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Characterization of Sulfur Radical Anions in Solutions of Alkali Polysulfides in Dimethylformamide and Hexamethylphosphoramide and in the Solid State in Ultramarine Blue, Green, and Red

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The characterization of the S_3^- radical anion as the blue species present in hexamethylphosphoramide and dimethylformamide solutions of alkali polysulfides and in ultramarine blue has been extended by the measurement of the depolarization ratios for the two a_1 bands of the ion, by the observation of two distinct resonance Raman progressions for the ion in solution, by the calculation of the S–S–S bond angle and the force constants for the ion, and by the estimation of the S–S bond length in the ion. The vibrational spectra of the red species formed by adding sulfur to blue solutions of Na_2S_4 in dimethylformamide are reported; the red species is thought to be the S_4^- radical anion. Both the S_2^- and S_3^- radical anions have been identified as the species responsible for the color of ultramarine green. Oxidation of the latter to ultramarine blue is associated with an increase in the S_3^-/S_2^- ratio. The force constants, harmonic frequencies, and anharmonicity constants of both the S_2^- and S_3^- radical anions are compared with those of other isoelectronic or effectively isoelectronic species. The resonance Raman spectrum of ultramarine red reveals the presence of the S_3^- and S_2^- radical anions together with a third, predominant species which may be the neutral S_4 molecule.

Introduction

The nature of the blue species formed when alkali polysulfides are dissolved in electron-pair donor solvents has, until recently, been highly controversial. However, conclusive work on the subject by Chivers and Drummond[1] and Seel et al.[2] has shown that this species, with an absorption band at ca. 600 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}), is the radical anion S_3^-. This species has also been identified as that responsible for the blue color of sulfur dissolved in a LiCl–KCl eutectic[3] and in ultramarine blue[4,5] and in its mineral equivalent lapis lazuli.[5] The S_3^- radical anion is directly analogous to the ozonide ion, O_3^-, recently characterized in an argon matrix at 16 K by Andrews and Spiker,[6,7] and it is also effectively isoelectronic with chlorine dioxide, which is another 19-valence-electron molecule.

Chivers and Drummond[1] have shown that the S_3^- ion behaves as a 1:1 electrolyte in HMPA, hexamethylphosphoramide (Λ_0 = 22 cm^2 Ω^{-1} mol^{-1} at 25 °C), and that it has a magnetic moment in solution of 1.53 μ_B, and they have also presented partial infrared and Raman data consistent with the ion having the expected bent (C_{2v}) structure. Seel and Güttler[8] have shown that, on addition of sulfur to blue solutions of Na_2S_4 in dimethylformamide, the absorption band at 617 nm reaches a maximum at the ratio S/Na = 3. Addition of further sulfur then causes this band to decrease in intensity, a new band to appear at 513 nm, and the solution to turn red; the new band was attributed to the S_4^- radical anion. Similar color changes take place on addition of sulfur to solutions of Na_2S_4 in HMPA, and similar conclusions have been reached as to the species present.[2] It seems probable that the red color in both solvents is caused by a mixture of species, viz., normal polysulfides and the S_3^- and S_4^- radical anions. It is also believed that the S_4^- ion may be formed in alkali-metal halide lattices,[9] to which it imparts a red coloration, consistent with the above results.

Other studies,[10] mainly ESR,[11] have shown that the S_2^- radical anion can be introduced as a substitutional impurity into the larger alkali halides, occupying a single halogen vacancy. Resonance Raman studies of NaI:S_2^- at 80 K, on excitation in the region of the $^2\Pi_u \leftarrow {}^2\Pi_g$ ($1\pi_g \leftarrow 1\pi_u$) transition, which is polarized parallel with the axis, at ca. 400 nm, have led to the observation of nine overtones of the S–S stretching mode.[12] The S_3^- radical anion has also been detected in alkali halides by ESR spectroscopy[9] and ENDOR[13] and shown in most cases to occupy a triple vacancy formed by one metal- and two halide-ion vacancies;[9] it is possible, however, that the ion occupies only a single vacancy[4] for host crystals of large lattice constants (e.g., KI, RbBr, and RbI).

The nature of the sulfur-containing species in ultramarine blue and lapis lazuli has long been a cause for speculation.[14,15] The idealized formula for the compound, $Na_8[Si_6Al_6O_{24}]S_4$, obscures the facts that it reportedly has ca. two sulfur atoms per unpaired electron,[16] one unpaired electron per formula unit (μ = 1.83 μ_B),[16,17] and an average oxidation state for sulfur of +0.3.[16] Resonance Raman studies have shown that the main sulfur-containing species present is the S_3^- ion, together with much smaller amounts of the S_2^- ion.[5] ESR results[18] suggest that the S_3^- ions form a face-centered cubic lattice in an elementary unit cell with a lattice constant that is twice that (9.06 Å) determined by the X-ray method (the space group for minerals of the sodalite type, to which ultramarine belongs, is T_d^4, $P\bar{4}3n$). To date, no vibrational information has appeared concerning the nature of the sulfur species in ultramarine green, and that on ultramarine red is slight and has seemingly led to an incorrect conclusion as to the nature of the sulfur species present.[15,16]

The present work had the aims of carrying out a thorough resonance Raman investigation of the sulfur species present in DMF, in HMPA, and in various ultramarines, of calculating and/or detailing the vibrational frequencies, harmonic frequencies, anharmonicities, force constants, bond angles, and bond lengths of the S_2^- and S_3^- ions, and of comparing these data with those for analogous ions with the same number of valence electrons.

