

The Infrared Absorption Intensity of the ν_3 Vibration of the UO_2^{2+} Ion in Nitrate and Thiocyanate Media

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The intensity of the asymmetric stretching vibration, ν_3 , of the UO_2^{2+} ion has been measured in a salt medium of NaNO_3 , keeping the ionic strength = 4 M. In order to try to correct for solvent effects, the IR absorption of aqueous SO_2 solutions was also determined and compared with gas phase data. For a series of solutions containing various concentrations of NaSCN it has been observed that the intensity increases with about 10 % when thiocyanate ions are coordinated to the uranyl group. The change of the ν_3 frequency has been used for a determination of the complex formation curve. This has been found to agree well with other data. Hence the frequency change is not a medium effect and it has been assumed that the same holds then for the intensity change. This change has been ascribed to a decrease of the bond order of the U—O bond caused by the coordination of thiocyanate ions.

From the absorption values the dipole moment derivative, $\partial\mu/\partial r$, has been calculated ($\pm 9.2 \times 10^{-10}$ e.s.u.) and the charge distribution of the UO_2^{2+} ion has been estimated as $-1 +4 -1$.

The bonds between the oxo ions and the U^{6+} ion in the uranyl(VI) ion are of considerable strength compared to other bonds that may be formed between the central uranium atom and ligands such as H_2O , OH^- , NO_3^- , and the like. This is illustrated, *e.g.* by the difference in bond lengths in $\text{UO}_2(\text{acetate})_3^-$, 1.71 Å for the axial and 2.49 Å for the equatorial U—O distances.¹ Hence the UO_2 group can be considered as a unit which is only slightly perturbed by the action of the equatorial ligands. In a way, therefore, the changes experienced by the UO_2 group can be used as a measure or at least an indication of the type and strength of the bonding between the U^{6+} ion and its equatorial ligands.

One such property of the UO_2^{2+} ion that is frequently used in investigations of this type is the frequency of infrared absorption corresponding to the asymmetric vibration (ν_3) of this linear three-atom group (Ref. 2 and references therein). Indeed, the variation of ν_3 is surprisingly great. It has been suggested² that the sequence of ligands arranged in relation to their frequency-decreasing is similar to that of the spectrochemical series or alternatively, and better,³

that of the nephelauxetic⁴ series. One then realizes that the decrease of ν_3 is due to the charge transfer from the equatorial ligands to the uranium atom. McGlynn and coworkers² suggest that the decrease is quite simply due to a collection of negative charge on the central atom, thus causing electrostatic repulsion between this charge and the axial oxygen atoms. They state explicitly that the accepting orbitals engaged in the charge transfer are not taking part in the bonding to the axial oxygen atoms.

As this proposition seems somewhat unrealistic, the present work was initiated to investigate the effect of equatorial coordination, not only on the frequency but also on the intensity of the ν_3 absorption. Although absolute infrared intensity measurements cannot usually be performed to a very high degree of precision, especially in aqueous solutions, comparison between intensities of similar molecules has been found^{5,6} to be very useful in cases, where the evidence on molecular structure from the frequency shifts is conflicting or uncertain.

The ultimate object⁷ of infrared intensity measurements is to estimate the derivative of the molecular dipole moment with respect to the normal or, still better, the internal coordinates of the molecule. In the case of a linear triatomic molecule, such as the UO_2^{2+} ion, the relevant calculations are straight-forward, and an attempt will be done to use the intensity data for this purpose. The results will be used for a discussion of the question of the bonding of the equatorial ligands raised by McGlynn *et al.*²

METHOD OF INVESTIGATION

In this work uranyl nitrate solutions rather than perchlorate ones were used as the IR absorption of the nitrate ion in the region of the UO_2^{2+} ν_3 frequency is not so strong as that of the perchlorate ion. Thus one can obtain a rather good base line of the recorded spectra also for high concentrations of nitrate ions.

There was no addition of nitric acid to suppress the hydrolysis of the UO_2^{2+} ion, but in most of the solutions investigated sodium nitrate was present in such concentrations that the ionic strength was 4 M.

