Vibrational Spectra and Force Constants of Tetrasulfurtetranitride, S_4N_4 [1]

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Infrared and Raman spectra of solid and dissolved $S_4{}^{14}N_4$ and of solid $S_4{}^{15}N_4$ have been recorded and assigned in accordance with the molecular point group D_{2d}. 22 of the 28 fundamental vibrations of both molecules have been identified and used to calculate force constants applying a modified Urey-Bradley force field with 9 independent constants. Good agreement between observed and calculated wavenumbers was obtained, and both Urey-Bradley and valence force constants are given. The results indicate that S_4N_4 basically contains eight SN single bonds and two extremely weak SS bonds.

Introduction

Tetrasulfurtetranitride (S_4N_4) is one of the best known sulfur compounds mainly due to its peculiar cage-like structure (Fig. 1) and its unique reactivity which makes it the starting material for the preparation of a large number of other sulfur-nitrogen compounds. The molecular structure and bonding properties have been studied by X-ray diffraction on single crystals at 25 °C [2] and at −153 °C [3], by molecular orbital calculations [4–8] and various spectroscopic techniques. These investigations show that the nitrogen atoms in S_4N_4 form a square while the sulfur atoms are located at the corners of a slightly distorted tetrahedron (elongated in the direction of the two-fold axis perpendicular to the plane defined by the nitrogen atoms resulting in a bisphenoid). The cage-like structure is based on eight strong SN covalent bonds of length 162 pm and at least two weak SS bonds of length 258 pm [2]. Some authors, however, suggest that there might be bonding interactions between all four sulfur atoms [3, 9] and others even claimed bonds between the four nitrogen atoms [10].

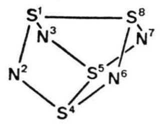

Fig. 1. Molecular Structure of S_4N_4 and numbering of atoms.

The strength of attractive and repulsive forces within a molecule can be elucidated by means of valence force constants to be calculated from vibrational spectra. A first attempt to assign the infrared and Raman spectra of S_4N_4 to the fundamental vibrations of the molecule and to calculate force constants was made by Lippincott and Tobin [11] but was based on a wrong molecular structure (the inverse cage structure with a square of sulfur and a tetrahedron of nitrogen atoms including two NN bonds). Later Bragin and Evans [12] reinvestigated the vibrational spectra and calculated 10 valence force constants from 12 observed fundamental frequencies. However, several of the force constants obtained by these authors have very unlikely values indicating that either the assignment is in error or the force field unsuitable (for a detailed discussion see below). In a recent investigation Turowski, Appel, Sawodny and Molt [13] remeasured the vibrational spectra of S_4N_4 and performed a force constants calculation. These authors felt, however, that the insufficient spectroscopic data did not allow the determination of all force constants in a unambiguous way and therefore did not report any details of their calculations nor complete results but just the SN and SS stretching force constants stating these "should be least doubtful".

In an attempt to finally solve the problem of vibrational assignment and to calculate reliable force constants, the infrared and Raman spectra of $S_4{}^{14}N_4$ and, for the first time, $S_4{}^{15}N_4$ were recorded and a normal-coordinate analysis based on a modified Urey-Bradley force field was carried out.

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Experimental

S_4N_4 was prepared according to the published method [14] and recrystallized several times (m.p. 180 °C). Samples from different batches gave identical spectra and no impurity bands could be detected. $S_4{}^{15}N_4$ was prepared according to the recently reported procedure [15] and kindly provided by Professor T. Chivers (Calgary).

Infrared spectra were recorded as nujol mulls, solutions in CS_2, or discs prepared from KBr, RbI or CsI utilizing the Perkin-Elmer i.r. spectrometers 325 and 580 B (180 – 4000 cm^{-1}) the latter one equipped with a data processing terminal. It was observed that the discs after storage at 40 °C for several days produced additional absorption bands at 1450 sh, 1397 vs, b, 1257 sh, 1237 vs, b, 1116 m, b, 1052 m, 1019 m – s, 983 m, 800 s, 676 sh, 655 m, 607 m – s, 591 s and 418 w (cm^{-1}). These bands were not present in freshly prepared samples, and the i.r. spectra of S_4N_4 were independent on the disc material.

Raman spectra were recorded at room and low temperatures on a Cary 82 spectrometer equipped with a triple monochromator and a krypton laser (647.1 nm). The spectrometer had been calibrated using solid indene. No Raman lines could be detected in the region 800 – 4000 cm^{-1}.

The force constant calculations were performed on a CYBER 170 computer utilizing the programs BGLZ and LSMA by Shimanouchi [16].

Vibrational Spectra and Assignment

The measured wavenumbers and intensities are given in Table 1. Comparison with the literature data shows good agreement with the i.r. spectrum reported by Chapman and Massey [17] and the Raman spectra published by Zallen and Slade [18], while the spectra reported by Lippincott and Tobin [11], Griffith and Rutt [19], Bragin and Evans [12], and Turowski et al. [13] show several weak features not present in our spectra and possibly caused by impurities. Since the spectra reported in this work have been reproduced with samples of different origin, they are believed to represent those of pure S_4N_4.

Assuming a molecular symmetry of D_{2d} tetrasulfurtetranitride must have 14 fundamental vibrations whose distribution to the 5 symmetry species of this point group is shown in Table 2. Seven fundamentals are i.r. active while 12 are allowed in the Raman spectrum.

