Vibrational spectra and force constants of heptasulfur imide S7NH

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Vibrational Spectra and Force Constants of Heptasulfur Imide

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Raman, infrared, and far-infrared spectra of solid and dissolved S_7NH, S_7ND, $S_7{}^{15}NH$, and $S_7{}^{15}ND$ have been recorded. All fundamental frequencies of heptasulfur imide have been observed and assigned in accordance with the molecular symmetry C_s. A normal-coordinate treatment was carried out using a modified Urey–Bradley force field with 16 independent force constants. Good agreement between observed and calculated frequencies was obtained and both Urey–Bradley and valence force constants are reported.

Introduction

In recent years the vibrational spectra of certain sulfur rings such as S_6,[1] S_8,[2] and S_{12}[3] have been definitely assigned. These rings belong to the degenerate point groups D_{3d} and D_{4d}, respectively, and since there are no substituents the spectra consist of relatively few absorptions and Raman lines, respectively. It has been shown that the spectra can be understood by means of very simple Urey–Bradley force fields with six or seven independent force constants only. For these reasons sulfur rings are ideal molecules to study the dependence of certain fundamental vibrations on ring size and molecular symmetry as well as possible relationships between force constants and structural parameters.[4,5]

Oxidation of S_8 with trifluoroperacetic acid yields S_8O[6] whose molecules still contain eight-membered puckered rings but with C_s symmetry.[7] The oxygen is linked to one of the sulfur atoms by a double bond in an axial position. The vibrational spectra of S_8O have been investigated[8] and force constants have been calculated.[9] The results show that the lowering of ring symmetry in S_8O compared with S_8 causes all bending and torsional modes degenerate in S_8 to split into their components but without much change in average frequency and Raman intensity.[9]

Another possibility to lower the symmetry of the S_8 ring is substitution of one sulfur atom by a heteroatom. The simplest compound of this type whose structure is known and which can be prepared in high purity is heptasulfur imide, S_7NH. S_7NH forms almost colorless crystals which can be prepared, for example, from S_8 by treatment with NaN_3 in tris(dimethylamino)phosphine oxide, subsequent hydrolysis in aqueous hydrochloric acid, and purification of the crude product by repeated recrystallization or column chromatography.[10] The molecular structure of S_7NH has been investigated several times[11,12] but only recently was it possible to determine the positions of all atoms including the hydrogen by x-ray diffraction on single crystals at −160 °C.[13] The molecules consist of crown-shaped S_7N rings containing almost planar groups S_2NH. The molecular and site symmetry is C_s and the centrosymmetric unit cell contains four molecules. The geometrical parameters are given in Table I; the numbering of atoms and bonds is shown in Figure 1.

The vibrational spectra of S_7NH were first investigated by Nelson[14] who recorded the Raman spectrum in the region 40–3500 cm^{-1} and the infrared spectrum in the region 200–4000 cm^{-1} using solid S_7NH and solutions in CS_2. However, Nelson did not observe all fundamental frequencies and made only a few assignments. Furthermore, some of the wavenumbers given in Tables 2 and 3 of Nelson's paper do not agree with the values which can be obtained from her Figures 2a and 2b.

TABLE I: Bond Distances (r, Å), Valence Angles (α, β, deg), and Dihedral Angles (τ, deg) of Heptasulfur Imide[a]

r_1, r_2	2.048	α_1	107.2	τ_1, τ_2	93.5
r_3, r_4	2.062	α_2, α_3	106.8	τ_3, τ_4	99.4
r_5, r_6	2.049	α_4, α_5	108.3	τ_5, τ_6	94.8
r_7, r_8	1.676	α_6, α_7	110.1	τ_7, τ_8	96.5
R_9	0.91	α_8	123.8	β_1, β_2	117.1

[a] The angle at atom i is termed α_i, the two angles SNH are termed β_1 and β_2, and the torsion angle at the bond r_i is called τ_i.

To remove these discrepancies and to determine all fundamental frequencies of the heptasulfur imide molecule we recorded the Raman, infrared, and far-infrared spectra of S_7NH, S_7ND, $S_7{}^{15}NH$, and $S_7{}^{15}ND$ in the solid state as well as in CS_2 solutions and made a normal-coordinate analysis.

Experimental Section

S_7NH was prepared from S_8 and NaN_3[10] since this method yields only traces of $S_6(NH)_2$ and $S_5(NH)_3$ which can be separated from S_7NH by chromatography only.[15] The crude product was extracted with boiling methanol from which on cooling S_8 crystallizes first followed by S_7NH on evaporation. The samples used for spectroscopy were purified by repeated recrystallization from CH_3OH and CCl_4 and in some cases by chromatography and showed melting points between 109 and 113 °C. All samples were free of $S_6(NH)_2$ as checked by thin-layer chromatography. Only traces of S_8 were present in some cases but since all strong IR absorptions and Raman lines of S_8 coincide with strong IR absorptions and Raman lines, respectively, of S_7NH no differences in the spectra of samples from different preparations were observed.

Since the hydrogen in S_7NH is fairly acidic ($pK_a = 5$[16]) S_7ND was easily obtained by recrystallization of S_7NH from excess methanol-d_1 (≥99 atom % CH_3OD) or alternatively by very slow precipitation of 2 g of S_7NH dissolved in 120 ml of dry acetone with 50 ml of D_2O (≥99.7 atom % D_2O) and subsequent drying under high vacuum for several hours.