As in all aqueous infrared work the length of the cell had to be extremely small due to the high infrared absorption of water. Consequently, the concentrations of uranyl ions had to be correspondingly high. In this work the values 0.2, 0.3, and 0.4 M $\text{UO}_2(\text{NO}_3)_2$ have been used. The intricate question then arises, to what degree the uranyl ions are polymerized. Fortunately, potentiometric determinations of the degree of hydrolysis have been carried out at high uranyl ion concentrations (0.4 M) by Hietanen and Sillén.⁸ In Fig. 1, their results are given graphically — recalculated to give the number (Z) of OH^- per UO_2^{2+} as a function of the hydrogen ion concentration $[\text{H}^+]$. From the condition that no extra acid is present in the solutions of the present work we have the stoichiometric relation that

$$Z = [\text{H}^+]/0.4 \quad (1)$$

The hydrogen ion concentration for which this relation is satisfied is obtained from the crossing point of the straight line representing eqn. (1) and the curve

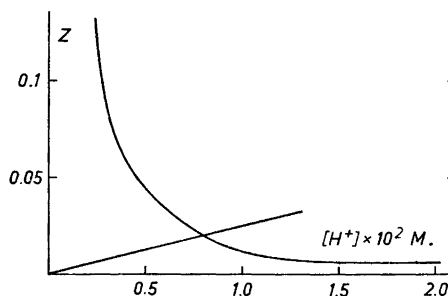


Fig. 1. Representation of the mean ligand number Z of the UO_2^{2+} — OH^- system from the investigation of Hietanen and Sillén.⁹ The straight line represents eqn. (1).

representing the experimental results of Hietanen and Sillén. From Fig. 1 it follows that $[\text{H}^+] = 8 \times 10^{-3}$ M, corresponding to a value of $Z = 0.02$.

Thus only a very small fraction of the uranyl ions is actually hydrolyzed. Furthermore, from the work of Kraus and coworkers⁹ it follows that the degree of polymerisation is then very low. Thus, although the figures given above cannot hold exactly in the present case, as the salt medium is different from that used in the potentiometric work,⁸ we can certainly state that the degree of hydrolytic polymerisation is very low. This must then hold also for the solutions of lower uranyl concentrations. Consequently, we can regard the infrared spectra as representative of the uranyl ion, UO_2^{2+} , as such. The ligands in the equatorial positions are then all oxygen-containing ones — mainly water and nitrate ions — and thus all occupying about the same place in the nephelauxetic series. Hence they may be expected to exert about the same influence on the ν_3 vibration of the UO_2^{2+} ion. It was then considered interesting to investigate the influence on this vibration by a ligand which had another position in the nephelauxetic series.

As such the thiocyanate ion was chosen, as it is one of the few ligands of notable coordination power with respect to the uranyl ion that are able to exist in acidic media. Earlier investigations⁵ have made it probable that the thiocyanate is coordinated *via* the nitrogen atom.

The nephelauxetic parameter,⁴ h , will then vary from about 1.0 for the oxo-ligands to about 1.3 for the nitrogenbonded thiocyanate. Although this is not a very great difference, rehybridization of the uranyl group may probably occur sufficiently to create observable differences of the infrared absorption intensity.

Another aspect that has to be considered in every IR intensity measurement in condensed phases is the dependency of the absorption intensity on the refractive index of the phase. Many relations have been proposed⁷ for converting the intensities measured in condensed phases to gas phase intensities. In reality, however, specific interactions seem to be equally important,⁷ especially in polar media. The best that can be done, therefore, is to relate the observed intensity of the uranyl ion to the intensities of a model substance that can be investigated in both aqueous solution and gas phase. As a model substance sulphur dioxide seemed suitable: The absorption frequency of the asymmetric stretching vibration¹⁰ is rather close to that of the uranyl ion and, furthermore, several independent measurements of the gas phase intensity

are reported in the literature.¹¹ The most obvious objection to this choice is that the sulphur dioxide is not a linear molecule. The differences between the two systems under discussion, caused by this non-linearity, are difficult to assess. Another objection is that the concentration of sulphurous acid present is not known very accurately. In this work it has been neglected as other investigations^{10,11} indicate that it is rather small. The systematic errors introduced in this way have been neglected, as we have no way to predict the third systematic error involved in the proposed comparison, *i.e.* the influence of specific interactions, notably solvation, of the two species in solution.

