

Figure 4. Relationship between the correlation times and the molecular radii of alkylgermanes ($R = 1.000$).

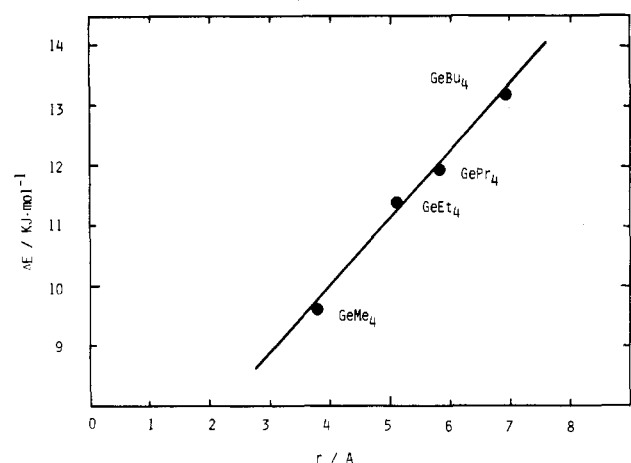


Figure 5. Relationship between the activation energies and the molecular radii of alkylgermanes ($R = 0.996$).

The linearity is also excellent. As T_1 decreases, τ_c proportionally increases.

The correlation time of $\text{Ge}(\text{CH}_3)_4$ was found to be 6.9×10^{-12} s. For the correlation time of a molecule of this size, the value we obtained seems reasonable since, for instance, the correlation

times of transition metals in aqueous tetrahedral oxo anions MO_4^{x-} ($M = {}^{51}\text{V}, {}^{53}\text{Cr}, {}^{97}\text{Mo}$, etc.; $x = 1-3$) obtained by viscosity measurements and eq 3 were in the range $(0.5-1.5) \times 10^{-11}$ s.³¹

Sekatsis et al. determined, however, the correlation time of $\text{Ge}(\text{CH}_3)_4$ in CDCl_3 at 23 °C as 0.5×10^{-12} s from the dipole-dipole relaxation of the methyl group by assuming the complete reorientation time of the $\text{Ge}(\text{CH}_3)_4$ molecule was longer than that of the methyl group by a factor of 9.¹¹ The assumption used by Sekatsis et al. that the methyl group rotates faster than the $\text{Ge}(\text{CH}_3)_4$ molecule by a factor of 9 is questionable, which was indicated by the relaxation time of the ^{13}C NMR spectrum of cholesteryl chloride.³² Thus the Stokes-Einstein-Debye model may be strictly inapplicable to a GeR_4 solution. The two methods give τ_c values different from each other by a factor of 10. Hence, the discrepancy between our τ_c (from the viscosity measurement) and that of Sekatsis (dipole-dipole relaxation) seems to arise from the difference of the method.

The activation energies for reorientation of tetraalkylgermanes are found in the range 9.6–13.2 kJ/mol. The activation energy of reorientation for $\text{Sn}(\text{CH}_3)_4$ is estimated to be 9.2 kJ/mol from the slope of $\ln T_1({}^{119}\text{Sn})$ against $1/T$.⁴ For CCl_4 , the activation energy is 7.6 kJ/mol from the temperature dependency of T_2 of the chlorine nuclei.³³ Furthermore, the activation energy of 13 kJ/mol for rotation of the sulfate ion was obtained from a plot of the correlation time at infinite dilution, $\tau(0)$, against the ratio of viscosity to temperature, (η/T) .³⁴

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Chemical Species in Solutions of Sulfur in Liquid Ammonia

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New results are given for absorption and Raman spectra of solutions of sulfur in liquid ammonia. These spectra have been obtained in a wide range of concentrations and temperatures. Our results give evidence that sulfur solubilization in liquid ammonia is in fact a redox dismutation, giving mainly the oxidized species S_4N^- and the reduced species S_6^{2-} , which is in equilibrium with the radical anion $\text{S}_3^{\cdot-}$. The identification of these species from absorption and Raman spectra is discussed. The redox dismutation equation is also discussed. It is indicated that the chemical species in these solutions are pH-dependent.

Introduction

It has been known for a long time that sulfur dissolves in liquid ammonia to give very colored solutions.¹ At the beginning of this century, the interpretation^{2,3} of these solutions was misled

by the identification of tetrasulfur tetranitride, S_4N_4 , after addition of silver iodide and evaporation of ammonia. It was not before the mid-1960s that the interpretation of Ruff and Geisel^{2,3} was recognized as incorrect by Zipp^{4,5} and by Nelson and Lagowski.⁶⁻⁸

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A significant progress in the understanding of these solutions was made by Chivers and Lau⁹ with the identification of the species S_4N^- and S_3^{2-} by Raman spectroscopy of $S-NH_3$ solutions. Our own experiments^{10,11} confirmed their results, but in addition, we have shown that sulfur-ammonia solutions are photosensitive, and this fact influences absorption and Raman spectra. It was then recognized by us¹¹ that the solubilization of sulfur in liquid ammonia is in fact a redox dismutation of sulfur. However, it is clear that our interpretation and the identification of the chemical species in these solutions^{12,13} needed a broader experimental basis, which will be given in the present paper.

