ON THE POSSIBILITY OF CHARACTERIZATION
OF URANYL GEL PHASES BY THEIR INFRARED SPECTRA*

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Attempts were made to characterize objectively uranyl gels of various types by means of infrared spectroscopy. It was found that the spectra can characterize the properties of the molecular units, of which the volume of the gel phase is built up, but not the gel phase as such. The molecular units mentioned are chemically closely related to uranates prepared by precipitating uranyl solutions with, *e.g.*, ammonia.

Microspheres of an uranyl hydrogel differ, in dependence on the conditions of preparation, by their optical, chemical, and mechanical properties[1]. For a more thorough evaluation of the various preparation procedures, an objective characterization of the quality of the gel prepared should be reached. Infrared spectroscopy is able to indicate, whether the differences are due to different arrangement of the basic molecular units (which are then identical in the various gels) in the bulk of the gel phase, or whether the changes pertain to these molecular units. In addition, their molecular structure could be characterized as well. Among the actinide elements, only spectra of a thorium gel have been measured[2].

EXPERIMENTAL

Infrared spectra were measured using a Perkin-Elmer 225 spectrometer in the region of 200 to 4000 cm^{-1} employing the nujol and fluorolube techniques. After a thorough washing with water or dilute ammonia (1 : 10), the hydrogel particles were converted to xerogel by heating at 105 or 220°C for 5 h; samples dried on air still attacked the CsI cell windows. Impregnation of the uranyl hydrogel microspheres with uranyl nitrate was performed from ether solution, since in aqueous solution the microspheres peptized considerably.

RESULTS

Most of the 77 spectra are essentially identical differing only insignificantly. None of them indicated the presence of residua of the gelation admixtures, *i.e.* hexamethylene-

tetramine and urea. A typical spectrum, obtained from various samples dried at 105°C, will be designated as Spectrum T. The Spectrum S (split) was found only for two samples; it differs from the T-Spectrum first of all by split bands of skeletal U-O vibrations. One of the samples with this spectrum (designated as S2) gave an additional type of spectrum (Spectrum I) after impregnation with uranyl nitrate. The corresponding data are summarized in Table I. In the further text the Spectrum T will be described and elucidated as the fundamental spectrum, the other types will be treated in relation to that one. A pictorial comparison of all the spectral types is facilitated by Fig. 1.

Range of $200 - 700\ cm^{-1}$. In this range, three intense bands dominate at $258 \pm \pm 5$, 385 ± 10, and $460 \pm 10\ cm^{-1}$; they can be attributed to the skeletal U-O vibrations[3]. In addition, broad bands, weak or medium intensity, are observed at 600 and 655 cm^{-1}; they are probably due to the libration of molecules of water in the gel lattice — on drying at 220°C their intensity decreases, sometimes they vanish completely.

In the S-type spectrum the dominant bands are split, the bands at 600 and 655 cm^{-1} are indistinct. The splitting vanishes on impregnation of the particles with uranyl nitrate, the bands of the skeletal vibrations being then identical with those in the typical spectrum (Table I, Fig. 1). In the Spectrum I a new intense band appeared at 575 cm^{-1}, which could represent a librational mode of molecular water.

Range of $700 - 1650\ cm^{-1}$. The most intense band in this range belongs to the anti-symmetric vibration of uranyl, $\nu_3(UO_2)$, appearing at $900 - 930$ cm^{-1}; after drying the sample at 220°C (12 spectra in the whole) the band shifts to lower wavenumbers in the range $890 - 900$ cm^{-1} (average 896 cm^{-1}). The energy of this vibration cha-racterizes the coordination state around the uranyl as the central ion[4]; for sodium[5] or ammonium[6] uranates, the vibrational frequency decreases with increasing content of the cations, from approximately 960 to 870 and 900 cm^{-1}, respectively. The uranyl gel impregnated with uranyl nitrate should be considered as an intimate mixture of two components affecting each other, rather than as a new compound: in fact, two bands of the uranyl vibrations appear in the spectra* at 911 and 949 cm^{-1}, which gives evidence of the occurrence of the ion in two thermodynamically different states. The former band, slightly more intense, displayed before the impregnation a value by 6 cm^{-1} higher.