The two A_2 fundamentals are completely inactive. While these rules apply to gaseous and dissolved S_4N_4, the behaviour of the solid is much more complicated. S_4N_4 crystallizes as monoclinic needles belonging to the centrosymmetric space group $P2_1/n$. The 4 molecules in the unit cell occupy general positions. The consequences of this situation for the vibrational spectra of solid S_4N_4 have been discussed in great detail by Zallen and Slade [18] as well as by Iqbal, Downs and Christoe [20].

As a result of the C_1 site symmetry the A_1, A_2, and B_1 fundamentals may become i.r. active and lead to weak absorption bands, while the E fundamentals may split into doublets. The two A_2 modes may also be observed in the Raman spectrum. However, since the deviation from D_{2d} symmetry is small, these effects are expected to be small too (the eight SN bond distances, for example, vary between 160 and 163 pm only, with a standard deviation of 2 pm [2]).

The factor group analysis of crystalline S_4N_4 predicts that all non-degenerate fundamentals of the D_{2d} point group may occur as quartets because of the presence of 4 molecules in the unit cell. Two components of each quartet (A_g and B_g) would be Raman active while the other two (A_u and B_u) would be i.r. active as a consequence of the center of symmetry of the unit cell. The four degenerate modes are predicted to split into octets (2 A_g, 2 B_g, 2 A_u, 2 B_u) resulting in multiplets of up to 4 lines in both the Raman and i.r. spectra [18]. Consequently, the internal fundamental modes of solid S_4N_4 may give rise to a maximum of 36 Raman lines and 36 i.r. absorption bands. However, since the intermolecular interactions are weak it can be expected that the spacings of the components of each multiplet should be small.

In addition to the internal modes 12 Raman active external (lattice) modes have been predicted [18]. By comparison with the spectra of S_8 [21] and other molecules of similar mass and structure the lattice vibrations can be expected in the region below 120 cm^{-1}. Since there are no Raman lines between 110 and 190 cm^{-1} in the spectra of S_4N_4 (Table 1), the internal and external modes obviously are well separated and can easily be classified as such. For a detailed discussion of the lattice vibrations see Ref. [18] and [20].

Table 1. Vibrational Spectra of S^{14} N_4 and $S_4{}^{15}N_4$ (wavenumbers in cm^{-1}; vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder, b broad; Raman intensities in brackets, p polarized, dp depolarized).

$S_4{}^{14}N_4$						$S_4{}^{15}N_4$		Assignment
Raman			Infrared			Raman	Infrared	
solid		in CS_2	solid		in CS_2	solid	in RbI	
20 °C	– 100 °C		in RbI	in CsI		– 100 °C		
	30 (10)					31 (13)		lattice vibrations
45	48 (48)					48 (44)		
53	54 (32)					54 (28)		
66	69 (1)					70 (1)		
76	90 (1)					87 (1)		
98	102 (11)					102 (11)		
	198 (sh)					198 (sh)		$\nu_{10}(B_2)$
200	201 (100)	177 m (dp)	188 m			201 (100)	186 m	
217	218 (89)	201 vs (p)				218 (92)		$\nu_3(A_1)$
222	224 (15)	216 w (dp)				225 (13)		$\nu_7(B_1)$
338	340 (4)					332 (sh)		$\nu_{14}(E)$
344	344 (5)	345 w, b	344 vs	346 vs		335 (5)	336 vs	
348	350 (13)					344 (13)		
			378 vvw					$\nu_3 + \nu_{10}(B_2)$
			418 vvw		–CS_2–		414 vw, b	
			446 vvw					ν_{14} + 102 (lattice)
517	518 (2, sh)		518 sh	521 vw	517 w	513 (sh)	513 w, sh	$\nu_{13}(E)$
520	521 (6)	520 w, b				517 (6)		
527	528 (4)		528 w	529 w		523 (3)		
			550 vs	549 vs	553 s-vs		534 vs	$\nu_9(B_2)$
560	558 (50)	565 s (p)				555 (44)		$\nu_2(A_1)$
			623 w-m	629 w			628 w, b	ν_9 + 75 (lattice)
			701 vs, b	700 vs	704 vs		684 vs, b	$\nu_{12}(E)$
720	720 (34)	720 s (p)				700 (39)		$\nu_1(A)$
726	728 (5)		727 m	729 m	722 vw, sh	714 (5)	709 m	see text
764	765 (4)	762 w	760 m 767 m	761 w 769 w	764 w	745 (5)	740 m 747 m	$\nu_8(B_2)$
			800 w	803 w			790 vw	$\nu_4(A_2)$?
			927 vs	929 vs	939 s-vs		904 vs	$\nu_{11}(E)$
			954 sh, w				933 vw, sh	$\nu_6(B_1)$?
			1006 w	1009 w	999 vw		985 w	$\nu_{12} + \nu_{14}$
			1048 vw	1047 w	1058 vw		1023 sh	$\nu_1 + \nu_{14}$
			1066 w-m	1067 w			1040 w-m	$\nu_8 + \nu_{14}$
			1405 w, b	1410 vw			1376 vw	$\nu_1 + \nu_{12}$; $\nu_{11} + \nu_{13}$
							1423 sh	
			1460 sh				1441 w	$\nu_1 + \nu_8$
			1478 w	1482 w				$\nu_6 + \nu_{13}$; $\nu_4 + \nu_{12}$
			1623 b, sh					$\nu_1 + \nu_{11}$
			1648 w	1652 vw			1605 vvw, b	$\nu_8 + \nu_{11}$

