VIBRATIONAL SPECTRA
OF N-METHYLAMIDOSELENATES AND N-METHYLAMIDOSULFATES

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On the basis of vibrational spectra assignments of the anions SeO_3NXY^- (X, Y = H, CH_3), the quadratic potential constants were calculated in the diagonal valence force field approximation. The assumption has been confirmed that the unexpectedly low force constant value of the SeO bond in $NH_4Se_3ONH_2$ is due to the H bonding formation to which the NH_4^+ cations considerably contribute. The influence of hydrogen bonds formed by —NH_2 groups on the SeO bond force constant was examined by means of a gradual substitution of hydrogen atoms by methyl groups. The vibrational spectra of the SO_3NXY^- (X, Y = H, D, CH_3) anions were also measured and calculation of the quadratic potential constants attempted.

The passage from the ZO_4^{2-} anion to Zo_3X^- anions (Z = S, Se; X = CH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, OCH_3, OH, F) is accompanied by rehybridization of the electron valence sphere of the central Z atom. With increasing electronegativity of the substituent X, the s-character of ZO bonds and also the p-character of ZX bond increase. Consequently, the bond angles between ZO bonds increase and the bonds become stronger and shorter. These effects should manifest themselves in the growing valence force constant f_{ZO} value. The same consequence results from the distribution of the two π-bonds over only three ZO bonds and not over four bonds as in the case of the ZO_4^{2-} anions[1].

In the series of $CH_3ZO_3^-$, $NH_2ZO_3^-$, $HOZO_3^-$, $CH_3OZO_3^-$, and FZO_3^- anions, the force constant of the ZO bond should increase in the order given, i.e., from $CH_3ZO_3^-$ to FZO_3^-. With the selenium compounds, such a dependence was confirmed by experiments. Only the f_{SeO} value in the amidoselenate anion calculated on the basis of vibrational spectra of $NH_4SeO_3NH_2$, was too low to correspond to the series mentioned[2]. This anomaly was ascribed[2] to the formation of hydrogen bond which in ammonium amidoselenate may occur under the participation of both the —NH_2 group and the NH_4^+ cation.

Calculations of quadratic potential constants of the $SeO_3NH_2^-$ anion were therefore attempted on the basis of vibrational spectra of the potassium salt where the cation effect mentioned above cannot interfere. Notwithstanding, also in this compound there may exist hydrogen bond due to the —NH_2 groups. In this connection it was of interest to observe the influence of the gradual substitution of hydrogen atoms in the —NH_2 group by methyl groups on the force constant values of the SeO bonds. The vibrational spectra of N-methylaminosulfate anions were also measured and discussed.

TABLE I

Assignments of Infrared Spectra of SeO_3NXY^- Anions

b, broad band; s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder; Σ, overtone or combination.

$SeO_3NH_2^-$	$SeO_3NHCH_2^-$	$SeO_3N(CH_3)_2^-$	Assignment
		227 w	$\tau Se-NC_2$
		248 wsh	$\tau_{s+as}NC_2$
		256 wsh	
	272 vw	268 wsh	$\omega NC_2 + \tau NHC$
296 vw	285 vw	285 w	$\varrho_s SeO_3$
314 w	313 w	320 vw	$\varrho_{as} SeO_3$
	344 w		$\tau Se-NHC$
		348 vw	ϱNC_2
369 m	380 w		$\delta_s SeO_3$
385 m	389 w		
		374 wsh	$\delta_s SeO_3 + \delta NC_2$
		408 m	
	414 w		ωNHC
404 m	428 m	425 m	$\delta_{as} SeO_3$
512 vw			$\tau Se-NH_2$
655 s	614 w		νSeN
		574 w	$\nu SeN + \varrho NHC$
		833 w	$\nu_s NC_2$
	839 w		δNHC
857 s			ωNH_2
864 s	866 s	869 s	$\nu_s SeO_3$
		893 ssh	$\nu_{as} NC_2$
	903 vs		νNC
891 vs	916 vs	905 vs	$\nu_s SeO_3$
919 vs	934 s	917 vssh	$\nu_{as} SeO_3$
	1 032 w	1 036 vw	$\varrho_s CH_3$
	1 127 vw	1 163 w	$\varrho_{as} CH_3$
1 123 w			δNH_2
	1 400 vw	1 408 vw	$\delta_s CH_3$
	1 417 vw		
superimposed by absorption bands of nujol			$\delta_{as} CH_3$
1 518 vw			δNH_2
2 020 vw			
2 262 vw		2 445 w	Σ
2 620 vw	2 540 vw	2 508 vw	
	2 784 vw	2 790 m	$\nu_s CH_3$
superimposed by absorption bands of nujol			$\nu_{s+as} CH_3$
	3 135 m		νNH
3 151 vs			$\nu_s NH_2$
3 187 vs			$\nu_{as} NH_2$

