Table V. Calculated and Observed Electronic Transitions in OsNCl$_4^-$

$^1A_1 \rightarrow$	$\bar{\nu}_{max}$(obsd), cm^{-1}	$\bar{\nu}_{max}$(calcd), cm^{-1}
E(^{3}E)	19 300^a	19 596
A$_1$(^{3}E)	b	20 395
E(^{3}A$_2$)	b	21 360
A$_1$(^{3}A$_2$)	22 810	22 749
A$_2$(^{1}A$_2$)	25 490	25 246
E(^{3}B$_2$)	30 340	29 544
E(^{1}E)	34 710	32 675

^{a} Average position of the two components. ^{b} Not observed.

V). More precise fitting would be meaningless in view of the crudeness of the theory. It is somewhat reassuring that the assigned values of parameters F_2, F_4, and Δ_1 for OsNCl$_4^-$ are in good agreement with those obtained[20] from a detailed analysis of the electronic spectrum of PtCl$_4^{2-}$ ($F_2 = 1406$, $F_4 = 54$, $\Delta_1 = 25 961$ cm^{-1}). Such close correspondence is to be expected, as the Os–Cl (2.31 Å)[10] and Pt–Cl (2.32 Å)[21] bond distances are nearly equal.

It should be pointed out that in *all* of our computations,[18] even when the values of F_2 and F_4 were greatly reduced, the ^{1}E–^{3}E splitting was found to be greater than 6000 cm^{-1}. This is the main basis of our assignment of both components of band system I to transitions to a split E(^{3}E) state. It is not likely that the higher component is $^1A_1 \rightarrow$ E(^{1}E), as in that case the implied singlet–triplet splitting would be well below the lower limit set by theory.

The unusually high energies of the osmium d orbitals (e, a$_1$) that interact with the nitrido group are particularly noteworthy. Indeed, the antibonding character of the e level in Os≡N appears to be much greater than that inferred for M≡O from spectral studies of oxo cation complexes containing second- and third-row metals.[22,23] We take this result to mean that nitride is a much better π donor than is oxide, a conclusion not incompatible with recent Mössbauer spectral experiments on Ru(VI)[24] and Os(VI)[25] nitrido complexes that clearly indicate the presence of a high degree of ligand → metal electron donation. It should also be emphasized that our analysis suggests that both σ and π nitrido–osmium bonds are very strong. As electron donation from N^{3-} to a metal center increases, the nucleophilic character of the coordinated nitrido group decreases. Our electronic structural model for Os≡N, then, would suggest a rather low nucleophilicity for the nitrido ligand, which accords well with experimental

observations made previously.[26]

References and Notes

(1) W. P. Griffith, *Coord. Chem. Rev.*, **8**, 369 (1972), and references therein.
(2) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(3) R. A. Wentworth and T. S. Piper, *J. Chem. Phys.*, **41**, 3884 (1964).
(4) C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).
(5) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
(6) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
(7) W. P. Griffith and D. Pawson, *J. Chem. Soc., Chem. Commun.*, 418 (1973).
(8) W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1315 (1973).
(9) S. R. Fletcher, W. P. Griffith, D. Pawson, F. L. Phillips, and A. C. Skapski, *Inorg. Nucl. Chem. Lett.*, **9**, 1117 (1973); F. L. Phillips and A. C. Skapski, *J. Cryst. Mol. Struct.*, **5**, 83 (1975).
(10) A preliminary report of the spectra of K$_2$[OsNCl$_5$] and [(n-Bu)$_4$N]-[OsNCl$_4$] has been published: C. K. Poon and H. B. Gray, *Proc. XII Int. Conf. Coord. Chem.*, **12**, 26 (1969).
(11) A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, **6**, 204 (1960).
(12) O. Siiman and C. K. Poon, unpublished results; C. D. Cowman, Ph.D. Thesis, California Institute of Technology, 1974.
(13) J. Chiang, M.S. Thesis, University of Southern California, 1974 (R. Bau, private communication).
(14) E. I. Solomon and C. J. Ballhausen, *Mol. Phys.*, **29**, 279 (1975).
(15) R. J. Collin, W. P. Griffith, and D. Pawson, *J. Mol. Struct.*, **19**, 531 (1973).
(16) The band splitting cannot be a result of a low-symmetry Os site, as the anion in a crystal of [(n-Bu)$_4$N][OsNCl$_4$] is rigorously C_{4v}.[12,13]
(17) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand-Reinhold, Princeton, N.J., 1966, p 140.
(18) Supplementary material.
(19) W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **2**, 109 (1959); J. C. Eisenstein, *J. Chem. Phys.*, **34**, 310 (1961).
(20) H. H. Patterson, J. J. Godfrey, and S. M. Kahn, *Inorg. Chem.*, **11**, 2872 (1972).
(21) H. J. M. Bowen, *Chem. Soc., Spec. Publ.*, No. 11 (1958).
(22) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).
(23) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).
(24) T. C. Gibb, R. Greatrex, N. N. Greenwood, and R. H. Meinhold, *Chem. Phys. Lett.*, **29**, 379 (1974).
(25) F. E. Wagner, D. Kucheida, U. Zahn, and G. Kaindl, *Z. Phys.*, **266**, 223 (1974).
(26) J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, 508 (1974).

