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

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The Raman and infrared spectra of K_2S_3, K_2S_4, K_2S_5, and K_2S_6 have been investigated for the polycrystalline and molten states and, with the exception of K_2S_3, for the glassy states. For K_2S_3, K_2S_4, and K_2S_5, the spectral features of the sulfur-containing anionic species appear well defined, with only minor changes as temperatures are increased to the melting points of the respective polysulfides. With K_2S_6, by contrast, features are observed that are indicative of a transformation to K_2S_5 and sulfur occurring in the solid state at temperatures as low as 150 °C. Application of point group symmetry analysis leads to the assignment of C_{2v} symmetry for S_3^{2-} in K_2S_3 and C_2 symmetry for S_4^{2-} in K_2S_4. A strong correlation between the glassy and polycrystalline spectra is observed, and quantitative studies in the glassy state with S_n^{2-} ions as structural sensors appear possible. A very marked band broadening is observed with the process of melting making useful structural interpretation of melt composition difficult for this series of polysulfides.

Introduction

The Raman technique has been of considerable value in elucidating structural features of several polyatomic anions,[3–7] e.g., ClO_3^-, NO_3^-, SCN^-, CO_3^{2-}, and CrO_4^{2-}, but no systematic studies have been performed for polyatomic anions made up exclusively of atoms of the same element, as is the case for the sulfur-bearing anionic species S_n^{2-} (where $n = 2, 3, 4, 5, \ldots$).

A laser-Raman study of the S_3^{2-} anion, using BaS_3 as model compound, was undertaken as part of a program to characterize the sulfur-bearing species in inorganic polysulfides.[8] While the low-temperature and ambient-temperature spectra for BaS_3 are in accord with simple bent S_3^{2-} anions, marked spectral changes with increasing temperatures were observed. The potassium tri-, tetra-, penta-, and hexasulfides have well-defined stoichiometry, and it appeared of interest to use this series of inorganic polysulfides to characterize, structurally, the sulfur-bearing anionic species. In this work the results of such studies are reported for K_2S_3, K_2S_4, K_2S_5, and K_2S_6 as polycrystalline solids and as glasses (K_2S_3 excepted) with laser-Raman spectroscopy as the principal technique.

Experimental Section

The compounds K_2S_3 and K_2S_5 were prepared from metallic potassium and H_2S in absolute alcohol according to the procedures of Thomas and Rule[9] and described later in greater detail by Pearson and Robinson[10] and by Feher.[11,12] The preparative steps were carried out with glovebox techniques (dry nitrogen atmosphere) since the decomposition of the polysulfides to thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), and elemental sulfur occurs with the presence of water and oxygen, as trace impurities.[13]

The tetrasulfide has usually been prepared by reaction between stoichiometric proportions of potassium and sulfur in liquid ammonia[11] or by the thermal decomposition of K_2S_5,[13] since the preceding procedure normally yields[10] a mixture of K_2S_3 and K_2S_5. In our work, a third and basically more simple approach to the synthesis of K_2S_4 was developed. Stoichiometric amounts of K_2S_3 and sulfur were weighed, mixed intimately, and sealed under vacuum in glass ampules. These were heated to 350 °C over a 4-h period, during which the contents were frequently mixed by manually removing and briefly shaking the ampules. Following this period, the ampules were placed in a 120 °C oven for several hours to promote crystal growth. Without this "tempering" period, the tetrasulfide was generally obtained as a glass. For K_2S_6, we used the method of Feher and Berthold,[12] starting with pentasulfide and sulfur as reactants, and the "two-temperature steps" technique just described. Further details on the preparation of the potassium polysulfides are given elsewhere.[14]

The polysulfides were characterized by melting points (dta), elemental analysis, and x-ray powder diffraction analysis. The salient observations are as follows.

Melting Point Data. **K_2S_3.** Aliquots from four batch preparations were examined; the lowest observed melting point was 285 °C, and the highest, 299 °C (cf. Auroux et al.,[15] 279 ± 3 °C; Feher and Berthold,[12] 292 °C).

K_2S_4. Samples taken from two preparations gave dta traces with a rather broad peak exhibiting a melting point at about 133 °C (cf. Feher and Berthold,[12] sintering at 145 °C and melting at about 159 °C).

K_2S_5. Samples from three separate batch preparations were examined; the observed melting points ranged from 199 to 205 °C (cf. Feher and Berthold,[12] 211 °C).