EXPERIMENTAL

The experimental technique was essentially the same as used before,¹³ with the exception that 25 μ spacers were used. The actual cell thickness was determined from the interference patterns of the empty cell.

The chemicals were all of analytical grade.

RESULTS AND CALCULATIONS

Frequency shifts. The shifts, $\Delta\nu$, of the ν_3 frequency caused by the addition of increasing amounts of sodium thiocyanate are given in Table 1 and graphi-

Table 1. Frequency shifts for the $\text{UO}_2^{2+} - \text{SCN}^-$ system.

$I = 4 \text{ M}$						Variable ionic strength			
$C_M = 0.2 \text{ M}$		$C_M = 0.3 \text{ M}$		$C_M = 0.4 \text{ M}$		$C_M = 0.2 \text{ M}$		$C_M = 0.4 \text{ M}$	
C_L	$\Delta\nu$	C_L	$\Delta\nu$	C_L	$\Delta\nu$	C_L	$\Delta\nu$	C_L	$\Delta\nu$
0.47	9	0.47	5.5	0.53	7.5	0.48	10	0.48	5
0.94	14	0.94	12	0.80	10.5	1.20	17	1.20	14
1.40	18.5	1.10	16	1.07	13	1.60	20	1.60	16
1.87	22	1.38	16.5	1.20	15	1.92	21	1.92	18
2.10	21.5	1.65	18	1.60	18.5	2.40	24.5	2.40	21
2.80	24.5	2.20	21.5						
○		△		□		●		■	

cally in Fig. 2. One observes a continuous change of the magnitude of these shifts. This can be explained, if it is assumed that more than one thiocyanate complex exist in the system, each with its characteristic frequency of absorption. As even the largest shift observed is smaller than the half-width of the ν_3 peak, it is not possible to resolve the component peaks of the successively formed complexes. However, just because of this, the observed frequency of maximum absorption will be dependent in some way on the relative amounts

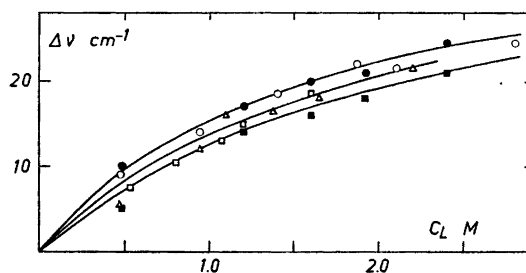


Fig. 2. The frequency shifts of the ν_3 absorption peak of the UO_2^{2+} ion caused by increasing thiocyanate concentration. The meaning of the symbols is found in Table 1.

of the complex present. Indeed, this effect gives the monotonous change of $\Delta\nu$ with C_L that is shown in Fig. 2. From the arguments above we can assume rather safely that the main part of the uranyl species in the solution is the unhydrolyzed, monomeric UO_2^{2+} unit. Furthermore, as the investigation of Ahrland,¹⁵ performed at low C_M values, did not show any evidence of polynuclear thiocyanato complexes, one can probably assume that this will hold also here. Then the degree of formation of the n 'th complex, α_n , is determined only by the concentration of the free thiocyanate ions, $[\text{L}]$. Then it must also hold that a certain value of $\Delta\nu$ corresponds to a certain value of $[\text{L}]$.

The mean ligand number, \bar{n} , is defined as usually¹⁴

$$\bar{n} = \frac{C_L - [\text{L}]}{C_M} \quad (2)$$

Consequently, if the curves in Fig. 2 are cut for a series of $\Delta\nu$ -values and the corresponding C_L values are plotted against C_M one obtains \bar{n} from the slope and $[\text{L}]$ as the intercept of a straight line.