On standing in air S_7ND changes to S_7NH within 24 h. Therefore, due to the conventional sample preparation the IR spectra of S_7ND exhibited additional weak absorptions belonging to S_7NH.

$S_7{}^{15}NH$ was prepared from $K^{15}NN_2$ (95 atom % ^{15}N at one terminal atom of the azide anion) which first had to be converted into $Na^{15}NN_2$ by ion exchange since KN_3 does not react with S_8 to give S_7NH in good yields. 1.6 g of $Na^{15}NN_2$ was stirred with 1.7 g of S_8 in 33 ml of

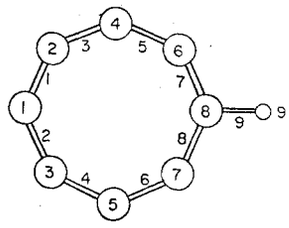

Figure 1. Numbering of atoms and bonds in heptasulfur imide.

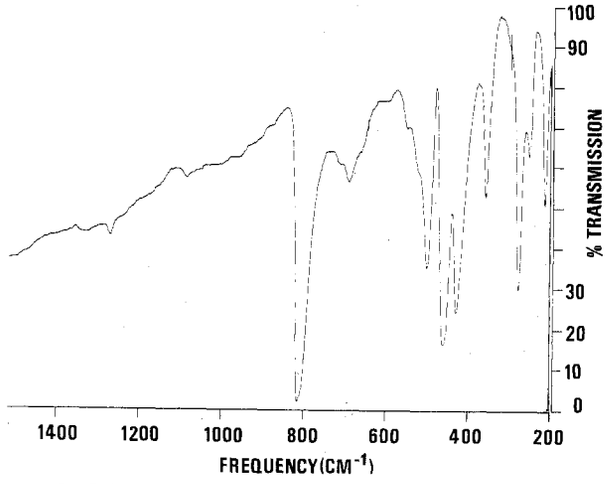

Figure 2. Infrared spectrum of solid S_7NH at 25 °C.

$[(CH_3)_2N]_3PO$, the reaction bottle being placed in a nitrogen filled desiccator over $CaCl_2$. After hydrolysis in 40 ml of 10% hydrochloric acid and drying under high vacuum the crude product was extracted with 140 ml of hot methanol for 1 hr. After cooling and filtration the solvent was evaporated and the residue dissolved in CS_2. This solution was used for column chromatography on silica gel eluting with a mixture of equal volumes of CCl_4 and *n*-hexane. The presence of S_7NH in the eluate was checked with alcoholic potassium hydroxide (turns violet with S_7NH). After evaporation of the medium fraction and drying under high vacuum colorless crystals of a $S_7{}^{14}NH/S_7{}^{15}NH$ mixture (1:1) were obtained (melting point 113 °C). In the following this mixture is denoted S_7*NH. All chemicals used were of the highest commercially available quality.

The Raman spectra were recorded in the region 10–3500 cm^{-1} using a Cary 82 spectrometer with triple monochromator and the 488.0-, 514.5-, and 647.1-nm lines of Ar and Kr lasers. Powdered samples as well as solutions in CS_2 (freshly distilled from P_4O_{10}) were investigated. With Ar laser excitation a rotating sample holder was used for solid samples. Polarization measurements were possible for the strongest Raman lines only since the solubility is not very high.

The infrared spectra in the region 200–4000 cm^{-1} were recorded using two grating spectrometers (Beckman IR 12 and Perkin-Elmer 325). KBr, CsBr, and CsI disks were prepared with 5–35 mg of heptasulfur imide. Low temperature spectra were recorded using a device described earlier.[17] Solutions in CS_2 were investigated in matched 0.1–1.0-mm cells of CsI. The region 50–400 cm^{-1} was also investigated with a Polytec FIR 30 Fourier transform spectrometer using sample disks prepared from pure S_7NH.

Vibrational Spectra and Frequency Assignment

The observed infrared bands and Raman lines are listed in Tables II–IV and the spectra are shown in Figures 2–4. For a molecule of C_s symmetry consisting of 9 atoms, 21

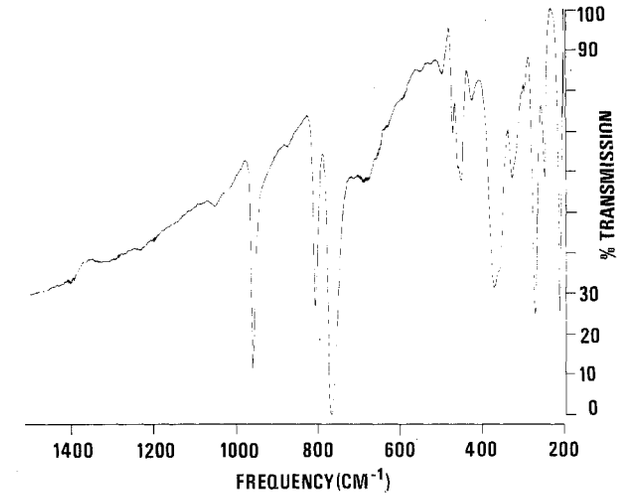

Figure 3. Infrared spectrum of solid S_7ND at 25 °C (containing approximately 10% S_7NH).

