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Raman Studies of Sulfur-Containing Anions in Inorganic Polysulfides. Sodium Polysulfides

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The present work reports the results of structural studies for Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5 as polycrystalline compounds, with laser-Raman and infrared spectroscopy as the principal technique. The measurements were extended from -135 °C to the respective melting points and, for the tri-, tetra-, and pentasulfides, to aqueous solutions, the glassy state, and the molten states. A complete vibrational assignment was achieved for S_2^{2-} (in the β-Na_2S_2 lattice), whereas for S_3^{2-}, S_4^{2-}, and S_5^{2-} exact analytical characterizations were achieved, but with less complete vibrational assignments. An instability of S_3^{2-} and S_5^{2-} in the corresponding polycrystalline polysulfides, respectively, is observed; at moderately high temperatures the former disproportionates to S_4^{2-} and S_2^{2-}, whereas the latter disproportionates to S_4^{2-} and elemental sulfur. The marked line broadening that accompanies the process of fusion limits the structural insight for the molten polysulfides but qualitative observations confirm the S_3^{2-} species as quite improbable in the composition range Na_2S_3 to Na_2S_5. The aqueous solution studies support the views advanced earlier from acidimetric rapid-mixing experiments, that S_4^{2-} and S_5^{2-} exist as an equilibrium mixture, irrespective of the parent polycrystalline polysulfide used as solute.

Introduction

In the Na_2S-S phase diagram,[5-7] Na_2S_2, Na_2S_4, and Na_2S_5 appear as well-defined compounds whereas Na_2S_3 corresponds to a eutectic mixture of the corresponding di- and tetrasulfides. Structural studies on the nature of these polysulfides appear to be limited to two works, the x-ray crystallographic study of Tegman[8] and a laser-Raman investigation of aqueous solutions by Ward,[9] both for Na_2S_4 only. The former established that Na_2S_4 crystallizes as the tetragonal space group $I\bar{4}2d$, with unit cell dimensions $a = 9.596$ Å, $c = 11.7885$ Å, and $Z = 8$, containing the tetrasulfide as unbranched S_4^{2-} ions. The latter demonstrated that high-quality Raman data could be gained for Na_2S_4 in aqueous solutions although the magnitude of the half-bandwidths appeared large for well-defined single-solute species. The spectra were interpreted[9] as due to a scattering species of C_2 point group symmetry and assigned to S_4^{2-} as the solute species in aqueous solutions. These results conflict with the interpretation advanced by Schwarzenbach and Fischer[10] based on an analysis of the rapid-mixing acidimetric studies of aqueous solutions, with Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5 as solutes. Structural data for the disulfide, trisulfide, and pentasulfide compositions in the sodium polysulfide series are apparently nonexistent. The present work reports the results of an investigation of this series of sodium polysulfides with laser-Raman as the principal technique, to gain insight on the structure and stability of the sulfur-containing species S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-} in the polycrystalline state. Low-temperature (-135 °C) and glassy-state measurements were investigated; some limited Raman studies of these polysulfides as molten salts were also undertaken to see whether useful structural insight could be gained into the nature of these polysulfides as high-temperature molten electrolytes. The studies were extended to aqueous Na_2S_4 to clarify the existing differing viewpoints[9,10] on the stability of the S_4^{2-} species in aqueous solutions.

Experimental Section

All preparative and analytical work, sample transfers, and filling of Raman cell assemblies were carried out under dry nitrogen atmospheres using glovebox and all-glass vacuum-manifold techniques, much as described in the related studies of BaS_3[11] and the potassium

polysulfides[12] in this laboratory, and the remarks will be limited to experimental aspects for the sodium polysulfides relevant to this investigation. Unless noted otherwise, the methods of Rosen and Tegman[13] were used throughout as the preparative procedure for the samples of this study, starting with $Na_2S \cdot 9H_2O$ and elemental sulfur. Further preparative information on the sodium polysulfides is given elsewhere.[14] The Raman spectra were recorded using a Jarrell-Ash 25-300 spectrometer coupled to a digital computer as described previously.[11,12] For polycrystalline samples a spectral slit width of 2 cm^{-1} was used while a slit width of 4 cm^{-1} was used for glassy, molten, and solution spectra. A rotating-cell scattering arrangement was used in order to prevent decomposition or heating of the colored (yellow) samples. A Perkin-Elmer Model 621 spectrometer and the KBr pellet technique were used for the infrared measurements.

Na_2S. This starting material for the synthesis of the polysulfides was not available commercially. It was prepared from $Na_2S \cdot 9H_2O$ by the two-step process of Rosen and Tegman.[13] In subsequent high-temperature preparative steps, in which this pure white product was used as starting material, no etching of glass was observed; this indicates absence of NaOH and is additional support for the high purity of the Na_2S thus gained.

