strongly involve the empty iron 4p orbital, which is satisfactorily described by basis II but not by basis I. As can be seen from Table III, the iron p-orbital populations are almost identical in the fragment and in the two complexes (basis I), whereas the population is larger in the CH_2S complex (basis II).

Comparative Study of the Iron–Formaldehyde and Iron–Acetone Bonds. $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ show a bonding structure entirely comparable to the one described for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$. The molecular orbital analysis again shows that in both the iron–tetraphosphine formaldehyde and acetone complexes there is essentially one bonding orbital, i.e. the highest occupied molecular orbital (HOMO), which describes a π-back-donative interaction between the iron d_π orbital and the π^* orbital of formaldehyde and acetone. The fact that bonding is dominated by a net electron charge flow from the iron substrate to the unsaturated ligand is again confirmed by the net negative charge residing on the coordinated ligand (see Table III). From Table II we notice, however, that the formaldehyde adduct of iron–tetraphosphine is found to have a binding energy remarkably higher than that of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. This larger binding energy results from the nearly doubled iron–formaldehyde interaction energy, which overcompensates the increased deformation energy of CH_2O itself. As has previously been discussed,[17] an increase in interaction energy is to be expected upon replacement of carbonyl ligands with the stronger electron donor phosphine ligands, leading to an increased π-back-donative capability of the iron atom toward CH_2O. Indeed, the presence of electron-donor ligands, such as the phosphine, increases the electron density at the iron atom and hence the π-back-donation and the strength of the interaction between Fe and CH_2O. We see from Table III that the increase in Mulliken population (basis I) on formaldehyde upon coordination is 0.64 for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and 0.83 for $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$. This increase of π-back-donation implies an increase of the strength of the iron–formaldehyde bond, as suggested by the interaction energy, which is −45.9 and −86.7 kcal·mol^{-1} for the iron–dicarbonyl–diphosphine and iron–tetraphosphine compounds, respectively (see Table II). The ligand influence can be explained in a different way by considering the energy of the fragment d_π orbital, which lies at −0.2657 au in $Fe(CO)_2(PH_3)_2$ and at −0.1647 au in $Fe(PH_3)_4$. The replacement of CO by PH_3, therefore, decreases the gap between the CH_2O π^* and the fragment d_π orbitals: hence, the overlap increases.

As shown in Table II, the acetone adduct of $Fe(PH_3)_4$ is computed to have a binding energy (−36.8 kcal·mol^{-1}) substantially smaller than that of the corresponding complex of CH_2O (−59.2 kcal·mol^{-1}). The difference in stability of the two complexes is understood by analyzing the deformation and interaction contributions to the binding energy. Once formaldehyde and acetone have undergone the geometry rearrangement required for coordination, they give rise to interactions with the iron substrate of entirely comparable strengths (the interaction energy for acetone is actually computed to be even higher than that for CH_2O). This result is in line with the comparable π^*-orbital energies of CH_2O and CMe_2O, which are computed to be 0.1094 and 0.1356 au, respectively, at the equilibrium geometries and 0.0507 and 0.0582 au, respectively, at the distorted geometries. We are thus led to the interesting conclusion that the lesser overall stability of the acetone complex can be entirely attributed to the higher deformation energy of CMe_2O, which is nearly twice that of CH_2O, rather than to a weaker acidity of the C=O unit.

Conclusions

The study of "ab initio" LCAO–MO–SCF level of the systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ has shown that the main bonding interaction between the iron fragment and the unsaturated molecule is the π-back-donation from the transition metal to the π-acceptor ligand. The π-back-donation is the driving force of the ligand deformation, which allows a better overlap between the π^* ligand and the d_π iron orbitals and therefore leads to an increased interaction energy. The deformation of the unsaturated molecule upon coordination is seen to be satisfactorily reproduced when comparison with experimental data is possible.

Bonding to iron is found to be stronger with thioformaldehyde than with formaldehyde. The reasons are that the former is a better π-acceptor ligand than the latter; furthermore, some nonnegligible contribution to the bonding comes from ligand-to-metal σ-donation.

The π-back-donation is comparable in $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$. Nevertheless, the acetone molecule exhibits a weaker bond than formaldehyde since the destabilization energy required by the geometrical deformation of CMe_2O upon coordination is higher.

Acknowledgment. Thanks are due to the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome) for provision of computing facilities and visiting grants. Support from the Italian National Research Council (CNR), the Ministry of Public Education (MPI), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly acknowledged.

Registry No. $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, 111113-06-5; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, 111113-07-6; $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, 111113-08-7; $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$, 111113-09-8.

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Identification and Characterization of Lithium Polysulfides in Solution in Liquid Ammonia

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Received February 20, 1987

This study uses Raman spectroscopy and UV–visible spectrophotometry for the identification and the characterization of lithium polysulfides in liquid ammonia solutions. It is shown that S_6^{2-} is the least reduced polysulfide; S_6^{2-} is in equilibrium with the radical $S_3^{\bullet-}$. This equilibrium is strongly temperature dependent, and the equilibrium constant is 4.3 × 10^{-3} M at 293 K. A weak disproportionation of S_6^{2-} is shown, through the observation of S_4N^-. The existence of S_4^{2-} in solution is proved. This species was found to disproportionate as demonstrated by the observation of $S_3^{\bullet-}$. The equilibrium constant for the disproportionation of S_4^{2-} is about 10^{-6} M, estimated from the absorbance of $S_3^{\bullet-}$. The disulfide S_2^{2-} exists in solution and has low solubility. The possible existence of S_5^{2-} in solution is also discussed.

Introduction

The aim of the present work is to contribute to the identification and the characterization of the lithium polysulfides in liquid ammonia solutions. Bergstrom,[1] Zintl et al.,[2] Watt and Otto,[3] and Nelson[4] have already contributed to the identification of the alkali polysulfides in solution in liquid ammonia. Nelson[4] was

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[1] Bergstrom, F. W. *J. Am. Chem. Soc.* **1926**, *48*, 146.

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the first, to our knowledge, to give a spectrophotometric characterization of alkali polysulfides in solution in liquid ammonia. He claims that the absorption bands of a given polysulfide do not depend upon the alkali cation in solution. For Nelson,[4] the di-and tetrasulfides are the only polysulfides in solution in ammonia. Letoffe et al.[5] have studied the synthesis of lithium polysulfides from the reaction of lithium and sulfur in liquid ammonia.

The studies aimed at the identification of alkali polysulfides in solution must, of course, take into account some results unknown at the time of the above mentioned papers. The identification of $S_3^{\bullet-}$,[8,9] the study of the equilibrium[15,18,19] between S_6^{2-} and $S_3^{\bullet-}$ in various media, and the synthesis[10] of S_4N^- advanced the understanding of the solutions of sulfur in liquid ammonia. It is now recognized[11,12] that the slow solubilization of sulfur in liquid ammonia is a redox disproportionation process. It has also been observed that the solutions are photosensitive.[11-13] It is now well-known that the solutions of alkali metals in liquid ammonia decompose to give alkali amides; this decomposition is catalyzed by traces of impurities. Such a decomposition must be minimized when alkali metal solutions in liquid ammonia are used for the synthesis of alkali polysulfides. This decomposition induces an error in the stoichiometry of the prepared polysulfide and also basifies the solution. Another point is the possible disproportionation of the polysulfides, well-known in aqueous media.[6,7] In ammonia, only Nelson[4] has considered this possibility.

In the present work, we give the first Raman spectra of solutions of lithium polysulfides in liquid ammonia, together with their absorption spectra. Both types of spectra have been obtained, from 200 K to room temperature, for Li_2S_n–NH_3 solutions with various well-defined values of *n*. From the results, an analysis of the polysulfides existing in solution, together with their spectrophotometric and Raman characterization, is given.