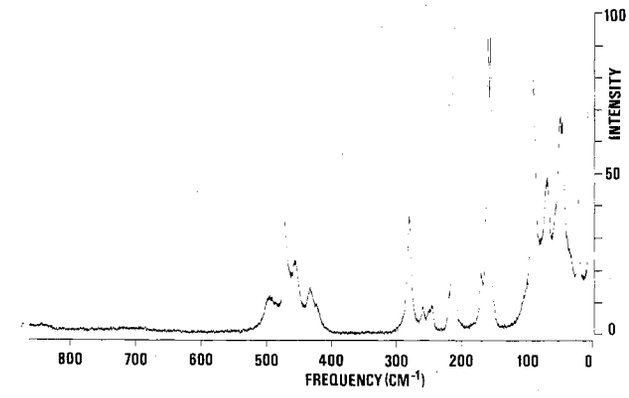

Figure 4. Raman spectrum of solid S_7NH at 25 °C (spectral bandwidth 1.5 cm^{-1}).

fundamental vibrations are to be expected, 12 of which belong to the species a′ and 9 to a″ and all of which are infrared and Raman active. There must be 9 stretching, 10 bending, and 2 torsion vibrations (cf. S_8O[9]). The NH stretching wavenumber of S_7NH at 3334 cm^{-1} in CS_2 shifts to 3270 cm^{-1} in the solid due to weak intermolecular H···S hydrogen bonding.[13] In S_7ND it occurs at 2475 cm^{-1} corresponding to a H/D ratio of 1.35. S_7*NH shows ν_{NH} at 3331 cm^{-1} (in CS_2) but no splitting was observed which, according to the mass difference between ^{14}N and ^{15}N, should amount to 7 cm^{-1}.

The SN stretching wavenumbers can be expected in the region 600–1000 cm^{-1} since the planar HNS_2 group can be compared with the molecules OCl_2 (673, 634[18]), $H^{11}BCl_2$ (892, 740[19]), and $HNCl_2$ (687, 666[20]) whose XCl stretching wavenumbers are given in parentheses. The antisymmetric SN vibration is of high IR intensity but does not show up in the Raman spectrum. It shifts on deuteration much more than on ^{15}N substitution because of some coupling with $\delta_{ND}(a'')$ in S_7ND. This mode occurs at 1288 cm^{-1} in S_7NH and at 970 cm^{-1} in S_7ND. The coupling also causes a substantial increase in IR intensity of δ_{ND}. In $HNCl_2$ the corresponding vibration occurs at 1295 cm^{-1}.[20] The symmetric SN vibration of S_7NH does also not occur in the Raman spectrum and is of very low IR intensity at 25 °C but can be easily detected in IR spectra taken at −185 °C. The wavenumbers are listed in Table IV.

The six SS stretching wavenumbers (3a′, 3a″) can be expected in the region 400–500 cm^{-1} since there is a linear relationship between SS bond distances and average SS frequency[5] from which ν_{SS} = 458 cm^{-1} is obtained. Since

TABLE II: Vibrational Wavenumbers of S_7NH (cm^{-1})[a]

Raman		Infrared		
Solid	In CS_2	Solid	In CS_2	Assignment
21 m				Lattice
47 vs				Lattice
50 vs				Lattice
		52 vw		Lattice
56 w,sh				
		63 w		
71 s	obsc	75 w		a′ τ
91 vs	89 s	96 vw		a″ τ
105 w,sh		107 m		91 + 21 or 63 + 52
158 vs		168 m		a′ + a″ δ_{SSS}
162 vs	160 vs,dp			
171 w	170 vw,sh			2·91
		212 s	204 s	a″ δ_{SSS}
215 vvs	212 vvs,p		211 m	a′ δ_{SSS}
220 vw,sh				160 + 71
247 w	249 w	250 m	249 m	a′ δ_{SSS}
251 vw				160 + 91
261 w		260 w		a″ δ_{SSN}
282 s	272 m,p	276 s	272 m	a′ δ_{SNS}
		295 w		212 + 91
		356 m	358 w-m	a′ δ_{SSN}
424 w,sh		427 s	424 s	a″ ν_{SS}
433 m	440 m			a′ ν_{SS}
456 m	460 w	456 s	446 s	a″ ν_{SS} + a′ γ_{NH}
			467 w,sh	a′ ν_{SS}
473 s	478 m			a″ ν_{SS}
496 m	487 m	500 m	494 m	a′ ν_{SS}
		522 w,sh	517 w,sh	272 + 249
		552 vw		500 + 52 or 500 + 63
		660 vw,sh		500 + 160 or 456 + 212
		694 w	680 w	a′ ν_{SN}
		718 vw		456 + 261 or 2·356
		740 vw		456 + 279
		816 vvs	805.8 s	a″ ν_{SN}
		1274 vw	1288 m	a″ δ_{SNH}
3258 m-s		3270 m	3334 m	a′ ν_{NH}

[a] v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad; p, polarized; dp, depolarized; obsc, obscured by CS_2; ν, stretching; δ, bending; τ, torsion vibration.

the bond distances vary by only 0.014 Å, vibrational coupling only causes the ν_{SS} to be spread over a certain region. The spectra of S_7NH and S_7ND show considerable differences in the 400–500-cm^{-1} region. In the case of S_7ND five frequencies of low or medium intensity are found in the IR and Raman spectra and can be assigned to the six SS stretching fundamentals assuming one incidental degeneracy at 463 cm^{-1}. Since all the calculations show the SS stretching modes distributed in alternating order to the two symmetry species (a′ > a″ ≈ a′ > a″ > a′ > a″) we assign the wavenumbers in the 420–480-cm^{-1} region accordingly.