Experimental Section

Materials. The air-sensitive blue and red solutions were handled in a dry oxygen-free atmosphere.

HMPA (BDH laboratory reagent grade), DMF (Hopkin and Williams, Synchemica), Na_2S_4 (Alfa Products), $Na_2S\cdot 9H_2O$ SLR (Fisons laboratory reagent), and sulfur (Fisons laboratory reagent) were used without further purification.

Blue solutions ($\sim 5 \times 10^{-3}$ M) in HMPA or DMF were prepared in the drybox by dissolving Na_2S_4 in the appropriate solvent or by addition of $Na_2S\cdot 9H_2O$ followed by sufficient sulfur to cause the blue color to appear. Red solutions were prepared from the blue solutions by addition of further sulfur.

Samples for Raman spectroscopy were filled into rotatable solution cells[19,20] in a drybox and then rapidly transferred to a vacuum line and sealed under vacuum. Samples so prepared could be preserved indefinitely.

Samples for infrared and visible absorption spectroscopy were filled into variable path length IR cells or 1-mm path length quartz UV

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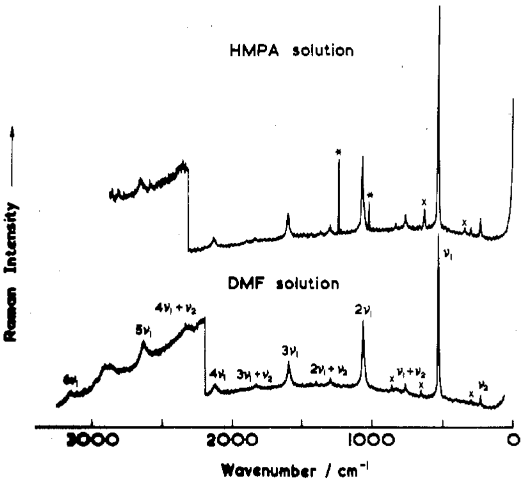

Figure 1. Raman spectra of the blue sulfur-containing solutions in HMPA and DMF with 647.1-nm excitation. Bands due to the solvent or plasma lines are indicated by an asterisk or a cross, respectively.

cells, respectively, in the drybox. If care was taken to ensure that all gases within the cells were displaced by the liquid, then these solutions were stable for several hours once removed from the drybox.

Physical Measurements. Raman spectra were recorded using a Spex 1401 double monochromator and a Spex Ramalog 6 double/triple monochromator in conjunction with Coherent Radiation Model 52 Kr^+ or Model CR12 Ar^+ lasers. The powers available at various exciting lines were as follows: 457.9 nm (2 W), 488.0 nm (10 W), 514.5 nm (>10 W), 568.2 nm (200 mW), 647.1 nm (500 mW). Detection was by means of photon counting in conjunction with a cooled RCA C31034 phototube (Spex 1401) or a cooled RCA C31034 SSR phototube (Spex Ramalog 6).

Liquid samples contained in rotatable cells, and solid samples pressed into a rotatable die, were rotated at ca. 1200 rpm in order to minimize thermal decomposition of the sample at the beam focus.[19,20] Spectra were calibrated by reference to neon emission lines which were superimposed directly onto the recording. Band areas were measured using a planimeter and were corrected for the relative spectral response of the instrument.

Infrared spectra were recorded on a Perkin-Elmer 225 infrared spectrometer. Spectra of the ultramarine samples were recorded as Nujol mulls between CsI plates and spectra of the colored solutions using a variable path length IR cell with KBr windows.

Visible absorption spectra were recorded using a Cary 14 spectrometer. Spectra of ultramarine samples were recorded using the spectrometer in the diffuse reflectance mode. Spectra of the colored solutions were recorded with the spectrometer in the transmission mode and the samples were contained in 1-mm path length quartz cells.

Results

Blue Solutions in DMF and HMPA. The Raman spectra of the blue solutions formed in DMF and HMPA are shown in Figure 1 for 647.1-nm excitation. The spectra are characterized by a progression in which ν_1, the symmetric stretching mode of the S_3^- ion, acts as the progression-forming mode; the progression $v_1\nu_1$ reaches $v_1 = 6$. The overtone bands show a continuous increase in half-bandwidth and a continuous decrease in band area as the vibrational quantum number, v_1, increases. In addition a second progression, $v_1\nu_1 + \nu_2$ to $v_1 = 3$, is observed for which ν_2 (the symmetric bending mode of the S_3^- ion) acts as the enabling mode. Such a subsidiary progression has been observed previously for the S_3^- ion as it occurs in ultramarine blue[5] but not for blue sulfur-containing solutions. The assignments for ν_1 and ν_2 have been confirmed by the observation that for the blue DMF solutions both the 535- and 233-cm^{-1} bands are polarized ($\rho \approx 0.23$ for both) and hence that both arise from totally symmetric fundamentals; accordingly the ion must be bent. The vibrational band assignments, together with values for the harmonic frequency (ω_1) and anharmonicity constant (x_{11}) calculated from a plot of $\nu(v_1\nu_1)/v_1$ vs. v_1,[19] are listed in Table I.

