

## VIBRATION SPECTRA OF IMIDODISELENATE AND IMIDODISULPHATE ANIONS

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*Dedicated to Professor K. Dostál, on the occasion of his 60th birthday.*

Infrared and Raman spectra of potassium salts of  $\text{N}(\text{SeO}_3)_2^{-3}$ ,  $\text{N}(\text{SO}_3)_2^{-3}$ , and  $\text{HN}(\text{SO}_3)_2^{-2}$  anions have been measured. Normal coordinate analysis has been used for their interpretation and characterization of bonding relations in the anions studied.

The method of preparation of salts of imidodiselenic acid was developed only recently<sup>1</sup>, and structure of the anion  $\text{N}(\text{SeO}_3)_2^{-3}$  has not yet been investigated. Therefore, we tried to contribute to its description by a study of vibration spectra of  $\text{KN} \cdot (\text{SeO}_3\text{K})_2 \cdot \text{H}_2\text{O}$  (*I*). We chose vibration spectra of  $\text{K}_2\text{Se}_2\text{O}_7$  (*II*),  $\text{KN}(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$  (*III*) and  $\text{HN}(\text{SO}_3)\text{K}_2$  (*IV*) as a suitable comparison material for the interpretation. So far only the compounds *II* (ref.<sup>2</sup>) and *IV* (refs.<sup>3,4</sup>), have been submitted to spectroscopic study. However, the vibration spectra<sup>3,4</sup> do not show satisfactory agreement, and their interpretation is only partial. Therefore, another aim of this work was to complete and define with more precision the available data. Interpretation of the vibration spectra of all the investigated anions and characterization of the bonding relations therein were carried out on the basis of normal coordinate analysis.

### EXPERIMENTAL

*Preparation of the compounds studied.* For the measurement of vibration spectra of the compound *I* we used a sample whose preparation, purification and purity check were described in ref.<sup>1</sup>. The compound *II* was prepared by thermal condensation of  $\text{KHSeO}_4$  (ref.<sup>5</sup>), and its purity was checked on the basis of its vibration spectra only.

Condensation of ammonium amidosulphate at about 300°C and recrystallization from aqueous ammonia solution gave triammonium imidodisulphate monohydrate<sup>4</sup> which was converted into the respective sodium salt by action of 50% aqueous sodium hydroxide; the sodium salt gave the compound *IV* on action of  $\text{KCl}$  (ref.<sup>6</sup>). Neutralization of *IV* with concentrated potassium hydroxide solution gave the compound<sup>7</sup> *III*.

For  $\text{KN}(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$  (309.5) calculated: 20.72% S, 37.90% K, 4.52% N; found: 21.05% S, 37.64% K, 4.40% N. For  $\text{HN}(\text{SO}_3\text{K})_2$  (253.3) calculated: 25.31% S, 30.87% K, 5.52% N; found: 25.60% S, 30.32% K, 5.38% N.

*Analytical methods.* In the imidodisulphates prepared sulphur was determined gravimetrically as barium sulphate after hydrolysis of the sample in concentrated hydrochloric acid and after reaction of the potassium amidosulphate formed with potassium nitrate. Potassium was determined gravimetrically, too (as potassium sulphate), and nitrogen was determined volumetrically according to Dumas. Purity of the compound *III* was also checked by paper chromatography<sup>8</sup>.

The infrared spectra of the solid samples in the region 3 600 to 400 cm<sup>-1</sup> were measured with a UR-20 apparatus (Zeiss, Jena) in Nujol suspension using cells with KBr windows. The Raman spectra inclusive of the polarization measurements were obtained with a Ramalog 3 apparatus (Spex, Metuchèn). The samples were located in glass capillary cells, the spectra were excited by the line 488 nm generated in an argon laser SP 165 03 (Spectra Physics, Mountain View) with the output of about 200 mW.

## RESULTS AND DISCUSSION

*Vibration spectra.* The anions *I*, *II*, and *III* belong, in the optimum case, to the  $C_{2v}$  point group with fully reduced vibration representation

$$\Gamma^{C_{2v}} = 7A_1^{P,\alpha} + 4A_2^\alpha + 6B_1^{P,\alpha} + 4B_2^{P,\alpha}.$$

Lowering of symmetry to  $C_2$ ,  $C_s$  or  $C_1$  (e.g. by anisotropic field in the crystal) results in all the vibrations being active in the both types of spectra, and in the two former cases 11 of them are fully symmetrical. For the anion of the salt *IV* the  $C_s$  point group represents the highest possible symmetry group, and the fully reduced vibration representation has the form

$$\Gamma^{C_s} = 13A'^{P,\alpha} + 11A''^{P,\alpha}.$$

If the group NH is considered to be a vibrating unit, then the fully reduced representation  $\Gamma^{C_{2v}}$  applies to the anion *IV*, too.

