VIBRATION SPECTRA OF SULPHUR TETRANITRIDE

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Received June 10th, 1980

Available data on infrared and Raman spectra of S_4N_4 in solid state and solutions have been verified and completed. On the basis of normal coordinate analysis an attempt has been made to define with more precision the interpretation of vibration spectra of this compound given in earlier reports.

Crystal and molecular structure of S_4N_4 has been attracting attention for a long time. It was found by X-ray analysis that S_4N_4 crystallizes in monoclinic system[1] (the space symmetry group C_{2h}^5) with four molecules in the elementary cell in the positions of trivial symmetry C_1 (ref.[2]). On the basis of electron difraction two different cage structures were suggested for the S_4N_4 molecule[3,4], the both belonging to the D_{2d} symmetry point group. Choice of the correct alternative was made on the basis of the complete X-ray analysis which proved plane arrangement of the four nitrogen atoms in combination with tetrahedral configuration of the four sulphur atoms[2,5] (Fig. 1a).

The first attempt to interpret the vibration spectra of S_4N_4 was based on an incorrect presumption of existence of N–N bonds in this molecule[6]. Later reports were based on the structure of sulphur tetranitrile found by X-ray analysis[7–9]. Recently, Raman spectra of the oriented S_4N_4 single crystal have also been published[10]. The suggested interpretation alternative was also rationalized with the use of normal coordinate analysis[8,9].

Several different results in the reports published so far (*e.g.* in the value of the potential constant f_{SS}) made us to try to complete the available experimental material and verify the results of normal coordinate analysis.

EXPERIMENTAL

S_4N_4 was prepared by reaction of dichlorodisulphane with ammonia in chloroform[11] and purified by repeated crystallization from benzene. The solvents used were dried and purified by usual methods.

The infrared (IR) spectra were obtained with a prism apparatus UR 20 (Zeiss, Jena) using cells with KBr windows. The Raman (RA) spectra were measured in capillary glass cells using a Ramalog 3 apparatus (Spex, Metuchen). The excitation was accomplished with the 488 nm line of an argon laser SP 165—03 (Spectra physics, Mountain View) with the output of about 50 mW.

RESULTS AND DISCUSSION

The vibration spectra of S_4N_4 obtained by us agreed very well with the published ones[9,10] except for slight insignificant differences in the wave number values. Their more precise interpretation was enabled, first of all, by the RA spectra of the solutions. Fig. 2 gives RA-spectrum of S_4N_4 in 1,4-dioxane. The measurements carried out in CCl_4 and CS_2 gave no additional information and served only as a verification of the results obtained in 1,4-dioxane. From Fig. 2 it can be seen than four bands could be differentiated in each vibration region (valence vibrations within 770 to 690 cm^{-1} and deformation vibrations within 570 to 520 cm^{-1}) of the S_4N_4

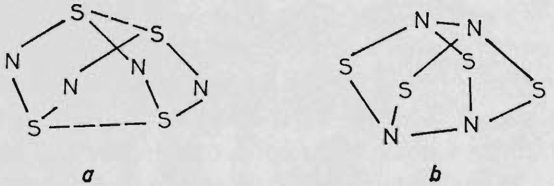

FIG. 1
The suggested structures of the S_4N_4 molecule

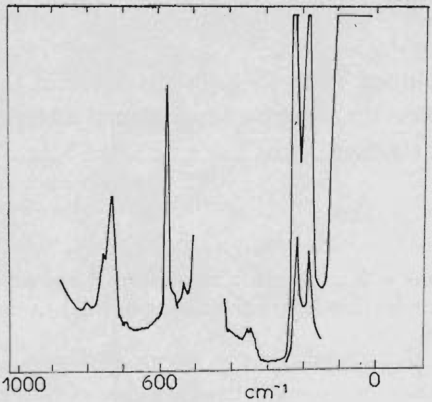

FIG. 2
The Laser-Raman spectrum of saturated solution of S_4N_4 in 1,4-dioxane

cycle. Table I (containing also data of refs[8,9]) suggests their interpretation on the basis of results of polarization measurements and with the use of selection rules for the D_{2d} point group. A somewhat different assignment of some bands (as compared with ref.[9]) resulted predominantly from the results of normal coordinate analysis, and it was indirectly supported also by the character of splitting of these bands in IR spectrum of the solid sample.