We give here new results on absorption and Raman spectra, which have been obtained for the first time vs. temperature and for a wide range of concentrations. These results confirm the previous interpretation and allow us to interpret absorption and Raman spectra. It is also shown that the chemical species in these solutions are the same in the whole range of concentration.

Experimental Section

Solutions for spectrophotometry experiments were prepared in quartz optical cells that could sustain ammonia vapor pressure at room temperature. A weighed amount of sulfur was introduced into the cell, which was then pumped down to about 10^{-6} Torr for several hours. The amount of ammonia, previously dried on alkali metal, was controlled by gas volumetry and condensed into the cell, which was sealed off. The cell was then kept at room temperature, in the dark. It must be emphasized that the solubilization of sulfur in liquid ammonia is slow. Absorption spectra were regularly recorded at room temperature until invariant spectra were obtained. At least 3 days after the preparation of the solution is completed is required to obtain invariant spectra. Absorption spectra have been recorded on a Beckman 5240 UV-visible spectrophotometer. Absorption spectra have been recorded vs. temperature, between about -70 °C and room temperature, with an Oxford Instruments DN 704 cryostat; the temperature of the sample was regulated within ± 0.1 °C.

Solutions for Raman spectroscopy experiments were prepared with the same procedure, but in Pyrex cylindrical tubes. Solutions were also kept at room temperature and in the dark for several days before recording Raman spectra. Raman spectrometers (Ramanor HG2 and Dilor RT) from the "Laboratoire de Spectroscopie Infra-Rouge et Raman" (LA-SIR) of Lille University were used. Raman spectra for the most concentrated sulfur-ammonia solutions were obtained with back-scattering experiments. It must be emphasized that, for dilute solutions (less than 0.01 M), the full Raman spectrum cannot be obtained because the S_4N^- Raman lines disappear quickly under the influence of the laser excitation line, while the vibration bands of S_6^{2-} are apparently unaffected. For concentrated sulfur-ammonia solutions (concentration greater than 1 M), the Raman spectra are invariant under the influence of the laser excitation line. In the intermediate-concentration range (between about 0.01 and 0.5 M), the bands of S_4N^- decrease continuously with time until a stationary intensity is reached. Of course these limits are somewhat dependent on the light power received by the sample and on the excitation wavelength. It must therefore be pointed out that Raman spectra are obtained for sulfur concentrations higher than for absorption spectra.

Results

The identification of S_4N^- and S_3^{2-} in sulfur-ammonia solutions was done by Chivers and Lau⁹ using Raman spectroscopy. With the same technique, we identify S_6^{2-} as the polysulfide in these solutions. With resonance Raman conditions, we identify S_3N^- , another sulfur imide more oxidized than S_4N^- , the concentration of S_4N^- being much larger than that of S_3N^- . Therefore, it appears that Raman spectroscopy is extremely useful for the identification

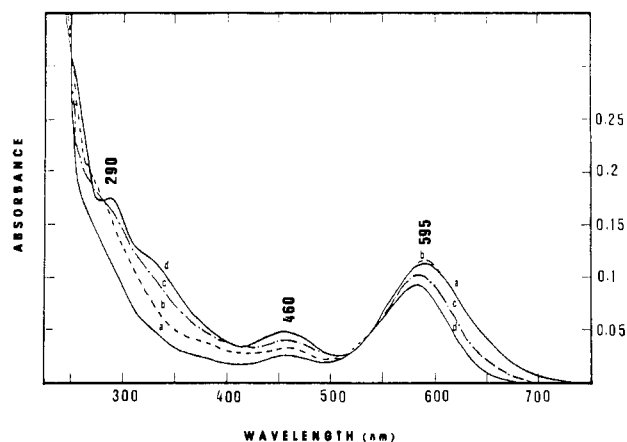


Figure 1. Absorption spectra of a dilute $S-NH_3$ solution (4.1×10^{-4} M) for various temperatures (optical path length 5 mm): (a) 293 K; (b) 265 K; (c) 225 K; (d) 200 K.

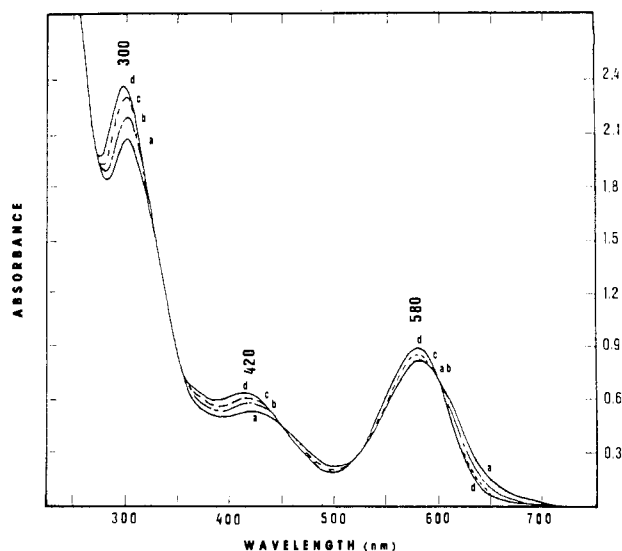


Figure 2. Absorption spectra of a $S-NH_3$ solution (3.5×10^{-2} M) for various temperatures (optical path length 0.5 mm): (a) 293 K; (b) 265 K; (c) 225 K; (d) 200 K.

of species, but Raman spectra depend very sensitively on the absorption spectrum of the solution. The absorption spectra vs. temperature display the equilibrium between S_3^{2-} and S_6^{2-} . We shall first discuss the results related to the variations of the absorption spectra vs. concentration and temperature. We shall then discuss the Raman spectra obtained under various conditions of concentration, temperature, and excitation wavelength.