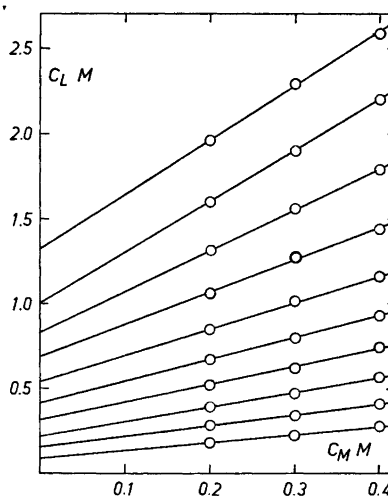


Fig. 3. C_L plotted against C_M for a series of constant $\Delta\nu$ values; $\Delta\nu = 4, 6, 8, \dots, 22$ cm^{-1} .

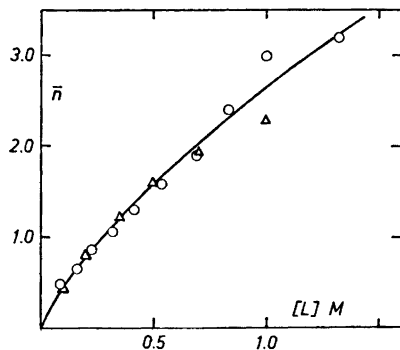


Fig. 4. Corresponding values of \bar{n} and $[L]$ from the slopes and intercepts of the lines of Fig. 3 (O). The values calculated from the data of Ahrlund¹⁵ are represented by (Δ). It should be noted that the range of measurements of this latter investigation was $0 < [L] < 0.35$ M.

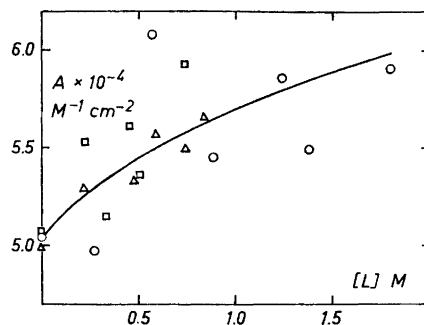


Fig. 5. The absolute intensities of the ν_3 absorption band plotted against $[L]$. The meaning of the symbols is given in Table 2.

It can be seen from Fig. 2 that in the actual case the scattering of the points is considerable. The curves are drawn so as to take into consideration also the measurements made at variable ionic strength. They are, furthermore, drawn to be equally spaced. It is therefore not surprising that linear plots of C_L versus C_M are found (Fig. 3). What is surprising, however, is that the complex formation curve (Fig. 4) obtained in this way so closely resembles the one given by Ahrlund.¹⁵ Without doubt therefore, the frequency shifts used for this "calculation" are caused by the formation of thiocyanato uranyl complexes and not by a non-specific solvent effect. This conclusion is important, as it justifies us to assume that any intensity change that may be observed is also caused by coordination of thiocyanate ions.

The UO_2^{2+} -intensities. All intensities were determined with the "Method I" described by Ramsay. Hence the products $\epsilon \cdot \Delta\nu_{1/2}$ were multiplied by $2.303 K$, where K was taken as equal to 1.56, *i.e.* slightly less than the theoretical value $\pi/2$ in order to give a reasonable correction for the finite slit-widths of the spectrophotometer. The results of the intensity measurements for the solutions of constant ionic strength are given in Table 2. From the complex formation curve obtained above, the $[L]$ values were calculated for each (C_M , C_L) couple. Then the intensities were plotted against $[L]$ (Fig. 5). The large scattering of the points arises mainly from the large experimental errors (5–10 %). Nevertheless, the tendency of increase is clear. A curve is drawn to emphasize the trend — it should not be given more meaning than that. The important point to be remembered in the discussion to come is that we find an increase and not a decrease of intensity.

The SO_2 -intensity. The results of the intensity measurements of two different preparations of aqueous solutions of sulphur dioxide are given in Table 3. The mean value was found to be $(1.9 \pm 0.1) \times 10^4 \text{ cm}^{-2} \text{ M}^{-1}$. This should be

Table 2. Intensity measurements of the $\text{UO}_2^{2+}-\text{SCN}^-$ system at $I = 4 \text{ M}$, $d = 24.8 \mu$,
 $A = 3.59 \times \varepsilon \times \Delta\nu_{1/2}$. $\varepsilon = \log T_0/T \cdot C_M^{-1} d^{-1}$.