Lithium polysulfides in liquid ammonia are, of course, considered as sulfur–ammonia solutions reduced by a lithium–ammonia solution. Sulfur is solubilized in liquid ammonia by a redox disproportionation process;[11,12] an oxidized species of sulfur in S–NH_3 solutions is S_4N^-, with a visible absorption band at 580 nm; a reduced species of sulfur in these solutions is S_6^{2-}, in equilibrium with the radical anion $S_3^{\bullet-}$. The $S_3^{\bullet-}$ species is well identified[20] by its absorption band at 610 nm and its Raman lines at 535 and 232 cm^{-1}. These characteristics of $S_3^{\bullet-}$ have been observed in various media.[8,9] The equilibrium between S_6^{2-} and $S_3^{\bullet-}$ is known to be temperature dependent.[15] We have proposed[11,12] that the solubilization of sulfur in liquid ammonia could be described by

$$10S + 4NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \tag{1}$$

$$S_6^{2-} \rightleftarrows 2S_3^{\bullet-} \tag{2}$$

However (1) does not describe completely the S–NH_3 solutions, since Raman spectroscopy experiments in resonance conditions at low temperatures (−40 °C) have shown[12] the presence of a small concentration of S_3N^-. This fact is not included in the above equation. The chemical reduction of an S–NH_3 solution by lithium should make the oxidized species in these solutions disappear.

A spectrophotometric characterization of S_6^{2-} will first be presented. The evidence of the weak disproportionation of this species will then be given and the equilibrium between S_6^{2-} and $S_3^{\bullet-}$ quantitatively analyzed. The existence and the characterization of S_4^{2-} will then be presented. It will then be shown that S_6^{2-} is the least reduced lithium polysulfide and that the existence of S_5^{2-} is difficult to ascertain.

Experimental Section

The preparation of a Li_2S_n–NH_3 solution was done in such a way that the average stoichiometry of the polysulfide, i.e. the value of *n*, was a priori chosen, according to reaction 3.

$$nS + 2Li + NH_3 \rightarrow Li_2S_n + NH_3 \tag{3}$$

Lithium metal (Alfa Ventron 3N5), stored in a glovebox with a dry, oxygen- and nitrogen-free argon atmosphere, was taken from freshly cut surfaces and weighed with a precision of ±0.1 mg in the glovebox. Sulfur (Fluka, >99.999%) was used without further purification and weighed with a precision of ± 0.1 mg in the glovebox; the amount of sulfur was adjusted for the preparation of a given Li_2S_n. The glassware was treated by a standard procedure[14] in order to minimize the decomposition of alkali metal–ammonia solutions. The glassware was connected to a vacuum line, pumped down to about 10^{-5} Torr for several hours. Ammonia, dried over potassium, was distilled and condensed into the cell at the temperature of liquid nitrogen. The amount of ammonia was controlled by gas volumetry. All the samples were sealed off. The completion of the reaction was done either at room temperature or at 0 °C. The samples were kept at this temperature for at least 3 days before an absorption or a Raman spectrum was recorded. The preparation of dilute samples (ca. 10^{-3} M) was done in two steps to obtain a satisfactory accuracy for the value of *n* (±0.1).

For all the experiments reported in the present work, there was no indication of decomposition, given by a residual vapor pressure of hydrogen at the temperature of liquid nitrogen.

Quartz optical cells that could sustain ammonia vapor pressure at room temperature were used. These cells have an optical path length of 0.5, 1, or 5 mm. The absorption spectra have been recorded on a Beckman UV–visible 5240 spectrophotometer. The absorption spectra have been recorded versus temperature, between 200 K 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. Raman spectrometers (RAMANOR HG2 and DILOR RT) from the Laboratoire de Spectroscopie Infra-rouge et Raman (LASIR) of the Université de Lille I were used. Raman spectra for the concentrated solutions were obtained with backscattering geometry.

Unless otherwise stated, the concentrations are always given at room temperature. However the absorbance data have been corrected for the thermal variations of the density of the solutions. It was observed that the color of the solutions strongly depends upon *n*, temperature, and concentration. For instance, a dilute (ca. 10^{-3} M) Li_2S_6–NH_3 solution is blue at room temperature, and pale yellow at 200 K, but a concentrated solution (ca. 1 M) has a dark red color at room temperature and turns to bright red at 200 K.

The solutions of lithium polysulfides in ammonia can be prepared with a different procedure, by reaction of sulfur with lithium sulfide. It must be emphasized that reaction of Li_2S with $(n-1)S$ in ammonia gives the same solution as the one prepared by following eq 3, if the latter preparation is free of decomposition. Since commercial Li_2S is often hydrated and is difficult to handle for small quantities because it is finely divided, the present authors have preferred the preparation of the solutions following eq 3. This procedure requires a careful preparation of the glassware but leads to a more accurate value of *n*.

Results

Observation of $S_3^{\bullet-}$ and of S_6^{2-} by Spectrophotometry. We first present the spectrophotometric observation of $S_3^{\bullet-}$ and S_4N^- in Li_2S_n–NH_3 solutions in order to obtain a spectrophotometric

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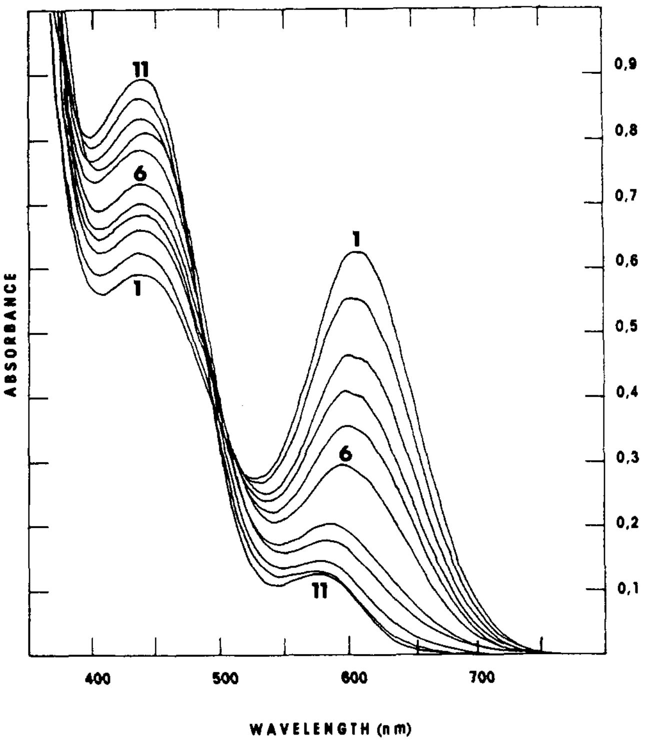

Figure 1. Absorption spectrum of a Li_2S_{10} solution (4.3×10^{-3} M) at different temperatures (K): (1) 294.3; (2) 286.8; (3) 278.8; (4) 273.5; (5) 268.4; (6) 262.5; (7) 247.3; (8) 239.6; (9) 229.4; (10) 219.8; (11) 202.0. Optical path length = 0.5 mm.