K_2S_6. The melting points for aliquots from the independently prepared batches were found to be 190 °C (cf. Feher and Berthold,[12] sintering at 184 °C and melting at 196 °C).

Elemental Analysis. Potassium was determined according to Scott's standard procedure[16] and sulfur according to the procedure of Pearson and Robinson.[17] Anal. Calcd for K_2S_3: K, 44.8; S, 55.2. Found: K, 44.2; S, 54.1. Calcd for K_2S_4: K, 32.8; S, 67.2. Found: K, 32.3; S, 67.4. Elemental analyses were not undertaken for K_2S_4 or K_2S_6; the stoichiometry of these compounds is supported by the x-ray diffraction results, the melting point data (dta), and the preparative procedure by which the reactants are used in the exact stoichiometric ratio to yield the desired compounds.

X-Ray Powder Diffraction Analyses. Good agreement for the prominent lines was obtained for K_2S_3, K_2S_4, and K_2S_6, but some discrepancies were observed in the case of K_2S_5 (cf. Feher and Berthold,[12] Cu Kα, 20 lines). For the latter, identical powder diffraction data (spacings, intensities) were obtained for samples from two batches of separately synthesized K_2S_5. The elemental analysis, dta traces, Raman spectra, and the internal consistency of the x-ray diffraction data of the separate preparations support the present results as reference-quality data for K_2S_5; these data are, accordingly, summarized in Table I. The *d* values for the prominent lines of the related potassium polysulfides are also tabulated since the Feher and Berthold[12] data were presented graphically rather than as numerical values.

Spectral Measurements. Raman spectra were obtained in digital form using a rotating-cell scattering arrangement as described previously.[8,18,19] Asymmetric Raman peaks were resolved into their components using a modification of Jones' program 10.[19,20]

Infrared spectra (200–4000 cm^{-1}) were obtained with a Perkin-Elmer 621 spectrophotometer and conventional KBr pellet techniques, with due care, as noted earlier, to exclude traces of moisture and oxygen.[8]

Results and Discussion

The Raman and infrared frequencies of peaks observed for K_2S_3, K_2S_4, K_2S_5, and K_2S_6 as polycrystalline samples at room temperature are given in Table II and the Raman spectra are compared in Figure 1. Inspection shows that the spectra appear well defined; for K_2S_6 at room temperature a rather broad band, from about 280 to 400 cm^{-1}, is observed. The spectrum of K_2S_6 over a wide temperature range is illustrated in Figure 2. It is seen that at −130 °C this band resolves into three component peaks; these frequencies are indicated by asterisks in Table II.

All four polysulfides darken markedly on heating, with a resultant loss of intensity in their Raman spectra. In the cases of K_2S_3, K_2S_4, and K_2S_5, no new spectral features appear as

Table I. Relative Line Intensities and *d* Values (Å) from X-Ray Diffraction Patterns of Potassium Polysulfides

K_2S_3		K_2S_4		K_2S_5		K_2S_6	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
20	5.90	50	4.26	40	5.27	20	5.90
15	4.95	20	3.96	70	4.50	20	5.53
25	4.62	15	3.54	20	4.36	25	5.24
25	4.13	30	3.27	10	4.11	40	4.54
25	3.74	90	3.10	60	3.64	15	3.79
15	3.64	100	2.93	10	3.31	15	3.56
100	3.15	60	2.75	50	3.25	100	3.22
35	3.01	50	2.62	25	3.18	100	3.12
70	2.79	40	2.51	80	3.09	100	3.00
70	2.73	70	2.34	100	2.91	40	2.83
60	2.61	50	1.77	100	2.84	40	2.75
15	2.49	50	1.68	80	2.79	40	2.62
60	2.35	70	1.54	100	2.64	50	2.55
25	2.31			20	2.47	30	2.44
50	2.23			70	2.30	90	2.14
15	2.07			70	2.25	10	1.96
50	2.00			20	1.90	25	1.91
50	1.90			70	1.81	25	1.88
50	1.83			35	1.80	25	1.75
50	1.67			35	1.67	10	1.62
60	1.59			25	1.59	10	1.59
30	1.51						
25	1.38						
20	1.35						

Table II. Raman and Infrared Frequencies (cm^{-1}) for Polycrystalline K_2S_n at 25 °C

K_2S_3		K_2S_4		K_2S_5		K_2S_6	
Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir
57 m		220 m, p		53 w		132 w	
105 m		266 m, dp		172 m		157 w	
238 m		434 s, p		252 m		254 m	
466 s	466	478^b sh, dp	477	268 w	270	337^a m	
		485^b s, p	486 sh		416	358^a m	
				432 s		373^a s	
				485 w	481	453 m	
				496 m	494	495 w	493
						504 w	502

[a] Values derived from low-temperature spectrum. [b] Values obtained through curve resolution.

