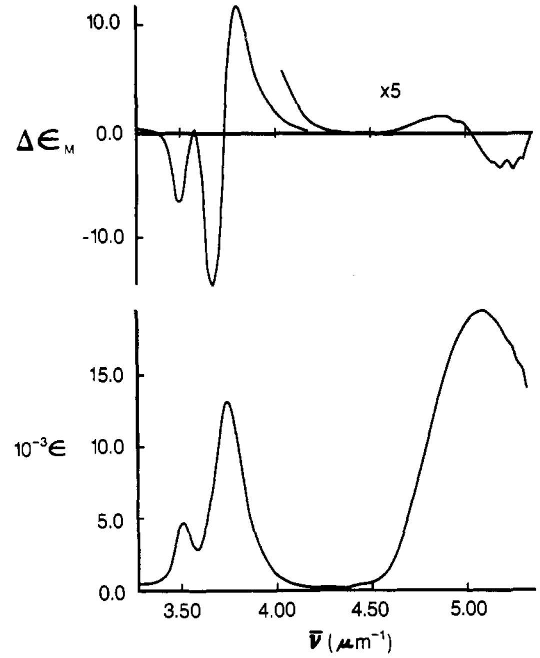

Figure 2. MCD (upper curves) and absorption (lower curve) spectra for aqueous solutions of $K_2Ni(CN)_4$. The MCD data between 4.1 and 5.3 μm^{-1} were multiplied by a factor of 5 before plotting.

analysis[2] noted that the $\mathcal{A}$ term for the 3.7-μm^{-1} band was also larger than could be explained on the basis of the $3d_{xz}3d_{yz}$ orbitals alone and explained the larger magnitude in terms of a pseudo $\mathcal{A}$ term contribution originating from $\mathcal{B}$ terms of opposite sign for the E_u state and a neighboring A_{2u} state at 3.5 μm^{-1}, which originates from the $a_{1g}(z^2) \rightarrow a_{2u}$ excitation. An upper limit of $\bar{\mathcal{A}}_1/\bar{\mathcal{D}}_0$ was estimated to be +2.6 (see ref 2 for details). Thus, it appears that the earlier interpretation[2] including the pseudo $\mathcal{A}$ term contribution provides a better explanation of the magnitude of the $\mathcal{A}$ term for the 3.7-μm^{-1} band than does the ADFM proposal. The negative $\mathcal{A}$ term observed cannot be explained by the ADFM assignment. However, the excitation $a_{1g}(z^2) \rightarrow e_u$, which would be expected at slightly higher energies than the $3d \rightarrow a_{2u}$ excitations, is expected to give an $\mathcal{A}$ term the same in magnitude but opposite in sign compared to the $\mathcal{A}$ term for the $b_{2g}(xy) \rightarrow e_u$ excitation or $\bar{\mathcal{A}}_1/\bar{\mathcal{D}}_0 = \sim -0.3$, on the basis of the earlier estimates.[2] This value compares favorably with the observed value (−0.15). Therefore, the assignment of the 5.0-μm^{-1} band to the $a_{1g}(z^2) \rightarrow e_u$ excitation is proposed here.

In conclusion, the MCD results reported here and earlier[2] are explained easily by the generally accepted $3d \rightarrow a_{2u}$ assignments for $Ni(CN)_4^{2-}$. The new data support the logical extension of these assignments to the higher energy e_u orbital for the 5.0-μm^{-1} band. The ADFM crystal results are not so easily explained, but however they are explained, the solution spectrum is still best interpreted by the conventional excitation scheme.

Registry No. $Ni(CN)_4^{2-}$, 48042-08-6.

Contribution from the Laboratoire de Chimie-Physique
(UA 253 du CNRS), HEI, 59046 Lille Cédex, France

Photochemical Observations in Solutions of Sulfur in Liquid Ammonia

P. Dubois, J. P. Lelieur,* and G. Lepoutre

Received March 14, 1988

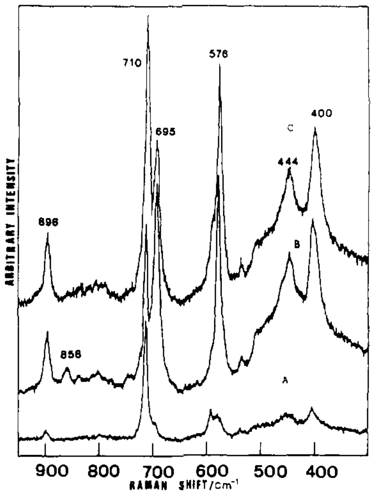

Figure 1. Raman spectra of sulfur–ammonia solutions (1 M) recorded with the 514.5-nm excitation line: (A) sample at 223 K recorded just at the beginning of the laser irradiation; (B) sample at 200 K recorded after the laser irradiation had been focused for 2 h on the sample after which the spectrum was then stationary; (C) sample at 223 K recorded after the laser irradiation had been focused for 1 h on the sample after which the spectrum was then stationary.