Three of the internal modes must belong to the symmetry species A_1 and therefore should give rise to intense and polarized Raman lines. Several authors [12, 13] reported the lines at 720, 565 and 201 cm^{-1} (in solution) to be the only polarized ones and assigned them accordingly. This is in agreement with the present results (Table 1). From the symmetry coordinates given below (Table 4) it can be seen that one of the A_1 modes (ν_3) must be the symmetric SS stretching vibration. In agreement with earlier authors [18, 20] the Raman line at 218 cm^{-1} of solid S_4N_4 is assigned to this fundamental since it does not shift on ^{15}N substitution. In CS_2 solution this line occurs at 201 cm^{-1} with a weak but well developed shoulder at 216 cm^{-1}. This shoulder becomes a well resolved line when polarized laser radiation is used causing the strong A_1 line at 201 cm^{-1} almost to disappear. In the solid the weak line occurs at 222 (25 °C) resp. 224 (– 100 °C) cm^{-1}; it is assigned as $\nu_7(B_1)$, see below. Several authors [18, 20] explained the Raman doublet at about 201/224 cm^{-1} as $\nu_3(A_1)$ split by intermolecular interactions. Our solution spectra show this interpretation to be in error. When the Raman spectrum is recorded in dioxane solution, however, as most earlier authors have done [11 – 13, 18], the ν_3

Table 2. Number and activity of the fundamental vibrations of S_4N_4 belonging to the different symmetry species of point group D_{2d}.

Species	Number	Infrared activity	Raman activity
A_1	3 ($\nu_1 \ldots \nu_3$)	–	+
A_2	2 ($\nu_4 \ldots \nu_5$)	–	–
B_1	2 ($\nu_6 \ldots \nu_7$)	–	+
B_2	3 ($\nu_8 \ldots \nu_{10}$)	+	+
E	4 ($\nu_{11} \ldots \nu_{14}$)	+	+

mode occurs at 218 cm^{-1} and completely covers the weak ν_7 line.

The asymmetric SS stretching vibration belongs to the symmetry species B_2 and therefore is i.r. and Raman active. Since the two SS bonds are orthogonal, the vibrational coupling between them should be very small and symmetric and asymmetric stretch should occur at almost identical wavenumbers. The B_2 mode can therefore be assigned to the Raman line at 200 cm^{-1} of solid S_4N_4 which in solution is observed at 177 cm^{-1}. This line is also unaffected by ^{15}N substitution and splits into a doublet a low temperatures [18, 20]. The A_u and B_u components of this mode occur in the i.r. spectrum of solid S_4N_4 unresolved at 188 cm^{-1} (Table 1).

The assignment of the two SS stretching modes is further supported by the Raman spectrum of $NH_4[S_4N_5O]$ given in Table 3 (not published before). This salt contains an anion which is structurally related to S_4N_4 but possesses only one SS bond (the other one being bridged by the additional nitrogen atom) [22]. The wavenumbers in Table 3 show that there is now only one strong Raman line in the 100 – 300 cm^{-1} region. In aqueous solution this line occurs at 193 cm^{-1} and is clearly polarized.

Of the many i.r. absorption bands of S_4N_4 which should belong to the B_2 and E species the one at 344 cm^{-1} must represent a degenerate mode since it occurs as a triplet in the Raman spectrum (only doublets are allowed for B_2 modes). For the same reason the two i.r. bands and three Raman lines clustered at 517 – 528 cm^{-1} must be caused by an E mode observed as only one signal in solution. The two remaining E vibrations are assigned to the very strong and relatively broad i.r. absorptions at 925 and 701 cm^{-1}. All attempts to assign the 925 cm^{-1} band to the B_2 species resulted in unacceptable force constants (see below). The assignment of both the 925 and 701 cm^{-1} bands to E modes is further supported by the following observations. The cage-like anions $S_4N_5O^-$ [22] and $S_4N_5^-$ [23] are both of C_S symmetry. Their i.r. spectra show pairs of strong bands near 925 and 701 cm^{-1} which obviously are the A′ and A″ components of the two modes degenerate in S_4N_4:

$S_4N_5O^-$: 975/942, 749/704 cm^{-1} [24],
$S_4N_5^-$: 950/915, 745/700 cm^{-1} [25, 26].

After this assignment the 764 cm^{-1} Raman line of S_4N_4 can only belong to the highest B_2 mode (ν_8) which in the infrared spectrum is split into a doublet but in case of solid S_4N_4 only. The strong i.r. band at 550 cm^{-1} must then be the second highest B_2 fundamental (ν_9).

After all A_1, B_2, and E modes have been identified the two Raman active B_1 modes ν_6 and ν_7 have to be found. The wavenumber calculations (see below) with a variety of assumed force constants showed that ν_7 can be expected in the 150 – 300 cm^{-1} region. Therefore this mode is assigned to the weak line at 223 cm^{-1} which is the only unexplained feature in the corresponding spectral region.