The trivial position symmetry of S_4N_4 molecules in the elementary crystal cell should cause activity of all 18 normal vibrations in the IR and RA spectra inclusive of splitting of bands of all degenerated vibrations. Out of four vibrations of the same type generated by the presence of four S_4N_4 molecules in the elementary cell two are IR-active and two are RA-active due to centrosymmetric factor group C_{2h}. The bands of all (in the D_{2d} point group) the non-denegerated and degenerated vibrations should thus be split into two or four components, respectively, in the both types of spectra. In study of polycrystalline samples, and due to random degeneration,

TABLE I

Fundamental frequencis of S_4N_4 (cm^{-1}) for D_{2d}

Symmetry type	No	Ref.[8]	Ref.[9]	This report[a]		Assignment	Distribution of potential energies[b], %
				found	calc.		
A_1	1	716	720	720	720	$\nu_s$cycl	$61\nu_1 + 38\nu_2$
	2	530	568	567	567	$\delta_s$cycl	$38\nu_2 + 51\nu_3$
	3	213	218	213	213	ν_sSS	$26\nu_2 + 62\nu_3$
A_2	4	557[c]	805[c]	615[d]	615	ν'_scycl	$58\nu_4 + 42\nu_5$
	5	428[c]	248[c]	350	347	δ'_scycl	$31\nu_4 + 69\nu_5$
B_1	6	888	698	734	534	ν_{as}cycl	$84\nu_6$
	7	615	528	532	532	δ_{as}cycl	$31\nu_6 + 69\nu_7$
B_2	8	705	710	693	693	ν'_{as}cycl	$88\nu_8$
	9	564	563	522	522	δ'_{as}cycl	$89\nu_9$
	10	178	180	180	180	ν_{as}SS	$91\nu_{10}$
E	11	938	942	937[e]	937	$\nu_e$cycl	$53\nu_{11}$
	12	766	760	765	765	ν'_ecycl	$46\nu_{12}$
	13	519	522	556	556	$\delta_e$cycl	$30\nu_{12} + 69\nu_{13}$
	14	341	346	350	350	δ'_ecycl	$31\nu_{11} + 65\nu_{14}$

[a] The wave numbers read from RA spectrum of solution of S_4N_4 in 1,4-dioxane; [b] only the contributions higher than 25% are given; [c] the calculated values; [d] taken from IR spectrum of the solid sample; [e] taken from IR spectrum of solution of S_4N_4 in 1,4-dioxane.

it is, of course, impossible to except the splitting of bands in the theoretically possible extent. Mostly, doublet splitting of bands of the degenerated vibrations can only be observed, and the rule of alternative inhibition causes somewhat different wave number values of the mutually corresponding bands in IR and RA spectra.

For the above-given reasons the spectra of the solid samples can exhibit non-active vibrations of the A_2 type even in the D_{2d} point group. Their identification in IR spectrum was enabled by results of normal coordinate analysis, whereas in RA spectrum they could not be observed.

The Normal Coordinate Analysis

The model for the analysis, its structural parameters, and the set of 18 internal coordinates of the S_4N_4 molecule were the same as in ref.[8]. Calculation of the quadratic potential constants was carried out by the Wilson **GF**-matrix method using a Tesla 200 computer and a set of programs described in refs[12,13]. For transformation of **G** and **F** matrices into the block diagonal form we used the following set of symmetrical coordinates:

$$S_1 = 1/\sqrt{8}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6 + \Delta r_7 + \Delta r_8),$$

$$S_2 = 1/\sqrt{8}(\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3 + \Delta\phi_4 + \Delta\phi_5 + \Delta\phi_6 + \Delta\phi_7 + \Delta\phi_8),$$

$$S_3 = 1/\sqrt{2}(\Delta D_1 + \Delta D_2) \text{ for the block } A_1,$$

$$S_4 = 1/\sqrt{8}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4 + \Delta r_5 - \Delta r_6 + \Delta r_7 - \Delta r_8),$$