Tables I to IV give vibration spectra of all the compounds studied. From the results of polarization measurements it follows that the anions *I* and *III* in aqueous solution belong to the point group  $C_{2v}$ . For evaluation of symmetry in solid state the region of antisymmetric valence vibrations of SO bonds is only applicable in which only three out of four possible vibrations of this type should appear in the infrared spectrum due to operation of the selection rules valid in the point group  $C_{2v}$ . The four bands observed in this region of infrared spectrum of *III* indicate that this anion belongs to a point group lower than  $C_{2v}$ . It is, however, impossible to decide which of the groups  $C_2$ ,  $C_s$  and  $C_1$  really applies. The two bands observed for these vibrations in infrared spectra of *I* and *II* represent a lower number than that required for the most symmetrical possible case of the  $C_{2v}$  point group. This finding obviously results from random degeneration of vibrations and lower symmetry of these anions in the crystal, which is probable but not directly provable. Similar situation is encountered with the anion *IV* whose highest possible symmetry is  $C_s$ , and in spite of that three bands of antisymmetrical valence vibrations of SO bonds can only be observed in the infrared spectrum.

In the spectra of the anions *I* and *III* the wave number difference between symmetrical and antisymmetrical bridge valence vibration is about  $200\text{ cm}^{-1}$ , whereas that of the anion *IV* is almost 10 times smaller. This phenomenon is obviously due to bonding relations at the central nitrogen atom which forms two and three bonds in the first two and the third cases, respectively. The presence of two free electron pairs at the nitrogen atoms in the anions *I* and *III* increases, according to expectation, the average value of wave numbers of valence bridge vibrations. Further consequences of this state are decrease of the angle between the bridge bonds and an increase of polarity of the terminal ZO bonds ( $Z = \text{S, Se}$ ) (ref.<sup>9</sup>), which is reflected in the vibration spectra (see the values in Tables I to III).

Assignment of majority of the experimentally observed bands to the deformation vibrations of the angles OZO, OZN, and ZNZ did not follow until from the preliminary results of the normal coordinate analysis, and, hence, its reasoning is briefly discussed in the following paragraph.

TABLE I  
Vibration spectra of  $\text{KN}(\text{SeO}_3\text{K})_2 \cdot \text{H}_2\text{O}$  (*I*)

IR, s		RA, s		RA, solution		Assignment
$\tilde{\nu}, \text{cm}^{-1}$	<i>I</i>	$\tilde{\nu}, \text{cm}^{-1}$	<i>I</i>	$\tilde{\nu}, \text{cm}^{-1}$	<i>I</i>	
		161	vw	130 b, p	vw	$\delta\text{SeNSe}$ ( $A_1$ )
				154 dp	vw	$\tau\text{SeO}_3$ ( $B_2$ )
		255 b	w	258 dp	w	$q' \parallel \text{SeO}_3$ ( $B_1$ ), $q \perp \text{SeO}_3$ ( $A_2$ )
		281	w	267 p	w	$q \parallel \text{SeO}_3$ ( $A_1$ )
		345	vw	376 p	w	$\delta'_s\text{SeO}_3$ ( $A_1$ )
		376	w			$\delta'_s\text{SeO}_3$ ( $B_1$ )
398	w	388	w	307 Sh, b	vw	$\delta'_{as} \parallel \text{SeO}_3$ ( $A_1$ ), $\delta'_{as} \parallel \text{SeO}_3$ ( $B_1$ ), $\delta'_{as} \perp \text{SeO}_3$ ( $B_2$ )
419	w	414	vw	422 Sh	vw	$\delta_{as} \perp \text{SeO}_3$ ( $A_2$ )
452 Sh	w	454	vw	435	vw	$q' \perp \text{SeO}_3$ ( $B_2$ )
625	vw	623	m	621 p	m	$\nu_s\text{SeNSe}$ ( $A_1$ )
820	s	822	vw	822 dp	vw	$\nu_{as}\text{SeNSe}$ ( $B_1$ )
862 Sh	m	863	vs	862 p	vs	$\nu_s\text{SeO}_3$ ( $A_1$ )
868	m			868 <sup>a</sup> Sh, dp	vw	$\nu'_s\text{SeO}_3$ ( $B_1$ )
886	vs	876 Sh	w	873	vw	$\nu_{as} \perp \text{SeO}_3$ ( $A_2$ ), $\nu'_{as} \parallel \text{SeO}_3$ ( $B_1$ )
897	vs	890	w	884 <sup>a</sup> Sh	vw	$\nu_{as} \parallel \text{SeO}_3$ ( $A_1$ ), $\nu'_{as} \perp \text{SeO}_3$ ( $B_2$ )

The band intensities (*I*) are denoted as follows: vw very weak, w weak, m medium, s strong, vs very strong; sh shoulder; b broad band, p polarized, dp depolarized band; <sup>a</sup> obtained in the polarization measurements.