EXPERIMENTAL

The test substances were prepared and purified by reported methods[3-5]. The deuterated substances were obtained by a 6—8 fold recrystallisation from D_2O. Infrared spectra were measured on a PE 621 apparatus in nujol suspension in KRS-5 cells (200—400 cm^{-1} region) and on a UR-20 apparatus in nujol suspension and KBr cells (400—3600 cm^{-1} region). The derivatives of KSO_3. .NH_2 were measured also in KBr discs. The Raman spectra of potassium amidosulfate derivatives were obtained from solid samples on a Spex-Ramalog apparatus.

RESULTS AND DISCUSSION

Vibrational spectra of N-*methylamidoselenates and* N-*methylamidosulfates.* From the anions examined only two, namely, $NH_2ZO_3^-$ and $N(CH_3)_2ZO_3^-$, may in an optimum case belong to the point group of symmetry C_s, while the $NHCH_3ZO_3^-$ anion is quite unsymmetrical. The occurrence of all fundamental vibrations in infrared and Raman spectra may therefore be expected.

The infrared spectra of SeO_3NXY^- anions are given in Table I. Because of an easy hydrolysis of these anions, it was not possible to prepare deuterated specimens by recrystallisation from D_2O. For this reason, the spectra were interpreted merely by comparison with those of the structurally related compounds of selenium[2], sulfur[6-16], and phosphorus[17]. Use was also made of the known assignments of methylamine, dimethylamine, and trimethylamine[18,19].

The infrared spectrum of $KSeO_3NH_2$ in the 400—3600 cm^{-1} region has been recently discussed[2]. All the assignments are accepted in the present paper except for the band position belonging to the ω_{NH_2} vibration. On the basis of an analogy with spectra of the amidosulfate anion, the absorption band belonging to this vibration is assumed[2] to be at about 970 cm^{-1} in spite of the absence of any absorption band in this region in the infrared spectrum of $KSeO_3NH_2$. On the other hand, the splitted band at about 860 cm^{-1} is assigned to $\nu_s SeO_3$ and the splitting is attributed to the presence of several ions in unequal positions in the crystal unit cell. Despite the impossibility to measure the infrared spectrum of $KSeO_3ND_2$, the effect mentioned might be explained by the assumption that ω_{NH_2} lies in the region of $\nu_s SeO_3$ stretching vibrations. The partially overlapped band at 857 cm^{-1} would then belong to ω_{NH_2} and the band at 864 cm^{-1} to $\nu_s SeO_3$. In the 200—400 cm^{-1} region, the earlier authors[2] obtained only the Raman spectrum of $NH_4SeO_3NH_2$. On the basis of our measurements of infrared spectra of $KSeO_3NH_2$ and $NH_4SeO_3NH_2$, we have somewhat changed assignments of bands belonging to δ_s, ϱ_s, and $\varrho_{as} SeO_3$ as it may be seen from Table I. We did not observe the band at 235 cm^{-1} reported in the earlier paper[2] and interpreted as $\varrho_{s+as} SeO_3$. This band may belong to the crystal lattice vibration with a poorly intensive absorption in infrared spectra or to decomposition products of $NH_4SeO_3NH_2$ formed by irradiation of the test substance during measurement of the Raman spectrum.

Assignments of infrared spectra of the anions $SeO_3NHCH_3^-$ and $SeO_3N(CH_3)_2^-$ were performed in agreement with the discussed spectrum of $SeO_3NH_2^-$ discussed above using the data from papers[18,19]. In the $200-400$ cm^{-1} region, the assignment is only of informative value because of the small extent of the compared experimental material.