Further the bands of coordinated nitrate ions occur in this range too[8,9]. The pre-sence of those ions was proved also chemically in the samples studied; the content of NO_3^-/U, which is ~ 0.5 after washing with water, decreases to a half after washing with dilute ammonia. The values of the wavenumbers for vibrations of coordinated nitrates are given in Table II for all the types of spectra. In several cases some fre-

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*   In $UO_2(NO_3)_2.6\,HO$ itself, the frequency has the value[7] of 950 cm^{-1}.

TABLE I

Infrared Spectra of Various Types of Gels in the Range of $200-700$ cm^{-1}
  For symbols see the text[a].

| | Type of spectrum | | | Assignment |
S 1	S 2	I[b]	T	
232 sh				
250 sh				
269 s, sp	270 s, sp	260 s, sp	258 ± 5 s, sp	U-O skeletal
278 sh				vibrations
330 s	335 s			
3<u>57</u> s	3<u>59</u> s	375 s	385 ± 10 s-vs	U-O skeletal
388 m-s	387 s, sh			vibrations
4<u>47</u> s, sp	4<u>48</u> s	460 s, b	460 ± 10 m-s, b	U-O skeletal
487 m	485 s			vibrations
521 m	515 sh			
600 vw	—	575 s	600 m, b	H_2O librations
650 vw, b	685 w, sp	—	655 m, b	

[a] Band intensities: s strong, m medium, w weak, v very, sh shoulder, sp sharp; under-lined bands are the most intense within the group. [b] Spectrum of the sample prepared from the sample with the spectrum S 2 by impregnation with solution of uranyl nitrate.
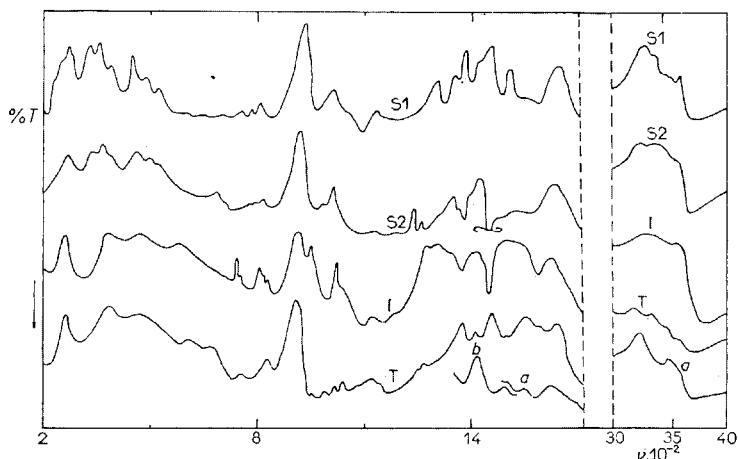

FIG. 1

Comparison of the Various Spectra

  For symbols see the text. a Spectrum T, the sample dried at 220°C; b the range of nujol ab-sorption, the spectra measured in fluorolube mulls (the sample dried at 105°C).

quency is supposed to be split to several bands, which indicates the nonequivalence of the nitrate coordination. After drying at 220°C the bands of the nitrate vibrations vanish completely.

In the range in question, the bands of the bending vibrations of coordinated hydroxyl groups, $\delta(OH)$, of molecular water, $\delta(HOH)$, and of ammonium groups, $\delta(NH_4)$, appear as well (Table II). If our assignment of the $\delta(OH)$ bands is correct (in some cases the bands can correspond to overtones or combinations), then their number and the broad span of energies (from $\sim 780\ cm^{-1}$ to $\sim 1190\ cm^{-1}$) suggests a variety of types of their bonding in the gel phase. The bands vanish almost completely on drying at 220°C, similarly as in the case of the nitrate bands.