*Normal coordinate analysis.* The model used for calculation of the quadratic potential constants of all the four anions is represented in Fig. 1. In the anion *IV* the NH group was considered to be a vibrating unit with relative mass about 15, and, for simplicity, this anion was considered to belong to the  $C_{2v}$  point group. The structural parameters of the anion *III*, i.e.  $r = 166$  pm,  $R = 146.8$  pm,  $\alpha = 110.2^\circ$ ,  $\beta = 108.7^\circ$ ,  $\varphi = 120.8^\circ$ , and those of the anion *IV*, i.e.  $r = 168$  pm,  $R = 146.2$  pm,  $\alpha = 113^\circ$ ,  $\beta = 105.7^\circ$ ,  $\varphi = 124.2^\circ$ , were found by complete X-ray analysis<sup>10</sup>. The respective values of *I* and *II* were assessed as follows:  $r = 163$  and  $160$  pm,  $R = 166$  and  $170$  pm,  $\varphi = 120^\circ$ , the angles  $\alpha$  and  $\beta$  were considered tetrahedral. The calculations used the wave number values of the fundamental transitions read from the Raman spectra of the aqueous solutions except for *IV* (little solubility) and *II* (ready hydrolysis) where it was necessary to use the wave number values from the Raman spectra of the solid samples.

The calculation of the quadratic potential constants was carried out by the Wilson **F,G**-matrix method using a Tesla 200 computer and a set of programs described

TABLE II  
Vibration spectra of  $K_2Se_2O_7$  (*II*)

IR, s <sup>a</sup>		RA, s		Assignment
$\tilde{\nu}$ , cm <sup>-1</sup>	<i>I</i>	$\tilde{\nu}$ , cm <sup>-1</sup>	<i>I</i>	
		106	w	$\delta SeOSe$ ( $A_1$ )
		156 b	vw	$\tau_{as} SeO_3$ ( $B_2$ )
		229	m	$\varrho \perp SeO_3$ ( $A_2$ )
		238	s	$\varrho \parallel SeO_3$ ( $A_1$ ), $\varrho' \parallel SeO_3$ ( $B_1$ )
		331	vw	?
		363	vw	$\varrho'_s \perp SeO_3$ ( $B_2$ )
		378 Sh	vw	$\delta'_s SeO_3$ ( $B_1$ )
		386	w	$\delta_s SeO_3$ ( $A_1$ )
		413	vw	$\delta_{as} \parallel SeO_3$ ( $A_1$ ), $\delta'_{as} \parallel SeO_3$ ( $B_1$ )
425 Sh	m	422 Sh	vw	$\delta'_{as} \perp SeO_3$ ( $B_2$ )
		433	vw	$\delta_{as} \perp SeO_3$ ( $A_2$ )
555	m	560	w	$\nu_s SeOSe$ ( $A_1$ )
680	vs	671	vw	$\nu_{as} SeOSe$ ( $B_1$ )
879	m	873	vw	$\nu'_s SeO_3$ ( $B_1$ )
896	m	896	vs	
		935	vw	$\nu_{as} \perp SeO_3$ ( $A_2$ ), $\nu'_{as} \parallel SeO_3$ ( $B_1$ )
946	vs	944	vw	
967	vs	960	w	

<sup>a</sup> Ref.<sup>2</sup>; for denotation of the band intensities (*I*) see Table I.

in refs<sup>11,12</sup>. The following set of internal symmetrical coordinates was used for transformation of the **G** and **F** matrices to the block diagonal form:

$$S_1 = 2^{-1/2}(\Delta R_1 + \Delta R_2),$$

$$S_2 = 6^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6),$$

$$S_3 = 12^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3 + 2\Delta r_4 - \Delta r_5 - \Delta r_6),$$

$$S_4 = \Delta\varphi,$$

TABLE III

Vibration spectra of  $\text{KN}(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$  (III)