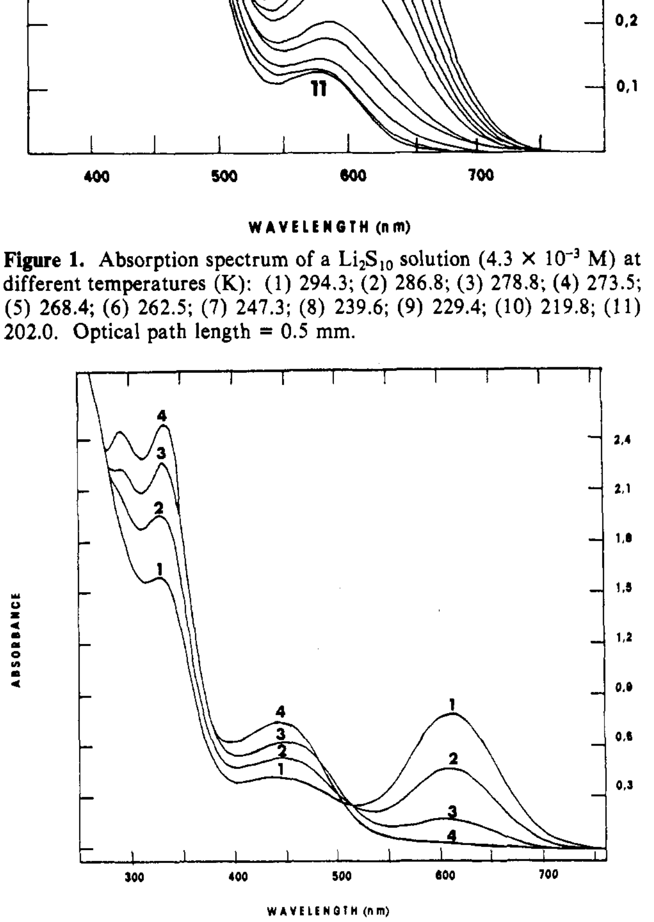

Figure 2. Absorption spectrum of a Li_2S_6 solution (4.3×10^{-3} M) at different temperatures (K): (1) 292.0; (2) 274.2; (3) 253.0; (4) 215.0. Optical path length = 0.5 mm.

characterization of S_6^{2-}. In Figure 1, the variations of the absorption spectrum for a Li_2S_{10} solution (4.5×10^{-3} M) with temperature are given; i.e., the average stoichiometry of this solution is Li_2S_{10}. At room temperature, an absorption band located at 610 nm is observed; this band decreases and shifts as temperature decreases, while a band at 440 nm increases. But, for the lowest temperature studied (200 K), this absorption band does not disappear completely: a small residual absorption band at 580 nm is observed at 200 K. This observation must be compared to the spectra obtained (Figure 2) for a Li_2S_6 solution (4.5×10^{-3} M). For this solution, the band located at 610 nm at room temperature disappears completely at 200 K while the other band in the visible range, near 450 nm, increases. The absorbance obtained at 610 nm at room temperature and the absorbance found at 580 nm at 200 K, are then plotted versus n, for the same concentration of the solutions (Figure 3). Figure 3 shows that the absorbance at 610 nm at room temperature increases sharply between $n = 2$ (for which A(610 nm) is zero) and $n = 6$ and then decreases for $n > 6$. An absorbance at 580 nm and 200 K was not observed for $n < 6.5$ but was observed for $n = 8$ and $n = 10$. The absorbance at 610 nm must be assigned to $S_3^{\bullet -}$ exclusively[8,9] as long as the absorbance at 580 nm at 200 K is equal to zero. This contribution at 580 nm can be assigned to S_4N^-.[10-12]

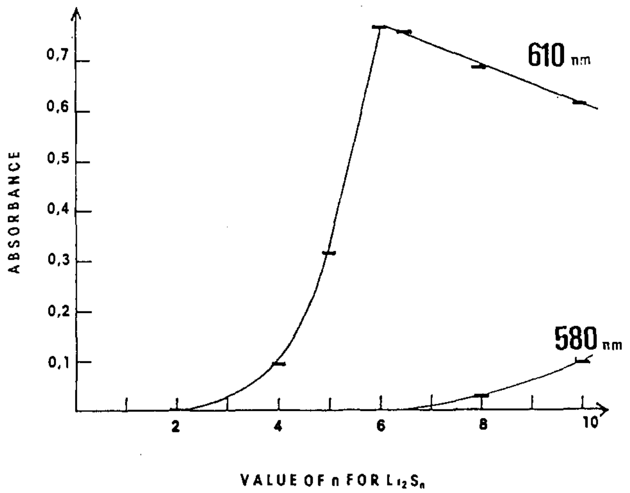

Figure 3. Absorbance $A(610)$ measured at room temperature and absorbance $A(580)$ measured at 200 K for Li_2S_n solutions versus n. All solutions have the same concentration: 4.3×10^{-3} M. Optical path length = 0.5 mm.

The chemical species in equilibrium with $S_3^{\bullet -}$ is S_6^{2-}. The visible absorption band of this species does not have a sharp peak for the maximum. For the sake of simplicity, it will be said that this band is located near 450 nm, but this band slightly shifts (less than 5 nm) toward the higher wavelengths when the concentration increases from 10^{-4} to 10^{-2} M and toward the lower wavelengths when temperature decreases from 300 to 200 K. It must also be mentioned that the UV part of the absorption spectrum of Li_2S_6 is significantly temperature dependent (Figure 2). In these solutions, at low temperatures, two UV bands are well resolved at 290 and 330 nm; they increase when temperature decreases and as the concentration of S_6^{2-} increases. However, the assignments of the UV bands are not going to be discussed in the present paper. The characteristics of the equilibrium between S_6^{2-} and $S_3^{\bullet -}$ will be described below on the basis of the thermal variations of the bands located at 610 nm and near to 450 nm. First, evidence will be given that the anion S_6^{2-}, aside from its dissociation equilibrium with $S_3^{\bullet -}$, is also slightly disproportionated.

Disproportionation of S_6^{2-}. Our Raman experiments under resonance conditions show that S_6^{2-} disproportionates, giving S_4N^- as the oxidized species. However the disproportionation of S_6^{2-} is weak.

The Raman spectra of solutions of Li_2S_5, Li_2S_6, and $Li_2S_{6.5}$ in liquid ammonia (all of concentration 1 M), recorded at room temperature with the 647.1-nm excitation line from an ionized Krypton laser, are displayed in Figure 4. These spectra show the presence of S_4N^- from the Raman line at 710 cm^{-1}. The species S_4N^- has other Raman lines[10-12] at 570, 590, and 898 cm^{-1}, but the line at 710 cm^{-1} is the most intense and is the only line of S_4N^- detected in the spectra of Figure 4. This line was not detected in Li_2S_4 solutions. The reproducibility of the results displayed in Figure 4 and the variations of the results with the value of n show that the observation of S_4N^- cannot be due to the uncertainty on the value of n in Li_2S_n. It was observed that the 710-cm^{-1} line observed at room temperature and shown in Figure 4 has an intensity independent of the duration of the illumination of the sample by the excitation line. However the line at 710 cm^{-1} is no longer observed under illumination at low temperatures and for rather dilute solutions. This finding confirms the attribution of this line to S_4N^-, because the photosensitivity of this species has already been demonstrated.[11-13]

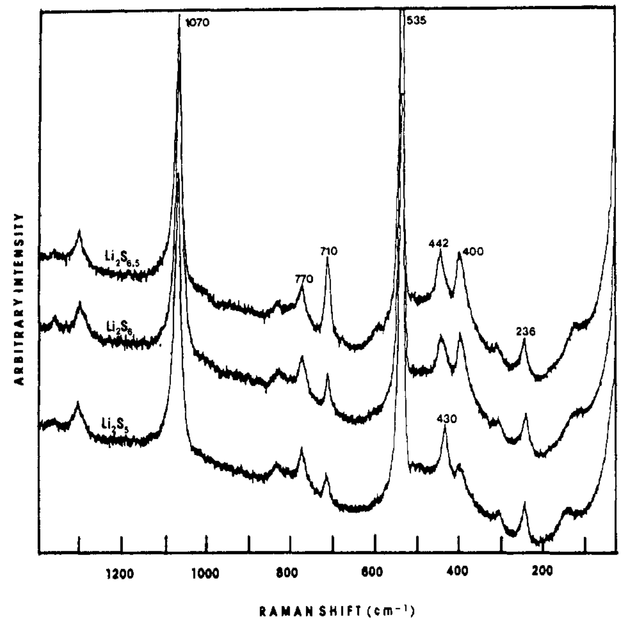

Figure 4. Raman spectra of 1 M Li_2S_5, Li_2S_6, and $Li_2S_{6.5}$ solutions recorded at room temperature, with the 647.1-nm excitation line from an ionized krypton laser.