Absorption Spectra of Sulfur-Ammonia Solutions vs. Concentration. The first absorption spectra of sulfur-ammonia solutions were published by Nelson and Lagowski,^{6,8} who observed three bands at 585, 430, and 297 nm, for a 2.5×10^{-4} M solution. Kerouanton et al.^{14,15} published an absorption spectrum, with a second visible absorption band located at 450 nm. They observed a shift of the main visible absorption band with time from 580 to 620 nm. Zipp and Evers⁵ confirmed the main characteristics of the absorption spectra given by Nelson and Lagowski.^{6,8} From these different studies no interpretation of the absorption bands of $S-NH_3$ solutions could be retained. The work of Chivers and Lau⁹ identified S_4N^- and S_3^{2-} in these solutions by Raman spectroscopy. The absorption bands of S_4N^- and S_3^{2-} were not known in liquid ammonia but were known to be located at 580 and 610 nm, respectively, in other media.^{16,17} We have shown

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previously¹¹ that sulfur-ammonia solutions are sensitive to traces of reducing agents and are photosensitive. These observations are very important in order to obtain satisfactory absorption spectra. We have obtained absorption spectra of these solutions between 4.1×10^{-4} and 8.8×10^{-2} M and from room temperature to about -70 °C.

A typical spectrum for a dilute S-NH₃ solution (concentration less than 10^{-3} M) is shown in Figure 1; at room temperature, absorption bands are found at 595 and 460 nm, while at 200 K, they are found at 580, 460, and 290 nm with a shoulder at ca. 330 nm.

We have observed that the absorption spectrum is concentration-dependent. A typical absorption spectrum of solutions of concentration larger than 2×10^{-3} M is shown in Figure 2. At room temperature, three bands are observed at 580, 420, and 300 nm. The comparison of Figures 1 and 2 shows that the intensities of the visible absorption bands have a larger difference for the more dilute solutions. But we have found that the absorbance at 580 nm is always larger (for any concentration or temperature) than the absorbance at ca. 420 nm. Nelson and Lagowski^{6,7} have observed the opposite situation, and our opinion is that their results are a consequence of the photosensitive nature of these solutions, which induces a decrease of the main visible absorption band, or a consequence of a partial reduction of the solution by impurities.

Our experiments show that the position of the second visible absorption band is concentration-dependent; this absorption band shifts from 460 nm for the more dilute solutions to 420 nm for the solutions in the 10^{-2} - 10^{-1} M range (Figure 5).

The variations of absorbance vs. concentration for the three absorption bands have been plotted in Figure 4; these curves have been plotted at 200 K, because for the most dilute solutions the absorption band at 290 nm is detectable only at low temperatures and because, as will be explained later, at 200 K the main visible absorption band is only due to S₄N⁻, without contribution of S₃⁻. It is shown that for the absorption bands located at 580 and 290 nm, Beer's law is satisfied up to about 1.5×10^{-3} M. From these curves the extinction coefficients at 290 and 580 nm are found to be equal to 1090 and 729 M⁻¹ cm⁻¹, respectively. These values are very different from those given by Nelson and Lagowski^{6,8} (130 and 7.6 M⁻¹ cm⁻¹, respectively, at -35 °C) or by Zipp and Evers^{4,5} ($\epsilon_{580} = 100$ M⁻¹ cm⁻¹, $\epsilon_{430} = 130$ M⁻¹ cm⁻¹ at -40 °C). If the absorbance of the second visible absorption band is plotted vs. concentration, a deviation from Beer's law is observed at about 10^{-3} M, but the position of this band is shown to be concentration-dependent. It must also be mentioned that the UV band is in fact located at 290 nm for the dilute solutions (Figure 1), while for more concentrated solutions ($\sim 10^{-2}$ M) this band is close to 300 nm (Figure 2).

Absorption Spectra of Sulfur-Ammonia Solutions vs. Temperature. Variations of the absorption spectra of S-NH₃ solutions with temperature were first given by Nelson and Lagowski.⁸ Their results show that the 580-nm absorption band disappears at -77 °C. Our own results with carefully prepared solutions do not show that the 580-nm absorption band disappears at low temperatures. For the most dilute solutions, the variations of the absorption spectrum with temperature are shown in Figure 1. For temperature decreasing from room temperature to 200 K, the absorbance decreases in the long-wavelength part of the main visible absorption band, while an increase of absorbance is observed for the other visible absorption band and in the UV region. These variations are assigned to dimerization of S₃⁻ into S₆²⁻ with decreasing temperature.