IR, s		RA, s		RA, solution		Assignment	
$\tilde{\nu}$ , $\text{cm}^{-1}$	<i>I</i>	$\tilde{\nu}$ , $\text{cm}^{-1}$	<i>I</i>	$\tilde{\nu}$ , $\text{cm}^{-1}$	<i>I</i>		
		150 Sh	vw	160 Sh, p	vw	$\delta\text{SNS}$ ( $A_1$ )	
		195 Sh	vw	196 Sh	vw	$\tau\text{SO}_3$ ( $B_1$ )	
		210	vw			}	
		139 Sh	vw	242 Sh	vw		?
		270 Sh	vw				
		334	m	343 Sh, dp	vw		$\rho \perp \text{SO}_3$ ( $A_2$ )
		356	m	360 p	w	$\rho \parallel \text{SO}_3$ ( $A_1$ )	
		373	s			$\rho' \parallel \text{SO}_3$ ( $B_1$ )	
485 b	vw	480	vw	472 Sh	vw	$\delta'_s\text{SO}_3$ ( $B_1$ )	
521	w	521	m	521 p	vw	$\delta_s\text{SO}_3$ ( $A_1$ )	
560	vw	554	vw	549 dp	vw	$\rho' \perp \text{SO}_3$ ( $B_2$ )	
572 Sh	vw	574 Sh	vw	609 p	vw	$\delta_{\text{as}} \parallel \text{SO}_3$ ( $A_1$ ), $\delta'_{\text{as}} \parallel \text{SO}_3$ ( $B_1$ )	
623	s	621	w	620 Sh, b	vw	$\delta_{\text{as}} \perp \text{SO}_3$ ( $A_2$ ), $\delta'_{\text{as}} \perp \text{SO}_3$ ( $B_2$ )	
675 Sh	vw	680	vw	681 p	vw	?	
778	w	780	vs	783 p	m	$\nu_s\text{SNS}$ ( $A_1$ )	
988	vs	979	vw	981 dp	vw	$\nu_{\text{as}}\text{SNS}$ ( $B_1$ )	
1 049	s	1 042	vw	1 029 dp(p)	vw	$\nu'_s\text{SO}_3$ ( $B_1$ )	
1 073	s	1 075	vs	1 061 p	vs	$\nu_s\text{SO}_3$ ( $A_1$ )	
1 129	s	1 122	vw			$\nu_{\text{as}} \perp \text{SO}_3$ ( $A_2$ )	
1 162	vs	1 152	w	1 129	vw	$\nu'_{\text{as}} \parallel \text{SO}_3$ ( $B_1$ )	
1 178	vs	1 160 Sh	w	1 140	vw	$\nu'_{\text{as}} \perp \text{SO}_3$ ( $B_2$ )	
1 195	vs	1 187	w	1 155	vw	$\nu_{\text{as}} \parallel \text{SO}_3$ ( $A_1$ )	
1 645	vw					$\delta_{\text{HOH}}$	
3 482	w					$\nu_s + \nu_{\text{as}}\text{OH}$	
3 540 Sh	w						

For denotation of the band intensities (*I*) see Table I.

$$S_5 = 12^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 + 2\Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6),$$

$$S_6 = 12^{-1/2}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + 2\Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6),$$

$$S_7 = N^{-1}[P(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6)],$$

$$S_R = N^{-1}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6) + P(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6)] \text{ for the block } A_1,$$

$$S_8 = \frac{1}{2}(\Delta r_2 - \Delta r_3 - \Delta r_5 + \Delta r_6),$$

TABLE IV

Vibration spectra of  $\text{HN}(\text{SO}_3\text{K})_2$  (IV)

IR, s		RA, s		Assignment
$\tilde{\nu}, \text{cm}^{-1}$	<i>I</i>	$\tilde{\nu}, \text{cm}^{-1}$	<i>I</i>	
		161 Sh	vw	$\delta\text{SNS} (A')$
		189	vw	$\tau\text{SO}_3 (A')$
		236 Sh	vw	?
		329	s	$\rho \parallel \text{SO}_3 (A'), \rho' \parallel \text{SO}_3 (A''), \rho \perp \text{SO}_3 (A'')$
465	vw	463	vw	$\delta'_s\text{SO}_3 (A'')$
541	w	526	w	$\delta_s\text{SO}_3 (A')$
555 Sh	vw	554	w	$\rho' \perp \text{SO}_3 (A')$
603	s	578	vw	$\delta_{as} \parallel \text{SO}_3 (A'), \rho'_{ae} \perp \text{SO}_3 (A'),$
		603 b	vw	$\delta_{as} \perp \text{SO}_3 (A''), \delta'_{as} \parallel \text{SO}_3 (A'')$
668	vw	671	vw	?
835 Sh	vw	842	m	$\nu_s\text{SNS} (A')$
874	s	863 Sh	vw	$\nu_{as}\text{SNS} (A'')$
?		947	vw	$\gamma\text{NH}$
1 028	vs	1 026	vw	$\nu'_s\text{SO}_3 (A'')$
1 088	m	1 089	vs	$\nu_s\text{SO}_3 (A')$
1 232	vs	1 198	vw	$\nu_{as} \perp \text{SO}_3 (A'')$
		1 214	vw	$\nu'_{as} \parallel \text{SO}_3 (A'')$
1 245 Sh	vs	1 238	vw	$\nu'_{as} \perp \text{SO}_3 (A')$
1 270	vs	1 252	vw	$\nu_{as} \parallel \text{SO}_3 (A')$
1 383	w			$\delta\text{NH} (A')$
3 232	w			$\nu\text{NH} (A')$

For denotation of the band intensities (*I*) see Table I.