$$S_5 = -1/\sqrt{8}(\Delta\phi_1 - \Delta\phi_2 + \Delta\phi_3 - \Delta\phi_4 + \Delta\phi_5 - \Delta\phi_6 - \Delta\phi_7 + \Delta\phi_8) \text{ for } A_2 \text{ block},$$

$$S_6 = 1/\sqrt{8}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4 + \Delta r_5 + \Delta r_6 - \Delta r_7 - \Delta r_8),$$

$$S_7 = -1/\sqrt{8}(\Delta\sigma_1 - \Delta\phi_2 + \Delta\phi_3 - \Delta\phi_4 - \Delta\phi_5 + \Delta\phi_6 + \Delta\phi_7 - \Delta\phi_8) \text{ for } B_1 \text{ block},$$

$$S_8 = 1/\sqrt{8}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4 + \Delta r_5 - \Delta r_6 - \Delta r_7 + \Delta r_8),$$

$$S_9 = 1/\sqrt{8}(\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3 + \Delta\phi_4 - \Delta\phi_5 - \Delta\phi_6 - \Delta\phi_7 - \Delta\phi_8),$$

$$S_{10} = 1/\sqrt{2}(\Delta D_1 - \Delta D_2) \text{ for the block } B_2,$$

$$S_{11} = 1/2(\Delta r_1 - \Delta r_4 - \Delta r_5 + \Delta r_8),$$

$$S_{12} = -1/2(\Delta r_2 - \Delta r_3 - \Delta r_6 + \Delta r_7),$$

$$S_{13} = -1/2(\Delta \phi_1 - \Delta \phi_2 - \Delta \phi_3 + \Delta \phi_4),$$

$$S_{14} = -1/2(\Delta \phi_5 - \Delta \phi_6 + \Delta \phi_7 - \Delta \phi_8),$$

$$S'_{11} = -1/2(\Delta r_2 + \Delta r_3 - \Delta r_6 - \Delta r_7),$$

$$S'_{12} = 1/2(\Delta r_1 + \Delta r_4 - \Delta r_5 - \Delta r_8),$$

$$S'_{13} = -1/2(\Delta \phi_5 + \Delta \phi_6 - \Delta \phi_7 - \Delta \phi_8),$$

$$S'_{14} = 1/2(\Delta \phi_1 + \Delta \phi_2 - \Delta \phi_3 - \Delta \phi_4) \text{ for the blocks } E.$$

The greatest problem in the course of the normal coordinate analysis consisted in suitable choice of adjusted set of quadratic potential constants (QPC). Presuming $f_{r_1r_3} = f_{r_1r_7}$, $f_{\phi_1\phi_5} = f_{\phi_1\phi_8}$, and $f_{r_1\phi_6} = f_{r_1\phi_7}$ (analogous relations are also valid for the other symmetrically equivalent pairs of internal coordinates), the **F** matrix contains 27 QPC, and 12 experimentally found frequencies do not suffice for their calculations. Therefore, according to the results of preliminary calculations a set of 14 potential constants was chosen (Table II). The first-rate crite-

TABLE II

Quadratic potential constants (QPC) of the S_4N_4molecule

QPC	[N m^{-1}]	QPC[a]	[N m^{-1}]
f_{RR}	146·9	$f_{\alpha_1\alpha i}$	123·5
f'_{RR}	69·3	$f_{\alpha_1\alpha 2}$	27·4
$f_{r_1r_1}$	323·4	$f_{\alpha_1\alpha 3}$	−14·9
$f_{r_1r_2}$	46·8	$f_{\alpha_1\alpha 4}$	−16·2
$f_{r_1r_5}$	−19·9	f_{r_1r5}	−36·9
$f_{r_1r_6}$	35·8	$f_{r_1\alpha 8}$	−23·2
$f_{r_1r_8}$	40·4	$f_{R\alpha}$	23·0

[a] The deformation and interaction potential constants were modified with the use of the lengths of the bonds including the respective angle, so that their dimension size might be the same as that of the valence potential constants, *i.e.* Nm^{-1}.