If S_6^{2-} is the least reduced lithium polysulfide in ammonia, the observation of S_4N^- in a $Li_2S_{6.5}$ solution is understandable, although it could not be evidenced from spectrophotometry experiments. But the observation of S_4N^- in Li_2S_6 and in Li_2S_5 shows that S_6^{2-} and S_5^{2-} are disproportionated. The production of S_4N^- from the disproportionation of S_6^{2-} and of S_5^{2-} is probably the result of several steps that will not be discussed herein.

The amount of the disproportionation of S_6^{2-} cannot be estimated. We have mentioned in the previous section that a solution of $Li_2S_{6.5}$ (1.5×10^{-2} M) does not display, for a 0.5-mm optical path length, a contribution to the absorbance from S_4N^- at 200 K. Therefore this contribution from S_4N^- must be considered as lower than 0.005. We have estimated[12] recently the extinction coefficient of S_4N^- to be about 7290 M^{-1} cm^{-1} in S–NH$_3$ solutions, while Chivers et al.[10] have proposed a value of 16 000 M^{-1} cm^{-1} for a salt of S_4N^- in acetonitrile. One can therefore conclude that a $Li_2S_{6.5}$ solution (1.5×10^{-2} M) contains less than 10^{-5} M of S_4N^-, i.e. less than 10^{-3} S_4N^- per S_6^{2-}. The concentration of S_4N^- should therefore be lower for solutions of Li_2S_5 and Li_2S_6 of a concentration of 1.5×10^{-2} M. One can now try to determine the concentration of S_4N^- corresponding to a Li_2S_6 solution (1 M) (Figure 4). The determination of the concentration of S_4N^- in this solution is not possible from spectrophotometry experiments. However, it is obvious that the disproportionation of S_6^{2-} will not increase with concentration. Therefore, the relative concentration of S_4N^- observed for 1 M solution (Figure 4) is certainly less than 10^{-3} M. The observation of S_4N^- in 1 M solutions (Figure 4) is made possible in Raman spectroscopy with resonance conditions, obtained with the 647.1- or the 514.5-nm excitation line. It is understandable that it was not possible to detect any temperature dependence of such a weak disproportionation.

The weak disproportionation of S_6^{2-}, evidenced by the oxidized species S_4N^-, must also produce a reduced form of sulfur. It is shown below that the polysulfide S_4^{2-} exists in liquid ammonia and that S_5^{2-} cannot be identified but could be considered. It can therefore be postulated that the disproportionation of S_6^{2-} produces also S_5^{2-} and/or S_4^{2-}, but S_4^{2-} cannot be detected at a concentration on the order of 10^{-3}–10^{-2} M when there is a much higher concentration of S_6^{2-}. Therefore, the disproportionation of S_6^{2-} can only be shown through the observation of S_4N^-.

Dimerization Equilibrium between $S_3^{\bullet-}$ and S_6^{2-}. The absorption spectra of Li_2S_6 solutions (Figure 2) show that when the temperature decreases, the absorption band of $S_3^{\bullet-}$ at 610 nm decreases while the absorption band at 450 nm increases. This is interpreted as the dimerization of $S_3^{\bullet-}$ into S_6^{2-}, which is complete at a temperature of about 200 K (Figure 2). We will now determine the equilibrium constant from the variations of the absorbance with temperature.

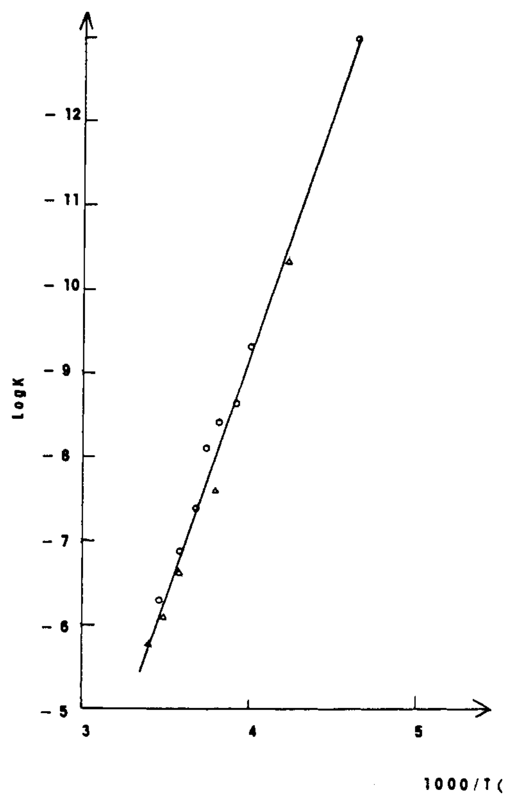

Figure 5. log K versus $1/T$ for two Li_2S_6 solutions: (○) 1.5×10^{-2} M; (△) 4.3×10^{-3} M.

For a Li_2S_6 solution at 200 K, we consider, following the experimental result, that $S_3^{\bullet-}$ is completely dimerized and the weak disproportionation of S_6^{2-} is ignored. At 200 K, let C_0 be the concentration of S_6^{2-}. Given α, the dissociation coefficient of S_6^{2-} for temperatures above 200 K, the S_6^{2-} concentration is $C_0(1 - \alpha)$ and the $S_3^{\bullet-}$ concentration is $2C_0\alpha$. It is then easily shown that $A(450)$ is related to $A(610)$ by

$$A(450) = -\frac{\epsilon(450)}{2\epsilon(610)}A(610) + C_0\,\epsilon(450)\,d \qquad (4)$$

where $\epsilon(\lambda)$ is the extinction coefficient of the species absorbing at λ, and d is the optical path length. Equation 4 implies a linear relationship between $A(450)$ and $A(610)$. The experimental low-temperature absorbances display a deviation from such a linear relation. However, when the experimental absorbance data are corrected for the thermal variations of the density of the solution, a linear variation is obtained between $A(450)$ and $A(610)$. It is necessary to make this correction to obtain accurately the values of the extinction coefficients and the variation of the equlibrium constant with temperature.

The corrected value of $A(450)$, read when $A(610) = 0$, allows the determination of $\epsilon(450)$, found to be equal to 2450 ± 150 M^{-1} cm^{-1}. The slope of the linear relation between $A(450)$ and $A(610)$ is −0.24. Following (4) and the $\epsilon(450)$ value, the extinction coefficient $\epsilon(610)$ is 5100 ± 300 M^{-1} cm^{-1}. This value is close to those given in the literature, between 3800 and 4850 M^{-1} cm^{-1} for various solvents.[15-19] However, the value obtained for S_6^{2-} is rather different from published values, but the absorption band of S_6^{2-} has been reported at various wavelengths for different solvents: for CH$_3$CN,[17] 450 nm and 3100 M^{-1} cm^{-1}; for DMSO,[16] 475 nm and 3800 M^{-1} cm^{-1}.

The values obtained for the extinction coefficients of S_6^{2-} and $S_3^{\bullet-}$ and the assumption that they are temperature and concentration independent allow the determination of the dissociation constant K in the temperature range between 200 and 298 K. These values are reported in Figure 5 for two Li_2S_6 solutions. The

Table I. Raman Lines (cm^{-1}) of M_2S_4 Solids and M_2S_4 Solutions

	solid Na_2S_4[21]	solid K_2S_4[23]	solid Cs_2S_4[24]	aqueous Na_2S_4[22]	Na_2S_4 in alcohol[21]	Li_2S_4 in NH_3 at 293 K[a]	Li_2S_4 in NH_3 at 100 K[a]	Na_2S_4 in NH_3 at 293 K[a]
1 ($S_3^{\bullet -}$)					535 m	535 w		535 vs
2							494 w	
3	483 s	485 s	494 ms	484 ms	491 m	490 m	488 m	485 m
4	469 ms	478 sh	483 ms		475 w	472 m	476 m	469 m
5	445 vs	434 s	433 s	446 s	450 vvw	430 vs	439 vs	437 vs
6			422 s	410 ms	413 m			
7	241 w	266 m	250 m 240 w	256 w	247 mw	236 vw	235 w	
8	212 m	220 m	209 s 195 s	194 w	195 mw	188 vs	195 vs	191 vs
9	98 ms		140 m	144 vw	140 w		117 w	

[a] Present work.