C_M (M)	C_L (M)	[L] M	$\log T_0/T$	$\Delta\nu_{1/2}$ cm^{-1}	$A \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-2}$
0.2 ○	0	0	0.240	29.0	5.04
	0.47	0.27	0.218	31.5	4.97
	0.94	0.57	0.230	36.5	6.08
	1.40	0.89	0.215	35.0	5.45
	1.87	1.24	0.219	37.0	5.86
	2.10	1.38	0.223	34.0	5.49
	2.80	1.80	0.227	36.0	5.91
0.3 △	0	0	0.345	30.0	4.99
	0.47	0.22	0.327	33.5	5.29
	0.94	0.48	0.287	38.5	5.33
	1.10	0.59	0.296	39.0	5.57
	1.38	0.74	0.316	36.0	5.49
	1.65	0.84	0.335	35.0	5.66
	2.20	1.24	—	—	uncertain
0.4 □	0	0	0.560	25.0	5.07
	0.53	0.22	0.402	38.0	5.53
	0.80	0.33	0.395	36.0	5.15
	1.07	0.45	0.456	34.0	5.61
	1.20	0.51	0.390	38.0	5.36
	1.60	0.74	0.437	37.5	5.93

Table 3. Intensity measurements on aqueous solutions of sulphur dioxide. Cell thickness
 22.8μ .

C_{SO_2} M	$\log T_0/T$	$\Delta\nu_{1/2}$ cm^{-1}	$\varepsilon \times \Delta\nu_{1/2}$ $\text{M}^{-1} \text{cm}^{-2}$	ν cm^{-1}
0.366	0.168	25	5.0×10^3	1320
0.366	0.199	21	5.0×10^3	1322
0.352	0.206	20	5.2×10^3	1324
0.352	0.218	21	5.7×10^3	1323
Mean: $(5.2 \pm 0.2) \times 10^3$				1322
$A = 2.303 \times 1.56 \times (5.2 \pm 0.2) \times 10^3 = (1.9 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{cm}^{-2}$				

compared to the value of the absolute intensity in gas phase at S.T.P. found by Mayhood:¹¹ $A = 1.91 \times 10^4 \text{ cm}^{-2} \text{ M}^{-1}$. Consequently, the intensity value found in the aqueous phase at room temperature can be regarded, within experimental uncertainty, as equal to the gas phase value at S.T.P. Then, if the same situation is assumed to hold also for the uranyl ion intensities, we

can consider the intensity measured in the aqueous solution as equal in magnitude to the one for the hypothetical situation of an uranyl ion existing in the gas phase.

Calculation of $\partial\mu/\partial r$. In the following, the calculation of the derivative of the dipole moment of the molecule with respect to bond length, $\partial\mu/\partial r$, will be performed in close adherence to the procedure of Robinson.¹⁶ The model used is the one (discussed in detail by, *e.g.*, Nakamoto¹⁷) of a bent XY_2 molecule, with an $\text{Y}-\text{X}-\text{Y}$ angle θ . (In the actual case, of course $\theta = \pi$).

The nomenclature is that of Nakamoto,¹⁷ except that we denote the symmetry coordinates S instead of R' . The intensity, A_i , of the ν_i absorption band is related to the dipole moment derivative with respect to the normal coordinate Q_i by eqn. (3) derived by Thorndike, Wells and Wilson.¹⁸

$$A_i = \frac{n\pi}{3c} |\partial\mu/\partial Q_i|^2 \quad (3)$$

Here n means the number of molecules per cm^3 and c is the velocity of light. μ is, as stated implicitly above, the dipole moment of the molecule. In this relation A_i is expressed in $\text{sec}^{-1} \text{cm}^{-1}$.