Raman Studies of Sulfur-Containing Anions in Inorganic Polysulfides. Barium Trisulfide

G. J. JANZ,* E. RODUNER,[1] J. W. COUTTS,[2] and J. R. DOWNEY, Jr.

The present work reports an investigation of the S$_3^{2-}$ anion from −125 to 580 °C using laser-Raman and rotating scattering arrangements as principal techniques, with BaS$_3$ (mp 554 °C) as the model system. The room-temperature and low-temperature spectra are understood in terms of a C_{2v} symmetry for S$_3^{2-}$. A unique spectral transformation occurs at higher temperature and in addition the compound exhibits a temperature-independent but magnetic-field-dependent paramagnetism. These changes are discussed from the viewpoint of bond angle changes, resonance Raman effect, and rotation of the S$_3^{2-}$ species in the solid state.

Introduction

The alkali and alkaline earth metals form a series of polysulfides containing S$_n^{2-}$ anions. Since complex equilibria undoubtedly occur between species such as S^{2-} and S$_n^{2-}$, we have undertaken the characterization of some of the S$_n^{2-}$ anions using, as model systems, a series of inorganic polysulfides for which the structures have been well characterized by careful x-ray crystallographic studies. The present work reports the results of an investigation of the S$_3^{2-}$ anion using laser-Raman spectroscopy as the principal technique and, as
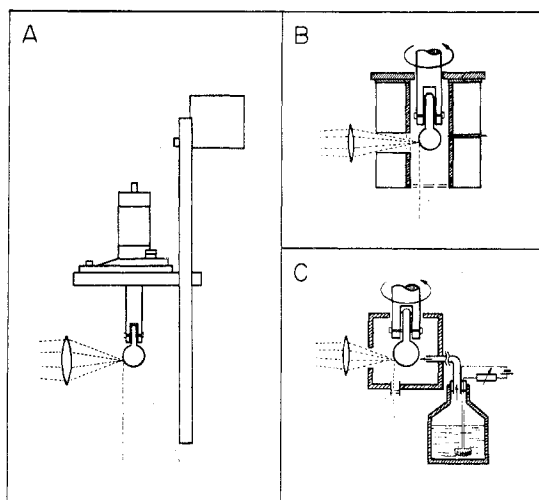
Figure 1. Rotating Raman cell assemblies for studies of polysulfides: (A) room-temperature configuration showing the spherical Pyrex glass cell coupled to the high-speed motor (3600 rpm); (B) details of the small resistance furnace (nichrome wire wound) and thermocouple for high-temperature studies; (C) cryogenic assembly showing the arrangements for the cold (nitrogen) gas stream.