TABLE II

Assignments of Vibrational Spectra of Anions $SO_3NH_2^-$, SO_3NHD^-, and $SO_3ND_2^-$

$SO_3NH_2^-$		SO_3NHD^- + $SO_3ND_2^-$	Assignment
IR	Raman	IR	
362 m	363 w	290^b s 321^a m	} $\varrho_{as}SO_3$
		366 w	$\tau S{-}ND_2$
403 vw	402 s	384^b w 394^a w	} $\varrho_s SO_3$
		438 vw	$\tau S{-}NHD$
503 w	503 vw		$\tau S{-}NH_2$
		546^b m 563^a vw	} $\delta_s SO_3$
586 s	584 w	585 m	} $\delta_{s\,+\,as}SO_3$
593 s		592 wsh	
		717 m	ωND_2
		776 vw	ωNHD
802 s	801 m	805 s	νSN
		818 wsh	ϱND_2
952 m	953 vw		ωNH_2
		1 017 vw	ϱNHD
1 049 vs	1 042 vs	1 048 s	$\nu_s SO_3$
1 123 s	1 133 vw	1 127 vw	ϱNH_2
		1 157 m	δND_2
1 228 vs b	1 191 w	1 215 vs	$\nu_{s\,+\,as}SO_3$
	1 265 vw		
		1 398 vw	δNHD
1545 m		1 542 vw	δNH_2
		2 404 w	$\nu_s ND_2$
		2 442 vw	νND
		2 489 m	$\nu_{as}ND_2$
3 269 s		3 263 vw	$\nu_s NH_2$
		3 287 w	νNH
3 320 s		3 318 vw	$\nu_{as}NH_2$

^{a} Belongs to the anion SO_3NHD^-; ^{b} belongs to the anion $SO_3NH_2^-$.

TABLE III
Assignments of Vibrational Spectra of $SO_3NHCH_3^-$ and $SO_3NDCH_3^-$ Anions

SO₃NHCH₃⁻		SO₃NHCH₃ + SO₃NDCH₃⁻	Assignment
IR	Raman	IR	
260 vw	263 vw	243 vw	} τS—N + τN—C
280 vw	284 vw	275 vw	
408 vw	409 w	390^a vw	} ϱ_sSO₃
		406^a vw	
440 w	438 m	435 w	ϱ_{as}SO₃
		535^b m	} δ_sSO₃ + ωNCD
		552^a w	
552 s	553 w		δ_sSO₃
570 w	574 vw	567 vwsh	ωNCH
577 w	604 w	575 w	} δ_{as}SO₃
603 m		595 m	
		635 wsh	} ϱNCD
		648 m	
718 msh		720 vwsh	ϱNCH
735 s	735 vw	735 m	νSN
		789 w	} δNCD
		807 w	
885 vw	877 vw	880 vw	δNCH
950 vw		944 vw	Σ
1 047 s		1 047 s	ν_sSO₃
1 064 m	1 057 vs	1 062 wsh	νCN
1 137 w	1 140 w	1 098 m	} ϱ_sCH₃
		1 139 vw	
1 184 vs	1 194 vw	1 182 vs	ν_{2s}SO₃
1 217 vs	1 224 w	1 203 vs	
1 243 m		1 227 s	} ϱ_{2s}CH₃
		1 246 m	
		1 381 vw	} δ_sCH₃
1 427 m	1 416 vw	1 428 vw	
1 445 vw	1 454 vw	1 444 vw	
1 456 vw	1 489 vw	1 460 vw	} δ_{as}CH₃
1 478 w		1 479 vw	
		2 405 m	} νND
		2 423 m	
2 813 vw		2 814 vw	
2 839 m		2 845 vw	} ν_sCH₃
2 895 vw		2 887 vw	
2 926 w		2 915 w	} Σ
		2 952 vw	
2 973 m		2 973 w	} ν_{as}CH₃
2 995 vw		2 995 vw	
3 249 s		3 245 w	νNH

^{a} Belongs to the anion $SO_3NHCH_3^-$; ^{b} belongs to the anion $SO_3NDCH_3^-$.

There is more experimental data for the SO_3NXY^- anions, since it was possible to prepare the deuterated analogues and make use of their spectra to a more detailed identification of absorption bands belonging to vibrations due to NH bands. Nevertheless, also in this case the interpretation of some band below 400 cm^{-1} is far from being quite unequivocal since the coordinate analysis of ions was performed on a considerably simplified model.