$$S_9 = \frac{1}{2}(\Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_5 + \Delta\alpha_6),$$

$$S_{10} = \frac{1}{2}(\Delta\beta_2 - \Delta\beta_3 - \Delta\beta_5 + \Delta\beta_6),$$

$$S_{11} = 2^{-1/2}(\Delta\tau_1 + \Delta\tau_2) \text{ for the block } A_2,$$

$$S_{12} = 2^{-1/2}(\Delta R_1 - \Delta R_2),$$

$$S_{13} = 6^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4 - \Delta r_5 - \Delta r_6),$$

$$S_{14} = 12^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3 - 2\Delta r_4 + \Delta r_5 + \Delta r_6),$$

$$S_{15} = 12^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 - 2\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6),$$

$$S_{16} = 12^{-1/2}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - 2\Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6),$$

$$S_{17} = N^{-1}[P(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6),$$

$$S'_R = N^{-1}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6) + P(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)] \text{ for the block } B_1,$$

$$S_{18} = \frac{1}{2}(\Delta r_2 - \Delta r_3 + \Delta r_5 - \Delta r_6),$$

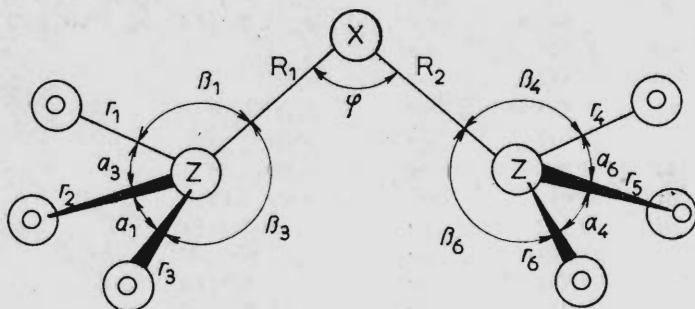


FIG. 1

The model of the anions  $X(\text{ZO}_3)_2^{-n}$  ( $Z = \text{S, Se}$ ;  $X = \text{N, NH, O}$ ;  $n = 2, 3$ ) used for normal coordinate analysis. *I*  $\text{N}(\text{SeO}_3)_2^{-3}$ , *II*  $\text{Se}_2\text{O}_7^{-2}$ , *III*  $\text{N}(\text{SO}_3)_2^{-3}$ , *IV*  $\text{HN}(\text{SO}_3)_2^{-2}$

$$S_{19} = \frac{1}{2}(\Delta\alpha_2 - \Delta\alpha_3 + \Delta\alpha_5 - \Delta\alpha_6),$$

$$S_{20} = \frac{1}{2}(\Delta\beta_2 - \Delta\beta_3 + \Delta\beta_5 - \Delta\beta_6),$$

$$S_{21} = 2^{-1/2}(\Delta\tau_1 - \Delta\tau_2) \text{ for the block } B_2,$$

where  $N$  is the normalization factor,  $P = [(2 + 4 \cos \alpha)/(1 + \cos \alpha)]^{1/2}$ ,  $S_R$  and  $S'_R$  are redundant coordinates.

Except for five fully symmetrical vibrations, the vibration spectra of all the studied anions could be interpreted only generally, and the detailed assignment was impossible until preliminary results of the normal coordinate analysis were available. In the approximation of diagonal valence force field the blocks  $A_2$  and  $B_2$  could only be solved in all the cases. The requirement of identical values for linear combinations of the potential constants  $f_\alpha - f'_\alpha$  and  $f_\beta - f'_\beta$  from the both blocks enabled a selection of bands belonging to deformation vibrations of the OZO and OZN angles of this symmetry type, because the wave number values of the bands due (in the given blocks) to the valence vibrations of the ZO bonds had no significant effect on the value of the quantities discussed. Introduction of the iteratively obtained values for  $f_\alpha - f'_\alpha$  and  $f_\beta - f'_\beta$  into the block  $B_1$  made it possible to consider two non-diagonal potential constants in its solution. On the basis of preliminary calculations we chose the elements  $F_{13,14}$  and  $F_{13,18}$  for the iteration process which gave a set of potential constants reproducing well the experimental wave numbers for vibrations of this symmetry type. The three elements ( $F_{16,16}$ ,  $F_{17,17}$ ,  $F_{18,18}$ ) already known in this calculation phase were introduced into the block  $A_1$ , which enabled to consider the non-diagonal constants  $F_{1,2}$ ,  $F_{1,4}$  and  $F_{1,7}$  therein. In this case a satisfactory agreement between the experimental and the calculated wave number values could be obtained, too.

With respect to number of the experimentally observed bands of fundamental frequencies (20 – no torsion vibration of the type  $A_2$  lying at very low wave numbers could be observed in any of the spectra) it was possible to adjust a maximum of 20 parameters in the overall calculation, and in some cases not the individual potential constants but their linear combinations (forming the elements of blocks of the factorized  $\mathbf{F}$  matrix) had to be considered. On the basis of the above-given procedure a set of 20 potential constants were chosen for the final calculation, the non-zero elements of the factorized  $\mathbf{F}$  matrix being expressed by this set in the following way:

$$F_{1,1} = f_R + f'_R,$$

$$F_{1,2} = 3^{1/2}(f_{Rr} + f'_{Rr}),$$

$$F_{1,4} = 2^{1/2}Rf_{R\phi},$$



$$F_{1,6} = (2Rr/3)^{1/2}(f'_{R\beta} - f''_{R\beta}),$$

$$F_{1,7} = 2^{1/2}N_1^{-1}[3Prf_{R\alpha} - (Rr)^{1/2}(3f_{R\beta} + f'_{R\beta} + 2f''_{R\beta})],$$