Table I. Raman Frequencies of BaS_3

Freq, cm^{-1}		Assignment
+25 °C	−125 °C	
80	82	Lattice modes
100.5	105	
157.5	156	
	163	
177	184	
	190	
227	229.5	Bending mode?
~238 sh	~240	
402	416.5	177 + 227
458 (457 ir)	458.5	Str modes
~472 sh	470	
476 (476 ir)	476	
549		472 + 80
640		458 + 177
685		458 + 227
703		476 + 227
		2 × 177 + 458
802 b		177 + 158 + 458
		177 + 158 + 472
917	918	2 × 458
947	947	2 × 472
954	960	2 × 476

the model system, BaS_3 for which crystal structure data have been reported recently by Schnering and Goh.[3]

The polysulfides are yellow samples at room temperature, and these turn dark red with increasing temperatures and are virtually black in the molten state. While our principal studies were at room temperature, a limited investigation of the temperature dependence of the spectra, from −125 °C up to the melting point (554 °C) and in the molten state to 580 °C, was undertaken, and these results were examined for a more exact characterization of the S_3^{2-} species.

Experimental Section

Since most polysulfides are sensitive to air and moisture, particular care was taken to carry out all operations under inert atmospheres [viz., preparative work, the characterization analyses (dta, x-ray, and elemental analysis), and Raman cell transfer]. All samples were stored in Pyrex Raman cells or in ordinary Pyrex tubes. They were evacuated to at least 10^{-3} mmHg and then carefully sealed off.

BaS_3. A two-step process was used to prepare BaS_3; in the first step we followed the work of Veley[4] for the preparation of the monosulfide from $Ba(OH)_2$ and H_2S, and in the second we reacted BaS with sulfur in the stoichiometry required for the trisulfide, as described by Robinson and Scott.[5] Fisher (CP) chemicals were used throughout. The color of the final product (mp 554 °C), after cooling to room temperature and grinding in a mortar and pestle, was yellow. Further synthetic details will be reported elsewhere.[6] Analytical characterization by elemental analysis, dta, and x-ray powder diffraction gave the following results: Ba found 58.5 ± 1% (complexometrically with DTPA) and 58.3% (gravimetrically as sulfate), (calcd. 58.81%); dta (Du Pont Model 900; 15°/min up to 375 °C), no indications of impurities or solid-state phase transitions; x-ray powder diffraction (Cu Kα; Mo Kα), d values for BaS and BaS_3 in excellent agreement with values in the ASTM files.[7]

Raman Work. Powdered (polycrystalline) samples, rather than single crystals, were used since the interest was in the analytical characterization and in significant spectral changes over a range of temperatures, through fusion, to 580 °C. The spectra were recorded with a Jarrell-Ash laser-Raman spectrometer (Model 25-300) using an argon ion laser as excitation source (5145 Å; 1.3 W maximum). Our spectrometer is interfaced with a PDP-15 computer for computer-assisted signal averaging and with seven functionally distinct software subsystems for data acquisition, storage, redisplay, and contour analyses. A complete description is given elsewhere.[8] The highly absorbing nature of the colored polysulfide samples required modification of the conventional Raman cell assemblies to prevent sample heating.[9] A rotating-cell technique, as shown in Figure 1, was designed. The rotating-cell assembly is basically that described by Gillespie and

Sowa[10] and Clark[11] and consists of a constant-speed motor (Globe CMC, 3600 rpm), an aluminum framework with *xyz* slide plate positioner, and an aluminum shaft with mounting screws. The cell itself must be capable of being evacuated and sealed due to the nature of polysulfide samples. The spherical design was adopted, and our cells were simply made from 7-mm o.d. Pyrex tubing. Care was taken to ensure exact spherical symmetry (~15-mm diameter) so as to maximize Raman scattering intensities. Furthermore care must be taken to align the incident laser beam to impinge equatorially, so as to avoid "alignment–temperature" effects, i.e., an irreproducibility of the Raman band intensities due to localized sample heating from laser energy absorption by highly colored samples.