TABLE IV

Assignments of Vibrational Spectra of the $SO_3N(CH_3)_2^-$ Anion

$SO_3N(CH_3)_2^-$		Assignment
IR	Raman	
237 w	236 vw	$\tau S-N$
245 wsh	259 vw b	$\tau_{s+as}NC_2$
267 vwsh		
285 vw	282 vw	ωNC_2
369 vw	376 m	$\varrho_s SO_3$
395 vw	395 vw	ϱNC_2
436 w	432 m	$\varrho_{as} SO_3$
475 vw	476 vw	δNC_2
553 w	555 s	$\delta_s SO_3$
586 m	589 m	$\delta_{as} SO_3$
726 s	734 vs	νSN
945 m	948 vw	$\nu_s NC_2$
1 043 ssh	1 047 vwsh	$\nu_{as} NC_2$
1 050 s	1 060 vs	$\nu_s SO_3$
1 100 vw	1 105 vw	$\varrho_s CH_3$
1 153 w	1 143 vw	
1 183 vs	1 185 vw	$\nu_{as} SO_3$
1 195	1 218 vw	
1 233 vs	1 235 vw	$\varrho_{as} CH_3$
1 252 ssh		
1 378 w	1 388 vw	$\delta_s CH_3$
1 427 vw	1 429 vw	
1 449 w	1 456 w	$\delta_{as} CH_3$
1 455 w		
1 468 w	1 476 vw	
2 789 vw		
2 833 w		
2 878 w		$\nu_{s+as} CH_3$
2 915 vw		
2 953 w		
3 002 vw		

The vibration spectra of the $SO_3NH_2^-$ and $SO_3ND_2^-$ anions have been reported many times[6-16]. The existing data were therefore only completed or more exactly formulated. Table II shows the infrared and Raman spectrum of KSO_3NH_2 and infrared spectrum of the deuterated analogue. Since the deuteration was not quite quantitative, the infrared spectrum relates to a mixture of three compounds, namely, KSO_3ND_2, KSO_3NHD, and a little of KSO_3NH_2 (the latter component manifests itself only by the most intensive bands). From the data of Table II, the following relations may be written for the isotopic ratio of analogous bands of NH_2, NHD, and ND_2 groups:

$$\nu NH : \nu NH = 1.35 : 1.00$$

$$\delta,\varrho,\omega_{NH_2} : \delta,\varrho,\omega_{NHD} : \delta,\varrho,\omega_{ND_2} = 1.33 : 1.12 : 1.00$$

It has also been observed, that the deuteration bears a great influence on the position of absorption bands belonging to bending vibrations of the $-SO_3$ group, obviously because of a strong coupling with some bending vibration of the $-NH_2$ group.

Vibrational spectra of the $SO_3NHCH_3^-$ and $SO_3NDCH_3^-$ anions are shown in Table III. Similarly to the preceding case, the infrared spectrum of $SO_3NDCH_3^-$ exhibits the most intensive bands of the $SO_3NHCH_3^-$ anion; moreover, we may observe doublets of absorption bands belonging to bending vibrations (ND bonds) and of the bond corresponding to ϱ_{CH_3}. The vibrational spectra of the $SO_3N(CH_3)_2^-$ anion shown in Table IV have been interpreted (similar to $SeO_3N(CH_3)_2$) on the basis of a comparison with those of $SO_3NH_2^-$ and $SO_3NHCH_3^-$.

Calculation of potential constants of N-methylamidoselenates and N-methyl-amidosulfates. In order to evaluate the bond relations in our test substances, calculations of quadratic potential constants of N-methylamidoselenate and N-methylamido-sulfate anions were attempted. Owing to a great number of the atoms involved and their low symmetry, considerable simplifications had to be introduced in spite of the use of a digital computer. In all cases, the $-NXY$ groups were taken as a vibrating unit and their active masses were calculated from the following relations:

$$m_{NH_2}^{akt} = m_N + 2m_H \; ; \quad m_{NDH}^{akt} = m_N + m_H + 3/4m_D \; ; \quad m_{ND_2}^{akt} = m_N + 3/2m_D \; ;$$

$$m_{NHCH_3}^{akt} = m_N + m_H + 1/4m_{CH_3} \; ; \quad m_{NDCH_3}^{akt} = m_N + 3/4m_D + 1/4m_{CH_3} \; ;$$

$$m_{N(CH_3)_2}^{akt} = m_N + 1/2m_{CH_3} \; .$$

The scheme of the anion model belonging to the point group C_{3v} with the fully reducible representation $\Gamma = 3A_1^{p,\alpha} + 3E^{p,\alpha}$ is shown on Fig. 1. The calculation of quadratic potential constants was performed by the Wilson **F**, **G**-matrix method on a E-503 digital computer. The **G** and **F** matrices expressed in internal coordinates