S_7NH exhibits only three strong IR absorptions in the 400–500-cm^{-1} region. These are absent not only in S_7ND but also in the spectrum of $(S_7N)_2S$[21] in which two S_7N rings are connected by a sulfur atom. The same holds for S_7NCH_3.[22] Therefore, we assume that the wavenumbers at 427, 456, and 498 cm^{-1} in the spectra of S_7NH are connected with the symmetric NH bending vibration (NH wagging). In S_7ND this mode occurs as a broad structured absorption at 367 cm^{-1}. In S_7NH it must be coupled to some extent with the SS stretching modes and we assign the 500-cm^{-1} frequency which occurs in the Raman spectrum at 496 cm^{-1} and is polarized to the highest SS stretching mode which is intensified and shifted from 474 cm^{-1} in S_7ND by mixing with δ_{NH}(a′). This assumption is supported by the normal-coordinate analysis (see below). The two remaining wavenumbers at 456 and 427 cm^{-1} are assigned to δ_{NH}(a′) assuming a splitting caused by a slightly asymmetric double minimum potential (DMP) as has been observed for NH stretching frequencies previously.[23] The

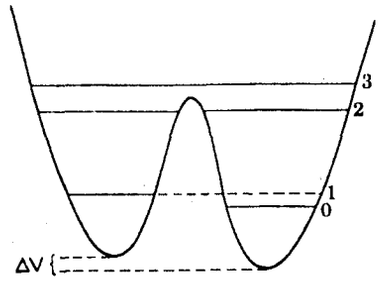

Figure 5. Assumed double minimum potential for the NH wagging mode of heptasulfur imide.

x-ray structure analysis of S_7NH showed the hydrogen in an axial position with respect to the S_7N ring but the angle between the NH bond and the plane formed by the neighboring atoms 6, 7, and 8 (see Figure 1) amounts to only 14° (in NH_3, 56°). Since there must be another position for the hydrogen on the other side of that plane (equatorial position) differing in energy only slightly (due to the different longe range SH interaction with atoms 4 and 5) the assumption of a DMP for the wagging vibration seems reasonable. The barrier between the axial and equatorial positions should be quite low causing the first vibrationally excited δ_{NH} level to be located near the top of the barrier which results in a splitting of this level (see Figure 5). In this case the relative IR intensities of the transitions 0–2 and 0–3 can be of comparable magnitude.[24,25] On deuteration the levels 0 to 3 decrease in energy and the splitting of levels 2 and 3 becomes much smaller leading to one broad but structured absorption

TABLE III: Vibrational Wavenumbers of S_7ND (cm^{-1})[a]

Raman solid	Infrared: Solid	Infrared: In CS_2	Assignment
22 m			Lattice
46 m			Lattice
49 m			Lattice
56 w,sh			Lattice
70 m			a′ τ
91 s			a″ τ
105 vw,sh			91 + 22
157, 161 vs			a′ + a″ δ_{SSS}
171 w			2·91
	211 vs	203 vs	a″ δ_{SSS}
214 vs		210 m	a′ δ_{SSS}
221 w			160 + 70
247 w	247 m	248 s	a′ δ_{SSS}
252 w			160 + 91
262 w	262 w		a″ δ_{SSN}
281 m	272 vs	270 s	a′ δ_{SNS}
	327 m	312 vs	a′ δ_{SSN}
	367 vs,b	368 vs	a′ γ_{ND}
	426 w	427 m	a″ ν_{SS}
439 w	435 vw		a′ ν_{SS}
	455 s	461 m	a″ ν_{SS}
460 w,b	464 m	469 m	a′ + a″ ν_{SS}
472 s	475 m	478 m	a′ ν_{SS}
	501 w		S_7NH
		517 w	270 + 248
	658 w	655 w	461 + 204
	680 w-m	676 vw	a′ ν_{SN}
709 vvw		697 w	427 + 270
715 vvw			
721 vvw	723 w	713 w	455 + 272
729 vvw			
	776 vvs	774.5 vvs	a″ ν_{SN}
	966 vs	970 vs	a″ δ_{SND}
	1055 vw,b	1050 vw	970 + 91 or 776 + 272
2425 w	2433 s	2475 s	a′ ν_{ND}

[a] For abbreviations see Table II.

TABLE IV: SN Stretching Wavenumbers of Heptasulfur Imide (cm^{-1})

Species	State	$S_7{}^{14}NH$	$S_7{}^{14}ND$	$S_7{}^{15}NH$	$S_7{}^{15}ND$
a′	Solid	694	680		
a″	In CS_2	805.8	774.5	787.0	762.0

band for δ_{ND}(a′). This explanation for the strong IR absorptions of S_7NH in the region 400–500 cm^{-1} is supported by the observation that these bands are observed in CS_2 solution too but shifted to lower wavenumbers due to the cleavage of the weak hydrogen bonds in solid S_7NH. Furthermore, S_7NH reacts with tris(dimethylamino)-phosphorus oxide (TDPO) to form the solid adduct $TDPO{\cdot}2S_7NH$ in which according to a x-ray structure analysis the two NH groups are hydrogen bonded to the oxygen atom.[26] In this compound δ_{NH}(a′) occurs at 671 cm^{-1} and δ_{ND}(a′) at 545 cm^{-1} which in both cases corresponds to a shift from $S_7NH(D)$ by a factor of 1.5 provided δ_{NH}(a′) is located near 450 cm^{-1} in S_7NH.