$$F_{2,2} = f_r + 2f'_r + f''_r + 2f'''_r,$$

$$F_{3,3} = f_r - f'_r + f''_r - f'''_r,$$

$$F_{4,4} = R^2 f_\varphi,$$

$$F_{4,6} = 2R(Rr/3)^{1/2}(f_{\varphi\beta} - f'_{\varphi\beta}),$$

$$F_{5,5} = r^2(f'_\alpha - f''_\alpha),$$

$$F_{6,6} = Rr(f_\beta - f'_\beta),$$

$$F_{7,7} = 6N_2^{-2}[P^2r^2(f_\alpha + 2f'_\alpha) + Rr(f_\beta + 2f'_\beta) - 2Pr(Rr)^{1/2}(f_{\alpha\beta} + 2f'_{\alpha\beta})]$$

for the block  $A_1$ ,

$$F_{8,8} = f_r - f'_r - f''_r + f'''_r,$$

$$F_{9,9} = F_{5,5},$$

$$F_{10,10} = F_{6,6},$$

$$F_{10,11} = R^{3/2}r^{1/2}(f_{\beta\tau} - f'_{\beta\tau}),$$

$$F_{11,11} = R^2 f_\tau \text{ for the block } A_2,$$

$$F_{12,12} = f_R - f'_R,$$

$$F_{12,13} = 3^{1/2}(f_{Rr} - f'_{Rr}),$$

$$F_{12,16} = -F_{1,6},$$

$$F_{12,17} = 2^{1/2}N_1^{-1}[3Prf_{R\alpha} - (Rr)^{1/2}(3f_{R\beta} - f'_{R\beta} - 2f''_{R\beta})],$$

$$F_{13,13} = f_r + 2f'_r - f''_r - 2f'''_r,$$

$$F_{14,14} = F_{8,8},$$

$$F_{15,15} = F_{5,5},$$

$$F_{16,16} = F_{6,6},$$

$$F_{17,17} = F_{7,7} \text{ for the block } B_1$$

$$F_{18,18} = F_{3,3},$$

$$F_{19,19} = F_{5,5},$$

$$F_{20,20} = F_{6,6},$$

$$F_{20,21} = R^{3/2} r^{1/2} (f_{\beta\tau} + f'_{\beta\tau}),$$

$$F_{21,21} = F_{11,11} \text{ for the block } B_2.$$

TABLE V

Quadratic potential constants (QPC) of the anions  $N(\text{SeO}_3)_2^{-3}$ ,  $\text{Se}_2\text{O}_7^{-2}$ ,  $N(\text{SO}_3)_2^{-3}$  and  $\text{HN}(\text{SO}_3)_2^{-3}$

QPC	$N(\text{SeO}_3)_2^{-3}$	$\text{Se}_2\text{O}_7^{-2}$	$\text{Se}_2\text{O}_7^{-2b}$	$\text{S}_2\text{O}_7^{-2b}$	$N(\text{SO}_3)_2^{-3}$	$\text{HN}(\text{SO}_3)_2^{-2}$
$f_R$	362.4	311.8	298	332	525.1	546.7
$f'_R$	16.5	42.6	42	62	61.1	194.8
$f_r$	592.2	677.6	667	794	720.6	814.8
$f'_r$	32.2	15.1	44	168	76.4	51.0
$f''_r$	0.9	6.3	-25	19	6.0	20.8
$f'''_r$	-4.9	-4.8	10	18	-0.2	4.0
$f_\varphi$	41.8	26.7	19	13	49.2	48.9
$f_\alpha - f'_\alpha$	53.0	55.1			112.2	99.9
$f_\beta - f'_\beta$	46.6	35.6			68.9	60.3
$F_{7,7}$	135.3	119.5			147.3	132.4
$f_\tau$	12.2	12.2			16.9	11.5
$f_{Rr}$	5.1	17.5			20.3	13.0
$f'_{Rr}$	-8.5	-9.6			-13.6	-7.7
$f_{R\varphi}$	20.3	2.2			23.9	26.6
$f'_{R\beta} - f'_{R\beta}$	18.5	22.7			19.5	3.6
$F_{1,7}$	-80.6	-30.5			-124.7	-93.9
$F_{12,17}$	-78.4	-34.8			-133.6	-79.5
$f_{\varphi\beta} - f'_{\varphi\beta}$	-4.7	-5.3			-3.7	-0.7
$f_{\beta\tau}$	-2.6	-2.1			-0.7	0.7
$f'_{\beta\tau}$	-8.2	-6.8			-12.0	-3.9

<sup>a</sup> All the QPC are given in  $\text{Nm}^{-1}$ ; <sup>b</sup> ref.<sup>13</sup>.