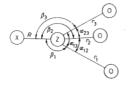were transformed to $\mathbf{G}_s$ and $\mathbf{F}_s$ with the use of the following set of symmetrical co-ordinates:

$$S_1^A 1 = R\;;\quad S_2^A 1 = 1/\sqrt{3}(r_1 + r_2 + r_3)\;;$$
$$S_3^A 1 = NP[(\alpha_{23} + \alpha_{13} + \alpha_{12}) - (\beta_1 + \beta_2 + \beta_3)]\;;$$
$$S_4^A 1 = N/P(\alpha_{23} + \alpha_{13} + \alpha_{12} + \beta_1 + \beta_2 + \beta_3)\;;$$
$$S_5^E = 1/\sqrt{6}(2r_1 - r_2 - r_3)\;;\quad S_6^E = 1/\sqrt{6}(2\alpha_{23} - \alpha_{13} - \alpha_{12})\;;$$
$$S_7^E = 1/\sqrt{6}(2\beta_1 - \beta_2 - \beta_3)\;;\quad S_5^E = 1/\sqrt{2}(r_2 - r_3)\;;$$
$$S_6^E = 1/\sqrt{2}(\alpha_{13} - \alpha_{12})\;;\quad \text{and}\quad S_7^E = 1/\sqrt{2}(\beta_2 - \beta_3)\;,\quad \text{wherein}$$
$$P = [(2 + 4\cos\alpha)/(1 + \cos\alpha)]^{1/2}\quad \text{and N is the normalization factor.}$$

The structural parameters of the ions were taken from papers[2,6].

Wave number values corresponding to the degenerated mode E were calculated as the arithmetic mean of observed bands for $\nu_{s+as}SeO_3$, $\delta_{s+as}SeO_3$, and $\varrho_{s+as}SeO_3$. The quadratic potential constant values calculated from the estimate of diagonal elements by the iteration method in approximation of the diagonal valence force field are shown in the first three columns of Table V. In the calculation, the relation $d'_{OSeN} = 1/10 d_{OSeN}$ was used[2]. The right part of Table V shows a set of quadratic potential constants calculated under the assumption that in the approximation used, all the three anions may be envisaged as isotopically substituted analogues. This procedure has been used to determine at least approximately the magnitude of the off-diagonal elements of the matrix $\mathbf{F}_s$ which must be otherwise neglected when vibrational spectra of several isotopically substituted derivatives are not at disposal for the calculation.

The potential constant f_{SeN} value* decreases in the order $SeO_3NH_2^-$, $SeO_3NHCH_3^-$, and $SeO_3N(CH_3)_2^-$ in accordance with the observed bond stability. This somewhat

Fig. 1

Model of the ZO_3X^- Anions ($Z = S$, Se; $X = NH_2$, $NHCH_3$, $N(CH_3)_2$) as Used for Calculations of Quadratic Potential Constants

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* As shown by the considerably higher f_{SeN} value when calculated from spectra of the three "isotopically substituted" analogues in contrast to the f_{SeN} values of the particular anions, negligence of the off-diagonal potential constants in the calculation leads to greatest errors in determination of the f_{SeN} value.

TABLE V
Quadratic Potential Constants of $SeO_3NH_2^-$, $SeO_3NHCH_3^-$, and $SeO_3N(CH_3)_2^-$ Anions (in mdyn/Å)

Force constant	$SeO_3NH_2^-$	$SeO_3NHCH_3^-$	$SeO_3N(CH_3)_2^-$	Force constant	SeO_3X^- [a]	
$f\,SeN$	3.37_4	3.32_4	3.18_8	$f\,SeN$	3.59_9	$g_{SeN} - g_{OSeN}$ -0.42_6
$f\,SeO$	6.13_9	6.21_1	6.22_0	$f\,SeO$	6.22_1	$g_{SeO} - g_{OSeO}$ 0.01_9
$f'\,SeO$	0.15_1	0.13_5	0.16_3	$f'\,SeO$	0.19_5	
$d\,OSeO$	0.50_9	0.55_4	0.55_5	$d\,OSeO$	0.55_0	$g_{OSeO} - g_{SeO}$ -0.00_5
$d'\,OSeO$	0.00_3	0.01_3	0.01_0	$d'\,OSeO$	0.02_2	
$d\,OSeN$	0.33_7	0.35_0	0.38_0	$d\,OSeN$	0.35_5	$g_{OSeN} - g_{OSeN}$ 0.01_5
$d'\,OSeN$	0.03_4	0.03_5	0.03_8	$d'\,OSeN$	0.03_5	

[a] $X = -NH_2$, $-NHCH_3$, $-N(CH_3)_2$.