For high-temperature studies a small nichrome wire furnace (upper limit 600 °C), as shown in Figure 1 is placed about the cell. Temperatures were monitored by a chromel–alumel thermocouple near the cell. For the low-temperature studies, a simple cryogenic jacket, from two styrofoam cups, also shown in Figure 1, was improvised. A cold flow of nitrogen (from liquid N_2) was adjusted to attain the desired temperature(s), and the positive flow prevented atmospheric moisture condensation.

A spectrometer slit width of 2.0 cm^{-1} at a scan speed of 20 cm^{-1}/min was used for most of the work with polycrystalline samples, the computer summing the pulses over 0.2 cm^{-1}. For the molten samples, a spectral slit width of 4.0 cm^{-1} at a scan speed of 50 cm^{-1}/min was used, the computer summing the pulses over 0.5 cm^{-1}. A band at 65 cm^{-1} was observed in all polycrystalline samples. This was shown to be a grating ghost. The wavenumber meter calibration was checked using a low-pressure mercury lamp. The accuracy of the calibration was ±0.5 cm^{-1} and the uncertainties of the low-temperature and room-temperature spectra were thus estimated to be ±1 cm^{-1}, while for the high-temperature studies they were somewhat greater (due to band-broadening effects). Polarization measurements are not possible with polycrystalline samples, and attempts to gain BaS_3 in the glassy state for this purpose were unsuccessful. Similarly, a solvent, in which this trisulfide was stable, was not found.

Spectral Results

The Raman frequencies are summarized in Table I, together with generalized assignments of the observed combination and overtone frequencies. A comparison of the results from 25 to 580 °C is in Figure 2, and that for the S–S stretching region from −125 to +435 °C, in Figure 3. The color of the molten polysulfide is virtually black, and the spectrum (nine scans averaged) is correspondingly very weak; it is nevertheless sufficient to show the greatly increased band broadening of the S–S stretching region that accompanies fusion. Inspection of Figure 3 shows clearly the increasing intensity of the 470-cm^{-1} peak relative to the two modes at 458 and 476 cm^{-1}; by 290 °C the 470-cm^{-1} frequency is dominant, with a

Table II. Symmetry and Activity of Vibrational Modes in Crystalline BaS₃

D_{2d}	Acoustical vib[a]	Ba²⁺ osc against S₃²⁻	Ba²⁺ osc against Ba²⁺	S₃²⁻ osc against S₃²⁻	Librations	Internal vib	Activity
A₁				1		2	Raman
A₂					1		
B₁			1		1		Raman
B₂	1	1				2	Ir, Raman
E	1	1	1	1	2	1	Ir, Raman
Modes	3	3	3	3	6	6	
Raman bands	2	2	2	2	4	5	

[a] Acoustical vibrations correspond to a translation of the complete unit cells. They are low in frequency and often are not observed spectroscopically.
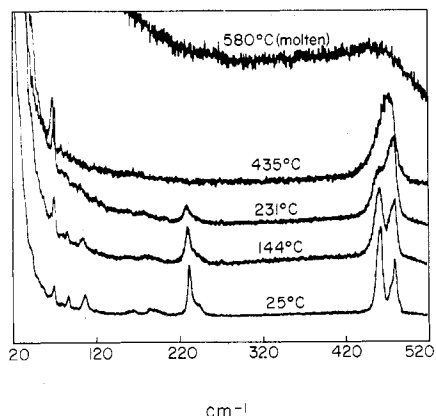

Figure 2. Comparison of the Raman spectrum of BaS₃ in the region 50–500 cm⁻¹ at room temperature and increasing temperatures to 580 °C. The molten spectrum (580 °C) is an average of nine scans.
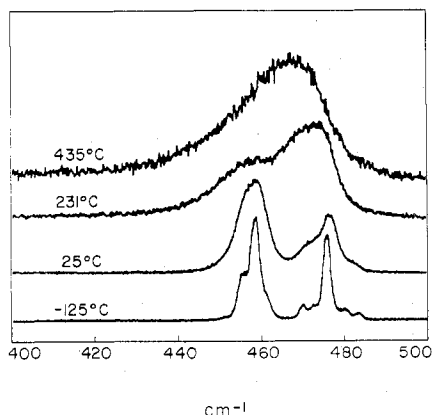