When A_i is expressed in $\text{M}^{-1} \text{cm}^{-2}$ the relation (3) turns into

$$A_i = \frac{N\pi}{3 \times 10^3 c^2} \left| \frac{\partial\mu}{\partial Q_i} \right| \quad (4)$$

where N is the avogadro number. In order to relate $|\partial\mu/\partial Q_3|$, the experimentally available quantity, to $|\partial\mu/\partial r|$, the theoretically interesting one, one has to make use of the symmetry properties of the molecule as prescribed by the G F matrix technique of Wilson.¹⁹

The internal coordinates, relevant in this connection, are Δr_1 and Δr_2 , *i.e.* the changes of the two $\text{U}-\text{O}$ bond distances, r_1 and r_2 .

Then the symmetry coordinates of the symmetric and asymmetric stretching modes in their normalized form are (Ref. 17, p. 52)

$$S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2) \quad (5 \text{ a})$$

$$S_3 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2) \quad (5 \text{ b})$$

Now in order to relate S_3 with Q_3 , one notices that, when the Wilson G and F matrices are applied in conjunction with the use of symmetry coordinates to the bent XY_2 molecule, they take the form of one-dimensional matrices, with matrix elements F_{33} and G_{33} , respectively, for the B_2 vibration mode (Ref. 17, p. 54).

The secular equation then takes the simple form (Ref. 17, p. 61)

$$\lambda_3 = G_{33}F_{33} \quad (6)$$

where $\lambda_3 = 4 \pi^2 c^2 \nu_3^2$, when ν_3 is expressed in cm^{-1} .

Furthermore, as the potential energy of the system, in the hypothetical case when only the asymmetric mode is excited, must be the same whether

it is expressed in terms of normal coordinates or symmetry coordinates, it holds that

$$V = \frac{1}{2} \lambda_3 Q_3^2 = \frac{1}{2} F_{33} S_3^2 \quad (7)$$

Hence combining eqns. (6) and (7), the relation between Q_3 and S_3 emerges

$$G_{33} Q_3^2 = S_3^2 \quad (8)$$

or

$$Q_3 = G_{33}^{-1/2} S_3 \quad (9)$$

Now G_{33} can be calculated from the formula (Ref. 17, Appendix II)

$$G_{33} = \frac{1}{m_Y} + \frac{1}{m_X} (1 - \cos \theta) \quad (10 \text{ a})$$

For the UO_2^{2+} ion we have then

$$G_{33} = \frac{1}{m_O} + \frac{2}{m_U} \quad (10 \text{ b})$$

Introducing the atomic masses one obtains

$$G_{33}^{-1/2} = 4.84 \times 10^{-12} \text{ g}^{-1/2} \quad (11)$$

Then from the experimental value $A = 5.03 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ (Table 2) and eqn. (4) one can calculate $|\partial\mu/\partial Q_3|$:

$$|\partial\mu/\partial Q_3| = 268 \quad (12)$$

By combining eqns. (9), (11) and (12) one gets

$$|\partial\mu/\partial S_3| = 268 \times 4.84 \times 10^{-12} = 12.97 \times 10^{-10} \text{ e.s.u.} \quad (13)$$

Then from the relation

$$\frac{\partial\mu}{\partial r_1} = \frac{\partial\mu}{\partial S_3} \times \frac{\partial S_3}{\partial r_1} + \frac{\partial\mu}{\partial S_1} \times \frac{\partial S_1}{\partial r_1} \quad (14)$$

and the fact that the symmetric stretching vibration causes no change of the dipole moment of the molecule, *i.e.* $\partial\mu/\partial S_1 = 0$, we have

$$\frac{\partial\mu}{\partial r_1} = \frac{\partial\mu}{\partial S_3} \times \frac{\partial S_3}{\partial r_1} \quad (15)$$

Combining eqns. (5 b), (13), and (15) and omitting the index of the internal coordinate we finally obtain

$$|\partial\mu/\partial r| = 9.17 \times 10^{-10} \text{ e.s.u.} \quad (16)$$

Calculation of the charge distribution

Now when the derivative of the dipole moment with respect to bond length has been calculated, it is tempting to try a determination of the charge distribution of the UO_2^{2+} ion.

If a linear molecule, Y X Y, is characterized by the fixed charges $-\varepsilon$ on each of the Y atom and $+2\varepsilon$ on the X atom, it can be easily derived that for the asymmetric stretching vibration

$$|\partial\mu/\partial r| = 2\varepsilon$$

This relation holds, if it is assumed that the charge distribution does not change during the vibration. This is by no means certain, but let us pursue the calculation as if it did hold.