Table I. Assignments, Depolarization Ratios, Harmonic Frequencies, and Anharmonicity Constants for Bands Observed in the Vibrational Spectra of Blue Sulfur Solutions in DMF[a] and HMPA[b]

	band max/cm^{-1}					
	HMPA[c]		HMPA[d]		DMF[d]	
assign	Raman	IR	Raman	IR	Raman	IR
ν_2	232		233		235.5 (0.23)[e]	
ν_1	533		533.5		535 (0.23)[e]	
ν_3		580		569		571[f]
$\nu_1 + \nu_2$			764		768	
$2\nu_1$	1067		1064.5		1067.5	
$2\nu_1 + \nu_2$			1296		1298.5	
$3\nu_1$	1597		1593.5		1595	
$3\nu_1 + \nu_2$			1822		1829	
$4\nu_1$	2126		2119		2124	
$5\nu_1$			2642		2646	
$6\nu_1$					3172	
ω_1/cm^{-1}			536.1		537.5	
x_{11}/cm^{-1}			1.3		1.3	

[a] DMF = dimethylformamide. [b] HMPA = hexamethylphosphoramide. [c] Reference 1. [d] Present work. [e] Depolarization ratios, measured with 647.1-nm excitation. [f] Observed at 573 cm^{-1} by T. Chivers and I. Drummond, *J. Chem. Soc., Dalton Trans.*, 631 (1974).

Table II. Assignments for Bands Observed in the Vibrational Spectra of Red Sulfur Solutions in DMF

band max/cm^{-1}		
Raman	IR	assign
318 w		DMF
359 w, sh		DMF
384 (0.21)[a] s, br		S_4^-
401.5 w, sh		DMF
439 (0.25)[a] m		S_4^-
518 (0.4)[b] w		S_4^-
	532 w, sh	S_4^-
535.5 (0.26)[b] m		$\nu_1(S_3^-)$
	541.5 m	S_4^-
659 s		DMF
815 (0.34)[a] w, br		S_4^- (384 + 439 = 823)
865.5 s		DMF

[a] Depolarization ratios, measured with 514.5-nm excitation.
[b] Depolarization ratios, measured with ~535-nm excitation from a dye laser (sodium fluorescein dye).

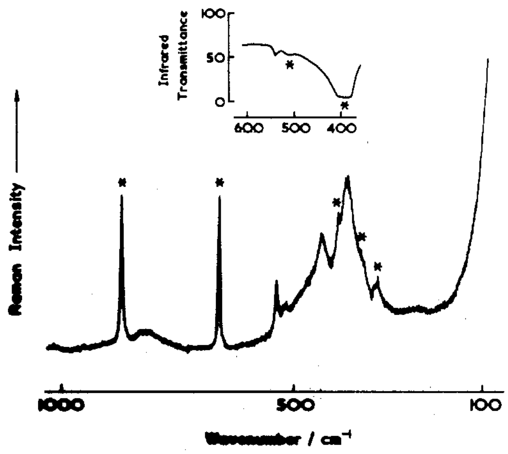

Figure 2. Raman spectrum of the red sulfur-containing solutions in DMF with 514.5-nm excitation. Bands due to the solvent are indicated by an asterisk. The inset shows the corresponding infrared spectrum.

Infrared spectra of the blue sulfur-containing solutions show a medium-intensity band at 571 cm^{-1} in DMF and a weak band at 569 cm^{-1} in HMPA. This is assigned to the asym-

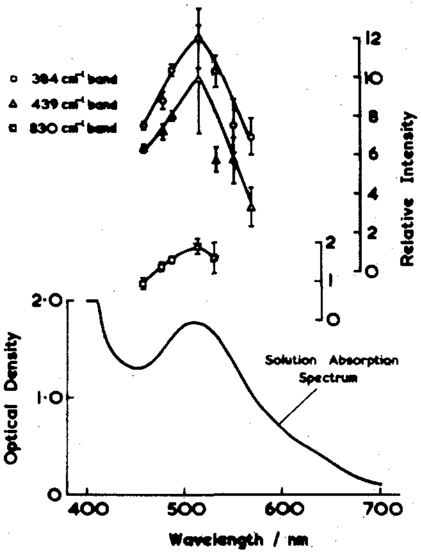

Figure 3. Excitation profiles for the 384-, 439-, and 830-cm^{-1} bands of the red sulfur-containing solutions in DMF. The full line shows the absorption spectrum. The reference band for the intensity measurements was the 661-cm^{-1} band of DMF.

metric stretching mode of the S_3^- ion, $\nu_3(b_1)$ in C_{2v} nomenclature.