Figure 3. Raman spectrum of BaS₃ in the S–S stretching region, showing details of the band changes from low temperatures −125 to +435 °C.

half-band width narrower than the doublet at 231 °C. This change of intensities occurs as a continuous process as the temperature is increased; on thermal cycling, a hysteresis was noted; i.e., the reverse changes occur at temperatures approximately 100 °C lower than in the heating cycle. Corresponding intensity changes are observed in the lower frequency regions (<300 cm⁻¹; bending and lattice modes); these are illustrated in Figure 4. One notes that only three frequencies remain at 290 °C (cf. eight at 125 °C) and that the relative intensities differ remarkably from those at the lower temperatures.

Certain observations in the Raman spectrum of BaS₃ suggested onset of rotation of the anions in the crystalline samples, and, accordingly, magnetic measurements were undertaken on a Gouy balance, using a 2.75-in. air gap. Acting forces were measured with a Mettler balance, and temperatures, with an iron–constantan thermocouple. Magnetic
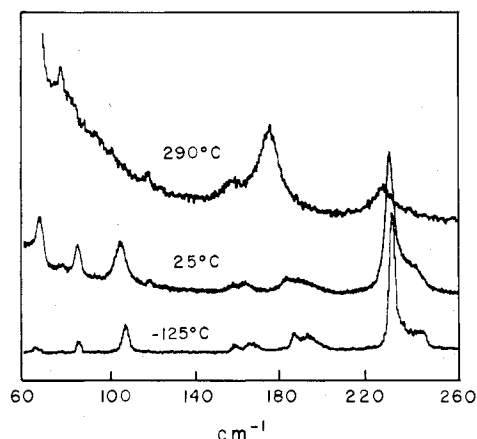

Figure 4. Comparison of the spectral changes occurring in the lattice and bending modes as a function of temperature. The 290 °C spectrum is an average of three scans.

susceptibilities were determined relative to CuSO₄·5H₂O as calibrant. The acting forces for BaS₃ (1.2883-g sample) corrected for the diamagnetism of the empty cell are summarized as follows. The magnetic susceptibility is independent of temperature in the temperature range −192 to +300 °C, but is dependent upon applied magnetic field strength. The magnetic susceptibility (cgsu/mol) is found to be 11.02 × 10⁻⁴ at 6000 G, 7.47 × 10⁻⁶ at 8000 G, 6.63 × 10⁻⁴ at 10 000 G, and 5.72 × 10⁻⁶ at 12 000 G. The reactants (BaS; sulfur) were examined and confirmed to be diamagnetic.

Limited ir spectra were undertaken in the S₃²⁻ stretching region, using the KBr pellet technique and a Perkin-Elmer Model 621 spectrometer. The two infrared-active stretching modes were observed at 457 and 476 cm⁻¹, respectively. The infrared studies were not extended to the low-frequency region.

Discussion

Crystal Structure of BaS₃ and Factor Group Analyses. The structure of BaS₃ was determined by Schnering and Goh[3] to be tetragonal with a unit cell of symmetry $P\bar{4}2_1m$ in crystallographic terms and $V_d^3 \equiv D_{2d}^3$ in spectroscopic nomenclature. The unit cell contains $Z = 2$ formula units and has the dimensions $a = 6.881$ Å and $c = 4.177$ Å. A bent trisulfide structure with an angle of 114.9° and an S–S bond length of 2.076 Å is reported. Therefore the symmetry of the free ion is C_{2v} and it also occupies C_{2v} sites in the lattice. The barium ions occupy S_4 sites in the crystal. An insight into the number and activity of the lattice modes and internal modes follows from a factor group analysis of the crystallographic data.[12,13] The symmetry and activity of the vibrational modes thus predicted for crystalline BaS₃ are summarized in Table II.