The assignment of the 10 ring bending and torsional modes is more difficult. The highest frequency at 356 cm^{-1} can be assigned to the symmetric SSN bending mode which according to the lower mass of nitrogen must be the highest ring bending mode.[27] No $^{14}N/^{15}N$ splitting has been observed for this mode which due to the calculations should amount to 6 cm^{-1}. In S_7ND δ_{SSN}(a′) is repelled by δ_{ND}(a′) and therefore shifted to 327 cm^{-1}.

The remaining nine modes can be expected between 300 and 60 cm^{-1} since all corresponding vibrations of S_8 and S_8O are found in this region. The two torsional modes degenerate in S_8 (85 cm^{-1}) and split in S_8O (84, 67 cm^{-1})

TABLE V: Comparison of Bending and Torsional Modes of Eight-Membered Rings (Symmetry Species, Wavenumbers, Raman Intensities)

S_8O (C_s)		S_8 (D_{4d})		S_7NH (C_s)
a′	219 vs	a_1	216 s	a′ 215 vvs
a′	250 vw	b_2	243 w	a′ 282 s
a′	190 w			a′ 356 –
		e_1	184 w	
a″	197 w			a″ 212 obsc
a′	67 s			a′ 71 s
		e_2	85 s	
a″	84 s			a″ 91 vs
a′	140 s			a′ 160
		e_2	152 s	vs
a″	157 vs			a″ 160
a′	(219)			a′ 250 vw
		e_3	243 w	
a″	235 vw			a″ 261 w

can be expected to be of strong Raman intensity and should be located near 80 cm^{-1}. We assign the strong Raman lines at 91 and 70 cm^{-1} to these modes and consider all wavenumbers below 70 cm^{-1} to be lattice modes. In contrast to the 91-cm^{-1} line the 70-cm^{-1} Raman line has not been observed for $TDPO{\cdot}2S_7NH$[26] and $(S_7N)_2SO$.[29] However, in S_7NH and S_7ND τ(a′) is strongly coupled with $\delta_{NH(D)}$ which may remove the incidental degeneracy of τ(a′) and τ(a″) which must be assumed for the two derivatives. The lattice vibrations of S_8 have been found below 65 cm^{-1} and some of them give rise to strong Raman lines.[30,31] In S_8O the lattice vibrations also occur below 65 cm^{-1}.[9] Since S_7NH is of similar shape and mass as S_8 and S_8O the wavenumbers of the lattice vibrations should be similar too. Since the unit cell of heptasulfur imide is centrosymmetrical (D_{2h}^{16})[11-13] the lattice vibrations may be either Raman or infrared active.

For the assignment of the remaining fundamentals it must be taken into account that only frequencies occurring in all compounds containing the S_7N unit can be ring bending modes of S_7NH. Since this is not the case for the Raman lines at 171, 220, and 251 cm^{-1} these frequencies must represent combination vibrations or overtones. The remaining wavenumbers are assigned according to their IR intensities and by analogy with S_8 and S_8O. The strong Raman line at 160 cm^{-1} slightly split in solid heptasulfur imide has been observed for S_8 at 152 cm^{-1} and for S_8O at 140/157 cm^{-1} and must represent two modes $\delta_{SSS}(\alpha' + a'')$ since there is no second line of similar intensity nearby. The splitting in the solid state may arise from correlation field interaction since it is not observed for solid $TDPO{\cdot}2S_7NH$.[26]

The strongest Raman line of S_7NH occurs at 215 cm^{-1}. This wavenumber is characteristic for eight-membered sulfur rings since it has been observed with high Raman intensity for S_8 (216) and S_8O (219) also but not for S_6, S_7, and S_{12}.[4] In the IR spectrum of dissolved S_7NH two bands occur at 204 and 211 cm^{-1} which correspond to the IR absorption of solid S_7NH at 212 cm^{-1} and the Raman line at 215 cm^{-1} and represent two SSS bending modes (a″ + a′).

The three bending modes left are assigned to the IR absorptions at 276(a′), 260(a″), and 250(a′) cm^{-1}. The 276-cm^{-1} frequency must be the SNS bending mode because of its high IR intensity and its shift on isotopic substitution (in CS_2: S_7NH 272, S_7ND 270, S_7*NH 270, S_7*ND 268 cm^{-1}).

In Table V the ring bending and torsional modes of S_8, S_8O, and S_7NH are compared. No differences in the spectra of S_7NH, S_7ND, S_7*NH, and S_7*ND were observed below 260 cm^{-1}.

Force Field

The force constant calculations were made using a modified Urey–Bradley force field since this field was shown to be suitable for S_8[2] as well as for $S_4N_4H_4$[32] and should therefore be applicable to S_7NH too. The details have been discussed in earlier papers.[1-4,9,32]

The following 16 independent force constants were used:

K_1 SS stretching
K_2 SN stretching
K_3 ND stretching
H_1 bending at S
H_2 SNS bending
H_3 SNH bending
H_4 NH wagging
F_1 SS repulsion
F_2 SN repulsion
F_3 SH repulsion
Y_1 SS torsion
Y_2 SN torsion
C long-range SS and SN repulsion
P_1 bond–bond interaction at S
P_2 bond–bond interaction at N
U NH wagging–SN torsion interaction