rion in their choice was the requirement of agreement between distribution of potential energy in the individual blocks and physically acceptable interpretation of the individual bands. In the first phase of the calculations the number of the adjusted parameters was lowered to 12 by introduction of the conditions $f_{r_1r_2} = f_{r_1r_8}$ and $f_{\varphi_1\phi_3} = f_{\varphi_1\phi_4}$ (analogously also for the other symmetrically equivalent pairs of the internal coordinates). The iteration procedure gives then a set of potential constants which reproduces well the experimental wave number values of normal vibrations at physically acceptable distribution of potential energy in all the blocks. The wave numbers 587 and 349 cm^{-1} were thus calculated for vibrations of the symmetrical type A_2. The valence vibration of this symmetry was, therefore, assigned the band observed in IR spectrum of the solid sample at 615 cm^{-1}, and the deformation vibration was assigned the band at 350 cm^{-1} belonging simultaneously to one of the degenerated deformation vibrations, too. Using these wave numbers, it was possible to cancel the two above-given limiting conditions and determine iteratively a 14-membered set of quadratic potential constants. The obtained values are given in Table II. From Table I it is seen that the wave number values calculated therefrom agree very well with the experimental data, and distribution of potential energy also stands in accordance with interpretation of the individual bands acceptably.

The value of potential constant $f_{SS} = 147 \text{ Nm}^{-1}$ calculated by us agrees approximately with that given in ref.[8] (161 Nm^{-1}), being about 3 to 5 times as great as further two published values (31 and 47 Nm^{-1}). The value of bond order $N_{SS} \approx 0{\cdot}9$ calculated from the relation

$$\log N = (-419{\cdot}4f^{-1/3} + r + 106{\cdot}8)/147{\cdot}7\,,$$

where f is the respective quadratic potential constant, and r is the bond length, indicates that the SS bond is most probably of a simple p–p σ-type (ref.[14,15]) and not an only partial bonding interaction, as it is stated most frequently. The bond order values calculated on the basis of the two above-given low f_{SS} values correspond to a practically negligible bonding interaction and, therefore, do not seem to be real.

The value of interaction potential constant f'_{SS} (69 Nm^{-1}) in unexpectedly high, being even greater than the usual value[14] for cumulated S–S bonds. However, if it is taken into account that the distance between the "non-bonded" sulphur atoms (269 pm) is only slightly greater than that between the "bonded" ones (258 pm) being still considerably smaller than the sum of their van der Waals radii (about 350 pm), then it is obvious that there exists a bonding interaction between all four sulphur atoms of the S_4N_4 molecule. This fact was not considered in the normal coordinate analysis, and its existence is obviously manifested in the unusually high value of the potential constant f'_{SS}.

On the contrary, the value of f_{SN} constant is the lowest of the values published so far[8,9] (411 and 505 Nm^{-1}, respectively), and it corresponds to the bond order $N_{SN} \approx 0{\cdot}8$, which contradicts the present opinion about partial π-character of these bonds. Their multiple character was inferred, first of all, from the found bond length S–N (162 pm), however, the bond angles found by X-ray analysis do not support this idea[5]. From average value of wave numbers of valence vibrations of the SN bonds in the S_4N_4 molecule (770 cm^{-1}, the wave number values of the degenerated valence vibrations being calculated twice) we obtain, according to the known[16] relation, the S–N bond length value 173 pm which is considerably higher than that found experimentally. A similar discrepancy was also observed with KSO_3NH_2 (ref.[15]) ($\nu_{SN} = 801\ \text{cm}^{-1}$, $r_{\text{exp}}^{SN} \approx 160$ pm, $r_{\text{calc}}^{SN} \approx 170$ pm), the value of potential constant f_{SN} (371 Nm^{-1}; ref.[17]) being consistent with an almost ideal S–N single bond in this molecule. This fact is explained[16] by strong mutual influence of S–N and S–O bonds in the KSO_3NH_2 molecule which was really confirmed by calculations[17]. Distribution of potential energy in the A_1 block (Table I) shows that S_4N_4 represents an analogous case of strong coupling of fully symmetrical valence and deformation vibrations of this cyclic molecule.

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Translated by J. Panchartek.