Red Solutions in DMF. The Raman spectra of the red sulfur-containing solutions in DMF are shown in Figure 2, for 514.5-nm excitation. The vibrational assignments for the bands observed in this spectrum are listed in Table II. Apart from those arising from the solvent and the S_3^- ion, four additional bands at 384, 439, 518.5, and 815 cm^{-1} were observed; all four were polarized. The bands at 384 and 439 cm^{-1}, as well as that at 815 cm^{-1} (which appears to be a combination band of the first two), are enhanced as the wavelength of the exciting radiation approaches the green region, reaching a maximum for 514.5-nm excitation. The excitation profiles of all three bands thus maximize at the same wavelength as that of the strong electronic transition, characteristic of the red solutions, at 512 nm (Figure 3). As the 384-, 439-, and 815-cm^{-1} bands all show the same wavelength dependence of their intensities, they clearly belong to the same species.

The infrared spectra of the red solutions show a medium-strength band at 541.5 cm^{-1}, which is characteristic of these solutions, together with a shoulder at 532 cm^{-1}. The latter is not due to the symmetric stretching mode of the S_3^- ion, because no strong band due to the corresponding asymmetric stretching mode is observed at 571 cm^{-1}. Thus both the 541.5- and 532-cm^{-1} bands appear to belong to the red sulfur-containing species.

Ultramarine Blue. The infrared spectrum of a thick Nujol mull of ultramarine blue contains a strong band at 582 cm^{-1} and a weak one at 547 cm^{-1}, which can be assigned, respectively, to the $\nu_3(b_1)$ and $\nu_1(a_1)$ fundamentals of the constituent S_3^- ion. These results are in good agreement with the resonance Raman spectra of this compound,[5] which gave the result $\nu_1 = 548.9$ cm^{-1}. The infrared–Raman coincidence for ν_1 indicates that the S_3^- ion is not linear, in agreement with polarization studies (vide supra).

Ultramarine Green. The Raman spectrum of ultramarine green with a variety of different exciting lines is given in Figure 4. Two entirely different resonance Raman progressions were observed. As the excitation wavelength approaches 615 nm, the 549-cm^{-1} band (attributable to $\nu_1(a_1)$ of the S_3^- ion) is greatly enhanced, and overtones to $4\nu_1$ are observed (Table III). On the other hand, as the excitation wavelength approaches 457.9 nm, the 591-cm^{-1} band (attributable to the stretching fundamental of the S_2^- ion) is enhanced instead. The absorption spectrum of ultramarine green in the visible region shows two strong bands at 393 and 607 nm. The excitation profile of the 549-cm^{-1} band maximizes near 615 nm, confirming the presence of the S_3^- ion, while that of the 591-cm^{-1} band only starts rising with the shortest wavelength exciting lines, consistent with the behavior expected for the S_2^- ion (Figure 5). The relative proportion of the S_2^- to the S_3^- ions is, from the relative Raman band intensities, much higher in ultramarine green than in ultramarine blue. Hofmann[15] has noted that the former may be converted to the latter on being heated in air to 600 °C. Our observations confirm this; on heating ultramarine green, both the absorption band at 393 nm and the Raman band at 591 cm^{-1} decrease substantially relative to the absorption band at 607 nm and Raman band at 549 cm^{-1}, respectively. Thus the color change

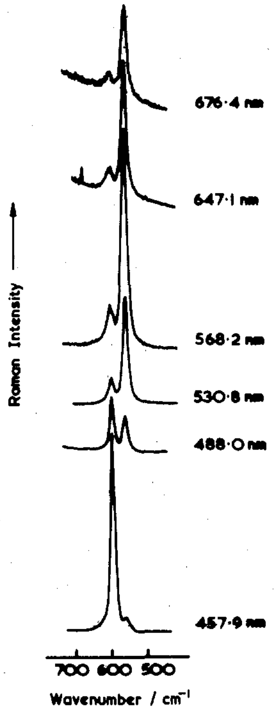

Figure 4. Raman spectra of ultramarine green with 676.4-, 647.1-, 568.2-, 530.8-, 488.0-, and 457.9-nm excitation.

Table III. Assignments of the Bands Observed in the Resonance Raman Spectra of Ultramarine Green, Together with Wavenumbers/cm^{-1} of Bands Assigned to S_2^- in Ultramarine Blue and Doped into a NaI Single Crystal

band max/cm^{-1}			
ultramarine green[a]	ultramarine blue[5]	NaI at 80 K[12]	assign
549			$\nu_1(S_3^-)$
589.6	586.5	594.5	$\nu(S_2^-)$
1096			$2\nu_1(S_3^-)$
1172.5	1168	1183.4	$2\nu(S_2^-)$
1641[b]			$3\nu_1(S_3^-)$
1752.5[d]	1747	1767.4	$3\nu(S_2^-)$
2187[c]			$4\nu_1(S_3^-)$
2324.5[d]	2320	2346.9	$4\nu(S_2^-)$
2894[d]		2919.9	$5\nu(S_2^-)$
		3487.9	$6\nu(S_2^-)$
		4051.1	$7\nu(S_2^-)$
		4609.6	$8\nu(S_2^-)$
594.7	590.4	599.8	ω_e/cm^{-1}
2.7	2.1	2.6	$\omega_e x_e$/cm^{-1}

[a] Present work. [b] Only observed using 530.8-, 568.2-, and 647.1-nm excitation. [c] Only observed using 568.2-nm excitation. [d] Only observed using 457.9-nm excitation.