For more concentrated solutions (Figure 2) the maximum of the main visible absorption band increases slightly with decreasing temperature. But a careful analysis of the thermal variations of the absorption bands must take into account the thermal variations of density. For a given species, whose concentration is supposed independent of thermal equilibrium, when the temperature decreases, the increase of density induces an increase of concentration. For an 8.8×10^{-2} M solution (Figure 3), with temperature

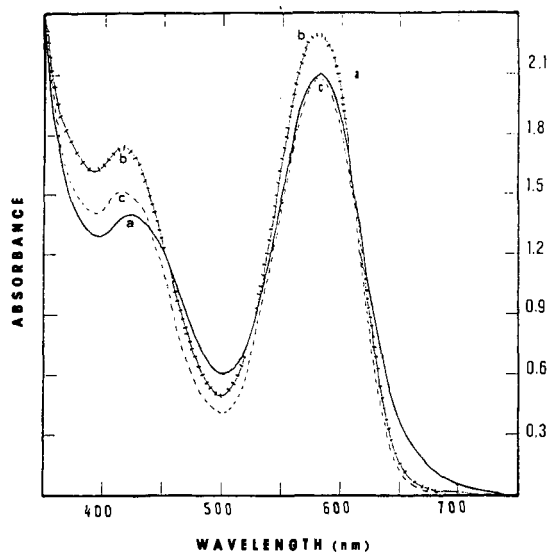


Figure 3. Influence of the thermal variations of density on the absorption spectrum (optical path length 0.5 mm): (a, —) experimental absorption spectrum at 293 K, with solution concentration 8.17×10^{-2} M calculated from the NH₃ density at 293 K; (b, +++) experimental absorption spectrum of the same solution as in (a) at 230 K, with solution concentration 9.18×10^{-2} M calculated from the NH₃ density at 230 K; (c, ---) absorption spectrum at 230 K corrected for the change of density, i.e. for a concentration of 8.17×10^{-2} M.

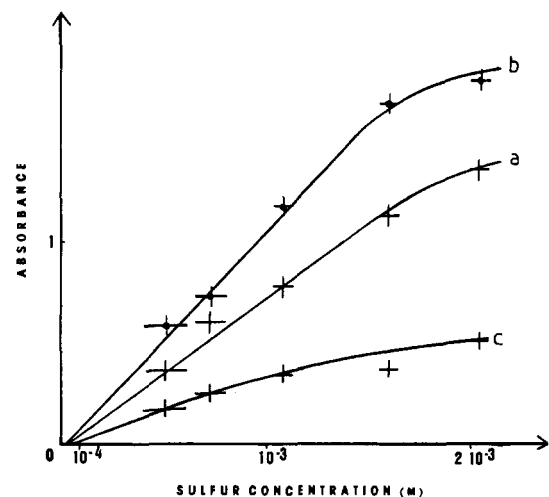


Figure 4. Beer's law for S-NH₃ solutions at 200 K, plotted from experimental (noncorrected) values for an optical path length of 1 cm: (a) 580 nm; (b) 290 nm; (c) $\lambda_2 = 420$ -460 nm.

decreasing from 293 to 230 K, we have shown that the apparent increase of absorbance of the 580-nm absorption band corresponds to the increase of density; the density of the solution and its thermal variations were supposed identical with those of pure liquid ammonia.

Therefore, it appears that the absorbance of the main visible absorption band at 580 nm does not vary with temperature, and this means that the equilibria in which S₄N⁻ may be involved do not depend significantly upon the temperature of the solution. But the long-wavelength part of the main visible absorption band decreases with decreasing temperature, and this results from the dimerization of S₃⁻. It is clear from Figure 1 and 3 that the relative contribution of S₃⁻ to the main visible absorption band at room temperature is larger for very dilute solutions, for which the dissociation of S₆²⁻ into S₃⁻ is large.

It must be noted that the absorption spectrum of S-NH₃ solutions, when the solubilization has been done at low temperature (-35 °C), displays differences^{12,13} with the absorption spectra shown in Figure 1 and 2.

Discussion on the Equilibrium between S₆²⁻ and S₃⁻. We have shown that, if the thermal expansion of the solution is taken into

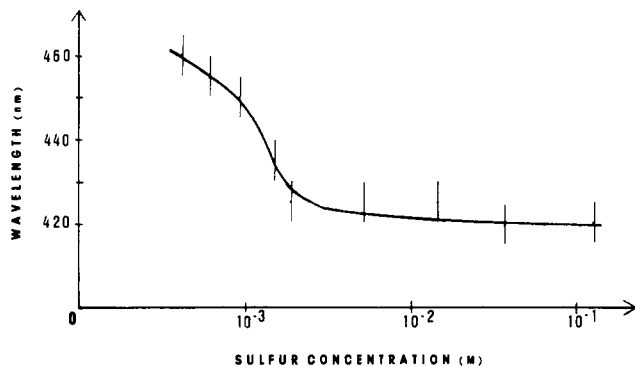


Figure 5. Shift of the second visible absorption band, at 200 K, vs. concentration.

account, the concentration of S_4N^- is temperature-independent. The decrease of the absorption band in the 600–650-nm range with decreasing temperature results from dimerization of S_3^{*-} . The simultaneous increase of the other visible absorption band can logically be assigned to S_6^{2-} . It must be emphasized that the main visible absorption band is at a constant position, located at 580 nm, while the maximum of the other visible absorption band is obtained for a wavelength λ_2 , which is concentration-dependent (Figure 5); we have found that the maximum of this band is located between 460 and 420 nm. If the absorbance of S_3^{*-} at 610 nm (A_{610}) obtained by the removal of the contribution of S_4N^- , correctly known by low-temperature measurements, is plotted vs. the absorbance of the other visible absorption band A_{λ_2} , a linear relation is experimentally obtained. The slope of this line is related to the ratio of the extinction coefficients of the species, as shown below.