TABLE VI

Interpretation of vibration spectra of anions  $N(\text{SeO}_3)_2^{-3}$ ,  $N(\text{SO}_3)_2^{-3}$ ,  $\text{HN}(\text{SO}_3)_2^{-2}$ , and  $\text{Se}_2\text{O}_7^{-2}$  and distribution of potential energy (PE)

No	Inter- pretation <sup>a</sup>	$\tilde{\nu}^b$ cm <sup>-1</sup>	$N(\text{SeO}_3)_2^{-3}$ distribution of PE <sup>c</sup> , %	$\tilde{\nu}^b$ cm <sup>-1</sup>	$N(\text{SO}_3)_2^{-3}$ distribution of PE <sup>c</sup> , %	$\tilde{\nu}^b$ cm <sup>-1</sup>	$\text{HN}(\text{SO}_3)_2^{-2}$ distribution of PE <sup>c</sup> , %	$\tilde{\nu}^b$ cm <sup>-1</sup>	$\text{Se}_2\text{O}_7^{-2}$ distribution of PE <sup>c</sup> , %
<b>A<sub>1</sub></b>									
1	$\nu_{\text{SZXZ}}$	621	44 $\nu_1$ + 27 $\nu_4$ + 28 $\nu_6$	783	52 $\nu_1$ + 19 $\nu_4$	842	60 $\nu_1$ + 15 $\nu_4$ + 15 $\nu_6$	560	59 $\nu_1$ + 19 $\nu_4$ + 21 $\nu_6$
2	$\nu_{\text{S}}\text{ZO}_3$	862	97 $\nu_2$	1 061	87 $\nu_2$	1 089	82 $\nu_2$ + 15 $\nu_1$	896	99 $\nu_2$
3	$\nu_{\text{AS}} \parallel \text{ZO}_3$	884	95 $\nu_3$	1 155	79 $\nu_3$	1 252	85 $\nu_3$	960	98 $\nu_3$
4	$\delta_{\text{ZXZ}}$	130	78 $\nu_4$ + 16 $\nu_6$	160	78 $\nu_4$ + 18 $\nu_6$	161	72 $\nu_4$ + 23 $\nu_6$	106	79 $\nu_4$
5	$\delta_{\text{AS}} \parallel \text{ZO}_3$	407	97 $\nu_5$	609	86 $\nu_5$	603	82 $\nu_5$	413	98 $\nu_5$
6	$\rho \parallel \text{ZO}_3$	267	58 $\nu_6$ + 37 $\nu_1$	360	52 $\nu_6$ + 30 $\nu_7$	329	41 $\nu_6$ + 46 $\nu_7$	238	72 $\nu_6$ + 17 $\nu_1$
7	$\delta_{\text{S}}\text{ZO}_3$	376	79 $\nu_7$ + 20 $\nu_1$	521	63 $\nu_7$ + 27 $\nu_1$	526	51 $\nu_7$ + 17 $\nu_6$ + 15 $\nu_1$	386	90 $\nu_7$
<b>A<sub>2</sub></b>									
8	$\nu_{\text{AS}} \perp \text{ZO}_3$	873	98 $\nu_8$	1 129	83 $\nu_8$	1 214	88 $\nu_8$	944	98 $\nu_8$
9	$\delta_{\text{AS}} \perp \text{ZO}_3$	422	90 $\nu_9$	625	82 $\nu_9$	609	85 $\nu_9$	432	89 $\nu_9$
10	$\rho \perp \text{ZO}_3$	258	94 $\nu_{10}$	343	94 $\nu_{10}$	329	96 $\nu_{10}$	229	89 $\nu_{10}$
11	$\tau_{\text{S}}\text{ZO}_3$	70	91 $\nu_{11}$	90	92 $\nu_{11}$	77	95 $\nu_{11}$	73	90 $\nu_{11}$
<b>B<sub>1</sub></b>									
12	$\nu_{\text{AS}}\text{ZNXZ}$	822	93 $\nu_{12}$	981	94 $\nu_{12}$	863	93 $\nu_{12}$	671	93 $\nu_{12}$
13	$\nu_{\text{S}}'\text{ZO}_3$	868	98 $\nu_{13}$	1 029	92 $\nu_{13}$	1 026	93 $\nu_{13}$	896	99 $\nu_{13}$
14	$\nu_{\text{AS}} \parallel \text{ZO}_3$	873	96 $\nu_{14}$	1 129	84 $\nu_{14}$	1 214	89 $\nu_{14}$	944	98 $\nu_{14}$
15	$\delta_{\text{AS}}' \parallel \text{ZO}_3$	407	98 $\nu_{15}$	609	88 $\nu_{15}$	597	91 $\nu_{15}$	413	99 $\nu_{15}$
16	$\rho' \parallel \text{ZO}_3$	258	97 $\nu_{16}$	360	91 $\nu_{16}$	329	92 $\nu_{16}$	238	97 $\nu_{16}$
17	$\delta_{\text{S}}'\text{ZO}_3$	376	87 $\nu_{17}$	475	78 $\nu_{17}$ + 20 $\nu_{12}$	463	89 $\nu_{17}$	378	97 $\nu_{17}$
<b>B<sub>2</sub></b>									
18	$\nu_{\text{AS}}' \perp \text{ZO}_3$	884	97 $\nu_{18}$	1 140	84 $\nu_{18}$	1 238	89 $\nu_{18}$	968	98 $\nu_{18}$
19	$\delta_{\text{AS}}' \perp \text{ZO}_3$	407	92 $\nu_{19}$	616	85 $\nu_{19}$	603	90 $\nu_{19}$	422	89 $\nu_{19}$
20	$\rho' \perp \text{ZO}_3$	435	81 $\nu_{20}$ + 16 $\nu_{21}$	549	82 $\nu_{20}$ + 15 $\nu_{21}$	554	82 $\nu_{20}$ + 15 $\nu_{21}$	363	83 $\nu_{20}$ + 15 $\nu_{21}$
21	$\tau_{\text{AS}}\text{ZO}_3$	154	95 $\nu_{21}$	196	96 $\nu_{21}$	189	88 $\nu_{21}$	156	95 $\nu_{21}$