The deformation of molecular water, $\delta(HOH)$, leads to two or three bands, sometimes strong, which indicates − similarly as in the case of $\delta(OH)$ − a multiple function of water molecules inside the gel. In xerogel, formed by drying at 105°C, the vibrations appear at 1 635 and 1 555 cm^{-1} as medium to strong bands (Table II); on drying at 220°C the intensity decreases − the bands are weak to medium − and the former band shifts to 1 615 cm^{-1}. The position of the other band is either preserved (1 550 cm^{-1}) or shifted to 1 535 cm^{-1}. No regularity with respect to the conditions of preparation or processing of the samples could be found. In addition, a new weak band appears at 1 500 ± 5 cm^{-1} in many cases, as the result of heating up to 220°C.

The sharp band of ammonium deformations $\delta(NH_4)$, attains rather high intensity and appears regularly at 1 410 ± 5 cm^{-1}; in most cases it is observable even between the absorption bands of nujol at 1 375 and 1 455 cm^{-1}. Drying at 220°C does not affect the band.

Range above 1 650 cm^{-1}. Besides the irregularly appearing minor bands, corresponding obviously to combinations and overtones, the stretching vibrations $\nu(OH)$ and $\nu(NH_4)$, appearing near 3 200 cm^{-1} and at higher wavenumbers, are typical of this range. In the typical spectrum these bands are usually broad and overlapping each other; the most intense one is the broad band at 3 200 ± 20 cm^{-1},* the intensity of the other bands (Table II) decreases gradually (sometimes they appear only as shoulders). If the sample is dried at 220°C, the first band retains its position at 3 210 ± 20 cm^{-1}, its resolution is better as a result of vanishing of the band at 3 330 cm^{-1}, whereas the band at 3 445 ± 10 cm^{-1} becomes medium intense and clear--cut, with an indistinct shoulder at 3 540 ± 30 cm^{-1}. Analogously, taking into account the invariability of the band intensities of the ammonium deformation vibrations, $\delta(NH_4)$, with temperature, we attribute the band at 3 200 cm^{-1} to the stretching vibrations of those groups, $\nu_3(NH_4)$, (the other band not affected by temperature, at $\sim 3 450\ cm^{-1}$, lies at too high wavenumbers[8]). It is also possible that all the bands

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* In a few cases the second band at 3 330 cm^{-1} was the most intense, with the band at 3 200 cm^{-1} absent.

TABLE II

Wavenumbers in the Region Above 700 cm^{-1}

For symbols see Table I.

S 1	S 2	I	T^a	Assignment
703 vw, sp	710 vw, sh	710 vw, sh	(713) vw	ν_5 [710]^b
752 w	765 vw, b	739 m, vsp	755 w, (b)	ν_3 [740]
—	—	748 m, sh	—	
782 w, sp	780 vw	—	(789)	δ(OH)
808 w-m	812 w-m	804 m, vsp	816 w-m	
—	—	815 w, sh	—	} ν_6 [810]
—	—	827 w	—	
930^c s	917 vs	911 vs	900—930 s-vs	} ν_3(UO$_2$)
—	—	949 s	—	
—	980 sh	—	990 w, (sh)	
1 008 m	1 008 m, sp	1 012 s, sp	1 017 w	} ν_2 [1 020]
—	—	1 033 sh	1 038 w-m, (sp)	
—	—	—	955 w, (sp)	
1 080 w, sh	—	—	1 088 w, (sh)	
1 128 w-m	1 128 w	1 125 w	1 125 w-m	} δ(OH)
—	—	—	(1 140) w, sh	
—	1 185 vw, b	1 188 vw, sh	(1 175) w, b	
—	1 235 m, sp	—	1 247 w, sh	
1 295 m	1 260 w-m, sp	1 270 s	1 260 w, sh	} ν_4 [1 275]
1 350 m	1 350 m	1 298 s	1 303 m	
1 415 sh	1 420 m-s	1 415 s, b	(1 410) m-s	δ(NH$_4$)
1 503 m	—	1 505 s, vb	1 505 w	ν_1 [1 500]
1 542 w, vb	1 540 w, vb	—	1 555 (m)-s	
—	—	—	(1 592) w	} δ(HOH)
1 638 m-s	1 625 m-s	1 615 m-s	1 635 (m)-s	
3 270 s	3 240 s, b	3 250 vs, vb	3 200 $\pm$ 20 s, b	
3 365 m, sh	3 370 s, vb	—	3 330 $\pm$ 20 (s)	
3 450 vw, sh	—	—	3 435 w, sh	} ν(OH)
3 500 vw, sh	3 560 s, sh	3 565 s, sh	3 550 w. sh	
3 570 w, sp	—	—	—	