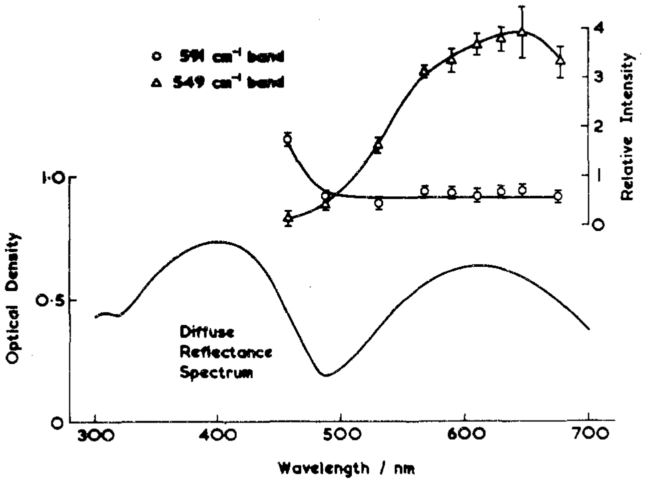

Figure 5. Excitation profiles of the 549- and 591-cm^{-1} bands of ultramarine green, together with the diffuse reflectance spectrum of the compound. The reference band for the intensity measurements was the $\nu_1(a_1)$ band of the periodate ion.

Table IV. Assignments of Bands Observed in the Resonance Raman Spectrum of Ultramarine Red

band max/ cm^{-1}	assign	band max/ cm^{-1}	assign
352 s, br	S_4	674 m	S_4 (ν_1?)
410 w, sh	?	1024 w, br	S_4 (352 + 674 = 1026)
547 w	$\nu_1(S_3^-)$	1093 w, br	$2\nu_1(S_3^-)$
580 w, sh	$\nu(S_2^-)$	1340 w, br	S_4 (2 × 674 = 1348)
653.5 w–m	S_4	1650 w, br	$3\nu_1(S_3^-)$

on oxidation of ultramarine green to ultramarine blue is, as suggested earlier,[3] undoubtedly caused by an increase in the S_3^-/S_2^- ratio.

Infrared spectra of ultramarine green showed no bands apart from those expected[21] for a sodalite mineral of (idealized) composition $Na_8[Al_6Si_6O_{24}]Cl_2$. The chemical composition of the ultramarine green used was approximately $Na_{7.7}[Al_{5.7}Si_{6.3}O_{24}]S_{1.94}Cl_{0.45}$, with about 40 sulfur atoms per unpaired electron and an average oxidation state for sulfur of −0.5.[15,16]

Ultramarine Red. The Raman spectrum of ultramarine red, excited with 514.5-nm radiation, is given in Figure 6. Vibrational assignments for the bands observed are listed in Table IV. The excitation profiles of the 352-, 653.5-, and 674-cm^{-1} bands of ultramarine red (Figure 7) all maximize in the region of the 520-nm electronic band maximum of the compound; in addition, a band at 1024 cm^{-1}, which appears to be a combination of the 352- and 674-cm^{-1} bands, shows the same behavior. The nature of the species giving rise to these Raman bands and to the electronic band at 520 nm will be discussed later.

The diffuse reflectance spectrum of ultramarine red also contains shoulders at 600 and 390 nm, indicative of the presence of both S_3^- and S_2^- radical anions. This is confirmed by the observation of a band at 547 cm^{-1} assignable to ν_1 of the S_3^- ion, together with a progression to $3\nu_1$, and by the observation of a band at 580 cm^{-1} assignable to the stretching fundamental of the S_2^- ion.

The chemical composition of the ultramarine red used was approximately $Na_{3.7}(NH_4)_{0.3}(H_3O)_2[Al_{4.8}Si_{7.2}O_{24}]S_3$, with about 75 sulfur atoms per unpaired electron and an average oxidation state for sulfur of +1.3.[15,16]

Discussion

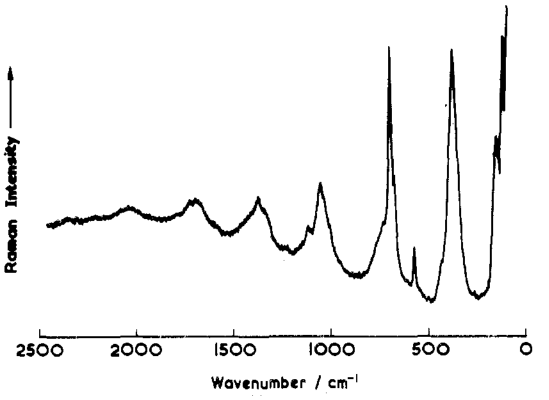

Figure 6. Raman spectrum of ultramarine red with 514.5-nm excitation.