The photosensitivity of solutions of sulfur in liquid ammonia was first observed by Bernard et al.[1,2] They have shown the influence of white-light illumination of the solutions on the absorption spectrum. They have also shown that the photosensitivity could be induced by laser excitation lines (488.0 and 514.5 nm). It was shown that the initial equilibrium state was recovered if the sample was kept for several days in the dark. The experiments of Bernard et al., carried out at room temperature, did not allow identification of the species resulting from the decrease of the S_4N^- concentration since the spectrophotometry experiments were performed only in the visible range. The observations of Bernard et al. were taken into account in the characterization of the equilibrium state of these solutions.[3,4] Prestel and Schindewolf[5-8] showed that sulfur–ammonia solutions contain several photosensitive species. They established that S_3N^- or S_4N^- can be produced through photoinduced reactions.[7,8] However, their experiments did not lead to an overall interpretation of the observed photochemical effects. Furthermore, it was shown recently that the solutions studied by Prestel and Schindewolf were not in the equilibrium state before illumination.[4,9] It is now well established that sulfur in ammonia undergoes a disproportionation process giving S_6^{2-} in equilibrium with S_3^- as reduced species and mainly S_4N^- as oxidized species. In the equilibrium state a large fraction of solubilized sulfur is still in the zero oxidation state.[4,13] This neutral form of sulfur, S_{am}, is not cyclic S_8, and likely involves ammonia molecules. For the sake of simplicity we call it $S_{n,am}$. We have proposed[4] the following disproportionation equilibrium to describe the equilibrium state, if the concentration of S_3N^- is neglected:

---

(1) Bernard, L. Thèse de docteur ingénieur, University of Lille, 1982.
(2) Bernard, L.; Lelieur, J. P.; Lepoutre, G. *Nouv. J. Chim.* **1985**, *9*, 199.
(3) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1987**, *26*, 1897.
(4) Dubois, P.; Lelieur, J. P.; Lepoutre, G. The Solubilization Process of Sulfur in Liquid Ammonia and the Equilibrium State of These Solutions. *Inorg. Chem.* **1989**, *28*, 195.
(5) Prestel, H.; Schindewolf, U. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 150.
(6) Prestel, H.; Seelert, S.; Schindewolf, U. *Z. Phys. Chem. (Munich)* **1986**, *148*, 97.
(7) Prestel, H.; Schindewolf, U. *Z. Anorg. Allg. Chem.* **1987**, *551*, 21.
(8) Prestel, H. Dissertation, University of Karlsruhe, 1986.
(9) Dubois, P. Thèse de doctorat No. 184, Université des Sciences et Techniques de Lille, 1987.
(10) Bojes, J.; Chivers, T.; Drummond, I. *Inorg. Synth.* **1978**, *18*, 203.
(11) Steudel, R. *J. Phys. Chem.* **1977**, *81*, 343.
(12) Chivers, T.; Lau, C. *Inorg. Chem.* **1982**, *21*, 453.
(13) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1988**, *27*, 3032.

0020-1669/89/1328-2489$01.50/0

$$(10/n)S_{n,\mathrm{am}} + 4NH_3 \rightleftarrows S_4N^- + S_6^{2-} + 3NH_4^+ \qquad (1)$$

with

$$S_6^{2-} \rightleftarrows 2S_3^- \qquad (2)$$

In the present note, new experimental results on the temperature dependence of the Raman spectrum of the solutions are given. These results show that the photochemical effects are temperature dependent, and this has been also investigated for the absorption spectrum. A general interpretation of the photochemical effects is proposed. It is also shown that S_7NH–NH_3 solutions display photochemical effects very similar to those observed for sulfur–ammonia solutions.

Experimental Section

Absorption spectra have been recorded on a Beckman 5240 UV–visible spectrophotometer. The temperature of the sample was regulated within ±0.1 °C with an Oxford Instruments DN704 cryostat. Raman spectrometers (Ramanor HG2 and Dilor RT) from the "laboratoire de Spectroscopie Infra-Rouge et Raman" (LASIR) of Lille University were used. The solid compound S_7NH was synthesized by following the method described by Bojes et al.[10] The Raman spectra we have recorded for solid S_7NH, and for solutions of S_7NH in CS_2 confirm published results.[11] The illumination of the sample with white light was done with a slide projector.