Let C_0 be the S_6^{2-} concentration at low temperatures (when S_3^{*-} is completely dimerized). Let α be the dissociation coefficient of S_6^{2-} . At any temperature, $2C_0\alpha$ is the S_3^{*-} concentration and $C_0(1-\alpha)$ the S_6^{2-} concentration. Therefore, the absorbances due to S_3^{*-} and to S_6^{2-} are respectively

$$A_{610} = 2C_0\alpha d\epsilon_{S_3^{*-}} \quad A_{\lambda_2} = C_0(1-\alpha)d\epsilon_{S_6^{2-}} \quad (1)$$

where d is the optical path length, which leads to the relation

$$A_{\lambda_2} = -\frac{\epsilon_{S_6^{2-}}}{2\epsilon_{S_3^{*-}}}A_{610} + C_0\epsilon_{S_6^{2-}}d \quad (2)$$

The linear relation (eq 2) between A_{λ_2} and A_{610} has been experimentally observed for temperatures between 200 and 293 K. The slope corresponding to the factor of A_{610} in eq 2 was found experimentally equal to -0.34 ± 0.05 ; this value is close to what can be expected from extinction coefficient values published for S_6^{2-} and S_3^{*-} in other media.^{18,19} The full use of this method leads, however, to values for $\epsilon_{S_6^{2-}}$ that have the right order of magnitude relative to published values but that are slightly concentration-dependent. This suggests that the linear relation between A_{λ_2} and A_{610} results indeed from the thermal equilibrium between S_6^{2-} and S_3^{*-} . But the possibility that A_{λ_2} might contain a contribution from a species other than S_6^{2-} cannot be presently discarded. The observation of small quantities of S_3N^- by Raman spectroscopy (see below), a species with an absorption band at 460 nm in liquid ammonia, implies a very critical approach for the determination of the extinction coefficient of S_6^{2-} and of S_3^{*-} . However, in spite of this difficulty, the equilibrium constant between S_6^{2-} and S_3^{*-} can be estimated to be on the order of 10^{-3} , which is the value typically obtained for equilibria in liquid ammonia.

Identification of Chemical Species in S-NH₃ Solutions from Raman Spectra. The presence of S_4N^- and S_3^{*-} in sulfur-ammonia solutions was first established by Chivers and Lau,⁹ using Raman spectroscopy. They observed the Raman lines of S_4N^- at 571,

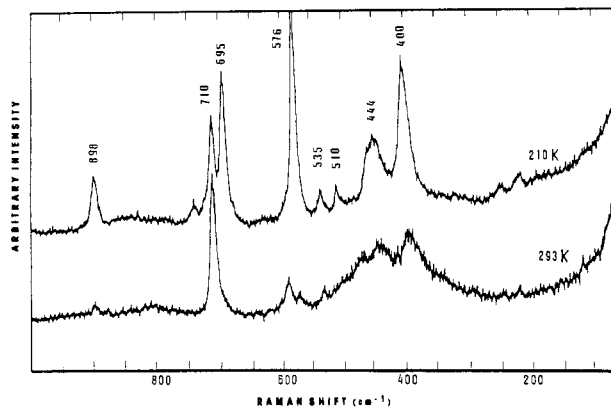


Figure 6. Raman spectra of a S-NH₃ solution (0.18 M) for the 514.5-nm excitation line of an argon laser, at 210 and 293 K.

592, 710, and 894 cm^{-1} , while the lines of S_3^{*-} were observed at 535 (vs) and 230 (w) cm^{-1} . They also observed Raman lines at 396 and 442 cm^{-1} and tentatively assigned them to the polysulfides S_6^{2-} and/or S_4^{2-} . From the results given in the previous section on absorption spectra and from unpublished Raman spectra on lithium and ammonium hexasulfides and tetrasulfides,²⁴ we assign the 396- and 442- cm^{-1} lines to S_6^{2-} . We have also recorded Raman spectra of sulfur-ammonia solutions vs. temperature, and we have observed, at low temperatures under resonance Raman conditions, new lines at 576, 695, and 898 cm^{-1} , which are assigned²⁰ to S_3N^- , a chemical species more oxidized than S_4N^- .

Sulfur-ammonia solutions contain, of course, the ammonium cation NH_4^+ . The Raman lines of NH_4^+ are not easily observed in the presence of NH_3 . In sulfur-ammonia solutions, Raman lines of NH_3 are not easily observed, particularly for concentrated solutions, as a consequence of the high absorbance of these solutions. Therefore, in the following sections, we shall mainly discuss the Raman lines of S_4N^- , S_3^{*-} , S_6^{2-} , and S_3N^- .