β-Na_2S_2.[15] This was prepared from stoichiometric amounts of Na_2S and elemental sulfur, initially mixed by grinding and heated in sealed evacuated Pyrex tubes for 6 h at 400 °C, followed by 1 h of heating at 600 °C and subsequent annealing at 200 °C for several hours. The color was yellow-orange after grinding. Analytical characterization was by dta thermograms and x-ray powder diffraction patterns: found mp 484 °C, lit.[13] mp 482 ± 2 °C; d-line spacings and relative intensities in accord with Rosen and Tegman's data.[13] The Raman spectrum of polycrystalline Na_2S_2 is illustrated in Figure 1 and numerical values of the observed frequencies are in Table I. At -135 °C, one observes the splitting of the 451-cm^{-1} band and the appearance of a new peak (27 cm^{-1}). These effects may be attributed to the intrinsically narrower line width at low temperature (and narrower spectrometer slit width) leading to increased resolution of overlapping peaks. The progressive loss of signal on heating is largely due to a gradual color change of the sample from yellow to gray-black. The spectrum for molten Na_2S_2 (500 °C) is illustrated in Figure 2; the very marked band broadening that accompanies melting is apparent (cf. Figure 1).

Na_2S_3. Reference to the phase diagram[5-7] shows that the stoichiometric trisulfide composition is a eutectic mixture of Na_2S_2 and Na_2S_4, melting at 230 °C. Na_2S_3 is apparently unstable with respect to the di- and tetrasulfides; an interest in the present investigation was to explore these features using the laser-Raman techniques. Two methods were used to prepare the stoichiometric trisulfide composition.
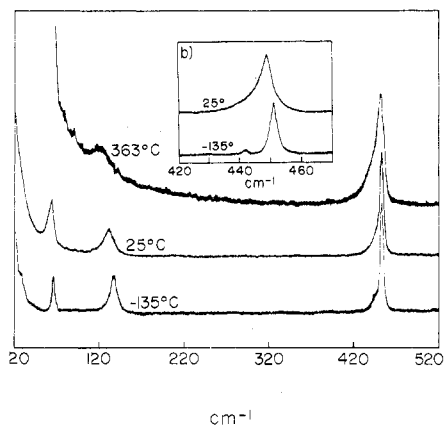
Figure 1. Raman spectra for polycrystalline β-Na$_2$S$_2$. The inset (b) illustrates the low-temperature splitting in the stretching region. All spectra were recorded with a spectral slit width of 2 cm^{-1} except the −135 °C spectrum in the inset for which the slit width is 0.7 cm^{-1}.
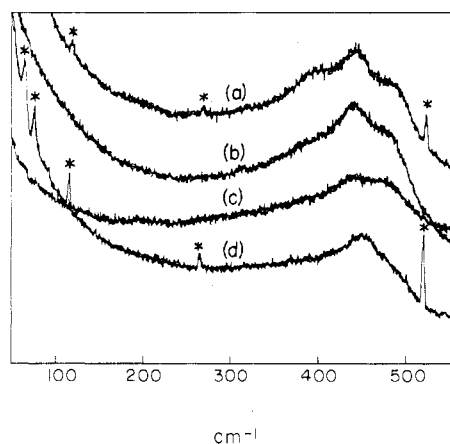

Figure 2. Raman spectra for molten sodium polysulfides: (a) Na$_2$S$_5$ at 270 °C (ten scans averaged); (b) Na$_2$S$_4$ at 300 °C (seven scans averaged); (c) Na$_2$S$_3$ at 265 °C (nine scans averaged); (d) Na$_2$S$_2$ at 500 °C (seven scans averaged). Asterisks indicate plasma laser lines.

(i) High-Temperature Reaction of Na$_2$S$_2$ and Na$_2$S$_4$, in Stoichiometric Amounts. This preparation showed a dta trace characteristic of the predicted eutectic (mp 230 °C); x-ray powder diffraction data[15] supported this. The Raman spectrum for this product was found to be an exact superposition of the spectra of the mechanical mixture before fusion of Na$_2$S$_2$ and Na$_2$S$_4$.