^{a} Data occurring often, but not always, are given in parentheses; ^{b} for nitrate vibrations, the probable wavenumbers according to[9], derived from various nitrate complexes of uranyl, are given in brackets; ^{c} a single band of ν_3(UO$_2$) with an asymmetrical sharp peak (possibly instrumental error?).

belong to the OH stretching vibrations, overlapping the $v_3(NH_4)$ band, the temperature-independent bands belonging probably to hydroxy groups, the temperature-dependent bands to molecular water.

From the broad range of frequencies $(3200 - 3550\ cm^{-1})$ as well as from the different intensities of the various bands and their shapes we can again infer the occurrence of a variety of O-H bonds, obviously with a significant contribution of hydrogen bridges (broad diffuse bands). The different weakening of the O—H bonds can be due to differently strong coordination of the hydroxy group to the uranium atom, *i.e.* U—O(H), as well as to differently strong hydrogen bridges, *i.e.*(O—)H$\cdots$O.

DISCUSSION

From the material collected it follows that all the gel phases — irrespective of the distinct differences in properties — are built up of essentially identical molecular units. Thus the differences in the properties of the gel phases must be associated with the way in that these molecular units are arranged into the bulk of the gel phase; and it is those intermolecular effects that show up only slightly in the infrared spectra.

The most marked difference in the spectra is the splitting of the bands of the skeletal uranium–oxygen vibrations, as found for two samples, always for the gel type E-II (ref.[1]); in two further attempted reproductions of the material exhibiting these S-type spectra, only the T-type spectra were obtained. The poor reproducibility appears more often in uranium chemistry and sometimes[10,11] it is called "black magic". The splitting of the skeletal bands is probably to be related to a different mutual arrangement of the molecular units in space, hence to the quasistructure of the gel phases. Having fixed particles, the gel resembles solid phase; on the other hand, however, the regular (not random) arrangement holding only in a limited distance causes the gel resemble liquids. This results in very small crystallites (in our case $200 - 300$ Å) and a relatively high freedom in their mutual arrangement. From experimental structural data we can draw an inference that materials with the S-type spectra have the same crystal structures as those exhibiting the T-type spectra. Diffraction lines of various gel samples correspond either to those of the hexagonal phases $3\ UO_3 . 2\ NH_3 . 4\ H_2O$ and $2\ UO_3 . NH_3 . 3\ H_2O$ or to the orthorhombic phase $3\ UO_3 . NH_3 . 5\ H_2O$ described in paper[12]. As the hexagonal and the monoclinic subcells of the two types are very close to each other (they have roughly equal parameters and volumes), the former subcell can be converted to the latter by a slight homogeneous deformation, so that a continuous transition between the hexagonal and the orthorhombic symmetries of the lattice is likely to exist, most probably in dependence on the content of ammonium ions[6].

The fact that on mere impregnation of the gel particles with uranyl nitrate the splitting of the skeletal bands bands vanishes, complies with the irreproducibility of the properties in the sense that the stability of the state, to which the spectrum S

corresponds, is very low indeed. It also conforms to the explanation of the pheno-menon based on the different spatial arrangement within the gel phase: it is feasible that a mere introduction of a new substance (uranyl nitrate) in the vacant sites of the uranyl gel can change the spatial arrangement of its building units. This assumes (or indicates) that bonds between these units in the gel are not very strong.