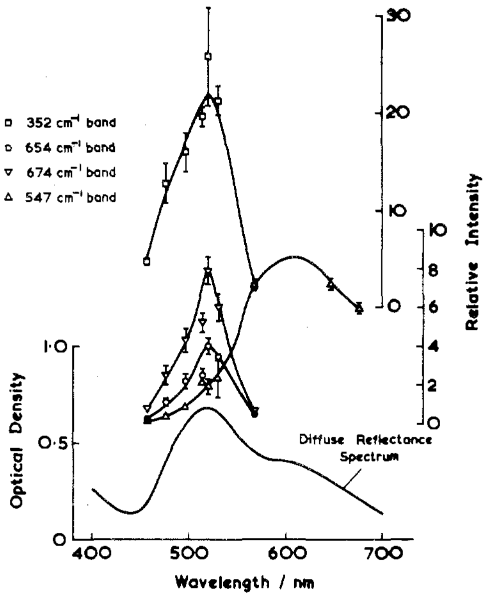

Figure 7. Excitation profiles of the 352-, 653.5-, and 674-cm^{-1} bands of the red sulfur-containing species (S_4?) and of the 547-cm^{-1} band of the S_3^- ion in ultramarine red. The reference band for the intensity measurements was the $\nu_1(a_1)$ band of the periodate ion. The diffuse reflectance spectrum of the compound is also indicated.

Sulfur Species in Solution. The present Raman results on the blue sulfur-containing species present in HMPA solutions are similar to, but more extensive than, those of Chivers and Drummond.[1] We have also extended the characterization of the blue species by the observation of overtones of $\nu_1(a_1)$ of the S_3^- ion to $6\nu_1$ in DMF solutions, by the observation of a second progression $v_1\nu_1 + \nu_2$ to $v_1 = 3$, and by the demonstration, by polarization studies, that both ν_1 and ν_2 are polarized, that they must, therefore, arise from a_1-type fundamentals, and hence that the ion must be bent (C_{2v}). The S_3^- ion, with ν_1 = 535 cm^{-1}, ν_2 = 235.5 cm^{-1}, and ν_3 = 571 cm^{-1}, is thus well characterized as being responsible for the blue color in these solutions. The electronic band at ca. 600 nm is equally characteristic of the ion; it is assigned to the $^2A_2 \leftarrow {}^2B_1$ ($2b_1 \leftarrow 1a_2$) orbitally allowed transition, by analogy with that at ca. 490 nm for the effectively isoelectronic species chlorine dioxide[22] and in agreement with the results of a scattered-wave SCF Xα calculation.[23]

The red sulfur-containing species in DMF, previously identified as the S_4^- ion by Seel et al.,[8] is shown to give rise to three polarized Raman bands at 384, 439, and 518.5 cm^{-1}, to a combination band at 815 cm^{-1}, and to infrared bands at 541.5 and 532 cm^{-1}. Although the existence of three polarized Raman bands, and no infrared–Raman coincidence, is consistent only with the trans-planar C_{2h} structure for the S_4^- ion (Table V), this structural suggestion cannot be put strongly owing to the possible nondetection of all formally active bands. The diamagnetic S_4^{2-} ion is known to have only C_2 symmetry in the solid state, the exact (chain) structure depending

Table V. Number of Spectroscopically Allowed Fundamentals for S_4 Molecules of Different Feasible Geometries

point group	stereochemistry	activities: Raman[a]	IR	coincidences
T_d	tetrahedral	3 (1)	1	1
D_{4h}	square planar	3 (1)	1	0
D_{3h}	trigonal planar	3 (1)	3	2
D_{2d}	puckered ring	5 (2)	2	2
C_{2h}	trans-planar chain	3 (3)	3	0
C_{2v}	cis-planar chain	6 (3)	5	5
C_2	gauche chain	6 (4)	6	6

[a] The number of polarized Raman bands is given in parentheses.

somewhat on the counterion (sodium salt,[24] r(S–S) = 2.074 Å (end) and 2.061 Å (middle), dihedral angle 97.81°; barium salt,[25] r(S–S) = 2.069 Å (all), dihedral angle 76.4°). The vibrational frequencies of this ion [ν_s(S–S′) 485 p, ν_s(S–S) 434 p, δ_s 220 p, τ 98, ν_{as}(S–S′) 478 dp, δ_{as} 266 dp,[26,27a] ν_1(a) 481, ν_2(a) 448, ν_3(a) 209, ν_4(a) 123, ν_5(b) 481, ν_6(b) 278 cm^{-1} [27b]] are lower, as expected, than those reported above and attributed to the S_4^- radical anion.

Sulfur Species in Ultramarines. It is clear from previous work on ultramarine blue[5] and from the present work on ultramarine green and red that the S_3^- and S_2^- ions are present in all three types of ultramarine. Electronic and Raman spectral data suggest that the S_3^- ion predominates in ultramarine blue, that they are present in comparable proportions in ultramarine green, but that, although present in ultramarine red, a third species predominates. Hofmann et al.[15] have identified this third species as S_2O, but the present vibrational studies show that this is not so. The Raman bands characteristic of this third species (352, 653.5, 674, 1024 cm^{-1}) do not match (except for one band) those of S_2O isolated in an argon matrix at 20 K (382, 673, 1157 cm^{-1});[28] neither do the bands match, either in frequencies or in intensities, those reported[28-30] for the S_3 molecule (310 (w)?, 490 (w)?, 585 (s), 650 (w) cm^{-1}).