This choice now leaves only one Raman line unassigned: the weak signal at 727 cm^{-1} which apparently corresponds with the medium intense i.r. band at 728 cm^{-1}. This i.r. absorption disappears almost completely on dissolution of S_4N_4 in CS_2. The isotopic shifts of the Raman line (14 cm^{-1}) and the i.r. band (18 cm^{-1}) indicate that the two signals may be of different origin. The i.r. band could be either a result of a solid state splitting of ν_{12}(E) or a combination of this mode with one of the lattice modes at 30 or 48 cm^{-1}. The very weak shoulder at 722 cm^{-1} observed for dissolved S_4N_4 could be assigned to the combination vibration $\nu_3 + \nu_{13}$ which is of E symmetry. The Raman line at 727 cm^{-1}, on the other hand, is probably not caused by the so far unassigned B_1 mode ν_6 since the calculations presented below show this mode to be expected near 880 cm^{-1} with an isotopic shift of 19 cm^{-1}. Neither can this

Table 3. Raman spectrum of solid $NH_4[S_4N_5O]$ (in cm^{-1}; for abbreviations see Table 1).

22 s	lattice	470 w	783 vw	ν_{SN}
48 m		475 w	819 w	
66 w		504 w	958 vw	
85 vw		551 w-m	1256 vw,	ν_{SO}
155 w		598 vw		
222 vs,	ν_{SS}	627 m		
346 w		645 vvw		
395 w				

line be the result of a solid state splitting of the A_1 fundamental at 720 cm^{-1} whose isotopic shift of 20 cm^{-1} is much larger. It therefore may also be interpreted as a combination vibration, for example $\nu_3 + \nu_{13}$ (E symmetry) or, more likely, $\nu_9 + \nu_{10}(A_1)$.

In the region of 1000 to 1650 cm^{-1} the i.r. spectra show several weak bands which can only arise from overtones or combination vibrations. Since only B_2 and E modes are i.r. active, the multiplication rules for symmetry species have to be taken into account as has been done with the tentative assignment given in Table 1.

Force Constant Calculation

The force constant calculations were made using a modified Urey-Bradley force field of the same type as has been succesfully applied in the vibrational analyses of other cyclic sulfur molecules, e. g. S_7NH [27], $(SNH)_4$ [28], S_6 [29], S_8 [30, 31], S_{12} [30, 32] and S_7 [33]. The details have been discussed in these earlier papers.

The cartesian coordinates of the atoms were calculated from the results of the room temperature X-ray structural analysis [2] averaged for the molecular symmetry D_{2d} (bond distances $r_{SN} = 161.6$ and $R_{SS} = 258.1$ pm, bond angles $\alpha_{NSN} = 104.5^\circ$ and $\beta_{SNS} = 112.8^\circ$, torsional angle $\tau_{NSNS} = 58^\circ$). The symmetry coordinates obtained from the character table of the D_{2d} point group are given in Table 4 (eight of the symmetry coordinates are redundant as can be seen from the comparison of Tables 4 and 5; redundant combinations yield wavenumbers of zero).

Table 4. Symmetry coordinates of S_4N_4 (the normalization and scaling factors have been omitted; the SN bonds r and torsional axes τ have been numbered starting from atom 1 [1–2: r_1, τ_1; 1–3: r_2, τ_2; 2–4: r_3, τ_3 etc.], the NSN bond angles α_{1-4} are located at sulfur atoms 1, 4, 5 and 8, and the SNS bond angles β at nitrogen atoms 2, 3, 6 and 7 (see Figure 1).

A_1	S_1	$\sim r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8$
	S_2	$\sim R_1 + R_2$
	S_3	$\sim \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$
	S_4	$\sim \beta_1 + \beta_2 + \beta_3 + \beta_4$
	S_5	$\sim \tau_1 - \tau_2 + \tau_3 - \tau_4 - \tau_5 + \tau_6 - \tau_7 + \tau_8$
A_2	S_1	$\sim r_1 - r_2 - r_3 + r_4 + r_5 - r_6 - r_7 + r_8$
	S_2	$\sim \tau_1 + \tau_2 - \tau_3 - \tau_4 - \tau_5 - \tau_6 + \tau_7 + \tau_8$
B_1	S_1	$\sim r_1 - r_2 + r_3 - r_4 - r_5 + r_6 - r_7 + r_8$
	S_2	$\sim \beta_1 - \beta_2 - \beta_3 + \beta_4$
	S_3	$\sim \tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_7 + \tau_8$
B_2	S_1	$\sim r_1 + r_2 - r_3 - r_4 - r_5 - r_6 + r_7 + r_8$
	S_2	$\sim R_1 - R_2$
	S_3	$\sim \alpha_1 - \alpha_2 - \alpha_3 + \alpha_4$
	S_4	$\sim \tau_1 - \tau_2 - \tau_3 + \tau_4 + \tau_5 - \tau_6 - \tau_7 + \tau_8$
E	S_1	$\sim r_1 + r_2 + r_3 + r_4 - r_5 - r_6 - r_7 - r_8$
	S_2	$\sim r_1 - r_2 + r_3 - r_4 + r_5 - r_6 + r_7 - r_8$
	S_3	$\sim r_1 + r_2 - r_3 - r_4 + r_5 + r_6 - r_7 - r_8$
	S_4	$\sim r_1 - r_2 - r_3 + r_4 - r_5 + r_6 + r_7 - r_6$
	S_5	$\sim \alpha_1 + \alpha_2 - \alpha_3 - \alpha_4$
	S_6	$\sim \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4$
	S_7	$\sim \beta_1 + \beta_2 - \beta_3 - \beta_4$
	S_8	$\sim \beta_1 - \beta_2 + \beta_3 - \beta_4$
	S	$\sim \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6 + \tau_7 - \tau_8$
	S_{10}	$\sim \tau_1 + \tau_2 + \tau_3 + \tau_4 - \tau_5 - \tau_6 - \tau_7 - \tau_8$
	S_{11}	$\sim \tau_1 - \tau_2 - \tau_3 + \tau_4 - \tau_5 + \tau_6 + \tau_7 - \tau_8$
	S_{12}	$\sim \tau_1 + \tau_2 - \tau_3 - \tau_4 + \tau_5 + \tau_6 - \tau_7 - \tau_8$