(ii) A Double-Displacement Reaction. Equation 1 was effected by

$$BaS_3 + Na_2SO_4 \rightarrow Na_2S_3 + BaSO_4\downarrow \tag{1}$$

adding, dropwise with stirring, a nearly saturated aqueous solution of Na$_2$SO$_4$ to BaS$_3$[11] at ∼5 °C. The water from the clear yellow filtrate was sublimed off using high-vacuum pumping on the frozen filtrate for a period of 48 h. Alternatively an identical product was obtained by dissolving a 1:1 mixture of Na$_2$S$_2$ and Na$_2$S$_4$ in deaerated water and removing the frozen solvent via vacuum sublimation. The Raman spectrum of the yellow polycrystalline product was confirmed to be a mixture of Na$_2$S$_3$ and Na$_2$S$_4$ by comparison with the spectra for Na$_2$S$_4$ and BaS$_3$,[11] as illustrated in Figure 3; the numerical values of the observed frequencies for Na$_2$S$_3$ are in Table I. From an analysis of the x-ray powder diffraction data (Cu Kα), the following values were assigned to Na$_2$S$_3$ [d, Å (intensity)]: 5.42 (m), 5.23 (w), 4.94 (m), 4.80 (s), 4.58 (m), 4.40 (m), 3.97 (w), 3.705 (m), 3.538 (s), 3.444 (m), 3.264 (m), 3.195 (w), 3.056 (ss), 2.803 (ss), 2.511 (ss), 2.357 (w), 2.157 (w), 1.954 (w), 1.912 (m), 1.873 (m), 1.803 (m), 1.720 (w). Initially this product has endothermic transitions at 93 and 102 °C and thus possibly contains some hydrate water. After heating of the compound to 130 °C (15 h, under vacuum), its dta thermogram was characteristic of the eutectic mixture of Na$_2$S$_2$ and Na$_2$S$_4$ (mp

Table I. Raman Spectra of Sodium Polysulfides (cm^{-1})

T, °C	ν, cm^{-1}
	β-Na$_2$S$_2$: Polycrystalline (mp 484 °C)
−135	27 (0.5, 2),^{a} 64.5 (3, 2), 134.5 (3, 10), 442.1 (0.2, 2), 451 (10, 5)
23	63.5 (4, 5), 129.5 (3, 20), 450.7 (10, 15)
412	∼62 (4, vb); ∼115 (3, vb); ∼449 (10, vb)
	Na$_2$S$_3$: Polycrystalline (dec pt <100 °C)
25	238 (0.5, 15), 458 (8, 10), 476 (10, 20)
	Na$_2$S$_4$: (a) Polycrystalline (mp 292 °C); (b) Glass; (c) Aqueous; (d) Molten
	(a) 48 (1, 2), 83 (1, 3), 97 (1, 2), 151 (1, 2), 171 (1, 4), 206 (3, 12), 239 (1, 15), 440 (2, 9), 445 (10, 3), 468 (2, 9), 482 (4, 6), 876 (0.1, 16), 883 (0.1, 8), 924 (0.2, 14), 935 (0.3, 14), 962 (0.1, 16)
25	(b) 222 (1, 29) (p),^{b} 267 (1, 22) (dp), 446 (10, 26) (p), 476 (3, 17) (dp), 487 (5, 17) (p)
	(c) 144 (<1, 103) (?),^{b} 194 (2, 44) (p), 256 (2, 54) (dp), 410 (6, 41) (p), 446 (10, 21) (p), 484 (6, 52) (dp)
365	(d) 396 (2, 62), 445 (10, 91), 484 (9, 84)
	Na$_2$S$_5$: (a) Polycrystalline (mp 256 °C) [α (Stable); β, γ (Metastable)]; (b) Glass
25	(a) (α) 103 (3, 5), 135 (2, 10), 214 (2, 10), 266 (2, 11), 391 (0.5, 6), 444 (10, 7), 488 (3, 12)
	(β) 75 (0.5, 4), 82 (1, 7), 95 (0.5, 5), 121 (1, 4), 139 (1, 4), 187 (1, 8), 208 (1, 44), 275 (1, 21), 419 (1, 13), 444 (10, 9), 449 sh (4, 8), 484 (3.5, 7)
	(γ) 209 (2, 7), 280 (2, 11), 427 (2, 15), 447 sh (6, 7), 451 (10, 4), 479 sh (2, 6), 485 (6, 6)
25	(b) 200 (<0.5, 10) (p), 275 (0.5, 10) (dp), 410 (5, 15) (dp), 444 (10, 15) (p), 480 (4, 10) (dp)