In a study of the photolysis products of various chlorosulfanes trapped in isopentane–methylcyclohexane glasses at 77 K, Meyer et al.[29] have assigned an absorption band system at 400 nm (ϵ 10^6 M^{-1} cm^{-1}) to S_3 and one at 530 nm (ϵ 10^5 M^{-1} cm^{-1}) to S_4. In view of the close proximity of this electronic band maximum to the 522-nm band of ultramarine red it is suggested, tentatively, that the sulfur species giving rise to this absorption band and responsible for the red color is the S_4 molecule. Such a suggestion appears not, however, to be consistent with the results of a study of the radio-frequency discharge products of sulfur dioxide;[30] the S_4 molecule was thought to be among the products and responsible for the Raman bands at 440, 601, and 668 cm^{-1}. A further possibility, however, is that both sets of Raman data correctly relate to the S_4 molecule but that it possesses a different stereochemistry in each environment. Of the seven isomers feasible for S_4, three are chain type (cis, C_{2v}; gauche, C_2; trans, C_{2h}) and the remaining four are the square plane (D_{4h}), the puckered ring (D_{2d}), the trigonal plane (D_{3h}) and the tetrahedron (T_d). Extended Hückel calculations suggest that the C_{2h} and D_{3h} structures would be the most stable ones, although thermodynamic and photoionization evidence favors the D_{3h} one.[31,32] The species responsible for the 522-nm band of ultramarine red may be one of the nonring forms of S_4, possibly the D_{3h} form which has no unpaired electrons, rather than a chain form which would be a diradical; the latter possibility seems unlikely in view of the large number of sulfur atoms (75) per unpaired electron reported for ultramarine red.[15,16]

A model of the ultramarine lattice, based on the work of Hofmann,[15] shows that a molecule of S_4 could easily fit into cavities in the lattice despite its larger size compared with that of the S_2^- and S_3^- ions.

Comparison of Oxygen and Sulfur Species. Andrews and Spiker[7] note that the electron added to ozone in forming the ozonide ion occupies a π-antibonding orbital; therefore the net bond order and force constant decrease and the bond length increases. We have calculated force constants for S_3^- and S_3 using our frequencies for S_3^- and the frequencies of Tang and Brown[28] for S_3, and we used these force constants to estimate the bond lengths. We find that the same trends apply as for the oxygen species. This lends support to Tang and Brown's assignments of bands to the S_3 molecule.

Andrews and Spiker[7] further note that qualitative molecular orbital theory gives a $\pi/2$ bond order for O_2^- and O_3, $\pi/4$ for O_3^-, and zero π bond order for O_2^{2-} in addition to the single σ O–O bond in all these species. It is therefore reasonable to expect the bond length and force constant for O_3^- to be approximately equidistant between the corresponding values

Table VI. Related Symmetrical Triatomic Species of Group 6 Elements

species	$\nu_1(a_1)$/cm^{-1}	$\nu_2(a_1)$/cm^{-1}	$\nu_3(b_1)$/cm^{-1}	r_0/Å	angle: exptl	angle: calcd	f_d[o]/mdyn Å^{-1}	$r_0^2 f_\alpha$/mdyn Å^{-1}	f_{dd}/mdyn Å^{-1}	$r_0 f_{d\alpha}$/mdyn Å^{-1}	ref
O_3	1110	705	1042.2	1.278[a]	116.8[a]	116.3	5.44	2.23	1.26	0.28	*a*
O_3^-	1016	600.9	802.3	(1.38)[b]	108[c]		3.49	2.42	0.86	0.03	*d*
ClO_2	945.5	447.4	1110.5	1.473[e]	117.6[e]	123	6.81	1.37	−0.19	0	*e*
SO_2	1151.4	517.7	1361.8	1.4321[f]	119.5[f]	122	9.87	1.67	−0.15	0	*f*
S_3	585	490 or 310	650	(1.97)[g]		111[h]	3.66[h]	1.97[h]	0.29[h]	0.32[h]	*i*
S_3^-	535	235.5	571	(2.04)[g]		103[j]	2.77	1.41	0.01	0	*k*
S_3^{2-}	458	227	476	2.076[n]	114.9[l]	102.1[m]	2.00	1.23	0.24	0	*n*