The following 9 independent force constants were used (the ranges within which the numerical values [in $N \cdot cm^{-1}$] of these constants have been varied in the early stages of the calculations are given in brackets):

K_1(SN)	SN bond stretching (r) (2.7 ... 4.0),
K_2(SS)	SS bond stretching (R) (0.2 ... 0.5),
P_1(NSN)	interaction between neighboring SN bonds at S (−0.9 ... 0.6),
P_2(SNS)	interaction between neighboring SN bonds at N (−0.4 ... 0.8),
H_1(NSN)	angle bending (α) (0.05 ... 0.4),
H_2(SNS)	angle bending (β) (0.15 ... 0.8),
F_1(SS)	repulsion between S atoms connected by N (−0.5 ... 0.9),
F_2(NN)	repulsion between N atoms connected by S (−0.5 ... 0.7),
Y	torsion of SN bond (τ) (0.04 ... 0.12).

When an additional bond-bond interaction force constant P_3(NSS) was introduced it adopted a very small negative value leading to an only slightly better agreement between calculated and observed wavenumbers. It was therefore not included in the final calculations.

With these constants the potential energy equation becomes:

$$\begin{aligned} 2V = {} & \sum^{8} K_1(\Delta r)^2 + 2\sum^{8} K_1' \, r(\Delta r) \\ & + \sum^{2} K_2(\Delta R)^2 + 2\sum^{2} K_2' \, R(\Delta R) \\ & + 2\sum^{4} P_1 \, \Delta r \, \Delta r' + 2\sum^{4} P_2 \, \Delta r \, \Delta r' \\ & + \sum^{4} H_1 (r\,\Delta\alpha)^2 + 2\sum^{4} H_1' \, r(r\,\Delta\alpha) \\ & + \sum^{4} H_2 (r\,\Delta\beta)^2 + 2\sum^{4} H_2' \, r(r\,\Delta\beta) \\ & + \sum^{4} F_1 (\Delta q_1)^2 + 2\sum^{4} F_1' \, q_1(\Delta q_1) \\ & + \sum^{4} F_2 (\Delta q_2)^2 + 2\sum^{4} F_2' \, q_2(\Delta q_2) \\ & + \sum^{8} Y (r\,\Delta\tau)^2 + 2\sum^{8} Y' \, r(r\,\Delta\tau) . \end{aligned}$$

Table 5. Observed and calculated wavenumbers (cm^{-1}) of S_4N_4 and potential energy distribution (≧10%) to the stretching (ν), bending (δ) and torsional (τ) symmetry coordinates; $\Delta\nu$ isotopic shift (cm^{-1}).

$S_4{}^{14}N_4$					$S_4{}^{15}N_4$		$\Delta\nu$	
		obs.	calc.	potential energy distribution	obs.	calc.	obs.	calc.
A_1	ν_1	720	717	48 ν(SN), 45 δ(SNS)	700	695	20	22
	ν_2	558	552	51 ν(SN), 25 δ(SNS), 21 δ(NSN)	555	552	3	0
	ν_2	218	229	54 δ(NSN), 33 ν(SS), 13 δ(SNS)	218	228	0	1
A_2	ν_4	—	928	100 ν(SN)	—	905	—	23
	ν_5	—	254	100 τ(SN)	—	246	—	8
B_1	ν_6	—	886	78 ν(SN), 22 δ(SNS)	—	867	—	19
	ν_7	224	227	86 δ(SNS), 13 ν(SN)	225	224	−1	3
B_2	ν_8	765	762	73 ν(SN), 25 δ(NSN)	745	743	20	20
	ν_9	550	549	40 δ(NSN), 38 τ(SN), 21 ν(SN)	534	531	16	18
	ν_{10}	201	194	58 ν(SS), 23 τ(SN), 17 δ(NSN)	201	194	0	0
E	ν_{11}	925	925	82 ν(SN), 13 δ(SNS)	904	904	21	21
	ν_{12}	701	708	82 ν(SN), 13 δ(SNS)	684	690	17	18
	ν_{13}	524	528	54 δ(NSN), 23 δ(SNS), 18 τ(SN)	520	517	4	11
	ν_{14}	344	348	44 δ(SNS), 33 τ(SN), 18 ν(SN)	336	343	8	5

The internal coordinates q are the distances between sulfur atoms bridged by one nitrogen atom ($q_1 = 256$ pm) respectively nitrogen atoms bridged by one sulfur atom ($q_2 = 269$ pm). The constants F' were constraint by the conventional assumption $F' = -0.1\,F$. All constants K', H' and Y' are eliminated in the removal of the redundant coordinates q.