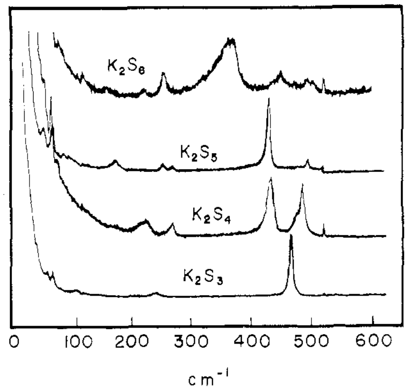

Figure 1. Raman spectra for the potassium tri-, tetra-, penta-, and hexasulfides as polycrystalline samples (25 °C).

the temperature is increased, but for K_2S_6, as is seen in Figure 2, a peak at 432 cm^{-1} becomes prominent (e.g., 150 °C, Figure 2). This frequency suggests the presence of K_2S_5, formed presumably from K_2S_6. A yellowish deposit was observed in the relatively cool neck of the Raman cell during the course of these measurements. The Raman spectrum of the latter confirmed sulfur.

For the molten polysulfides, the Raman scattering is extremely weak, due to the intensely black color of the samples; a general feature of the Raman spectrum is a very broad band in the 300–500-cm^{-1} region. While the spectrum of molten K_2S_5 shows some slight structure, those for the other molten polysulfides are virtually featureless. Without additional technique refinements, the quality of the molten-state spectra appears insufficient for structural interpretation, and this was not pressed further.

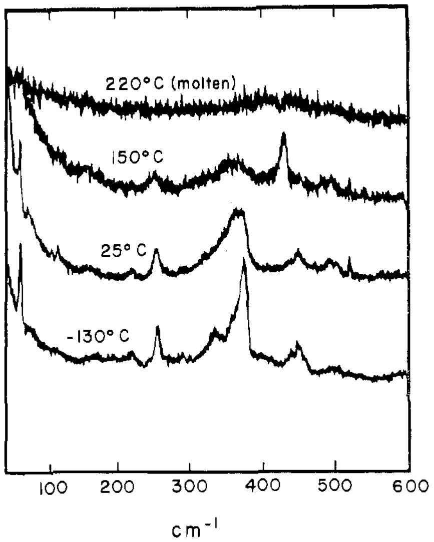

Figure 2. Raman spectra for K_2S_6 over a temperature range.

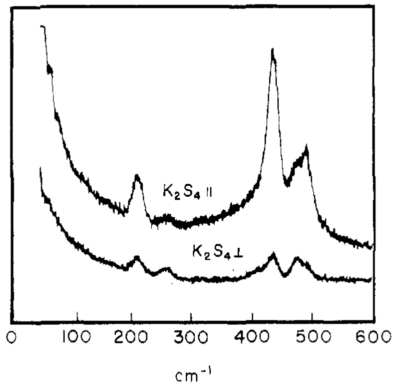

Figure 3. Raman spectra of glassy K_2S_4 (parallel and perpendicular polarizations).

Three of the polycrystalline potassium polysulfides (K_2S_4, K_2S_5, and K_2S_6) could be gained as glasses by plunging the molten samples into liquid nitrogen. When the same procedure was repeatedly attempted with K_2S_3, the spectrum corresponded to that of the polycrystalline sample; apparently the glassy state for K_2S_3 was not obtained by this simple technique. The peaks in the spectrum of glassy K_2S_4 (Figure 3) are of particular interest and utility since they can be identified with corresponding peaks in the spectrum of polycrystalline K_2S_4 and enable depolarization ratio studies. The values listed in Table II were thus determined. The maximum difference in the frequencies for glassy and polycrystalline states of K_2S_4 is about 12 cm^{-1} (e.g., 220 cm^{-1}, Table II). For K_2S_5 and K_2S_6, correspondences between peaks in the glassy and polycrystalline states are not always evident. In the spectrum of glassy K_2S_5 and K_2S_6, depolarized bands appear at 400 and 485 cm^{-1}, while a band at 438 cm^{-1} is polarized. The glassy spectra of these two compounds are very similar, the only difference being slight intensity variations between the three peaks.