[a] G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, p 604. [b] r_0 estimated from a plot of r_0 vs. f_d for various small oxygen species (ref *d*). [c] Bond angle calculated from isotopic ν_3 frequencies (ref *d*). [d] Frequencies for matrix-isolated $Cs^+O_3^-$: L. Andrews and R. C. Spiker, *J. Chem. Phys.*, 59, 1863 (1973). $\omega_1 = 1028.2$ cm^{-1}, $X_{11} = 4.95$ cm^{-1}. [e] Reference *a*, p 607. [f] Reference *a*, p 605. [g] r_0 estimated from a plot of r_0 vs. f_d for various sulfur species. [h] Bond angle and force constants calculated using $\nu_2 = 310$ cm^{-1}. [i] S.-Y. Tang and C. W. Brown, *Inorg. Chem.*, 14, 2856 (1975). [j] All bond angles calculated from a knowledge of the three vibrational frequencies by a method described by G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, p 169. [k] Present work. $\omega_1 = 537.5$ cm^{-1}, $X_{11} = 1.34$ cm^{-1}. [l] H. G. von Schnering and N. K. Goh, *Naturwissenschaften*, 61, 272 (1974). [m] On the bases of Walsh's rules (A. D. Walsh, *J. Chem. Soc.*, 2666 (1953)) one would expect the S–S–S angle to decrease in the order $S_3 > S_3^- > S_3^{2-}$ (18, 19, and 20-valence-electron species, respectively). However, this angle is very dependent (in the case of the anions) on the counterion and thus on the crystal forces, viz., S_3^{2-} in BaS_3 (S-S-S = 115°) and S_3^{2-} in SrS_3 (S-S-S = 108°) (H. G. von Schnering and N. K. Goh, *Naturwissenschaften*, 61, 272 (1974); S. Yamaoka, J. T. Lemley, J. M. Jenks, and H. Steinfink, *Inorg. Chem.*, 14, 129 (1975)). Hence no simple rationale of the angle changes on successive reduction of S_3 is possible. [n] Frequencies for BaS_3: G. J. Janz, E. Roduner, J. W. Coutts, and J. R. Downey, *Inorg. Chem.*, **15**, 1751 (1976). [o] Force constants calculated using a general valence force field. The force constant $f_{d\alpha}$ was allowed to vary only if a satisfactory fit to the observed frequencies could not be obtained with $f_{d\alpha} = 0$. The experimental bond angles were used in the calculation of force constants for O_3, O_3^-, ClO_2, SO_2, and S_3^{2-}. No experimental bond angles were available for S_3^- and S_3; therefore the angles calculated from the fundamental frequencies were used.

Table VII. Stretching Frequencies, Bond Lengths, Harmonic Frequencies, and Anharmonicity Constants for Diatomic Oxygen and Sulfur Species in Their Ground States

species	state	r(M–M)/Å	$\tilde{\nu}$/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e$/ cm^{-1}	f/mdyn Å^{-1}	ref
$^{16}O_2^+$	$^2\Pi_g$	1.1227[a]	1843.3[b]	1876.4	16.53	16.60[c]	*a*
$^{16}O_2$	$^3\Sigma_g^-$	1.20740[a]	1556.2[b]	1580.361	12.073	11.77	*a*
$^{16}O_2^-$	$^2\Pi_g$	1.28[d]	1113.4[b]	1131	8.8	6.03	*e*
$^{16}O_2^{2-}$	$^1\Sigma_g^+$	1.49[f]	794[g]			2.97[h]	
$^{32}S_2$	$^3\Sigma_g^-$	1.889[i]	719.98[b]	725.68	2.852	4.96	*i*
$^{32}S_2^-$	$^2\Pi_g$	(2.00)[j]	589.4[k]	594.3	2.5	3.33	*l*
$^{32}S_2^{2-}$	$^1\Sigma_g^+$	2.126[m]	473[n]			2.11[h]	

[a] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules", Van Nostrand, Princeton, N.J., 1950, p 560. [b] Calculated from ω_e and $\omega_e x_e$ using $\tilde{\nu} = \omega_e - 2\omega_e x_e$. [c] All force constants calculated using $f = 4\pi^2 \mu c^2 \omega_e^2$, where μ is the reduced mass and c is the velocity of light. [d] Bond length in crystalline KO_2: S. C. Abrahams and J. Kalnajs, *Acta Crystallogr.*, 8, 503 (1955). [e] ω_e and $\omega_e x_e$ for O_2^- in KBr: J. Rolfe, W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, 49, 963 (1968). [f] Bond length in BaO_2: S. C. Abrahams and J. Kalnajs, *Acta Crystallogr.*, **7**, 839 (1954). [g] Raman frequency in Na_2O_2: J. C. Evans, *Chem. Commun.*, 682 (1969). [h] Force constant calculated from $\tilde{\nu}$. [i] Reference *a*, p 566. [j] Bond length estimated from a plot of r_0 vs. f for various small sulfur species. [k] Raman frequency of S_2^- in ultramarine green (present work). [l] Present work. [m] Bond length in BaS_2: H. G. von Schnering and N.-K. Goh, *Naturwissenschaften*, **61**, 272 (1974). [n] Vibrational frequency in BaS_2: R. Steudel, *Z. Naturforsch.*, **306**, 281 (1975).

for O_2^- and O_2^{2-}. Examination of Tables VI and VII reveals that this is true, not only for the oxygen species but also for S_2^-, S_3^-, and S_2^{2-} species.

Bond angles calculated from a knowledge of the three vibrational frequencies (see footnote *j*, Table VI) are compared to published experimental bond angles for ClO_2, SO_2, and O_3 in Table VI. We therefore estimate our calculated bond angles for S_3^- and S_3 to be accurate to approximately ±5°. A value for the bond angle in S_3 could only be calculated using $\nu_2 = 310$ cm^{-1}, which is thought therefore to be the preferred value (cf. Table VI).

The changes in force constant and bond length with change in oxidation state are particularly clearly illustrated for the diatomic species in Table VII. We note that the sulfur species follow the same trends as the oxygen species in this respect. The similar trends observed in these two sets of compounds are not unexpected since the electronic structures of the two series are entirely analogous.

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Registry No. S_2^-, 12185-15-8; S_3^-, 12597-04-5; S_4^-, 37301-16-9; S_4, 19269-85-3.

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