TABLE VI
Percent Potential Energy Distribution in the ZO_3NXY^- Anions

Mode	$SeO_3NH_2^-$			$SeO_3NHCH_3^-$			$SeO_3N(CH_3)_2^-$			$SO_3NH_2^-$		
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
$\nu_1(A_1)$	92·41	4·43	3·16	90·60	3·58	5·82	88·06	2·78	9·16	44·99	21·49	33·52
$\nu_2(A_1)$	3·92	95·08	1·00	2·80	96·02	1·08	2·02	96·99	0·99	13·40	78·46	8·14
$\nu_3(A_1)$	3·78	0·39	95·82	6·61	0·36	93·03	9·88	0·27	89·85	40·49	2·75	56·76
	S_5	S_6	S_7	S_5	S_6	S_7	S_5	S_6	S_7	S_5	S_6	S_7
$\nu_1(E)$	98·30	1·14	0·56	98·19	1·24	0·57	98·06	1·32	0·62	98·31	6·44	1·25
$\nu_2(E)$	1·03	98·43	0·54	1·14	98·53	0·33	1·22	98·41	0·37	2·85	96·71	0·44
$\nu_3(E)$	0·67	0·39	98·94	0·66	0·29	99·05	0·73	0·01	99·26	0·22	0·02	99·76

TABLE VII
Multiplicity Solution of the GF Problem for the SO_3NXY^- Anions (in mdyn/Å)

	Solution, No	1	2	3	4	5	6
$SO_3NH_2^-$	$F_{11}(A_1)$	4·606	4·606	3·175	3·175	2·821	5·832
	$F_{22}(A_1)$	7·331	7·331	6·224	6·224	6·260	6·083
	$F_{33}(A_1)$	3·307	3·307	5·573	5·573	5·911	2·942
	$F_{11}(E)$	7·544	7·687	2·343	1·119	1·198	1·978
	$F_{22}(E)$	1·996	0·826	6·208	6·382	1·498	0·915
	$F_{33}(E)$	1·262	2·993	1·306	2·661	10·582	10·496
$SO_3NHCH_3^-$	$F_{11}(A_1)$	4·060	4·060	3·164	6·399	6·783	6·783
	$F_{22}(A_1)$	4·960	4·960	5·172	5·064	4·706	4·706
	$F_{33}(A_1)$	5·228	5·228	5·907	2·983	2·884	2·884
	$F_{11}(E)$	7·124	7·238	2·274	1·719	1·719	1·441
	$F_{22}(E)$	2·004	1·024	5·894	1·299	1·299	6·016
	$F_{33}(E)$	1·667	3·210	1·775	10·562	10·562	2·745
$SO_3N(CH_3)_2^-$	$F_{11}(A_1)$	4·453	4·453	3·631	6·823	8·004	8·004
	$F_2(A_1)$	4·892	4·892	5·040	4·959	3·971	3·971
	$F_{33}(A_1)$	5·208	5·208	5·803	3·139	2·840	2·840
	$F_{11}(E)$	6·984	7·094	2·278	1·931	1·387	1·278
	$F_{22}(E)$	1·980	0·918	5·771	1·048	1·448	5·912
	$F_{33}(E)$	1·576	3·347	1·658	10·771	10·849	2·885