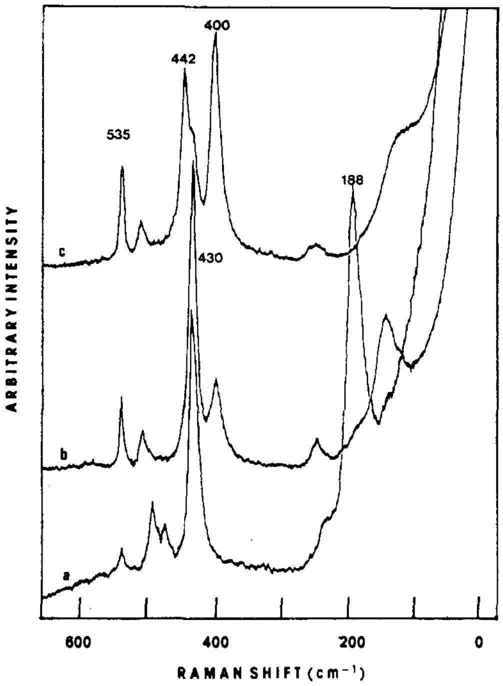

Figure 6. Raman spectra of Li_2S_n solutions recorded with the 647.1-nm excitation line: (a) Li_2S_4 (1.5 M) at room temperature; (b) Li_2S_5 (1 M) at 200 K; (c) Li_2S_6 (0.1 M) at 200 K.

dissociation equilibrium constant at 298 K is 4.3 × 10^{-3} M, and the enthalpy ΔH is 48 kJ M^{-1}.

Existence and Disproportionation of S_4^{2-} in Ammonia Solutions. Several recent papers have been concerned with the Raman characterization of sodium,[21,22] potassium,[23] and cesium[24] tetrasulfides in the crystalline or in the molten state (Table I). The coherence of these various experiments suggests that they are indeed a characterization of the tetrasulfide anion. The comparison of these results with our results (Table I) indicates that the S_4^{2-} anion exists in lithium polysulfides–ammonia solutions, but is disproportionated. The identification of S_4^{2-} in solution by Raman spectroscopy allows us to assign the corresponding absorption spectra.

A typical Raman spectrum of a solution of average stoichiometry Li_2S_4 (1.5 M) and the Raman spectra of Li_2S_6 (0.1 M) and Li_2S_5 (1 M) solutions are given in Figure 6. The measured frequencies for the Li_2S_4 sample, in the liquid and in the frozen state, are reported in Table I, together with the frequencies observed for the Na_2S_4, K_2S_4, and Cs_2S_4 solids. The Raman spectrum of a Li_2S_4–NH_3 solution (Figure 6) displays at 535 cm^{-1} a line that shows the existence of $S_3^{\bullet -}$ in these solutions, which will be confirmed by the spectrophotometry experiments. The line at 535 cm^{-1} decreases when the temperature decreases. This line is not observed when the solution is frozen. The observation of $S_3^{\bullet -}$ in Li_2S_4–NH_3 solutions shows the disproportionation of S_4^{2-}, but it must be emphasized that neither the Raman spectra nor the absorption spectra display, even at 200 K, the previously mentioned characteristics of S_6^{2-}.

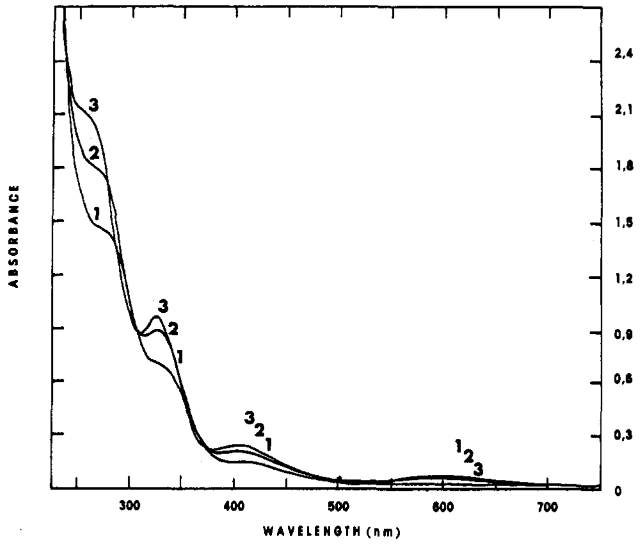

Figure 7. Absorption spectrum of a Li_2S_4 solution (3.1 × 10^{-3} M) at different temperatures (K): (1) 290.0; (2) 266.0; (3) 200.0 Optical path length = 0.5 mm.

The comparison of the Raman spectra of Li_2S_4–NH_3 solutions and of M_2S_4 solids enables us to say that S_4^{2-} exists in solution in ammonia. However a significant difference is observed. The relative intensity of the Raman line at 188 cm^{-1} is higher than that observed for solid M_2S_4, except for Cs_2S_4.[24] This high relative intensity for the line around 190 cm^{-1} was also observed[28] in a Na_2S_4–NH_3 solution (column 8 of Table I) (obtained from Na_2S_4 prepared in situ) and in K_2S_4–NH_3 solutions.[28] However, a Raman line was also observed[28] around 190 cm^{-1} in $(NH_4)_2S_4$–NH_3 solutions, but with a smaller relative intensity. It was found[28] that S_4^{2-} is more disproportionated in $(NH_4)_2S_4$ than in Li_2S_4. This suggests that the intense 188-cm^{-1} line cannot be due to a species resulting from the disproportionation of S_4^{2-}. The same conclusion can be reached from the fact that the intensity of the line at 188 cm^{-1} decreases as soon as the average stoichiometry is slightly smaller or higher than 4. The high relative intensity of this line appears to characterize the alkali tetrasulfides in liquid ammonia.

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It can be concluded that the Raman spectra of Li_2S_4–NH_3 solutions show the existence of S_4^{2-} and $S_3^{\bullet-}$ in solution but do not display lines that could be assigned to S_6^{2-} or to a another polysulfide, even for the concentrated solutions (1–3 M) we have studied.

Absorption Spectrum of S_4^{2-}. The absorption spectrum of Li_2S_4–NH_3 solutions is now presented (Figure 7). An absorption band is observed at 610 nm; this band decreases when the temperature is decreased and disappears at about 200 K. This absorption band corresponds to the 535-cm^{-1} Raman line and is assigned to $S_3^{\bullet-}$. Another absorption band is observed in the visible range at 410 nm. The absorbance of this band increases when the temperature is decreased (Figure 7); an isobestic point is observed between the 410- and the 610-nm bands. The absorbance of the 410-nm band, $A(410)$, is linearly related to the absorbance of the 610-nm band, $A(610)$, when the experimental data are corrected for the thermal variations of the density. We assign the band located at 410 nm to S_4^{2-}. The bands located at 330 and 250 nm have the same thermal variations as the band located at 410 nm and are also assigned to S_4^{2-}.