Raman Spectra of S-NH₃ Solutions vs. Concentration. As mentioned in the Experimental Section, the Raman spectra are concentration-dependent because the more dilute solutions are photosensitive under the laser radiations that have been used. For the more concentrated solutions, e.g. more than 0.5 M, the intensity of the Raman lines are constant vs. time. For a given excitation line, the Raman spectra are concentration-independent up to saturation at room temperature (about 5 M). This means that the relative intensities of the lines of S_4N^- and S_6^{2-} are concentration-independent. However, the intensity of the 535- cm^{-1} line, due to S_3^{*-} , decreases with increasing concentration for a given temperature and a given excitation line, and this will be discussed in the next section. Therefore, except for the relative intensity of the 535- cm^{-1} line, the Raman spectra are concentration-independent for concentrations larger than about 0.5 M, and this indicates that there is no modification of the chemical species in these solutions when the concentration increases.

Variations of the 535- cm^{-1} Raman Line (S_3^{*-}) vs. Concentration and Temperature. With the 647.1-nm excitation line, the 535- cm^{-1} Raman line is detected up to about 5 M. With the 488.0- or 514.5-nm excitation line the 535- cm^{-1} Raman line is detected up to about 0.4 M. When the 535- cm^{-1} Raman line is observed at room temperature, its intensity decreases with decreasing temperature (Figures 6 and 7), and this line is usually undetectable at temperatures below about $-70^\circ C$.

The temperature dependence of the 535- cm^{-1} line is a consequence of the temperature dependence of the equilibrium between S_6^{2-} and S_3^{*-} . It is indeed well-known²⁰ that the radical anion

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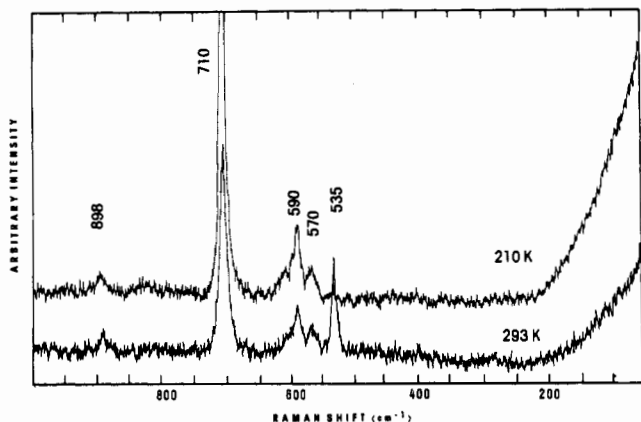


Figure 7. Raman spectra of a S-NH₃ solution (0.18 M) for the 647.1-nm excitation line of a krypton laser, at 210 and 293 K.

dimerizes into S₆²⁻ with decreasing temperature.

The decrease of the intensity of the 535-cm⁻¹ line with increasing concentration, for a given temperature and a given excitation line, results from the lesser dissociation of S₆²⁻ into S₃⁻ when the concentration increases and from the fact that the absorption band of S₃⁻ (610 nm) is masked by the absorption band of S₄N⁻ (580 nm). Consequently, the contribution of S₃⁻ to the main visible absorption band (580 nm) decreases relative to the S₄N⁻ contribution, when the concentration increases. This explains the relatively difficult detectability of S₃⁻ in sulfur-ammonia solution by Raman spectroscopy. But we have shown,²⁴ by electrochemical impedance measurements, that the S₃⁻ concentration increases with the sulfur concentration. In solutions for which the absorption band of S₃⁻ (610 nm) is not masked by the absorption band of another species, for instance in solutions of Li₂S₆ or (NH₄)₂S₆ in liquid ammonia, the intensities of the 535-cm⁻¹ lines increase with concentration, but in these solutions, these lines are also undetectable below about -70 °C.

Temperature Dependence of the Raman Lines of S₄N⁻. The variations of the Raman lines of S₄N⁻ with temperature are strongly dependent upon the excitation line (Figures 6 and 7). The intensity of these lines increases with decreasing temperature, with the 647.1-nm excitation line (Figure 7), while the intensity of the solvent lines is weak and approximately temperature-independent. The variations of the S₄N⁻ lines are then directly related to the variations of the absorbance with temperature. It has been observed (cf. above) that the absorbance decreases with temperature, for wavelengths larger than 580 nm, but this is a consequence of the dimerization of S₃⁻ into S₆²⁻, when the temperature decreases.

For the other excitation lines that have been used (488.0 and 514.5 nm), the variations of the Raman spectrum are unexpected, and both excitation lines give the same phenomena. For temperatures below 230 K, in addition to the S₄N⁻ lines, new lines are observed at 576, 695, and 898 cm⁻¹ (Figure 6). We assign these lines to the S₃N⁻ species, and it is our assumption that the lines of S₃N⁻ are observed as a consequence of resonance Raman conditions, because the variations of the absorption spectrum of a rather concentrated S-NH₃ solution (Figure 2) do not display evidence of a significant contribution of S₃N⁻, which should be located at 460 nm.^{20,24}

The synthesis of S₃N⁻ was first performed by Bojes et al.,²⁰ by reaction of S₄N⁻ with triphenylphosphine in acetonitrile. They have shown that the S₃N⁻ Raman lines, in the solid state, are observed at 574, 686, and 894 cm⁻¹ and that the absorption band of S₃N⁻ in CH₂Cl₂ is found at 465 nm. Chivers and Lau⁹ have indicated that the Raman spectrum of (Ph₃P=N=PPh₃)⁺S₄N⁻ in liquid ammonia displays the Raman lines of S₄N⁻ and S₃N⁻. However, these authors mention that the Raman lines of S₃N⁻ have not been detected in S-NH₃ solutions, at room temperature.