unexpected finding (owing to the +I-effect of methyl groups, the growing number of methyl groups should result in a stronger and not weaker SeN bond) clearly indicates the considerable influence of hydrogen bonds formed from the $-NH_2$ groups on the stability of the amidoselenate ion. Replacement of hydrogen atoms by methyl groups interferes in the formation of hydrogen bonds and the stability of the whole ion thus decreases. Quadratic potential constant values of SeO bonds increase in the order $SeO_3NH_2^-$, $SeO_3NHCH_3^-$, and $SeO_3N(CH_3)_2^-$. All these values are higher than the f_{SeO} value calculated on the basis of vibrational spectra of NH_4. $.SeO_3NH_2$ (6·01 mdyn/Å); this finding thus confirms the assumption on the influence of hydrogen bondings formed by the NH_4^+ cations. The SeO bond potential constants of the anions examined also reveal the influence of the hydrogen bonding formation by the groups $-NH_2$ and $-NHCH_3$. In spite of the decreasing electronegativity from $-NH_2$ to $-N(CH_3)_2$, the f_{SeO} value increases in the same direction. The influence of the substitution of hydrogen atoms by methyl groups resulting in a decreased formation or complete absence of hydrogen bonds is obviously stronger than that of the relatively small change in the substituent electronegativity. The f_{SeO} value calculated from spectra of all the three anions is very similar to that calculated for the particular anion. Since the use of the diagonal valence force field approximation as well as negligence of the interaction with NXY groups owing to the simplified model for calculations, are only of a little influence, the f_{SeO} values thus obtained may be regarded to reflect truly the virtual state of anions.

In view of the simplifications, the calculated bending and interaction potential constants can be hardly used for quantitative considerations on bond relations in the anions examined. Some differences between our constants for $SeO_3NH_2^-$ and those given in the earlier paper[2] are due to the different interpretation of vibrational spectral bands in the $200-400$ cm^{-1} region. The absolute value of off-diagonal force constants obtained by a simultaneous solution of vibrational spectra of all the three anions are in most cases lower than 0·1 mdyn/A. Only two of them, namely, g_{SeN}^{SeO} and $g_{OSeO}^{SeN} - g_{OSeN}^{SeN}$, are comparable to bending and interaction potential constants considered in the calculations of a particular molecule. Inaccurate results are obtained when they are neglected. As shown by the potential energy distribution in the anions examined (Table VI), all the vibrations are characteristic.

The calculation of quadratic potential constants of the SO_3NXY^- anions was attempted in an an analogous manner. In the solution of the simplified model, however, the use of diagonal valence force field led to incorrect results. The calculated f_{SO} potential constant values do not correspond to those expected on the basis of the $-NXY$ group electronegativity and to those of the anions $CH_3SO_3^-$, $NH_2SO_3^-$, $HOSO_3^-$, $CH_3OSO_3^-$, and FSO_3^-; moreover, they are not in agreement with the relationship between the f_{SO} and f_{SeO} constants proposed by Paetzold[20]. Thus, the f_{SO} values calculated from f_{SeO} values in the SeO_3NXY^- anions are 8·05$_5$ mdyn/Å (SO$_3$NH$_2^-$), 8·18$_0$ mdyn/Å (SO$_3$NHCH$_3^-$), and 8·19$_3$ mdyn/Å (SO$_3$N(CH$_3$)$_2^-$), while

TABLE VIII

Quadratic Potential Constants of the $SO_3NH_2^-$ Ion (in mdyn/Å)

f_{SN}	3.70_9	$g_{OSO}^{SN} - g_{OSO}^{SN}$	-0.12_1
f_{SO}	8.33_0		
f_{SO}'	0.33_3	$g_{OSO}^{SO} - g_{OSO}^{SO}$	-0.24_0
d_{OSO}	1.27_6		
d_{OSO}'	0.42_5	$g_{OSN}^{SO} - g_{OSN}^{SO}$	0.08_7
d_{OSN}	0.46_4		
d_{OSN}'	0.04_6	$g_{OSN}^{OSO} - g_{OSN}^{OSO}$	0.04_5
g_{SN}^{SO}	-0.30_8		

those obtained from the simplified model are considerably lower. The set of quadratic potential constants calculated for $SO_3NH_2^-$ is also considerably different from that reported in the paper of Siebert[6]. Because of the possibility that the iteration procedure converges to a solution without physical meaning, we have attempted calculations of all the multiplicity solutions[21] of the SO_3NXY^- anion. The results are summarised in Table VII. It may be seen that none of the solutions corresponds to data of the paper mentioned[6]. In all cases, the expected values are most similar to the solution 1 which is identical with that obtained by the iteration procedure. The greatest deviations from the expected values may be observed with the N-methyl substituted anions. Owing to the small atomic weight of sulfur. the model used is too rough and the estimate of the active masses of groups assumed as the vibrating unit is too inaccurate. These factors lead to such deviations in potential constant values that they hardly can reflect the virtual valence state of anions. With the use of vibrational spectra of isotopically substituted SO_3NHD^-, $SO_3ND_2^-$, and $SO_3NDCH_3^-$ anions, reasonable results were obtained only in the case of $SO_3NH_2^-$ while with $SO_3NHCH_3^-$, the results were similar to those of the multiplicity solution 1. The interaction of groups —SO_3 and —$NHCH_3$ or —$N(CH_3)_2$ is thus of such a character that it excludes a model analogous to that used with the corresponding selenium compounds.

