absorption spectrum[3] (the cation-anion interaction is quite weak) was 383 cm^{-1}; the ν_{UF} frequency value for the $(NH_4)_3UO_2F_5$ spectrum (with a considerably stronger cation-anion bond) was

354 cm^{-1}; and the same value for the $(R_3NH)_3UO_2F_5$ complex (with the strongest cation-anion bond) was found to be even lower[3] -- 348 cm^{-1}.

Using the method of V.M. Vdovenko et al.[6], we made quantitative evaluations of the changes that took place in the $M_3UO_2F_5$ complexes as a result of the change in the intensity of the outer-sphere cation-anion interaction. The calculation results are cited in Table 1, showing the maximum bond order alteration for U-O bonds in the scrutinized pentafluorouranylates to be 0.27, the change in the bond order of U-F bonds being only 0.108. Naturally, it is rather difficult to record such slight changes by means of vibrational spectroscopy.

To obtain direct information concerning the character of the U-F bonds in $M_3UO_2F_5$, we used the NMR method. The ^{19}F NMR spectra for the $M_3UO_2F_5$ complexes (M - K, Rb, Cs and NH_4) were rather symmetrical. The chemical shifts (δ_F), measured in respect to F_2 are cited in Table 1, which shows that δ_F has the lowest value with $Cs_3UO_2F_5$, and gradually increases when passing over to $Rb_3UO_2F_5$ - $K_3UO_2F_5$ - $(NH_4)_3UO_2F_5$ (the resonance signal shifts to the high field). This fact proves that the uranium-fluorine bond possesses the greatest covalency in $Cs_3UO_2F_5$, and the least in $(NH_4)_3UO_2F_5$. Consequently, the ^{19}F NMR data fully corroborate the conclusions based on the IR-spectroscopy studies concerning the nature of the alteration in the extent of the cation-anion interactions in $M_3UO_2F_5$.

A definite connection between the values of ν_{as} (UO_2^{2+}) and δ_F is apparent from Table 1. General considerations imply that this dependence will be of a quadratic nature. However, since the number of experimental points is not great, and they apparently lie far from the parabola peak, their positions are well expressed by the linear relationship:

$$\delta_F = 1.36\,\nu_{as} - 726.$$

It was also of interest to trace the influence of outer-sphere cations by luminescence spectra, since the latter, apart from giving data on the vibrational structure of the main electronic state, also give evidence concerning the excitation energy of the uranyl complex.

The luminescence spectra recorded at 77°K for $M_3UO_2F_5$ complexes appeared as 3 or 4 groups of equally separated lines. The frequencies of symmetric and asymmetric stretching vibrations for uranyl are known to be[7] linearly dependent, and it is obvious that the $\nu_s(UO_2^{2+})$ shifts observed in the luminiscence spectra are symbatic in respect to $\nu_{as}(UO_2^{2+})$ shifts.

The most interesting result in our study of the luminescence spectra of pentafluorouranylates is, to our mind, the regularity in the shift of resonance frequency transition $(n''_{v=0}\ \ n'_{v=0})$ with change in the intensity of the cation-anion interaction. As seen from Table 1, ν_0 increases in the series $Cs_3UO_2F_5$ - $Rb_3UO_2F_5$ - $K_3UO_2F_5$ - $(NH_4)_3UO_2F_5$, i.e. the change in the ν_0 frequency value coincides, in respect to sign, with the alteration of the stretching vibration frequency in the uranyl group and with the alteration of δ_F.

It is noteworthy that the ν_o shift with passing from one cation to another is much higher than the shift in the frequencies of $\nu_s(UO_2^{2+})$ and $\nu_{as}(UO_2^{2+})$. This indicates to a higher sensitivity to the outer-sphere interaction of the pure electron transition frequency as compared to stretching vibration frequencies.

We presume that the ν_o frequency shift in the luminescence spectra for $M_3UO_2F_5$ complexes is connected with the rise in the order of uranyl bonds, leading to an increase in the excitation energy of the anion, i.e. to the increase of the energy needed to transfer the electron from the bonding molecular orbital to the antibonding molecular orbital.

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