With these constants the potential energy becomes

$$\begin{aligned}2V = &\overset{6}{\Sigma} K_1(\Delta r)^2 + 2\overset{6}{\Sigma}K_1'r(\Delta r) + \overset{2}{\Sigma}K_2(\Delta r)^2 \\ &+ 2\overset{2}{\Sigma}K_2'r(\Delta r) + K_3(\Delta R)^2 + 2K_3'R(\Delta R) \\ &+ \overset{7}{\Sigma}H_1(r\Delta\alpha)^2 + 2\overset{7}{\Sigma}H_1'r(r\Delta\alpha) + H_2(r\Delta\alpha)^2 \\ &+ 2H_2'r(r\Delta\alpha) + \overset{2}{\Sigma}H_3(\bar{r}\Delta\beta)^2 + 2\overset{2}{\Sigma}H_3'\bar{r}(\bar{r}\Delta\beta) \\ &+ H_4(R\Delta\gamma)^2 + 2H_4'R(R\Delta\gamma) + \overset{6}{\Sigma}F_1(\Delta q_1)^2 \\ &+ 2\overset{6}{\Sigma}F_1'q_1(\Delta q_1) + \overset{2}{\Sigma}F_2(\Delta q_2)^2 + 2\overset{2}{\Sigma}F_2'q_2(\Delta q_2) \\ &+ \overset{2}{\Sigma}F_3(\Delta q_3)^2 + 2\overset{2}{\Sigma}F_3'q_3(\Delta q_3) + \overset{6}{\Sigma}Y_1(r\Delta\tau)^2 \\ &+ 2\overset{6}{\Sigma}Y_1'r(r\Delta\tau) + \overset{2}{\Sigma}Y_2(r\Delta\tau)^2 + 2\overset{2}{\Sigma}Y_2'r(r\Delta\tau) \\ &+ \overset{8}{\Sigma}C(\Delta q')^2 + 2\overset{8}{\Sigma}C'q'(\Delta q') + 2\overset{7}{\Sigma}P_1\Delta r\Delta r' \\ &+ 2P_2\Delta r\Delta r' + 2\overset{2}{\Sigma}U\Delta\gamma\Delta\tau\end{aligned}$$

The coordinates q and q' are the distances between atoms i and, respectively, $i + 2$ and $i + 3$, and r and r' are the distances of adjacent bonds within the ring. Since all the distances q' are very similar ($4.15 < q' < 4.45$ Å) only one force constant C was used.[33] Any long-range repulsion envolving the hydrogen atom was neglected. The constants F' and C' were constrained by the conventional assumptions $F' = -0.1F$ and $C' = -0.1C$. All constants K', H', and Y' are eliminated in the removal of the redundant coordinates q and q'.

Calculations

The calculations were performed by a CD 6500 computer using the programs UBZM by Schachtschneider[34] to calculate the Z matrix elements for the force constant C and BGLZ and LSMA by Shimanouchi[35] to calculate all matrices, the frequencies, and potential energy distribution. The valence force constants were obtained from the F matrix.

The Cartesian coordinates were taken from the recent low temperature x-ray structure analysis.[13] However, the NH bond length was assumed to be 1.03 Å which is the average in a large number of NH compounds and the hydrogen was assumed to be in the plane of the neighboring atoms ($\beta_1 = \beta_2 = 118.1°$).[36] The symmetry coordinates with exception of the NH wagging coordinate $S = \Delta\gamma$ were taken from S_8O[9] (γ is the angle between the NH bond and the plane of atoms 6–8).

Force Constants

The first set of frequencies was calculated with assumed Urey–Bradley force constants whose values were choosen using the force constants of S_8[2] and $S_4N_4H_4$.[32] To adjust the calculated to the observed frequencies by the least-squares method 38 observed values were used for $S_7NH(\nu_2-\nu_4, \nu_7-\nu_{14}, \nu_{18}-\nu_{21})$, $S_7ND(\nu_1-\nu_{21})$, $S_7{}^{15}NH(\nu_{14})$, and $S_7{}^{15}ND(\nu_{14})$. ν_{NH} was neglected because of its anharmonicity. Solution frequencies were taken above 750 cm^{-1}, otherwise solid state values were used.

First groups of force constants were varied but in the last run all 16 force constants were allowed to vary simultaneously until the corrections became zero. The frequencies obtained as well as the potential energy distribution are given in Table VI. The force constants are listed in Tables VII and VIII.

The maximum difference between observed and calculated wavenumbers amounts to 9 cm^{-1}.

Discussion

The Urey–Bradley and valence force constants of S_7NH can be compared with those of S_8[2] and $S_4N_4H_4$.[32] This comparison shows that all corresponding values are very similar indicating that the frequency assignment of S_7NH is correct and that the force field is appropriate. It should be pointed out, however, that the force constants connected with the wagging mode of S_7NH cannot be considered as reliable as those of $S_4N_4H_4$ which exhibits three wagging modes from which the force constants can be determined more accurately. The normal-coordinate treatment of $S_4N_4H_4$ has shown that in addition to the wagging–torsion interaction also wagging–stretching and wagging–bending interaction force constants are necessary which, however, could not be used in the case of S_7NH because of the only one wagging frequency. Nevertheless, all constants connected with the NH group are very similar in S_7NH and $S_4N_4H_4$.

There exist relationships between bond distances and SN[39] and SS[5] stretching force constants. The mean values calculated for S_7NH (Table VIII) are in agreement with these equations (calcd $f_r(SN) = 3.9$, $f_r(SS) = 2.47$ mdyn/Å). However, we have no explanation for the two different SS stretching force constants.