^{a} The first value in parentheses is the peak intensity relative to a scale of 10, and the second is the estimated half-bandwidth in cm^{-1}. ^{b} Band polarization could be determined for the glassy and aqueous states only.
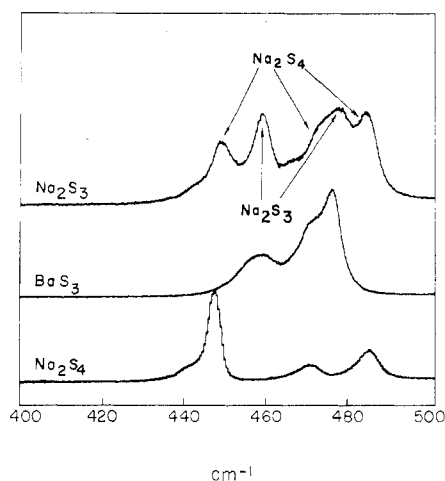

Figure 3. Raman spectra of polycrystalline Na$_2$S$_3$, Na$_2$S$_4$, and BaS$_3$ in the stretching region. For the Na$_2$S$_3$ spectrum the peaks are labeled to indicate their assignment to Na$_2$S$_4$ or Na$_2$S$_3$.

230 °C) and the d spacings assigned to Na$_2$S$_3$ had disappeared; the pattern was a composite of Na$_2$S$_2$ and Na$_2$S$_4$. The Raman spectrum corresponds to that of the product for the high-temperature synthesis (above), i.e., a mixture of Na$_2$S$_2$ and Na$_2$S$_4$, with the complete absence of the characteristic peaks assigned to Na$_2$S$_3$ (Table I and Figure 3). The spectrum of molten Na$_2$S$_3$ is compared with those of the other molten polysulfides in Figure 2.

Na$_2$S$_4$. Anhydrous Na$_2$S (above) was mixed with elemental sulfur in the stoichiometry required for the tetrasulfide; after being mixed thoroughly with grinding and after being sealed under vacuum in Pyrex ampules, the reactants were heated for 24 h at 210 °C, followed by 1 h at 500 °C. Upon cooling of the system to room temperature a reddish brown product was gained; on being ground, the product became yellow-orange (found mp 292 °C, lit.[13] mp 294 ± 2 °C). Anal.
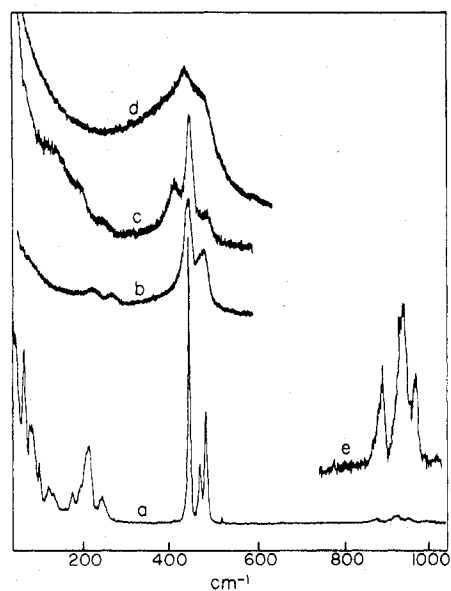
Figure 4. Raman spectra of polycrystalline (a), glassy (b), aqueous (c), and molten (d) Na_2S_4 demonstrating increased band broadening. Spectrum e illustrates the overtone region for the polycrystalline material with an expanded ordinate. [a, single scan; b, nine scans averaged; c, approximately 0.5 M (three scans averaged); d, 300 °C (seven scans averaged).] Spectra a, b, c, and e were recorded at room temperature.

Calcd for Na_2S_4: S, 73.6. Found: S, 72.3, 72.9, 73.8. The numerical values for the observed Raman frequencies of Na_2S_4 for the polycrystalline, glassy, aqueous, and molten states are in Table I, and the spectra are illustrated for the molten, glassy, aqueous, and polycrystalline solid states in Figures 2 and 4, respectively. The aqueous solution spectra (Table I) are in close accord with those of Ward,[9] with the qualification that the differences in the numerical values may be attributed to instrumental factors, e.g., such as slit widths: present work, 3.5 cm⁻¹; Ward,[9] 8 cm⁻¹).