Without knowledge of the geometry and hence the space group designations of these polysulfides, the factor analysis

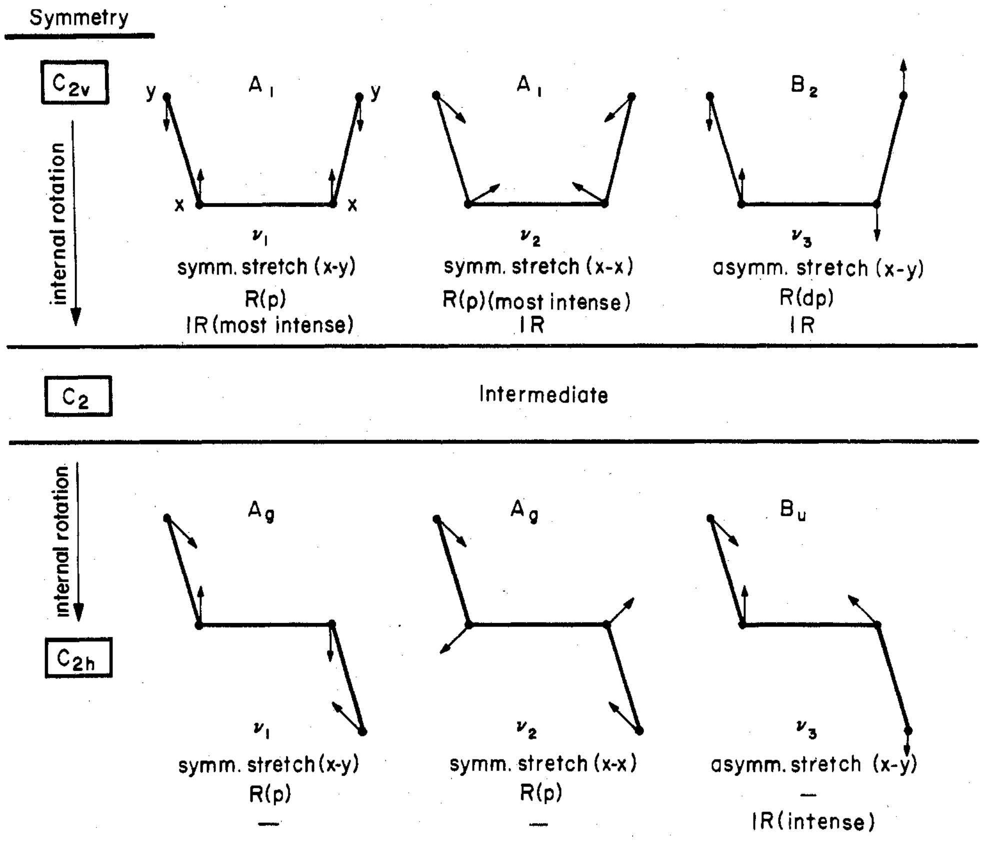

Figure 4. Spectroscopic activities of the stretching modes of a YXXY tetraatomic chain where the YXXY designation is used to distinguish between ν_1 (X-Y symmetric stretch) and ν_2 (X-X symmetric stretch).

required for a detailed vibrational assignment is not possible (cf. barium trisulfide[8]). Some insight is possible from the limited structural data available. Auroux and co-workers[15] determined the crystallographic constants for K_2S_3 and concluded that it belongs to the triclinic system, with seven formula units per unit cell. In view of the low symmetry and large number of ions per unit cell, one might expect the Raman spectrum of K_2S_3 to include a substantially larger number of peaks (many of them being lattice modes) than actually observed. A possible explanation for the relatively simple spectra of K_2S_3, K_2S_4, and K_2S_5 is that there may be relatively little interaction between the vibrations of polysulfide anions of the same unit cell. Therefore it appears worthwhile to examine the observed spectra relative to selection rules for isolated anions.