The presence of $S_3^{\bullet-}$ indicates the disproportionation of S_4^{2-}. The simplest hypothesis for the corresponding disproportionation equation, since neither S_5^{2-} nor S_3^{2-} are presently identified, is

$$2S_4^{2-} \rightleftarrows S_6^{2-} + S_2^{2-} \tag{5}$$

with S_6^{2-} in equilibrium with $S_3^{\bullet-}$ (eq 2). The decrease of the temperature leads to the dimerization of $S_3^{\bullet-}$ into S_6^{2-}. However, there is no direct evidence of either S_6^{2-} or S_2^{2-} in Li_2S_4–NH_3 solutions. The absorption band of S_6^{2-} has been observed at 450 nm in Li_2S_6–NH_3 solutions, but the absorption band of S_4^{2-} at 410 nm increases without shift or deformation when the temperature decreases (Figure 7). The Raman spectra of Li_2S_4–NH_3 solutions do not give evidence of S_6^{2-} or S_2^{2-}. Therefore, in these solutions, S_6^{2-} is detected neither by spectrophotometry nor by Raman spectroscopy. This suggests that the disproportionation equilibrium of S_4^{2-} could be written

$$2S_4^{2-} \rightleftarrows 2S_3^{\bullet-} + S_2^{2-} \tag{6}$$

Such an equilibrium has already been proposed by Martin et al.[19] for S_4^{2-} in DMSO. If the extinction coefficient of $S_3^{\bullet-}$ (5100 ± 300 M^{-1} cm^{-1}) deduced from the analysis of Li_2S_6–NH_3 solutions is used for Li_2S_4–NH_3 solutions, the proportion of $S_3^{\bullet-}$ at room temperature is between 5 and 10% of the analytical concentration of the solution. This disproportionation explains why S_2^{2-} is not observed. Equation 6 leads to a disproportionation constant on the order of 10^{-6} M. However, the determination of the extinction coefficients of the chemical species in these solutions leads to unsolved contradictions. The disproportionation equation of S_4^{2-} (eq 6) leads to a linear relation between $A(410)$ and $A(610)$:

$$A(410) = -\frac{\epsilon(S_4^{2-})}{\epsilon(S_3^{\bullet-})}A(610) + \epsilon(S_4^{2-})\, dC_0 \tag{7}$$

where d is the optical path length and C_0 is the analytical concentration of the solution at a given temperature. The linear relation between $A(410)$ and $A(610)$ is indeed observed experimentally. The value of $A(410)$, when $A(610)$ is zero, leads to $\epsilon(S_4^{2-}) = 1100 \pm 100$ M^{-1} cm^{-1}. This result is close to the corresponding value given by Martin et al.[19] However the slope of the linear relation between $A(410)$ and $A(610)$ is −0.5 ± 0.1, and this leads to a value of about 2000 M^{-1} cm^{-1} for $S_3^{\bullet-}$, which is 2.5 times smaller than the value obtained from Li_2S_6–NH_3 solutions. Such a contradiction suggests that other equilibria could possibly be involved. Equation 6 implies that S_5^{2-} does not exist in solution in ammonia or, differently stated, is completely disproportionated. The possible existence of S_5^{2-} in ammonia solutions will be examined in the discussion section.

Li_2S_n–NH_3 Solutions with $n < 4$. These solutions are much less colored than those with $n > 4$. Their clear yellow color is approximately temperature independent. These solutions are all saturated for concentrations of ca. 10^{-3}–10^{-2} M (respectively to Li_2S_n).

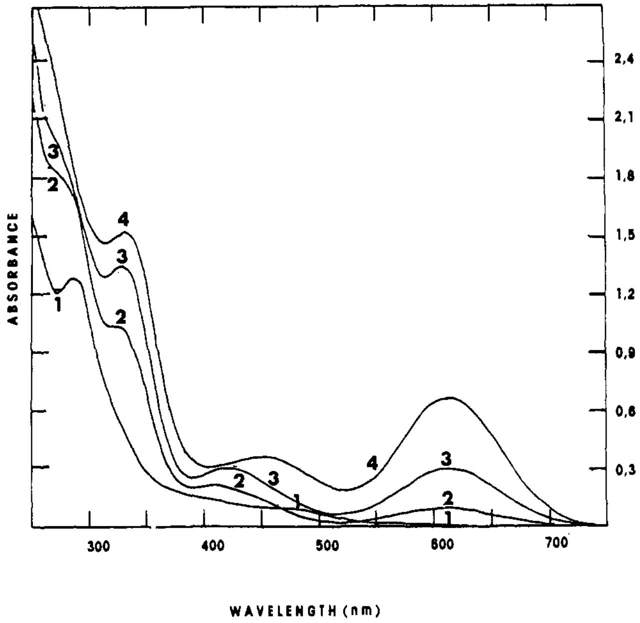

Figure 8. Absorption spectra, at room temperature, of Li_2S_n solutions: (1) Li_2S_2; (2) Li_2S_4; (3) Li_2S_5; (4) Li_2S_6. Optical path length = 0.5 mm. All the solutions have been prepared with the same concentration (4.3 × 10^{-3} M), but Li_2S_2 is saturated.

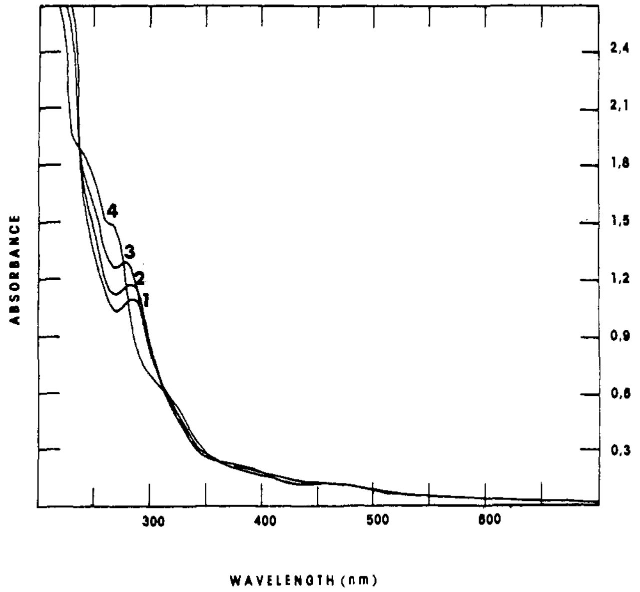

Figure 9. Absorption spectrum of a Li_2S_2 solution (4.3 × 10^{-3} M), at different temperatures (K): (1) 291.6; (2) 257.4; (3) 226.3; (4) 203.0. Optical path length = 0.5 mm.

Raman spectra have been obtained for saturated $Li_2S_{3.5}$–NH_3 solutions, which have only shown the presence of S_4^{2-}. Satisfactory Raman spectra have not been obtained for $n < 3.5$, because a thin solid layer was rapidly deposited at the impact of the laser beam even for a low power on the order of 50 mW. This film was characterized by a single Raman line located at 378 cm^{-1}. The origin of this band is not understood. We have verified with Raman spectroscopy the observation of Letoffe et al.[5] that dry Li_2S_2 is not thermally stable and decomposes to give Li_2S and S_8.

The absorption spectra for Li_2S and Li_2S_2 solutions in ammonia have been recorded. The absorption spectrum of a Li_2S_2–NH_3 solution is given in Figure 9 for various temperatures. The absorption spectrum of a Li_2S–NH_3 solution at 200 K is given in Figure 10 and compared with the absorption spectra obtained for solutions of higher values of n. The Li_2S_2 and Li_2S solutions have been prepared with concentrations equal to 4.3 × 10^{-3} and 1.7 × 10^{-3} M, respectively. However, it is very important to note that they are both saturated in the temperature range between 200

Table II. Comparison of the Experimental and Calculated Concentrations (M × 10^3) of S_6^{2-} in Li_2S_8 and Li_2S_{10} at 200 and 293 K[a]

	200 K		293 K				
	$[S_6^{2-}]^{\text{exptl}}$	$[S_6^{2-}]^{\text{calcd}}$	$[S_3^{\bullet-}]^{\text{exptl}}$	$[S_6^{2-}]^{\text{exptl}}$	$[S_6^{2-}]^{\text{tot exptl}}$	$[S_6^{2-}]^{\text{tot calcd}}$	dissoc const *K*
Li_2S_8	7	7	2.6	4.2	5.5	5.9	1.22
Li_2S_{10}	7.13	7.14	2.2	4.5	5.6	6.03	1.1

[a] All values have been multiplied by 10^3. The concentration of the Li_2S_8 solution is 4.9 × 10^{-3} M at 293 K and 5.8 × 10^{-3} M at 200 K. The concentration of the Li_2S_{10} solution is 4.3 × 10^{-3} M at 293 K and 5.1 × 10^{-3} M at 200 K.