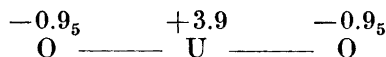
Then we obtain

$$2\varepsilon \times 4.8 \times 10^{-10} = 9.17 \times 10^{-10} \quad (18 a)$$

or

$$\varepsilon = 0.96 \quad (18 b)$$

Consequently, adding the positive charge of the central atom, we obtain the following charge distribution of the UO_2^{2+} ion



Remembering the uncertainties inherent in the intensity values that are the basis of the calculation, the errors of the charges may be estimated to about $\pm 10\%$.

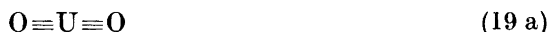
DISCUSSION

Let us first turn our attention to the just obtained charge distribution of the uranyl ion. It is very interesting to note that — within the error limits of both types of estimation — it is exactly the same that has been suggested by Connick and Huges²⁰ from entropy data of aqueous solutions of the uranyl ion. This gives us some support for the validity of the assumption that the charge distribution does not change appreciably during the vibration. As this assumption has been questioned, *e.g.* by Person and Hall,²¹ because of the striking disagreement between the intensities observed for the ν_3 and ν_2 vibrations of CO_2 and CS_2 , some comment is appropriate. Person and Hall,²¹ following Thorndike²² and Robinson,¹⁶ suggest that during the ν_3 vibration of, *e.g.*, CO_2 the two resonance structures



should be favoured, the one in one extreme phase of the vibration, the other in the other extreme phase. Thus, there should be a considerable variation of the dipole moment of the molecule during the vibration. This may very well be so, although the effect of the lone-pair contribution to the dipole moment during bending vibration is by no means clear⁷ and can also be of importance when explaining the observed anomalies.

The situation described by Person and Hall²¹ obviously arises from the fact that the carbon atom can form only four bonds. The uranium atom, however, has quite a number of orbitals available for bond formation that make possible the simultaneous use of the p_x and p_y orbitals of the oxygen atoms for the formation of π -orbitals. Thus the formal structure



may very well be one of the dominating resonance structures of the uranyl ion. Hence there is no possibility for the formation of resonance forms with a differing number of bonds to the oxygen atoms during the ν_3 vibration. For the resonance form



originating from the use of a smaller number of orbitals of the uranium atom for the bonding of the oxygen atoms, however, a situation, similar to that described for the CO_2 case should be possible.

With this picture in mind let us now turn to the effect of the coordination of other ligands, *e.g.* thiocyanate ions, on the intensity of the ν_3 vibration. If it were true, as suggested by McGlynn, Smith and Neely,² that the orbitals of the uranium atom used for the bonding of these extra ligands are not to any extent any of those engaged in the bonding of the axial oxygen atoms, coordination should only result in a decrease of the charge of the uranium atom. This, in turn, means that the intensity of the ν_3 absorption band should be unaffected by coordination or even decreased. Now, on the contrary, an increase is observed (Fig. 5). It seems to the present author that in order to explain this increase of intensity it is necessary to assume that the extra ligands are bonded by the interaction of ligand orbitals and some uranium orbitals that are also engaged in the hybridized orbitals that are responsible for the bonding of the axial oxygen atoms. This can be expressed also by saying that the resonance structure (19 b) is favoured in relation to the structure (19 a). This means that the polarity of the O—U—O bonds is increased and hence, from the model assumed, the intensity should increase. Furthermore, if the (19 b) structure is somewhat more important in the description of the O—U—O bonding, an increase of the contribution to $|\partial\mu/\partial r|$ originating from the effects described²¹ for the CO_2 case should be expected. Both these effects should then combine to the observed increase of intensity.

Once more, then, it seems that infrared intensity measurements can give more detailed information on molecular properties than does the mere observation of frequency shifts.

This work is part of a project financially supported by *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council). The technical assistance of Miss Karin Borg is gratefully appreciated.

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Received October 28, 1967.