By comparison with the observations of Bojes et al.,²⁰ the new lines observed below 230 K can be assigned to S₃N⁻. They are observed with the 488.0- and 514.5-nm excitations, and their

overtone and combination bands are observed; these lines are not detected with the 647.1-nm excitation line (Figure 7). These observations show that these lines are observed under resonance Raman conditions and that the corresponding absorption band is at a wavelength smaller than 488.0 nm. There is no evidence that the simultaneous presence of S₄N⁻ and S₃N⁻, detected at temperatures below 230 K, results from a temperature-dependent equilibrium between these species. The contribution of S₄N⁻ to the main visible absorption has been found to be temperature-independent; the other visible absorption band increases at ca. 420 nm (for rather concentrated solutions) with decreasing temperature, and this is interpreted as a consequence of the dimerization of S₃⁻ into S₆²⁻. Therefore, the absorption spectrum gives evidence neither of a contribution of S₃N⁻ nor of variations of the contribution of S₄N⁻ with temperature. It is concluded that the observations of S₃N⁻ below 230 K in Raman spectra result from the resonance Raman conditions and that the concentration of S₃N⁻ is much lower than the concentration of S₄N⁻. In the present situation, the resonance Raman conditions are apparently best satisfied at low temperatures.

Other experiments, which will be published later with more details,²⁴ confirm this interpretation. If the pH of S-NH₃ solutions is increased by progressive addition of an alkali-metal amide, the chemical species in the solutions are transformed: the oxidized form of sulfur becomes more oxidized, and the reduced form of sulfur becomes more reduced. These experiments show that S₄N⁻ is then transformed into S₃N⁻. The absorption and Raman spectra recorded under these conditions confirm that the Raman lines of S₃N⁻ are found in liquid ammonia at 576, 695, and 898 cm⁻¹, that the absorption band of S₃N⁻ in liquid ammonia is located at ca. 460 nm, and that the extinction coefficients of S₃N⁻ and S₄N⁻ are close.

Polysulfide Identification in S-NH₃ Solutions from Raman Spectroscopy. As mentioned previously, Chivers and Lau⁹ observed S₃⁻ in S-NH₃ solutions by Raman spectroscopy. They tentatively assigned the Raman lines observed at 396 and 442 cm⁻¹ to S₆²⁻ and/or S₄²⁻. We have observed the corresponding bands at 400 and 444 cm⁻¹ (Figure 6). We show here that the polysulfide present in S-NH₃ solutions is S₆²⁻ only. We have recorded Raman spectra of S-NH₃ solutions, chemically reduced by lithium or hydrogen sulfide, in a quantitative manner. Raman spectra of ammonia-polysulfide solutions corresponding to analytical compositions of Li₂S₄, (NH₄)₂S₄, Li₂S₆, and (NH₄)₂S₆ display such differences that the presence of S₆²⁻ in S-NH₃ solutions is evidenced: S₆²⁻ solutions display two intense lines in the 400-440-cm⁻¹ region, while S₄²⁻ solutions display only one intense line in this region. In addition, Li₂S_x or (NH₄)₂S_x solutions with x larger than 6 have Raman spectra showing the Raman lines of S₄N⁻. Since S₄N⁻ does not appear in solutions corresponding to an analytical composition of Li₂S₆, a more reduced species such as S₄²⁻ cannot be present either. This gives evidence that, in S-NH₃ solutions, there is no polysulfide less reduced than S₆²⁻.

It was observed that the Raman spectra of S₆²⁻ in various solutions depend upon the cation (Li₂S₆, (NH₄)₂S₆, ...) and display small differences about the position and relative intensity of S₆²⁻ lines. The expected geometric flexibility of such a chemical species might explain this difference. The Raman spectra of solid K₂S₆²² and Cs₂S₆²³ are also different from what we have observed for S₆²⁻ in liquid ammonia solutions.

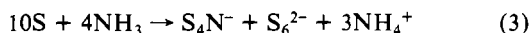
We have observed a marked excitation line effect on the Raman lines of S₆²⁻ (Figures 6 and 7). The intensity of these lines decreases with increasing wavelength. These lines are practically undetectable with the 647.1-nm excitation line, in S-NH₃ solutions, as a consequence of the strong absorbance at 580 nm. These observations are coherent with our assignment of the S₆²⁻ absorption band to the 420-450-nm region.

It is somewhat surprising that the Raman lines of S₆²⁻ do not increase significantly with decreasing temperature, while the intensity of the 535-cm⁻¹ line of S₃⁻ decreases to zero. This was first considered as surprising because S₃⁻ dimerizes into S₆²⁻ with decreasing temperature and this increases the S₆²⁻ concentration. In fact, in Raman spectroscopy experiments, the concentration

of the solutions is rather high, and S_6^{2-} is weakly dissociated. Therefore, the relative increase of S_6^{2-} when the temperature decreases from room temperature to -70°C is small. Also, the observation of S_6^{2-} by Raman spectroscopy is best done with the 488.0-nm excitation line under resonance conditions, and under these conditions, the species concentration is less easily related to the intensity of the Raman lines.