Na_2S_5. Some difficulties were encountered in the characterization of this polysulfide owing to the somewhat irreproducible behavior of samples of this stoichiometry relative to dta thermal analysis, Raman spectra, and x-ray powder diffraction patterns. Some aspects of these were clarified through the recognition that this polysulfide can be gained in three polycrystalline modifications, designated herewith as the α, β, and γ forms, of which the latter two are metastable; transformation to the α form may be induced thermally by tempering at 200 °C. Some of the results of the preparative studies are as follows. The pentasulfide may be prepared by mixing Na_2S_4 with a large excess of sulfur and heating the molten mixture in an evacuated sealed Pyrex ampule for a prolonged period (e.g., 350 °C, 4 days). During this period the ampule is removed for vigorous mechanical shaking to mix the two black immiscible liquid phases (refer to the phase diagram of ref 5). The pentasulfide is obtained as the more dense phase and is separated mechanically after cooling. Anal. Calcd for Na_2S_5: Na, 22.3. Found: Na, 21.6. X-ray powder diffraction data show exact correspondence with those reported by Rosen and Tegman[13] for Na_2S_5, with the exception of $d = 3.911$ Å which was not observed. From the dta thermogram the observed melting point is 254 °C; lit. mp 265 °C,[13] 258 °C,[7] 253 °C.[16] The Raman spectrum for this modification is that designated for α-Na_2S_5 in Table I and Figure 5. A metastable pentasulfide, melting at 227 °C, has been observed by Tegman.[17] In the present work two polycrystalline metastable forms were observed, and the Raman data for these, designated as β- and γ-Na_2S_5, respectively, are in Table I and Figure 5. Any one of these three modifications may crystallize arbitrarily from the supercooled melt. The β form was obtained by a preparation of Na_2S_4 and elemental sulfur mixed in exact pentasulfide stoichiometry and maintained for 4.5 days at 350 °C. Characterization: dta, found mp 255 °C, lit. mp 265 °C,[13] 258 °C,[7] 253 °C;[16] x-ray powder diffraction data, d (Å) = 4.86 (m), 4.40 (m), 3.94 (s), 3.38 (w), 3.19 (vw), 2.99 (m), 2.83–2.73 (ss (vb)), 2.62 (s), 2.40 (w), 2.21 (vw), 2.06 (w), 1.99 (w), 1.93 (w), 1.81 (w), 1.68 (m). Comparison with the d spacings reported for the stable modification,[13] designated as α-Na_2S_5, shows that these
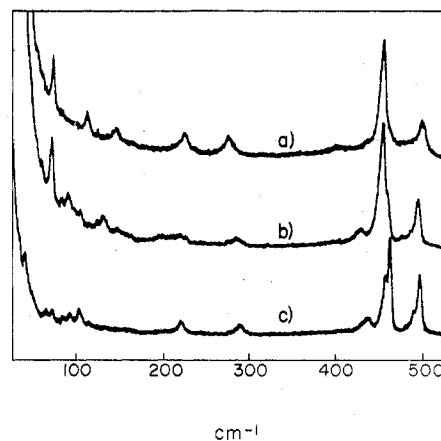
Figure 5. Room-temperature Raman spectra of the polycrystalline α (a), β (b), and γ (c) forms of Na_2S_5.

differ clearly. The Raman spectrum for γ-Na_2S_5 was gained from a preparation of Na_2S_4 similar to that for β-Na_2S_5 (vide supra), but in which the sample is additionally held at 200 °C for 40 h as a tempering period prior to cooling to room temperature. If the Raman spectrum for the product thus gained is taken before the sample is crushed and ground, the data reported as those for γ-Na_2S_5 in Table I and Figure 5 are obtained. The presence of lattice modes in the spectra for all three forms (α, β, γ) confirms the crystalline nature of these samples. The γ form is unstable; if the sample is ground (mortar and pestle) and the Raman spectrum of the powdered sample is observed, transformation to the α form is observed. The thermally induced conversion of the β form to the α form and that of the latter to the tetrasulfide can be monitored by the laser-Raman technique. Not much of β form is left after heating the ground sample at 160 °C (2.5 h), and after 1 h at 220 °C only the Raman spectrum of α-Na_2S_5 is observed. Conversion of the latter to Na_2S_4 appears complete within 0.5 h at 220 °C. Disproportionation of the pentasulfide to the tetrasulfide and sulfur is thus confirmed and in some instances may even occur in the laser beam at room temperature. The difficulties encountered in the analytical characterization of the pentasulfide by Debye–Scherrer x-ray techniques, dta thermal analyses, and Raman spectroscopy are thus understood as due to the existence of this polysulfide in more than one crystalline modification and the interconversion of these, as well as the pentasulfide disproportionation. Orthorhombic sulfur is a strong Raman scatterer; the fact that it is not always detected in the spectra after the disproportionation reactions raises the possibility that sulfur may have sublimed from the bulk phase. In the 200–250 °C temperature range and under vacuum, sublimation of sulfur from samples thus disproportionated was confirmed by a thermogravimetric analysis. Weight loss: found, 15.5%; theory, 15.5%, for complete conversion to the tetrasulfide. The identity of the sublimate was confirmed as orthorhombic sulfur by laser-Raman spectroscopy.