The average SS stretching frequency of S_7ND of 453 cm^{-1} is in agreement with the value of 458 cm^{-1} calculated from the bond distance–stretching frequency relationship.[5] The average SN stretching frequency of S_7NH (751 cm^{-1}), however, does not fit the known bond distance–stretching frequency relationship[40] derived from only a few values some of which are not longer valid. Therefore, this relationship should be reinvestigated.

Nelson[14] observed a number of very weak Raman lines in the SN stretching region of S_7NH whose frequencies do not agree with the two infrared active ν_{SN} modes. She explained these lines by factor group splitting of the ν_{SN}. However, we did not observe these lines and the small frequency shift of the two ν_{SN} modes on dissolution of S_7NH in CS_2 does not support the idea of any measurable correlation field splitting. We therefore believe that the weak Raman lines are combination vibrations. We did also not observe the splitting of $\delta_{SNH}(a'')$ reported by Nelson.

The most peculiar detail of the S_7NH spectrum is the NH wagging mode giving rise to three strong IR bands near

TABLE VI: Observed and Calculated Wavenumbers of S_7NH and S_7ND and Potential Energy Distribution to the Symmetry Coordinates[a]

	$S_7{}^{14}NH$			$S_7{}^{14}ND$		
	Wavenumber, cm^{-1}			Wavenumber, cm^{-1}		
	Obsd	Calcd	Potential energy, (%)	Obsd	Calcd	Potential energy, %
a' ν_1	(3334)	3393	100 ν_{NH}	2475	2475	99 ν_{ND}
ν_2	694	693	83 ν_{SN}, 13 δ_{SNS}	680	681	84 ν_{SN}, 12 δ_{SNS}
ν_3	498	498	45 γ, 44 ν_{SS}	474	477	88 ν_{SS}
ν_4	472	465	88 ν_{SS}	463	461	85 ν_{SS}, 12 δ_{SSS}
ν_5	(456)	450	93 ν_{SS}	439	448	97 ν_{SS}
ν_6	(433)	436	52 ν_{SS}, 38 γ	367	369	37 δ_{SSN}, 36 γ, 12 ν_{SS}
ν_7	356	357	60 δ_{SSN}, 12 τ_{SN}, 12 ν_{SS}	327	327	56 δ_{SSN}, 20 τ_{SN}, 15 γ
ν_8	279	281	39 δ_{SNS}, 22 γ, 13 τ_{SN}, 13 δ	276	274	37 δ_{SNS}, 33 γ
ν_9	249	245	75 δ_{SSS}	247	244	69 δ_{SSS}, 14 γ
ν_{10}	215	214	63 δ_{SSS}, 18 τ_{SS}	214	213	61 δ_{SSS}, 14 τ_{SS}
ν_{11}	160	162	77 δ_{SSS}	159	161	75 δ_{SSS}, 11 γ
ν_{12}	71	70	39 γ, 33 τ_{SN}, 21 τ_{SS}	70	70	39 γ, 33 τ_{SN}, 21 τ_{SS}
a'' ν_{13}	1288	1290	98 δ_{NH}	970	968	81 δ_{ND}, 19 ν_{SN}
ν_{14}	805.8	808	98 ν_{SN}	774.5	773	93 ν_{SN}
ν_{15}	(472)	462	93 ν_{SS}	463	462	93 ν_{SS}
ν_{16}	(456)	459	87 ν_{SS}	455	459	87 ν_{SS}
ν_{17}	(427)	423	99 ν_{SS}	428	423	99 ν_{SS}
ν_{18}	261	256	59 δ_{SSN}, 28 δ_{SSS}	262	255	58 δ_{SSN}, 29 δ_{SSS}
ν_{19}	212	214	58 δ_{SSS}, 18 τ_{SS}	211	213	57 δ_{SSS}, 22 τ_{SS}
ν_{20}	160	168	70 δ_{SSS}, 23 δ_{SSN}	159	168	70 δ_{SSS}, 23 δ_{SSN}
ν_{21}	91	92	65 τ_{SS}, 26 τ_{SN}	91	92	64 τ_{SS}, 25 τ_{SN}
$S_7{}^{15}NH$: ν_{SN}(a'') obsd 787.0, calcd 788				$S_7{}^{15}ND$: ν_{SN}(a'') obsd 762.0, calcd 760		

[a] $\geq$10%; wavenumbers in brackets were not used in the force constant calculation.

TABLE VII: Urey-Bradley Force Constants of Heptasulfur Imide (mdyn/Å)

K_1(SS)	1.751	H_4(NH)	0.180	Y(SS)	0.023
K_2(SN)	2.805	F_1(SS)	0.347	Y(SN)	0.045
K_3(ND)	5.749	F_2(SN)	0.703	C	0.039
H_1(S)	0.053	F_3(SH)	0.552	$U(\gamma/\tau)$	0.142
H_2(SNS)	0.199	P_1(S)	0.236		
H_3(SNH)	0.109	P_2(N)	0.572		

TABLE VIII: Valence Force Constants of Heptasulfur Imide (mdyn/Å)[a]

f_r(SS)	2.23 ($r_1 - r_4$)	f_a	0.23 ($a_1 - a_5$)
f_r(SS)	2.53 (r_5, r_6)	f_a	0.36 (a_6, a_7)
f_r(SN)	3.98	f_a	0.33 (a_8)
f_R(ND)	6.37	f_β	0.28
f_{rr}(SS/SS)	0.52	f_γ	0.18
f_{rr}(SS/SN)	0.80	f_τ	0.03 (SSSS)
f_{rr}(SN/SN)	0.90	f_τ	0.04 (SSSN)
f_{rR}(SN/NH)	0.41	f_τ	0.05 (SSNS)
$f_{r\alpha}$	0.15-0.31	$f_{\gamma\tau}$	0.14
$f_{r\beta}$(SN/NH)	0.31		

[a] f_i, diagonal constants; f_{ij}, interaction constants between the nearest coordinates indicated.