Discussion

We have previously suggested that the redox dismutation of sulfur in liquid ammonia could be described by the following equation, with the species arbitrarily written as completely ionized:



The polysulfide S_6^{2-} is in equilibrium with the radical $S_3^{\cdot-}$:



Reaction 3 is oversimplified, first because there must be many kinetic steps to yield such a result and second because S_4N^- is not the only oxidized species detected spectroscopically when solutions have reached equilibrium at room temperature and so other oxidized species may be present. For rather concentrated solutions, S_3N^- has been detected under resonance Raman conditions, at temperatures below 230 K, but the concentration of S_3N^- is certainly very low. If the concentration of S_3N^- were one-tenth of the concentration of S_4N^- , the band of S_3N^- should be clearly observed in the absorption spectrum of about 5×10^{-3} M solutions. It remains that the observation of S_3N^- limits the validity of eq 3. Equation 3 should be correct if the oxidized form of sulfur were only S_4N^- . From eq 3, it appears that the maximum concentration (molarity) of S_4N^- in solution is one-tenth of the sulfur (S) concentration. From Beer's law plotted for the 580-nm absorption band, the extinction coefficient, calculated relative to

the sulfur concentration, was found equal to $729\text{ M}^{-1}\text{ cm}^{-1}$; this implies that the extinction coefficient of S_4N^- is at least equal to $7290\text{ M}^{-1}\text{ cm}^{-1}$. This can be compared to the extinction coefficient of $1.6 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$ found for S_4N^- by Chivers et al.¹⁶ The difference cannot be accounted for by the presence of S_3N^- , which has a low concentration.

Other experiments show that the electrochemical impedance in $S-NH_3$ and in $(NH_4)_2S_6-NH_3$ solutions have thermal variations that are governed by eq 4. These experiments show that the S_6^{2-} concentration in $S-NH_3$ solutions is correctly given by eq 3.

It seems therefore that eq 3 describes correctly the redox dismutation of sulfur in liquid ammonia, except that S_4N^- is observed simultaneously with a low concentration of S_3N^- .

It must be emphasized that eq 3 is an overall equation, which does not account for possible transient chemical species during the dissolution process.

Let us say finally that the general type of eq 3 is checked by the fact that progressive addition of base (alkali-metal amide) in the solutions progressively transforms S_4N^- into more oxidized species and S_6^{2-} into more reduced species. Similar equations can easily be written with other oxidized species such as S_3N^- , or other reduced species such as S_4^{2-} , as will be necessary to explain the pH effects.

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Registry No. S, 7704-34-9; NH_3 , 7664-41-7; S_4N^- , 74273-17-9; S_6^{2-} , 12597-13-6; $S_3^{\cdot-}$, 12597-04-5; S_3N^- , 76468-83-2.

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Coordination Compounds of 5-Methyl[1,2,4]triazolo[1,5-a]pyrimidin-7-ol. Structures, Spectra, and Unusual Magnetic Properties of Tetraaquabis(5-methyl[1,2,4]triazolo[1,5-a]pyrimidin-7-olato)copper(II) and the Structurally Analogous Diammine Diaqua Compound

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The structures of diamminediaquabis(5-methyl[1,2,4]triazolo[1,5-a]pyrimidin-7-olato)copper(II), $Cu(C_6H_5N_4O)_2(H_2O)_2(NH_3)_2$ (**1**) and the analogous tetraaqua compound $Cu(C_6H_5N_4O)_2(H_2O)_4$ (**2**) have been determined from X-ray diffraction data. Crystals of both compounds are monoclinic, space group $P2_1/c$, with the following lattice constants: **1**, $a = 8.917$ (2) Å, $b = 13.998$ (2) Å, $c = 7.234$ (5) Å, $\beta = 106.77^\circ$, $Z = 2$; **2**, $a = 9.497$ (3) Å, $b = 13.748$ (2) Å, $c = 6.850$ (4) Å, $\beta = 110.34^\circ$, $Z = 2$. Both compounds appear to have a trans arrangement of the ligands around six-coordinated copper. For **1** Cu-OH₂(ax) is 2.554 (3) Å, Cu-NH₃ is 1.997 (3) Å, and Cu-N(lig) is 2.016 (3) Å. For **2** Cu-OH₂(ax) is 2.391 (2) Å, Cu-OH₂(eq) is 2.066 (2) Å, and Cu-N(lig) is 1.962 (2) Å. The structural features of the compounds are related to their spectral and magnetic properties. Though both compounds are essentially mononuclear, magnetic susceptibility measurements show that **1** has a significant magnetic interaction as deduced from the maximum in the susceptibility at 4.1 K. The magnetic exchange coupling in **2**, though it is isostructural, is much smaller. The different properties are explained by different orbital ground states for the two compounds. The magnetic exchange in the "pseudo linear chains" most likely proceeds through ligand-stacking interactions.

Introduction

Purine and pyrimidine derivatives are known to be metal-binding bases in all kinds of biological processes.¹ Therefore, the binding of metal ions to these types of molecules has been studied extensively during recent years. Studies on the naturally occurring bases in DNA have shown that the purine ligands

frequently use the imidazole type N(7) atom in coordination, but N(9) may also be used.² With adenine there is a bidentate bridge (coordination through N(3) and N(9)) has been reported for several copper(II) compounds^{3,4}. Pyrimidine bases are also known to use N(3) for coordination to a variety of metal ions.⁵ In addition

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