Discussion

The sodium di-, tri-, tetra-, and pentasulfides have been synthesized and a number of uncertainties in the preparative aspects and characterization have been clarified in the present studies. The Raman spectra, viz., Table I and Figures 1–5, are of high quality and are suitable for characterizing the generalized vibrational frequencies for the sulfur-containing anionic species in this series, as required for analytical characterization analyses. The present discussion accordingly will be limited to a brief examination of these results to see what additional structural insights are possible and to consider the evidence for the existence of some of these sulfur-bearing species in aqueous solution and at elevated temperatures in the crystalline and molten states. The polysulfides will be first discussed individually, followed by some general considerations of the aqueous-solution and molten-state spectra.

Na_2S_2. The preparative procedure, in which the disulfide is gained from the melt, leads to the formation of β-Na_2S_2.[13] X-ray crystallographic studies[18] have characterized the

Table II. Vibrational Assignments

Band, cm^{-1}	Symmetry	Description
		(a) Na$_2$S$_2$[a]
451.4 A	A$_{1g}$	Internal vib of S$_2$$^{2-}$, in phase
442.1	A$_{1g}$	Similar to 451.4 cm^{-1} but due to isotopic sulfur species
134.5	E$_{1g}$	Lib motion of the two S$_2$$^{2-}$ groups in opposite direction
64.5	E$_{2g}$	Out-of-phase oscn of S$_2$$^{2-}$ (2d) in (004) plane
27	E$_{2g}$	Out-of-phase oscn of Na$^+$ (2c) in (004) plane
		(b) Na$_2$S$_4$[b]
482 p	ν_1	Sym str, terminal S-S
445 p	ν_2	Sym str, central S-S
206 p	ν_3	Sym bend
468 dp	ν_4	Asym str
239 dp	ν_5	Asym bend
151 ?	ν_6	Torsion

[a] Polycrystalline β-Na$_2$S$_2$ (hexagonal space group D_{6h}^{4} and for S$_2$$^{2-}$ $D_{\infty h}$ symmetry). [b] Polycrystalline Na$_2$S$_4$ (tetragonal space group D_{2d}^{12} and for S$_4$$^{2-}$ C_2 symmetry).

structure as having a hexagonal space group D_{6h}^{4} = $P6_3/mmc$, with two formula units per unit cell. Based on these data, a factor group analysis predicts only four Raman-active fundamentals out of the 24 possible modes, i.e.

$$\Gamma_{\text{Raman}} = A_{1g} + E_{1g} + 2 E_{2g} \qquad (2)$$

Inspection of the results (Table I and Figure 1) shows that four Raman-active bands, as predicted by this analysis, are observed at −135 °C; apparently at 25 °C the lowest mode is masked by the wing of the Rayleigh line. The A$_{1g}$ and E$_{1g}$ modes correspond to the symmetrical stretching and the librational fundamentals for the disulfide, and the 451- and 134-cm^{-1} bands are assigned to these accordingly. The additional fundamental (442.1 cm^{-1}) is understood as due to isotopic splitting of the A$_{1g}$ mode; calculations predict that the ^{32}S–^{34}S peak would fall approximately 7 cm^{-1} below the ^{32}S–^{32}S Raman band. Inspection of the unit cell structure[17] shows that both Na$^+$ and S$_2$$^{2-}$ occupy sites of the same symmetry, and these two lattice modes are indistinguishable by group theory. Energetic considerations predict that the Na$^+$ interactions with the surrounding lattice will be much weaker than for the corresponding S$_2$$^{2-}$. The two bands 64.5 and 27 cm^{-1} are assigned to the S$_2$$^{2-}$ and Na$^+$ lattice modes, respectively. The vibrational assignments, using the numerical values observed at −135 °C, are summarized in Table II. The force constant thus found for S$_2$$^{2-}$ is 1.99 × 10^5 dyn/cm; by comparison, in elemental sulfur, S$_8$, the force constant for the symmetrical S–S stretching mode is 1.84 × 10^5 dyn/cm.[19]