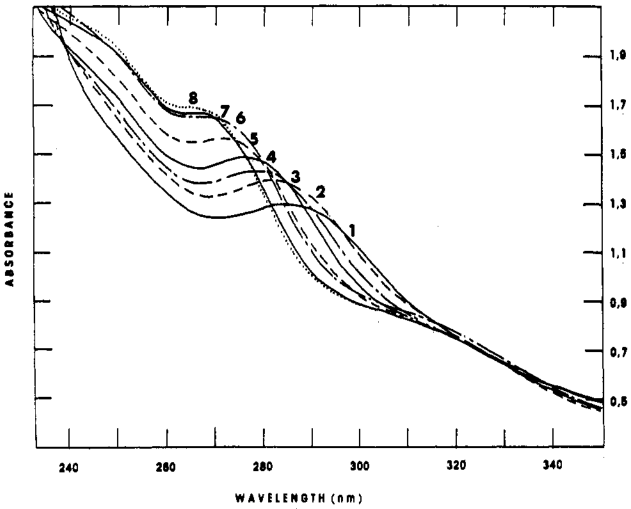

Figure 10. Absorption band observed at different temperatures (K) at about 285 nm in a Li_2S_2 solution (4.3 × 10^{-3} M, but saturated): (1) 291.6; (2) 274.4; (3) 257.4; (4) 242.5; (5) 226.3; (6) 215.2; (7) 208.0; (8) 203.0.

and 300 K. The absorption spectrum of Li_2S_2 (Figure 9) displays a UV band at 285 nm at room temperature, but when the temperature is decreased, weak bands or shoulders are observed at 250, 330, 380, and 460 nm. For the Li_2S_2–NH_3 solutions, an absorption band at 610 nm was never observed, and this can be seen as the best indication that S_2^{2-} is not significantly disproportionated. The absorption band observed around 285 nm in Li_2S_2–NH_3 displays an important temperature dependence, which is detailed in Figure 10. The variation of the energy $E_{\max}$ of this band versus the temperature is linear, except for the lowest temperatures, for which the resolution becomes less favorable. However the thermal variations of this band are interpreted as the signature of a ctts band.[26] The slope of the linear part of $E_{\max}$ versus temperature gives for $dE_{\max}/dT$ a value of 69 cal deg^{-1}. Similar variations attributed to ctts bands have been observed by Nelson and Lagowski[27] in H_2S–NH_3 and K_2S–NH_3 solutions, with $dE_{\max}/dT$ equal to 68 and 77 cal deg^{-1}, respectively. The comparison of the absorption spectra of Li_2S_2 and Li_2S (Figures 9 and 11) shows that the 285-nm band in Li_2S_2 must be assigned to S_2^{2-} and not to S^{2-}. However the position of the band around 285 nm in Li_2S was also observed to be temperature dependent, and a value of 68 cal $deg.^{-1}$ is obtained for $dE_{\max}/dT$. The observations of Nelson and Lagowski[27] for the ctts band in H_2S–NH_3 in the temperature range between 200 and 300 K have been confirmed.[28]

Discussion

Is S_6^{2-} the Least Reduced Lithium Polysulfide in Liquid Ammonia? This question is related to the interpretation of the *A*(610) versus *n* plot (Figure 3); the maximum of *A*(610) is obtained for $n = 6$.

A naive approach is to say that if S_6^{2-} is the least reduced polysulfide, a Li_2S_n solution with $n > 6$ can be viewed approximately as the addition of a Li_2S_6 solution and a sulfur ammonia solution resulting from the solubilization of the sulfur in excess ($(n - 6)$S). This approach suggests that a Li_2S_n solution with $n > 6$ contains more $S_3^{\bullet-}$ than a Li_2S_6 solution of the same concentration because the sulfur–ammonia solution contains $S_3^{\bullet-}$.[11,12,20]

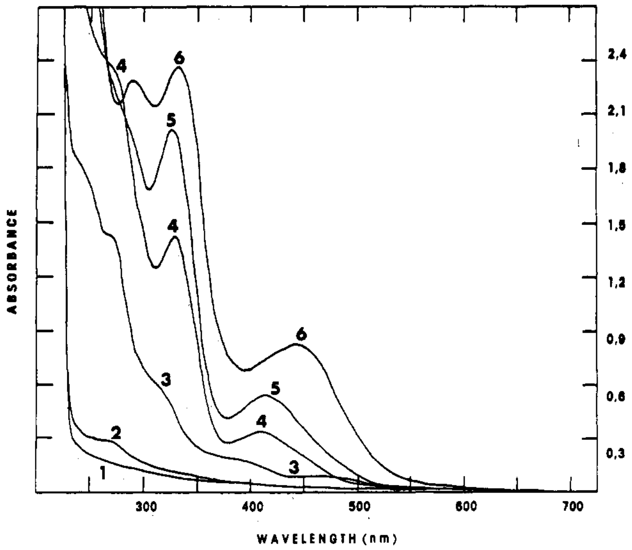

Figure 11. Absorption spectra of Li_2S_n–NH_3 solutions at about 200 K: (1) pure NH_3; (2) Li_2S (1.4 × 10^{-3} M, but saturated); (3) Li_2S_2 (5.1 × 10^{-3} M, but saturated); (4) Li_2S_4 (5.1 × 10^{-3} M); (5) Li_2S_5 (5.1 × 10^{-3} M); (6) Li_2S_6 (5.1 × 10^{-3} M). Optical path length = 0.5 mm.

Therefore, this approach cannot explain that *A*(610) is a maximum for $n = 6$.

The previous analysis could lead to the conclusion that a S_n^{2-} polysulfide with $n > 6$ exists and gives $S_3^{\bullet-}$ through disproportionation processes.[15,19] In some solvents, the existence of S_8^{2-} has been shown[15,18,19,29] with an absorption band between 480 and 520 nm. It is obvious that such a band does not exist in the solutions we have studied. In the Li_2S_n solutions with $n > 6$, there is no spectroscopic indication of chemical species other than S_6^{2-}, $S_3^{\bullet-}$, and S_4N^-. However another point must be taken into account. If S_6^{2-} is the highest polysulfide, Li_2S_n solutions with $n > 6$ contain NH_4^+ and are acidic. We have shown in the study of the ammonium polysulfides[28] in ammonia solutions that S_6^{2-} is less dissociated in ammonium polysulfides than in lithium polysulfides. This could explain why for Li_2S_n with $n > 6$ the concentration of $S_3^{\bullet-}$ is smaller than expected, because the Li_2S_n solutions are acidic for $n > 6$. This was directly confirmed[28] by the progressive introduction of NH_4Cl into a Li_2S_6 solution. It was then observed that the absorbance at 610 nm decreases when NH_4Cl is added.