The quadratic potential constant values of the anion $SO_3NH_2^-$ calculated on the above mentioned basis are shown in Table VIII; when used back in the secular equation, they give experimental wave number values with an error less than ± 22.4 cm^{-1}. The f_{SO} value is somewhat higher than that calculated on the basis of f_{SeO} in $SeO_3NH_2^-$. This difference may be ascribed to the absence of hydrogen bond in the anion $SO_3NH_2^-$ as indicated by comparison of potential constant values of NH bond ($SeO_3NH_2^-$, $f_{NH} = 5.56_7$ mdyn/Å; $SO_3NH_2^-$, $f_{NH} = 6.01_8$ mdyn/Å). Moreover, the

off-diagonal elemental of the **F**-matrix were neglected in calculations of potential constants of the $SeO_3NH_2^-$ anion, but were taken into account in the case of the $SO_3NH_2^-$ anion. This circumstance lowers the possibility to compare both sets of values.

As indicated by potential energy distribution in the anion $SO_3NH_2^-$ anion (Table VI), the vibrations νSN and $\nu_s SO_3$ belonging in the approximation used to the totally symmetric species A_1, cannot be regarded as characteristic because of the mutual interference. This is a considerable difference in comparison with the corresponding selenium compounds. Only the vibration $\delta_s SO_3$ and all the three vibrations of the type E may be regarded as sufficiently characteristic.

As suggested by the above results, the bonds in $SeO_3NH_2^-$ and $SO_3NH_2^-$ anions are not quite analogous. The earlier[2,3] proposal on the influence of hydrogen bonding formation is thus fully justified.

REFERENCES

1. Paetzold R.: Z. Chem. *4*, 272 (1964).
2. Paetzold R., Dostál K., Růžička A.: Z. Anorg. Allgem. Chem. *347*, 13 (1966).
3. Krejčí J., Horsák I., Dostál K.: Chem. zvesti *26*, 169 (1971).
4. Traube W., Brehmer E.: Chem. Ber. *52*, 1288 (1919).
5. Behrend R.: Lieb. Ann. *222*, 116 (1883).
6. Siebert H.: Z. Anorg. Allgem. Chem. *289*, 15 (1957).
7. Siebert H.: Z. Anorg. Allgem. Chem. *292*, 167 (1957).
8. Gupta J., Majumdar A. J.: J. Indian Chem. Soc. *18*, 1457 (1941).
9. Hoffman H. J., Andress K. R.: Naturwissenschaften *41*, 94 (1954).
10. Hoffman H. J., Andress K. R.: Z. Anorg. Allgem. Chem. *284*, 234 (1956).
11. Vaugnat A. M., Wagner E. L.: J. Chem. Phys. *26*, 77 (1957).
12. Biceli L.: Ann. Chim. *46*, 563, 661 (1956); *47*, 1380 (1957).
13. Dupuis T.: Compt. Rend. *242*, 2924 (1956).
14. Rocchiccioli M. C.: Compt. Rend. *243*, 1621 (1956); *255*, 1942 (1962).
15. Katiyar R. S.: Proc. Indian Acad. Sci. *A62*, 169 (1965); *A63*, 20 (1966).
16. Katiyar R. S.: Indian J. Pure Appl. Phys. *6*, 686 (1968).
17. Steger E.: Z. Anorg. Allgem. Chem. *309*, 304 (1961).
18. Barceló J. R., Bellanato J.: Spectrochim. Acta *8*, 27 (1956).
19. Dellepiane G., Zerbi G.: J. Chem. Phys. *48*, 3573 (1968).
20. Paetzold R.: Spectrochim. Acta *24*, 717 (1968).
21. Ruth J. M., Phillipe R. J.: J. Chem. Phys. *41*, 1492 (1964).

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