The first set of wavenumbers was calculated from assumed Urey-Bradley force constants whose values were choosen on the basis of the experiences with S_7NH [27], $(SNH)_4$ [28], $S_3N_2O_2$ [34] and other sulfur compounds [35]. To adjust the calculated to the observed wavenumbers by the least squares method the 22 observed values of $S_4{}^{14}N_4$ and $S_4{}^{15}N_4$ given in Table 5 were used. In the beginning, groups of force constants were varied but in the last run all 9 force constants were allowed to vary simultaneously until the alterations became negligible. The calculated wavenumbers as well as the potential energy distribution to the symmetry coordinates are given in Table 5. The maximum difference between observed and calculated wavenumbers amounts to 11 cm^{-1}. The final Urey-Bradley force constants as well as the valence force constants obtained from the F matrix are shown in Table 6.

It is pleasing to see that the observed $^{14}N/^{15}N$ isotopic shifts $\Delta\nu$ of 13 of the 14 fundamentals agree with the calculated shifts within 4 cm^{-1} (Table 5, last column). Only in case of the bending mode ν_{13}(E) the calculated shift exceeds the observed one by 7 cm^{-1} indicating that the potential energy distribution of this mode is not correctly reproduced by the force field applied.

Several attempts were made to adjust the calculated to alternatively assigned observed wavenumbers. The most reasonable alternatives seem to be $\nu_8(B_2) = 925$ and $\nu_{11}(E) = 765$ cm^{-1} or, on the other hand, $\nu_8(B_2) = 701$, $\nu_{11}(E) = 925$ and $\nu_{12}(E) = 765$ cm^{-1} as has been proposed by Turowski et al. [13]. Using the same force field as mentioned above it was, however, not possible to obtain a reasonably good agreement between observed and calculated wavenumbers for these two assignments. Furthermore, in the first case an unacceptably low stretching force constant f_r(SN) was obtained.

Finally, it should be mentioned that almost all of the 58 different calculations carried out showed $\nu_9(B_2)$ at higher wavenumbers than ν_{13}(E). Therefore, the assignment $\nu_9 = 552$ and $\nu_{13} = 521$ cm^{-1}, which is also supported by the quite different isotopic shifts of the two modes, seems to be well established.

In the introduction it has been mentioned that some authors claimed SS bonds between all sulfur

Table 6. Urey-Bradley (UB) and valence force constants (VF) of S_4N_4 and $S_4(NH)_4$ (in N · cm^{-1}; f_i diagonal constants, f_{ij} interaction constants between the nearest coordinates indicated).

S_4N_4 UB			S_4N_4 VF	$S_4(NH)_4$ VF
K_1(SN)	3.32	f_r(SN)	3.76	4.01
K_2(SS)	0.21	f_R(SS)	0.21	—
P_1(NSN)	− 0.71	f_{rr}(NSN)	− 0.64	0.79
P_2(SNS)	0.33	f_{rr}(SNS)	0.74	0.98
H_1(NSN)	0.46	f_α(NSN)	0.53	0.58
H_2(SNS)	0.49	f_β(SNS)	0.68	0.41
F_1(S...S)	0.58	$f_{r\alpha}$	0.06	0.41
F_2(N...N)	0.10	$f_{r\beta}$	0.32	0.23
Y	0.12	f_τ	0.12	0.09

atoms in S_4N_4. To check whether there is a bonding interaction between sulfur atoms bridged by one nitrogen atom it was attempted to assign a negative value to the "repulsion" constant $F_1(S\ldots S)$. However, with $F_1 = -0.5\,N\cdot cm^{-1}$ and all other constants as given in Table 6 unreasonably low wavenumbers for at least three normal modes were obtained: $\nu_2(A_1) = 367$, $\nu_7(B_1) = 123$ and $\nu_{14}(E) = 213\,cm^{-1}$. This shows that the $S\ldots S$ interactions must be repulsive. Similarly, a negative value ($-0.5\,N\cdot cm^{-1}$) of $F_2(N\ldots N)$ resulted in unacceptable values for the bending modes $\nu_9(B_2)$ and $\nu_{13}(E)$.

Discussion

It is interesting to compare the four observed wavenumbers assigned to SN stretching modes of S_4N_4 with those of $(SNH)_4$ which belongs to the point group C_{4v} (in both cases the A_2 and B_2 stretching modes have not been observed):

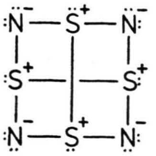
	S_4N_4	$S_4(NH)_4$ [28]
A_1	720	716
B_1	765	858
E	925	830
E	701	704
average	790 cm^{-1}	764 cm^{-1}

The average SN stretching wavenumbers are very similar in agreement with the SN stretching force constants f_r which are almost identical (Table 6). This indicates that the SN bond order in S_4N_4 cannot be much higher than in $S_4(NH)_4$ despite the somewhat smaller bond distance (S_4N_4: 162, $S_4(NH)_4$: 167 pm). Using the relationship

$$f_r(SN) = 145\, d_{SN}^{-7.00}\ (d \text{ in Å})$$

derived from the data of only seven SN compounds [36] one obtaines $f_r = 5.0\,N\cdot cm^{-1}$ for S_4N_4 and $4.1\,N\cdot cm^{-1}$ for $S_4(NH)_4$ indicating that this equation cannot be applied to S_4N_4.