<sup>a</sup> Z = S, Se; X = N, O. <sup>b</sup> The maximum difference between the calculated and experimental wave number values given in the Table does not exceed 1%. <sup>c</sup> Only the contributions greater than 15% are given rounded off to integers.

Table V gives the final values of the 20 adjusted parameters for all the four studied anions along with some values of the potential constants published<sup>13</sup> for the anions  $S_2O_7^{2-}$  and  $Se_2O_7^{2-}$ . Their introduction back into the secular equations reproduces the experimental values of fundamental frequencies with an accuracy better than 1%; in most cases absolute error does not exceed  $1\text{ cm}^{-1}$ . In the Raman spectra of the solid samples of *II* and *IV* there appear several bands (e.g.  $331$  and  $935\text{ cm}^{-1}$  for *II*;  $578$ ,  $671$  and  $1198\text{ cm}^{-1}$  for *IV*) which could not be assigned to their fundamental frequencies on the basis of the calculations carried out. Obviously they are generated by the presence of two or more anions in non-equivalent positions of the elementary cells of the crystals; in some cases they can be bands of combination or harmonic frequencies.

The  $f_{SeO}$  value of the anion *II* is higher than that of *I* by about 15%, and there is a similar ratio of the  $f_{SO}$  values in the pair of the anions *IV* and *III*. In the both cases the increase in the  $f_{ZO}$  value, i.e. decrease of polarity of the terminal ZO bonds, is due to higher electronegativity of the central bridge atom. From the  $f_R$  values it follows that a bonding  $\pi$ -contribution is insignificant at the bridge bonds of the anions *I* and *II* (the bond order is approximately unity). A quite different situation is encountered with the anions *III* and *IV* in which the respective bond order is about 1.5. The  $f_R$  value is about the same for these two anions, and different bonding relations at the bridge nitrogen atom make themselves felt (besides a marked, roughly tenfold lowering of the wave number difference between symmetrical and anti-symmetrical valence vibration of the bridge SNS bonds) also by about three fold increase of the interaction constant  $f'_R$  of the anion *IV* as compared with that of *III*.

Deformation vibration of the bridge bonds SeOSe in the anion *II* (ref.<sup>13</sup>) and in a number of other compounds of hexavalent selenium<sup>14</sup> has so far been connected with the intensive Raman spectral bands within  $240$  to  $230\text{ cm}^{-1}$ , which is obviously due to the earlier presumed<sup>15,16</sup> localization of  $\delta$ SOS of  $S_2O_7^{2-}$  at about  $330\text{ cm}^{-1}$ . However, on the basis of the calculations carried out it became clear that the band appearing in this region belongs to deformation vibrations of the  $—SeO_3$  end group, and that  $\delta$ SeOSe must be connected with a band lying at a substantially lower wave number ( $106\text{ cm}^{-1}$ ). Attempts to find such a set of the potential constants which would agree with the originally suggested interpretation always led to physically non-acceptable distribution of potential energy in the set of fully symmetrical vibrations and also to non-negligible differences between their experimental and calculated wave numbers. The interpretation suggested by us agrees well with the position of  $\delta$ SOS in  $S_2O_7^{2-}$  determined on the basis of normal coordinate analysis<sup>13</sup> (in the interval  $180–110\text{ cm}^{-1}$ ) and with the wave number values of deformation vibrations of the bridge ZNZ bonds in the spectra of the compounds *I*, *III*, and *IV* ( $160$  to  $130\text{ cm}^{-1}$ ).

Table VI gives the calculated distribution of potential energy along with a lucid interpretation of the vibration spectra of all the studied anions, and it is seen that

the vibrations belonging to the  $A_2$ ,  $B_1$ , and  $B_2$  symmetry types are always quite characteristic. Out of the fully symmetric vibrations,  $\nu_2$ ,  $\nu_3$ , and  $\nu_5$  can only be considered sufficiently characteristic. Among the four remaining vibrations there exists a considerable interaction which fundamentally decreases possibility of their identification in spectra of cognate compounds, unless results of normal coordinate analysis are applied.

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