The analysis of the spectrophotometry experiments for $n > 6$ is compatible with the hypothesis that S_6^{2-} is the least reduced polysulfide. For such solutions, the concentration of S_6^{2-} at 200 K can be calculated with the hypotheses that S_6^{2-} is the highest polysulfide and that the excess sulfur is solubilized according to eq 2; this means that the sulfur is excess gives one S_6^{2-} per 10 S. For these hypotheses, for the Li_2S_8 and Li_2S_{10} solutions we have studied, the calculated S_6^{2-} concentrations at 200 K were respectively 7 × 10^{-3} and 7.13 × 10^{-3} M. From the absorption spectra of these solutions at 200 K, the concentrations of S_6^{2-} are found (Table II) (by using $\epsilon(S_6^{2-})$ = 2450 M^{-1} cm^{-1}) to be equal to 7 × 10^{-3} and 7.13 × 10^{-3} M for Li_2S_8 and Li_2S_{10}, respectively. This indicates that the mentioned hypotheses allow an accurate

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determination of the concentration of S_6^{2-}.

At temperatures higher than 200 K, the concentration of $S_3^{\bullet -}$ depends upon the dissociation constant between S_6^{2-} and $S_3^{\bullet -}$. The present analysis, summarized in Table II, suggests that the dissociation constant of S_6^{2-} decreases when n increases from $n = 6$ to $n = 10$. At room temperature (293 K), for those Li_2S_8 and Li_2S_{10} solutions, the experimental absorbance at 610 nm can be corrected for the small contribution of S_4N^- measured at 200 K and assumed to be temperature independent; this corrected absorbance at 610 nm can then be used to obtain the $S_3^{\bullet -}$ concentration by using the value $\epsilon(S_3^{\bullet -}) = 5000\ M^{-1}\ cm^{-1}$. The absorbance at 440 nm can be used to obtain the concentration of S_6^{2-}. These concentrations of S_6^{2-} and $S_3^{\bullet -}$ can be used to obtain the total concentration of S_6^{2-} at 293 K, from

$$[S_6^{2-}]^{\text{tot exptl}} = [S_6^{2-}]^{\text{exptl}} + \tfrac{1}{2}[S_3^{\bullet -}]^{\text{exptl}} \qquad (8)$$

This experimental total concentration of S_6^{2-} can be compared to the calculated total concentration, obtained with the previously mentioned hypotheses. The comparison of these quantities is not as satisfactory as at 200 K, but still suggests that the existence of a polysulfide S_n^{2-} with $n > 6$ is unlikely. The experimental concentrations of $S_3^{\bullet -}$ and S_6^{2-} at 293 K also allow the determination of the dissociation constant K of S_6^{2-}. The values obtained for K (Table II) are found, as expected, to be lower than the corresponding value in Li_2S_6.

It can therefore be concluded that the existence of a polysulfide S_n^{2-} with $n > 6$ is unlikely and that the decrease of $A(610)$ for $n > 6$ (Figure 3) is a consequence of the lesser dissociation of S_6^{2-} in these solutions, due to the presence of NH_4^+. Simultaneously, the concentration of S_4N^- is less than expected from the above-mentioned naive hypotheses. Therefore, for $n > 6$, S_6^{2-} and S_4N^- have both a concentration lower than expected. This suggests that they are involved in chemical equilibria with other species not directly identified.

Does S_5^{2-} Exist in Solution in Ammonia? In Figure 8, the absorption spectrum at room temperature of a Li_2S_5–NH_3 solution is given, together with the spectra of Li_2S_4 and Li_2S_6 solutions at the same concentration. For each solution, a band is observed at 610 nm and assigned to $S_3^{\bullet -}$. The other band of the visible range is located at 420 nm for the Li_2S_5–NH_3 solution, and a linear relation is obtained between $A(420)$ and $A(610)$ when the temperature is decreased; the band at 420 nm increases and shifts slightly towards the lower wavelengths when the temperature is decreased (415 nm at 200 K). The observation of $S_3^{\bullet -}$ indicates at least a partial disproportionation of S_5^{2-}. However, the absorption spectrum of a Li_2S_5–NH_3 solution cannot be interpreted simply by a complete disproportionation of S_5^{2-}

$$2S_5^{2-} \rightleftarrows S_6^{2-} + S_4^{2-} \qquad (9)$$

The experimental absorbance of $S_3^{\bullet -}$ at 610 nm is not significantly different from the value expected from eq 9, and from the experimental absorption spectra of Li_2S_6 and Li_2S_4 solutions. However, the absorption band observed experimentally at 420 nm is narrower and better shaped than the absorption band that would result from the superposition, in the 400–500-nm range, of the spectra of the Li_2S_6 and Li_2S_4 solutions. Therefore, it is difficult to conclude, from the absorption spectra, that S_5^{2-} is completely disproportionated. It was hoped that S_5^{2-} could be detected by Raman spectroscopy. The Raman spectra of Na_2S_5 (of different crystalline forms), K_2S_5, and $(NH_4)_2S_5$ have been published.[22,23,25] Steudel and Schuster[25] have also indicated that $(NH_4)_2S_5$ is disproportionated when it dissolves in liquid ammonia. The Raman spectra of Li_2S_n–NH_3 solutions, at room temperature, are given in Figure 6 for $n = 4$, 5, and 6. Can the spectrum obtained for Li_2S_5–NH_3 give evidence of S_4^{2-}, S_6^{2-} or S_5^{2-}? This spectrum does not display the intense 188-cm^{-1} line observed in all the Li_2S_4–NH_3 solutions studied, even the moderately concentrated one (0.5 M). This spectrum displays a medium line at 400 cm^{-1}, which could be assigned to S_6^{2-}. However, the overall spectrum is somewhat similar to the spectra[22] of solid Na_2S_5. This observation, together with the absence of the relatively intense line at 188 cm^{-1}, observed in Li_2S_4 solutions, could lead to the conclusion of the existence of S_5^{2-}, partially disproportionated. However, it can be thought that the relatively high intensity sometimes observed for the line at 188 cm^{-1} could result from a small structural change of the S_4^{2-} species, resulting from the interactions of this species with the other species in solution. Obviously, if S_5^{2-} is completely disproportionated, it is difficult to interpret the absorption spectrum of Li_2S_5–NH_3, but if S_5^{2-} is not completely disproportionated, there is no unambiguous spectroscopic signature of this species. It will be concluded that the existence of S_5^{2-} cannot be presently ascertained, but the existence of S_5^{2-} should have important consequences on the equilibria between the polysulfides in ammonia solutions.

Conclusion

The present work confirms the complexity of polysulfides solutions, well established in aqueous media.[30] This complexity arises from the overlap of chemical equilibria. An important difference with aqueous polysulfides solutions is the existence, in ammonia, of S_6^{2-}. From the present work, S_6^{2-} (in equilibrium with $S_3^{\bullet -}$), S_4^{2-}, S_2^{2-}, and S^{2-} have been identified in ammonia. The S_6^{2-} and S_4^{2-} polysulfides are very soluble, but S_2^{2-} and S^{2-} are not. The S_6^{2-} and S_4^{2-} polysulfides are disproportionated. The existence of polysulfides less reduced than S_6^{2-} is unlikely, that of S_5^{2-} is questionable, and that of S_3^{2-} is also unlikely. $S_3^{\bullet -}$ is found to be the only radical in these solutions. It appears that Raman spectroscopy is essential for the identification of polysulfides species, but spectrophotometry is required for a quantitative approach of the chemical equilibria.

Acknowledgment. We are grateful to the Laboratoire de Spectroscopie Infrarouge et Raman (LASIR) de l'Université de Lille 1, for the use of their Raman spectrometers. We thank Drs. Lorriaux, Chapput, and de Bettignies, for experimental assistance and Dr. Corset for helpful discussions. This research was supported by the CNRS (ATP Application de l'électricité à la chimie No. 249) and by the AFME (Décision d'aide à la Recherche No. 42139261). We also thank Dr. F. X. Sauvage for a critical reading of the manuscript.

Registry No. NH_3, 7664-41-7; S_6^{2-}, 12597-13-6; $S_3^{\bullet -}$, 12597-04-5; S_4^{2-}, 12597-07-8; S_5^{2-}, 12597-12-5; S_4N^-, 51330-98-4; lithium polysulfide, 74432-42-1.

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