As the gel phase dried at 105°C contains in addition to hydroxyl groups also coordi-nated nitrate ions, chemically it should be a basic nitrate. Nevertheless, from the spectra as well as from chemical analysis it follows that ammonium ions are present in the gel too, which is indicative of ammonium uranate. Open to question remains the chemical nature of the molecular units of which the hydrogel is built up.

As the gelation was caused by homogeneous ammoniation, *i.e.* by releasing am-monia in the whole volume of a drop of the gelated solution during the decomposition of the hexamethylenetetramine dissolved, uranyl hydroxo complexes must have been formed in the solution. These converted gradually to micelles, which agglo-merated* to give a threedimensional net[13].

Uranyl hydroxo complexes are transformed to solid phase as amphoteric uranyl hydroxide (*i.e.* uranic acid), often written[14] as uranium trioxide dihydrate, UO_3 . . 2 H_2O. As the whole gelation process proceeds in slightly acidic medium and over-alkalinization does not appear locally either[15], the concentration of free hydroxyl ions is always low and the nitrate ions present — being in a high excess over the free hydroxyl ions — are able to bind partly on the hydroxo complexes formed. The primary gel phase is therefore represented by neutral hydroxo-nitrate complexes. Only secondarily, ammonium ions bind on this amphoteric solid phase (this is analogous to the formation of uranates by external alkalization of uranyl solutions). Although the concentration of free hydroxyls is very low during the gelation, the total concentration of hydroxyls and hence also that of ammonium ions, released by the decomposition of hexamethylenetetramine, is comparable with that of the ura-nyl ions. Therefore a part of the ammonium ions bind already during the gelation process, which manifests itself by a temporary increase of acidity[15], as the NH_4^+ ions substitute hydrogen of the hydroxyl bridges[6,16,17].

If the gel particles are washed with dilute aqueous solution of ammonia instead of water, the content of the ammonium ions additionally increases. This appears in the change of colour or transparency of the gel spheres; the treatment is of practical

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* Although the mechanism of gelation is not being discussed here, it should be noted that the second gelation admixture, urea, plays an important role in the process: its presence in the appropriate amount is the prerequisite for the formation of just a hydroxide gel: if the urea were present in an inadequate amount or if it were absent at all, hydroxidic precipitate would form instead. Moreover, urea enables the formation of a relatively stable feed, *i.e.* it enables the dissolution of massive portions of hexamethylenetetramine in a concentrated uranyl solution without formation of the solid phase[1].

importance, as the behaviour of the spheres during their processing to uranium dioxide usually improves, to say nothing of their lower peptization in ammonia than in water.

In addition to hydroxyl bridges, in which hydrogen can be substituted by a cation, the primary hydroxide solid phase contains also nonbridge hydroxyls, whose hydrogen cannot be substituted, but instead of which another ligand can be coordinated[17]. The scheme of arrangement of the molecular units in the solid (gel) phase is then as follows:*

$$= \quad [UO_2(OH)_2]_n \quad = \quad [UO_3.H_2O]_n$$
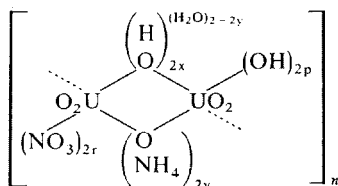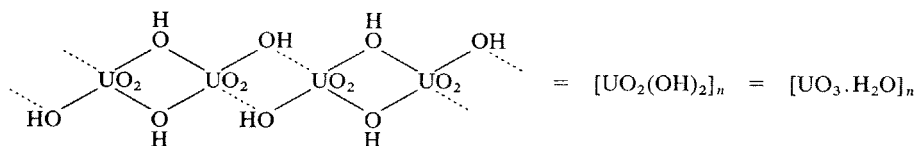
This scheme explains the amphoteric nature of the hydroxide uranyl phase: the acidic behaviour, *i.e.* the formation of uranates, is enabled by the presence of the hydroxyl bridges, the hydrogen of which can be substituted, the basic behaviour, *i.e.* the formation of basic salts, is conditioned by the substitution of the nonbridge hydroxyls by another ligand; to the uranyl gel it is peculiar that these two functions come in action simultaneously, as it contains both the ammonium and the nitrate ions. Its chemical nature can be described by the empirical formula

$$[UO_2(OH)_x(ONH_4)_y(OH)_p(NO_3)_r(H_2O)_{1-y}]_{n/2} ,$$

where $x + y = 1$ (pertaining to the bridge hydroxyls) and $p + r = 1$ (pertaining to the nonbridge hydroxyls of the primary gel phase). The corresponding scheme is the following:

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*   In this scheme molecular water, as corresponding to the formula $UO_3.2\,H_2O =$ $= UO_2(OH)_2.H_2O$, is omitted for simplicity. On substitution by ammonium[6] and sodium[17] ions it is spontaneously released, obviously for steric reasons. From this it follows that this molecular water is located in the close vicinity of the hydrogen of the hydroxyl bridges.

Changes in the content of the cation (*e.g.* the ammonium ion) or anion (*e.g.* the nitrate ion), which can occur in the gel probably more easily than in the usual precipitate, will generally affect the structural and thus also some spectroscopic properties of the hydroxide uranyl phase, because they will in some respect alter the distances of some atoms. The uranyl gel will therefore resemble by its properties ammonium uranate or basic nitrates or uranium trioxide dihydrate, but it will not be identical with them.

Molecular water and hydrogen bridges play certainly an important role in the structure of the gel; information on this topic which can be obtained from IR spectra is not, however, very detailed. First of all, from the bands of the bending vibrations $\delta(HOH)$ it can be concluded that the gel contains mostly molecular water bound in two (sometimes probably in three, see Spectrum T) ways. The bonding to which the band at 1635 cm^{-1} corresponds could be similar to that occurring in $UO_3 . 2 H_2O$ (with regard to the band shape and intensity, its energy being $5-30$ cm^{-1} higher), but not to that occurring in uranate, as the corresponding band has essentially lower intensity. The bonding corresponding to the band of $\delta(HOH)$ at 1555 cm^{-1} should differ from the preceding one either by considerably stronger bonding of the oxygen to uranium, *i.e.* U—O(H), or by appreciably weaker hydrogen bridges (O)H$\cdots$X, or combination of these effects.* Some of the hydroxyl groups are bonded by very strong hydrogen bridges.

The bands of the stretching vibrations $\nu(OH)$ are not in contrast with this explanation, nevertheless any more substantial information cannot be drawn from them.

CONCLUSION

Although we cannot explain the marked differences in the optical, mechanical, or chemical properties of gel phases[1] by employing their infrared spectra, we can use them to characterize the basic molecular unit, of which the gel phases are formed. The primary gel phase are the electroneutral hydroxo-nitrate uranyl complexes, which are able to bind secondarily ammonium ions (during the gelation or after its completion, *e.g.* during washing with ammonia). As a consequence, the gels contain both nitrate ions (thus resembling basic uranyl salts) and ammonium ions (thus resembling ammonium uranates). In addition they contain molecular water bound in several ways.

The different properties of the gel phases are obviously due to different arrangement of the molecular units inside these phases. Only exceptionally we could catch a case

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*   Since the spectra discussed pertain to xerogels, we must take into account that the water is that one which was a part of the uranium compound rather than the weaker-bound water, which represented an essential part of the volume of the starting hydrogel and which can be removed for a great part by drying at room temperature.

where this difference in the arrangement of the units appeared appreciably in the infrared spectrum, *viz.* by the splitting of the bands of the U-O skeletal vibrations. This splitting could be removed by impregnation of the corresponding hydrogel with uranyl nitrate, resulting in the formation of an intimate mixture of two compounds affecting each other. Regarding the practical demand for an objective characterization of the differences in properties of differently prepared gel phases as such, we must consider these results as an only partial success. To attain our aim, we directed our attention also to other methods, the most promising of which seems to be the emanation thermal analysis (ETA) $\left(refs^{18,19}\right)$; the results will be published later.

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