The factor group analysis was extended to the possible case of rotating S₃²⁻ units in crystalline BaS₃. Certain observations in the Raman spectrum, e.g., the appearance of the 470-cm⁻¹ peak with increasing intensities as the temperature is raised

from −125 to +435 °C (see Figure 3), could indicate onset of rotation of the anions in the (220) plane. If this rotation is sufficiently rapid, the anion symmetry will appear to be $D_{\infty h}$. Correspondingly the symmetry of the unit cell will change from $D_{2d}{}^3$ to $D_{4h}{}^5$ with Ba^{2+} in $C_{4h}(2)$ and $S_3{}^{2-}$(rotating) in $D_{2h}(2)$. Factor group analysis predicts that the Raman-active lattice modes will be limited to three librational bands

$$\Gamma = B_{2g} + 2\,E_g$$

Three bands are observed in the spectrum of BaS_3 at higher temperature (in addition to the stretching mode).

Trisulfide Structure. The $S_3{}^{2-}$ ion has a known bent structure with a bonding angle of 114.9°.[3] A free triatomic ion of C_{2v} symmetry is expected to show three normal modes, all active in ir and Raman spectra: a symmetric stretching mode (A_1); an asymmetric stretching mode (B_1); a symmetric bending mode (A_1). Usually the asymmetric stretching mode is of higher energy than the symmetric one, but in some cases (O_3, F_2O, $NO_2{}^-$) this is reversed. The appearance of two coincident stretching modes in the Raman and ir spectra (Table I) is in agreement with a bent trisulfide structure. It is, however, not clear whether the 227-cm^{-1} peak or its shoulder at 238 cm^{-1} has to be assigned to the bending mode. One of these could well be a libration. A normal-coordinate vibrational analysis using a valence force field predicts a bending frequency of 277 cm^{-1} with ν_1 458 cm^{-1} and ν_3 476 cm^{-1} and of 284 cm^{-1} with ν_1 476 cm^{-1} and ν_3 = 458 cm^{-1}. It is not possible to choose between the assignments on this basis. The force constants, with ν_1 458 cm^{-1}, are found to be k_1 = 1.77 × 10^5 dyn/cm and δ = 0.54 × 10^5 dyn/cm. This is to be compared with the values reported[14] for orthorhombic sulfur: k_1 = 1.84 × 10^5 dyn/cm; δ = 0.335 × 10^5 dyn/cm.

Factor group analysis predicts five internal modes for BaS_3, the two modes of symmetry A_1 each split into A_2 + B_2 due to coupling of the two ions in the elementary cell when they oscillate in phase or out of phase. In practice a correlation splitting of this type is usually weak and seldom observed. Therefore, and because of the temperature dependence, this splitting is not responsible for the shoulder at 470 cm^{-1}, but very likely it is seen as a splitting ($\sim$3 cm^{-1}) of the 458-cm^{-1} band at −125 °C. Accordingly this band should be assigned tentatively to the symmetric stretching mode. Final assignment must await polarization measurements. As noted elsewhere, attempts to obtain BaS_3 in the glassy state or in solution (for polarization measurements) were unsuccessful.

The High-Temperature Spectrum. The most likely explanation for the occurrence of only one spectral feature in the stretching region at high temperature (see Figures 1 and 2) would seem to be band broadening leading to increased overlap of the 458- and 476-cm^{-1} peaks to produce a single band at $\sim$470 cm^{-1}. However this explanation is not adequate since the half-width of the high-temperature peak is less than that of the doublet at lower temperatures. In addition band broadening cannot explain the changes in the lattice mode region illustrated in Figure 4.