450 cm^{-1}. The potential energy distribution shows γ_{NH} to be mixed with many other a' vibrations but this result may be partly unreal since the PED with respect to γ_{NH} was quite sensitive to the kind and the values of certain force constants (94 different sets of force constants were examined). We, therefore, doubt that the three IR bands at 427, 456, and 500 cm^{-1} arise all from coupling of γ_{NH} with two or three SS stretching vibrations. Only the highest band at 500 cm^{-1} is believed to be a mixture of γ_{NH} and ν_{SS}. The remaining "doublet" at 427/456 cm^{-1} must be caused by a double minimum potential as discussed above or by Fermi resonance of $\gamma_{NH} \approx 450$ cm^{-1} with a combination vibration. There are indeed several suitable binary combinations belonging to the a' species (for example, 2·214, 2·212, 356 + 71, 279 + 160). However, there are also combinations close to $\gamma_{ND} = 367$ cm^{-1} but no Fermi resonance is observed. We therefore favor the explanation by a double minimum potential.

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A Detailed Study of *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine Luminescence in Organic Glasses. Evidence for a Protonation Reaction

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The solvent and temperature dependence of an anomalous long-lived luminescence (λ_{max} 430 nm), observed simultaneously with the ordinary fluorescence and phosphorescence of tetramethyl-*p*-phenylenediamine (TMPD) in ethanol and in some other organic solvents at 77 K, has been studied. These results together with some complementary observations on absorption spectra have been interpreted as indicative of a protonation by ethanol of the TMPD molecule in its ground state. It is also shown that when excited to the first singlet, $TMPDH^+$ is partially decomposed to $TMPD^{S_1}$ the spectral properties of which are different from that of the directly excited TMPD. The mechanism of protonation and the importance of the environment on spin–orbit coupling of TMPD are discussed.

Introduction

Aromatic amines in organic glasses have been the subject of several luminescence studies in the last decade.[1-3] Among them, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) is of particular interest. Due to its low ionization potential, it is the most commonly used solute for photoionization studies in liquid or glassy solutions. Its UV excited luminescence[4] as well as the neutralization luminescence following photoionization[5] have been extensively studied. In a previous paper,[6] we reported the existence of a new type of long-lived luminescence characterized by excitation and emission spectra which appear quite distinct from the TMPD absorption and emission. The species responsible for this emission was tentatively identified with a solute–solvent charge transfer state, the existence of which had been repeatedly postulated in glasses[7] as well as in liquids[8] to account for some anomalies noted in photoionization studies.

Further experimental results do not support this early interpretation and the experimental evidence given below shows that the luminescence is associated with the protonated form $TMPDH^+$. Moreover, it has been observed that upon excitation $TMPDH^+$ is partly decomposed to TMPD* and that the luminescent properties of the latter are somewhat different from those of the directly excited TMPD molecule.

Experimental Section

Reagents. TMPD was liberated from the hydrochloride salt with NaOH and purified by several sublimations just before use. Methylcyclohexane (Eastman Kodak spectrograde) and 3-methylpentane (Koch Light) were purified by chromatography on activated silica gel and alumina ("standard" MCH and 3MP). Ethanol (Merck) was distilled on acid 2,4-dinitrophenylhydrazine and dried over I_2–Mg in accord with the Lund and Bjerrum method ("standard" ethanol). Triethylamine (TEA, Fluka) was distilled over potassium hydroxyde. The solvents were purified just before use and their purity was tested by absorption and emission spectroscopy. The classical methods of purification described above have been used in most experiments. However, for solvents denoted below as "dry" further dehydration was performed by keeping the solvent several hours on a sodium mirror (for MCH and TEA), on anhydrous $CaSO_4$ (for ethanol), or on molecular sieves (for MCH, ethanol, 2,2,2-trifluoroethanol (Fluka), acetonitrile (uvasol Merck)). In all cases, the treatment was done under vacuum and the solutions were prepared by dilution in the same vacuum system after distillation of the solvent. The samples were finally sealed in a nonfluorescent silica tube (3 mm i.d.) for low temperature measurements or in a 10-mm square silica cell for room temperature experiments.

Apparatus and Measurements. The absorption spectra were obtained with a Zeiss PMQ II spectrophotometer equipped to make low temperature measurements.[9] The luminescence spectra were recorded with a Jobin-Yvon "Bearn" spectrofluorimeter equipped with a phosphoroscope. The spectral bandwidth was 3–6 nm for excitation and 6–12 nm for analysis. The relative emission intensities were obtained from areas measured on intensity vs. wavenumber curves. It has been determined that the intensity vs. wavelength dependence of the analyzing monochromator and photomultiplier system is constant to within 10% in the 350–510-nm spectral range. An abrupt decrease of sensitivity only occurs for wavelengths longer than 550 nm. Thus the intensity data were determined from the observed uncorrected emission spectra. The observed excitation spectra were corrected to a constant number of photons in the exciting beam. The spectral composition of the exciting light was itself obtained by the use of rhodamine B as a quantum counter.