Na$_2$S$_3$. The Raman studies confirm that a 1:1 mixture of Na$_2$S$_2$ and Na$_2$S$_4$ is obtained from a melt of overall composition corresponding to the trisulfide. Relative to the existence of S$_3$$^{2-}$ in the melt at this composition, inspection of the Raman spectrum (Figure 2) shows that quantitative interpretations are ruled out owing to the very broad nature of the band. For the case of a mixture of S$_4$$^{2-}$ and S$_2$$^{2-}$, one would expect three polarized and one depolarized Raman bands. For a S$_3$$^{2-}$ species (cf. BaS$_3$[11] and K$_2$S$_3$[12]) one expects one polarized and one depolarized Raman band. Analyses of the polarization data for a melt of the trisulfide overall composition is in accord with two polarized bands; further, the spectrum of the "quenched liquid" is identical with that for glassy Na$_2$S$_4$. One concludes that it is not possible, by the laser-Raman technique, to detect S$_3$$^{2-}$, and the existence in molten polysulfides, accordingly, is not supported. This differs from the predictions by Tegman[17] of approximately 60 mol % S$_3$$^{2-}$ in molten polysulfides of this composition at 300 °C. Raman spectra and x-ray powder diffraction data support the

existence of Na$_2$S$_3$ in the polycrystalline state, possibly as the trihydrate as reported by Bottger.[20] The different x-ray powder diffraction data and dta thermograms reported by Oei[7] for Na$_2$S$_3$ synthesized in liquid ammonia compared to those for the aqueous preparation of this work are also thus understood. At approximately 100 °C, Na$_2$S$_3$ disproportionates to α-Na$_2$S$_2$ and Na$_2$S$_4$. This is in marked contrast to barium and potassium polysulfides, in which the S$_3$$^{2-}$ has been characterized[11,12] as a well-defined, stable triatomic species of C_{2v} point group symmetry.

Na$_2$S$_4$. This tetrasulfide has been structurally characterized by x-ray crystallographic studies[8] as having tetragonal symmetry, with eight molecules per unit cell (four per Bravais cell). The crystallographic space group is $I\bar{4}2d$ (D_{2d}^{12}), with the S$_4$$^{2-}$ on C_2 symmetry sites. A factor group analysis leads to the conclusion that the correlation field splitting is very weak. Accordingly the vibrational assignment for S$_4$$^{2-}$ will correspond closely with the analysis for tetraatomic species as an isolated species of C_2 point group symmetry. The selection rules[21] predict six Raman-active modes (4 A + 2 B), four polarized and two depolarized. The assignment of five of these fundamentals is possible by reference to that advanced for K$_2$S$_4$[12] and the assignments for the closely related species S$_2$Cl$_2$ and S$_2$Br$_2$ by Stamreich and Forneris;[22] the vibrational assignment thus advanced for the internal modes of S$_4$$^{2-}$ in sodium tetrasulfide is summarized in Table II. Comparison with the results for K$_2$S$_4$[12] shows that the numerical values of the frequencies are in close accord but that the relative intensities of the fundamentals differ; the differences are in accord with S$_4$$^{2-}$ having a somewhat larger dihedral angle in polycrystalline K$_2$S$_4$ than in Na$_2$S$_4$ (97.81°); by contrast the glassy-state spectra for Na$_2$S$_4$ and K$_2$S$_4$ are virtually identical, implying that the dihedral angles for S$_4$$^{2-}$ species are nearly equal in that state. The assignment of the torsional mode is tentative and was strictly by analogy with S$_2$Cl$_2$ and S$_2$Br$_2$ (102 cm^{-1} (dp?), 66 cm^{-1} (dp?), respectively);[22] it was observed in the polycrystalline state (151 cm^{-1}) and the aqueous state (144 cm^{-1}) but not in the glassy state for Na$_2$S$_4$ (Table I). As noted earlier, the aqueous spectra are in accord with the results reported by Ward,[9] but an assignment solely to S$_4$$^{2-}$ is questioned. This is considered later, together with the results for aqueous Na$_2$S$_5$.

Na$_2$S$_5$. The experimental observations and Raman data for the pentasulfide are understood in terms of three crystalline forms which we have designated, arbitrarily, as α, β, and γ modifications; it is also apparent that the β and γ forms are metastable relative to the α form. From the viewpoint of a vibrational assignment, five point group symmetries are possible for S$_5$$^{2-}$, and the selection rules have been given elsewhere.[12] The point groups D_{5h} and $D_{\infty h}$ are ruled out from the limited depolarization data (Table I, glassy state), leaving C_{2v}, C_s, and C_2 as the most probable. The depolarization data appear incomplete, and without additional studies (preferably single crystal) one cannot advance this further. A generalized assignment is possible, much as for K$_2$S$_5$ and K$_2$S$_6$,[12] assuming an unbranched pentasulfide species. Using the observed values for α-Na$_2$S$_5$ (Table I) and the skeletal selection rules of Pitzer[23] and assuming either of the above point group symmetries, one obtains for S$_5$$^{2-}$ the following assignments.

Skel vib modes Descripn	No.	ν, cm^{-1}
Stretch	4	391, 429, 444, 488
Bend	3	214, 266
torsion	2	103, 135

As for the potassium polysulfides, K$_2$S$_5$ and K$_2$S$_6$, refinement of this generalized assignment must await additional results.