That the shorter SN bonds in S_4N_4 than in $(SNH)_4$ do not indicate any appreciable double bond character has also been concluded from molecular orbital calculations [6, 7] and is in agreement with measurements of the ^{14}N [37] and ^{15}N [15] chemical shifts which correspond better with the values found for nitrogen in SN single bonds than in SN double bonds. If one prefers a valence bond picture, the following structure seems to represent the bonding situation best:

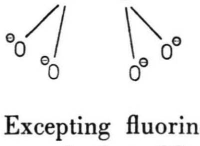


This structure was first proposed by Lindqvist [38]. In this connection it is interesting to note that S_4N_4 readily reacts with Lewis acids with adduct formation while $(SNH)_4$ and S_7NH do not since in these compounds the "lone pairs" at the nitrogen atoms are partly delocalized into unoccupied sulfur orbitals (the geometry at the nitrogen atoms is planar). The smaller SNS bond angle of 112.8° in S_4N_4 compared with 124.0±0.2° in S_7NH [39] and $(SNH)_4$ [40] further supports the assumption of basically SN single bonds in S_4N_4.

Comparison of the other valence force constants of S_4N_4 with those of $(SNH)_4$ in Table 6 shows good agreement excepting the interaction constant $f_{rr}(NSN)$ which is negative in case of S_4N_4 only. This may, however, be a consequence of the additional SS bonds. The SS stretching force constant $f_R = 0.21\,N\cdot cm^{-1}$ is roughly in agreement with the relationship

$$f_R(SS) = 460\, d_{SS}^{-7.26}\ (d \text{ in Å}),$$

which has been established for f_R values between 1.45 and 6.29 $N\cdot cm^{-1}$ [41, 42]. For $d_{SS} = 2.58$ Å one obtains $f_R = 0.47\,N\cdot cm^{-1}$. Comparison with the SS stretching force constant in S_8 (2.32 $N\cdot cm^{-1}$ [31]) shows the SS bond order in S_4N_4 to be very small. Several authors suggested these bonds might be bent and arise from pure 3 p orbitals of the sulfur atoms [5 – 7]. The weakness of the SS bonds can, however, also be explained by the rather high positive charges [43] on the sulfur atoms. In this respect S_4N_4 resembles the dithionite anion which also contains a very long SS bond (239 pm) between tri-coordinated sulfur atoms (symmetry C_{2v}) [44, 45]:



Excepting fluorine compounds, it is generally observed that SS bonds involving tri-coordinated sulfur atoms are much weaker than with two-coordinated S atoms [41].

As pointed out above, Bragin and Evans [12] have published the only detailed force constant calculation of S_4N_4 based on the correct molecular structure. The general valence force field used by these authors consists of the following 10 constants: f_r, f_R, f_{rr}, f_{RR}, f_α (for both angles α and β), $f_{\alpha\alpha}$, $f_{r\alpha}$, $f'_{r\alpha}$, $f''_{r\alpha}$ and $f_{R\alpha}$. With a wavenumber assignment somewhat different from the present one these force constants assumed values which, in some cases, are highly unlikely. For example, $f_R = 1.61$, $f_\alpha = 1.62$ and $f_{R\alpha} = 0.57\ \mathrm{N \cdot cm^{-1}}$ are all much too large. Also, the interaction between the two orthogonal SS bonds separated by two SN bonds should be negligibly small, while Bragin and Evans calculated $f_{RR} = 0.32\ \mathrm{N \cdot cm^{-1}}$. The assignment preferred by these authors differs from that in Table 5 with respect to the following five modes: $\nu_2(A_1) = 530$, $\nu_6(B_1) = 888$, $\nu_7(B_1) = 615$, $\nu_8(B_2) = 705$ and $\nu_{12}(E) = 766\ \mathrm{cm^{-1}}$ [12]. This assignment is not in agreement with the presently available polarization data. Furthermore, the 888 and 615 $\mathrm{cm^{-1}}$ Raman lines have not been observed by Bragin and Evans but were taken from the spectra by Lippincott and Tobin [11] who observed these lines for S_4N_4 dissolved in dioxane only. Other authors failed to observe these lines both for S_4N_4 dissolved in dioxane or CS_2 and for the solid ([13] and Table 1). The assignment and force constants reported by Bragin and Evans [12] are, therefore, obviously in error.

Another assignment was recently proposed by Turowski et al. [13]. It differs from the present one only by exchange of two wavenumbers: $\nu_8(B_2) = 701$ and $\nu_{12}(E) = 765\ \mathrm{cm^{-1}}$. However, in the present wavenumber calculations ν_8 was always larger than ν_{12}, and the small splitting of the 765 $\mathrm{cm^{-1}}$ i.r. band of solid S_4N_4 considered by Turowski et al. as an indication for a degenerate mode can also be explained by intermolecular interaction within the unit cell as pointed out above. Therefore, the above assignment by Turowski et al. may be in error too. These authors also calculated force constants but reported only two values: $f_r(\mathrm{SN}) = 5.05$ and $f_R(\mathrm{SS}) = 0.31\ \mathrm{N \cdot cm^{-1}}$. The latter one is in agreement with the present results while the former, for unknown reasons, is considerably higher (see Table 6). No information about the total number and kind of force constants used was given [46].

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[1] Sulfur Compounds, Part 76; for Part 75 see R. Steudel, J. Mol. Struct. in press.

[2] B. D. Sharma and J. Donohue, Acta Cryst. **16**, 891 (1963).