Another aspect to be considered is the anomalous magnetic behavior of BaS_3 as a function of temperature. The magnetic susceptibility is typical of a paramagnetic substance except for the fact that it is independent of temperature (the Curie law predicts a $1/T$ dependence) and dependent on applied magnetic field. Some explanation must be sought for this very complex magnetic behavior; it is not clear whether this behavior arises from the same causes as the spectral changes.

The observed spectral changes in both the lattice and the intramolecular regions of the spectrum seem to imply a structural change in BaS_3 as the temperature increases. From this view, three contributing causes seem possible: (a) a change in crystalline structure associated with a decrease in triatomic bond angle such that the two stretching vibrations become accidentally degenerate; (b) onset of free rotation for the $S_3{}^{2-}$ species with accompanying change to $D_{\infty h}$ point group symmetry and $D_{4h}{}^5$ lattice symmetry; (c) the appearance of a resonance Raman effect (in accord with the dark color of the sample at high temperature). Free rotation of $S_3{}^{2-}$ leads to predicted spectral behavior in accord with the observed number of peaks (see above) and would also lead to magnetic properties due to the rotating charge. However this cannot explain the anomalous magnetic behavior of BaS_3 and, coupled with the extremely rare occurrence of anionic free rotation in the crystalline state, rules against the suggestion of onset of free rotation.

No support for a phase transition (to 375 °C) is gained by dta observations during thermal cycling, and, in addition, an x-ray powder diffraction pattern at 350 °C is identical with that at room temperature except for the usual thermal expansion of the lattice. It is interesting to note that K_2S_3 has a spectrum with only one Raman and ir peak (466 cm^{-1}) in the stretching region at all temperatures from −130 °C to its melting point.[15] This spectrum has been interpreted in terms of accidental degeneracy of the two stretching vibrations. The same color changes on heating that are observed for BaS_3 are also observed for the polysulfides of potassium[15] and sodium[16] but do not lead to anomalous spectral changes for these materials. These observations make it very difficult to choose between the remaining two possibilities (a or c), and without additional data further discussion would be speculative.

Registry No. $S_3{}^{-2}$, 12597-05-6; BaS_3, 12231-01-5.

References and Notes

(1) Research Assistant, Rensselaer Polytechnic Institute 1974–1975.
(2) Visiting Professor, Rensselaer Polytechnic Institute, 1974–1975; on leave from Lake Forest College, Lake Forest, Ill.
(3) H. G. v. Schnering and N. K. Goh, *Naturwissenschaften*, **61**, 272 (1974).
(4) V. H. Veley, *J. Chem. Soc.*, **49**, 369 (1886).
(5) P. L. Robinson and W. E. Scott, *J. Chem. Soc.*, 693 (1931).
(6) G. J. Janz et al., unpublished work.
(7) ASTM X-Ray Powder Diffraction Data File, No. 3-0824.
(8) J. R. Downey, Jr., and G. J. Janz in "Advances in Infrared and Raman Spectroscopy", R. J. H. Clark and R. E. Hester, Ed., Heyden & Son, London, 1975.
(9) W. Kiefer and H. J. Bernstein, *Appl. Spectrosc.*, **25**, 609 (1971).
(10) R. J. Gillespie and J. M. Sowa, private communication, Sept 1973.
(11) R. J. H. Clark, *Spex Speaker*, **18**, 2 (1973).
(12) T. R. Gilson and P. J. Hendra, "Laser Raman Spectroscopy", Wiley-Interscience, London, 1970.
(13) W. G. Fately, N. T. McDevitt, and F. F. Bentley, *Appl. Spectrosc.*, **25**, 155 (1971).
(14) K. Venkateswarlu and P. Thirugnanasambandam, *Trans. Faraday Soc.*, **55**, 1993 (1959).
(15) G. J. Janz, J. W. Coutts, J. R. Downey, Jr., and E. Roduner, *Inorg. Chem.*, **15**, 1755 (1976).
(16) G. J. Janz, J. R. Downey, Jr., E. Roduner, G. J. Wasilczyk, J. W. Coutts, and A. Eluard, *Inorg. Chem.*, **15**, 1759 (1976).