The pentasulfide ion disproportionates to S$_4$$^{2-}$ and elemental sulfur at moderately high temperatures and reduced pressures.

Details have been noted in the Experimental and Section; e.g. the conversion to Na_2S_4 appears complete after 0.5 h at 220 °C. This does not rule out the possible existence of S_5^{2-} in the molten state, but the very marked band broadening on fusion does not make the melt spectra (Figure 2) very informative. Some further thoughts on this follow.

Aqueous Solutions and Molten Polysulfides. The present work was limited to some careful investigation of the Raman spectrum of aqueous Na_2S_4. A comparison of the Raman spectra for the skeletal modes of polycrystalline and molten Na_2S_4 with the aqueous solutions is illustrated in Figure 4; the numerical values of the frequencies and depolarization results are in Table I. The spectra are the average results of repeated scans (four to ten) to increase the signal to noise ratio. The aqueous spectra show the same marked line broadening that accompanies the melting of the polysulfides (cf. Figures 2 and 4). While the band contour for the aqueous solutions shows more structure than for the molten-phase spectra, the unusually large broadening in the aqueous and molten states is such that the band contour virtually overlaps completely the skeletal frequencies for the individual di-, tri-, tetra-, and pentapolysulfides as crystalline solids (Table I and Figures 3–5). While factors such as rotational, conformational, and anharmonicity contributions undoubtedly feature in this band broadening, the magnitude is more in accord with contributions due to the equilibrium coexistence of a series of polysulfide species. From this viewpoint the results of Schwarzenbach and Fischer[10] are informative. It was thus shown that for the tetrasulfide the equilibrium properties of the aqueous solution may be ascribed to 64% S_4^{2-}, 27% S_5^{2-}, and 9% of S^{2-} and that the equilibrium composition is established rapidly (10^{-2} s). Similarly, rapid disproportionation of the di- and trisulfides, with the formation of S_5^{2-} and S_4^{2-} species, was noted. Tegman[17,24] has shown that the assumption of an equilibrium distribution of several polysulfide species is required to account for the thermodynamic equilibria between the molten polysulfides and sulfur vapor at high temperatures. The magnitude of the Raman band broadening (aqueous solutions; molten

polysulfides) is additional support for these observations.

Registry No. Na_2S_2, 22868-13-9; Na_2S_3, 37488-76-9; Na_2S_4, 12034-39-8; Na_2S_5, 12034-40-1; Na_2S, 1313-82-2.

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Synthesis and Structural Aspects of the Vanadium-Substituted Niobium Diselenides[1]

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Solid solutions of formula $Nb_{1-x}V_xSe_2$ ($0 < x < 1$) have been prepared by direct synthesis from the elements under minimum-gradient conditions. Single crystals of $NbSe_2$ and VSe_2 have been made by chemical transport using iodine as transporting agent. X-ray studies by single-crystal and Debye–Scherrer techniques have been used to define regions of homogeneity. Monophasic regions occur for $0 \le x \le 0.01$ (where the structure is that of the 2H-$NbSe_2$ polytype), $0.11 \le x \le 0.20$ (structure 4Hb), and $0.30 \le x \le 1.00$ (structure 1T). It is proposed that vanadium substitutes for niobium in trigonal-prismatic coordination in only the first of these regions; otherwise, the vanadium goes into octahedral coordination and produces the 4Hb polytype by enhancing octahedral coordination of the niobium. The variation of structural parameters with composition is described in terms of a pure size effect attendant on the vanadium-for-niobium substitution.

Introduction

The layered dichalcogenides are of great interest as model compounds for study of electrical interactions and critical phenomena in quasi-two-dimensional systems. Excellent summaries of the structural and physical properties have been given by Wilson and Yoffe[2] and by Yoffe.[3] Two distinguishing characteristics of the compounds are metallic vs. nonmetallic behavior and trigonal-prismatic vs. octahedral coordination. As an approximate rule, groups 4 and 6 dichalcogenides are semiconductors, whereas group 5 compounds are metals; however, there is not a 1:1 correlation between metallic be-

havior and coordination. The principles that govern adoption of trigonal-prismatic rather than octahedral coordination have not been definitively worked out, but Gamble[4] and Madhukar[5] have had considerable success in correlating trigonal-prismatic preference within a given group with large metal-to-chalcogen radius ratio and small bond ionicity. The fact that it does not seem to matter whether covalent or ionic radii are used in the classification suggests that relative sizes are more important than bond ionicity in setting the coordination.

One possible way to get more precise information on the factors that influence coordination is to look in detail at a