[3] M. L. DeLucia and P. Coppens, Inorg. Chem. **17**, 2336 (1978).

[4] P. S. Braterman, J. Chem. Soc. **1965**, 2297.

[5] A. G. Turner and F. S. Mortimer, Inorg. Chem. **5**, 906 (1966).

[6] R. Gleiter, J. Chem. Soc. A **1970**, **3174**.

[7] M. S. Gopinathan and M. A. Whitehead, Can. J. Chem. **53**, 1343 (1975); A. Millefiori and S. Millefiori, J. Chem. Res. (S), **1980**, 244.

[8] K. Tanaka, T. Yamabe, A. Tachibana, H. Kato, and K. Fukui, J. Chem. Phys. **82**, 2121 (1978).

[9] A. Banister, Nature London, Phys. Sci. **239**, 69 (1972); P. Cassoux, O. Glemser, and F. Labarre, Z. Naturforsch. **32b**, 41 (1977).

[10] D. Chapman and T. C. Waddington, Trans. Faraday Soc. **58**, 1679 (1962).

[11] E. R. Lippincott and M. C. Tobin, J. Chem. Phys. **21**, 1559 (1953).

[12] J. Bragin and M. V. Evans, J. Chem. Phys. **51**, 268 (1969).

[13] A. Turowski, R. Appel, W. Sawodny, and K. Molt, J. Mol. Struct. **48**, 313 (1978).

[14] G. Brauer (Ed.), Handbuch der Präparativen Anorganischen Chemie, Vol. 1, p. 403, Stuttgart 1975.

[15] T. Chivers, R. T. Oakley, O. J. Scherer, and G. Wolmershäuser, Inorg. Chem. in press.

[16] T. Shimanouchi, Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules, Tokyo 1968 (distributed privately).

[17] D. Chapman and A. G. Massey, Trans. Faraday Soc. **58**, 1291 (1962).

[18] R. Zallen und M. L. Slade, Phys. Rev. B **18**, 5775 (1978).

[19] W. P. Griffith and K. J. Rutt, J. Chem. Soc. A **1968**, 2331.

[20] Z. Iqbal, D. S. Downs and C. W. Christoe, J. Phys. Chem. Solids **38**, 263 (1977).

[21] G. Gautier and M. Debeau, Spectrochim. Acta **30 A**, 1193 (1974) and **32 A**, 1007 (1976), and references cited therein.

[22] P. Luger, H. Bradaczek, and R. Steudel, Chem. Ber. **109**, 3441 (1976).

[23] W. Flues, O. J. Scherer, J. Weiß, and G. Wolmershäuser, Angew. Chem. **88**, 411 (1976).

[24] R. Steudel, Z. Naturforsch. **24b**, 934 (1969).

[25] O. J. Scherer and G. Wolmershäuser, Angew. Chem. **87**, 485 (1975).

[26] J. Bojes and T. Chivers, Inorg. Chem. **17**, 318 (1978).

[27] R. Steudel, J. Phys. Chem. **81**, 343 (1977).

[28] R. Steudel and F. Rose, Spectrochim. Acta **33 A**, 979 (1977).

[29] L. A. Nimon and V. D. Neff, J. Mol. Spectrosc. **26**, 175 (1968).

[30] D. W. Scott, J. P. McCullough, and F. H. Kruse, J. Mol. Spectrosc. **13**, 313 (1964).

[31] R. Steudel and H. J. Mäusle, Z. Naturforsch. **33a**, 951 (1978).

[32] R. Steudel and D. F. Eggers, Spectrochim. Acta **31**A, 871 (1975).

[33] R. Steudel and F. Schuster, J. Mol. Struct. **44**, 143 (1978).

[34] R. Steudel, J. Steidel, and N. Rautenberg, Z. Naturforsch. **35b**, 792 (1980).

[35] R. Steudel, Spectrochim. Acta **31A**, 1065 (1975).

[36] O. Glemser, A. Müller, D. Böhler, and B. Krebs, Z. Anorg. Allg. Chem. **357**, 184 (1968).

[37] J. Mason, J. Chem. Soc. A **1969**, 1567.

[38] I. Lindqvist, J. Inorg. Nucl. Chem. **6**, 159 (1958).

[39] H.-J. Hecht, R. Reinhardt, R. Steudel, and H. Bradaczek, Z. Anorg. Allg. Chem. **426**, 43 (1976).

[40] S. N. Nabi, M. B. Hursthouse, and K. M. A. Malik, Acta Cryst. B **33**, 2309 (1977).

[41] R. Steudel, Angew. Chem. Int. Ed. Engl. **14**, 655 (1975).

[42] R. Steudel, Z. Naturforsch. **30b**, 281 (1975).

[43] W. R. Salaneck, J. W-p Lin, A. Paton, C. B. Duke, and G. P. Caesar, Phys. Rev. (B) **13**, 4517 (1976).

[44] O. Foss and A. Hordvik, Acta Chem. Scand. **12**, 1700 (1958).

[45] C. T. Kiers and A. Vos, Acta Cryst. **B34**, 1499 (1978).

[46] From the Dissertation of A. Turowski (University of Bonn, West Germany 1977, p. 60–61) it can be seen that f_r(SN) was calculated neglecting the sulfur-sulfur bonds while f_R(SS) was obtained by an alternative calculation with different symmetry coordinates neglecting the torsional coordinates.