K_2S_3. Three possible configurations for the isolated S_3^{2-} are linear, bent, and cyclic. The selection rules for Raman and ir absorption bands for these are summarized in Table III. The linear configuration can be ruled out since the infrared peak at 466 cm^{-1} is coincident with a Raman peak (Table I), and the selection rules do not predict coincidences (center of inversion). For the cyclic structure (D_{3h}), one predicts two Raman frequencies, one high (ring stretch) and one low (ring deformation); the low-frequency mode would also be ir active. The observed ir absorption is not in accord with these selection rules and the cyclic structure, accordingly, appears improbable. A bent structure (C_{2v}) allows three Raman-active vibrations (symmetric and asymmetric stretches at high frequency; bend at low frequency); all of these are also allowed in the ir spectrum. Inspection of Table I and Figure 1 shows that only two Raman frequencies (apart from very low frequencies, attributable to lattice modes) are observed for K_2S_3, i.e., 466 and 238 cm^{-1}. This suggests either that the two high-frequency modes are accidentally degenerate (at 466 cm^{-1}) or, less probable, that one of these is too weak to be detectable. By comparison, the S_3^{2-} anion in BaS_3 exhibits two high-frequency peaks (plus a shoulder) in the neighborhood of 460 cm^{-1}, in accord with C_{2v} point group symmetry.[8] It is interesting to note that these two high-frequency peaks merge at higher temperature[8] and that the resulting spectrum corresponds closely with that observed for the S_3^{2-} species in K_2S_3.

K_2S_4. For S_4^{2-}, the six possible configurations, assuming equivalence of bond length and bond angles in each, and the selection rules are given in Table III. To the extent that the isolated ion treatment is justifiable, three of the possible structures—trans planar (C_{2h}), cyclic planar (D_{4h}), and linear ($D_{\infty h}$)—can be ruled out because of the observed coincidences between ir and Raman frequencies (Table II and Figure 1). For the puckered-ring configuration (D_{2d}), one predicts two polarized bands whereas three are observed (Figure 3); thus this configuration appears equally improbable. The remaining symmetry possibilities are C_2 and C_{2v}. The Raman activity of these differs only in the polarization of one mode, the torsion mode. This vibrational frequency is expected to be somewhat less than 200 cm^{-1}; it was not observable in the glassy state of K_2S_4 so that, within the limits of this approach, a distinction between C_2 and C_{2v} is not possible. For either of these two point group symmetries, the assignment of three of the Raman frequencies is possible for S_4^{2-}, as shown below.

Mode	ν_3	ν_4	ν_5
Descripn	Sym bend	Asym str	Asym bend
Assignt	220 cm^{-1}	478 cm^{-1}	266 cm^{-1}
Polarizn	p	dp	dp

The vibrational modes for C_{2h} and C_{2v} are schematically illustrated in Figure 4. Consideration of these and the observed relative intensities of the three stretching modes leads to the selection of C_2 as the most probable point group symmetry for S_4^{2-}. Some of the supporting points are as follows.

Table III. Summary of Number of Spectroscopically Allowed Peaks for Tri-, Tetra-, and Pentaatomic Species

Point group	Structure	Normal modes		Comments
		Raman	Ir	
		Triatomic		
$D_{\infty h}$	Linear	1 p	2	*a*
C_{2v}	Bent	3 (2 p, 1 dp)	3	*b*
D_{3h}	Cyclic	2 (1 p, 1 dp)	1	*c*
		Tetraatomic		
C_{2v}	Cis planar	6 (3 p, 3 dp)	5	*b*
C_{2h}	Trans planar	3 p	3	*a*
C_2	Nonplanar	6 (4 p, 2 dp)	6	*b*
D_{4h}	Cyclic planar	3 (1 p, 2 dp)	1	*a*
$D_{\infty h}$	Linear	3 (2 p, 1 dp)	2	*a*
D_{2d}	Puckered ring	5 (2 p, 3 dp)	2	*d*
		Pentaatomic		
D_{5h}	Cyclic planar	3 (1 p, 2 dp)	1	*a*
$D_{\infty h}$	Linear	3 (2 p, 1 dp)	4	*a*
C_{2v}	Planar "W" chain	9 (4 p, 5 dp)	8	*b*
C_s	Planar chain	9 (5 p, 4 dp)	9	*b*
C_2	Nonplanar chain	9 (5 p, 4 dp)	9	*b*

[a] No coincidences (mutual exclusion). [b] All coincident. [c] One coincidence (the depolarized, low-frequency line). [d] Two coincidences.

The intensities of Raman (ir) bands are proportional to the square of the change in polarizability (dipole moment) during a vibration. A large change in polarizability accompanies the symmetrical stretching mode, ν_2, and one predicts that this will be stronger than ν_1 in the Raman spectrum, at least for C_{2v}. The corresponding ir band is predicted to be weak for C_{2v} and inactive for C_{2h}. Inspection of the results shows that the 434-cm^{-1} Raman band is the most intense and that this band is not detected in the ir spectrum. This frequency is, accordingly, assigned as ν_2, and the dihedral angle in S_4^{2-} is closer to that for C_{2h} than for C_{2v}. The 486-cm^{-1} frequency may thus be assigned to ν_1; the fact that the intensities of ν_1 and ν_2 do not differ markedly in the Raman spectrum but vary significantly in the ir spectrum is additional support for a symmetry closer to C_{2h} than to C_{2v}. The remaining two fundamentals are, correspondingly, assigned to C_2 symmetry (dihedral angle greater than 90°):

Mode	ν_1	ν_2
Descripn	Sym str	Sym str
Assignt	485 cm^{-1}	434 cm^{-1}
Polarizn	p	p

where the tetraatomic species has been generalized as Y–X–X–Y to distinguish between ν_1 and ν_2.

K_2S_5 and K_2S_6. For S_5^{2-}, five possible structures are summarized in Table III, together with the symmetry point groups and selection rules. Two may be readily ruled out, i.e., D_{5h} and $D_{\infty h}$, since the selection rules predict only three Raman-active modes and no coincidences between Raman and ir activity. Inspection of the results (Table III) shows six Raman bands at frequencies greater than 100 cm^{-1} and four ir bands, with two bands coincident (Raman, ir). It appears impossible to choose between the remaining symmetries without more complete polarization data from single-crystal studies. From a more general viewpoint,[21] one can advance a generalized assignment of numerical values from Table II for the skeletal vibrational modes for S_5^{2-} and S_6^{2-}. Thus for an unbranched polysulfide species of n atoms, one may expect $(3n - 3)$ vibrational fundamentals, with $(n - 1)$ skeletal stretching modes, $(n - 2)$ skeletal bending modes, and $(n - 3)$ skeletal torsional modes. The frequencies for the former two, by comparison with the more exact analyses for BaS_3[8] and for K_2S_3 and K_2S_4 (this work), fall in the ranges 400–500 and 200–300 cm^{-1}, respectively; the torsional modes are expected at frequencies <200 cm^{-1} and may be difficult to distinguish from lattice modes. Accordingly the values in Table IV from the observed results (Table II) are assigned for the generalized S_5^{2-} and S_6^{2-}. More exact assignments await further data, such as would follow from studies of band depolarization using single-crystal spectroscopy or the dissolved and glassy states of these polysulfides.

Table IV

Skel vib modes		Freq assignment lines, ν, cm^{-1}
Descripn	No.	
	(a) S_5^{2-} (K_2S_5)	
Stretching	4	496, 485, 432, 416
Bending	3	252, 268
Torsion	2	172
	(b) S_6^{2-} (K_2S_6)	
Stretching	5	504, 495, 455, 373, 358
Bending	4	337, 254
Torsion	3	132, 157

Relative to the stabilities of the polyatomic sulfur species in the potassium polysulfides, it is apparent that the S_6^{2-} disproportionates to S_5^{2-} and elemental sulfur in the solid state under relatively mild conditions; i.e., this reaction occurs as low as 150 °C. The other polysulfides reported here remain stable at least to the melting point. A very marked band broadening accompanies the process of melting (S_3^{2-}, S_4^{2-}, S_5^{2-}), and while various factors (such as rotational broadening, conformational broadening, contributions due to anharmonicity) undoubtedly contribute, the magnitude is more in accord with an equilibrium coexistence of a series of the polysulfide ions in the molten state. Further studies are necessary to clarify this from the viewpoint of useful structural insight into the nature of the molten polysulfides.

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Registry No. K_2S_3, 37488-75-8; K_2S_4, 12136-49-1; K_2S_5, 12136-50-4; K_2S_6, 37188-07-1.

References and Notes

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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, irrrespective 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 $I\bar{4}2_d$, 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.