Results

Photosensitivity of Sulfur–Ammonia Solutions and Temperature Dependence of Their Raman Spectra. The Raman spectra of sulfur–ammonia solutions at room temperature are well interpreted.[1-3,12] The dependence of the Raman spectra upon the excitation line is understood, because the main features of the absorption spectrum in the visible range are interpreted.[2-4] For the 647.1-nm excitation line, the lines of only two species, S_3^- and S_4N^-, are observed while for the 514.5- and 488.0-nm excitation lines, the lines of the reduced species S_6^{2-} are observed in addition to those of S_3^- and S_4N^-, because S_4N^-, S_3^- and S_6^{2-} absorb at 580, 610, and ca. 440 nm, respectively. The dilute solutions are photosensitive under the laser radiation.[1-3] For the most dilute solutions (less than 0.1 M) the intensity of the S_4N^- Raman lines decreases gradually to zero, while the intensity of the other observed Raman lines is constant. For concentrated solutions (more than 0.5 M), the intensity of all the Raman lines is time independent. In the intermediate concentration range, the intensity of the S_4N^- lines reaches a stationary value under laser irradiation. These observations have been made at room temperature.[3,9]

For temperatures below about 230 K, the characteristic S_3N^- Raman lines at 576, 695, and 898 cm^{-1} are observed, while the intensity of the S_4N^- Raman lines decreases.[3] In order to interpret the temperature dependence of the Raman spectrum,[3] new experiments have been carried out. The sample was cooled down in the dark, and Raman spectra were recorded versus time at a constant temperature.

In Figure 1, spectrum A has been recorded at 223 K immediately after the sample had been irradiated with the 514.5-nm excitation line. Spectrum A is identical (as far as the S_4N^- lines are concerned) with the room temperature spectrum of this sample. It must be noted that spectrum A shows no S_3N^- Raman line. However the spectra recorded with the same conditions, after a longer time of irradiation with the 514.5-nm excitation line, change drastically with time: the lines of S_3N^- are observed and increase by comparison with the intense line of S_4N^- at 710 cm^{-1}. Simultaneously, the intensity of the NH_3 Raman lines increases, as a consequence of the decrease of the absorbance of the solution.

The time required to obtain a stationary intensity of the Raman lines depends upon three factors: temperature, laser light power, and concentration. The influence of temperature and time on the Raman lines is shown in Figure 1. For a constant laser light power, when the temperature decreases, the intensity of the S_3N^- lines increases while that of the S_4N^- lines increase. For temperatures over about 230 K, S_3N^- has never been observed in sulfur–ammonia solutions. For temperatures below about 230 K, S_3N^- was observed for concentrations larger than 10^{-2} M.[3]

The Raman spectra recorded with this procedure (cooling down of the sample in the dark and irradiating the cold sample) show that S_3N^- results from the photosensitivity of S_4N^-. The formation of S_3N^- may occur by cleavage of a sulfur–sulfur bond:

$$S_4N^- \rightleftarrows S_3N^- + S \qquad (3)$$

The sulfur atom extruded from S_4N^- will probably give S_{am}. The photoinsensitivity of Raman spectra at room temperature for concentrated solutions (more than 0.5 M) suggests that the forward and reverse processes of eq 3 have the same rates. The observation of S_3N^- is possible at temperatures below about 230 K because the rate of the backward reaction has decreased.

At room temperature for dilute solutions (less than 10^{-2} M), the Raman lines of neither S_4N^- nor S_3N^- are observed. This gives evidence that S_3N^- is a photosensitive species, as already shown by Prestel and Schindewolf.[5-8] From spectrum B of Figure 1 (200 K), another evidence of the photosensitivity of S_3N^- is given. Indeed the two Raman lines at 695 and 576 cm^{-1} display unusual relative intensities, and a new weak line is observed at 858 cm^{-1}. We have previously suggested the formation of S_2N^- from S_3N^- in sulfur–ammonia solutions after addition of an alkali-metal amide.[13] A Raman line at 858 cm^{-1} was then tentatively assigned to S_2N^-. It is suggested that the photoinduced reaction on S_3N^- might produce S_2N^- by the cleavage of a sulfur–sulfur bond, as for eq 3. However, for dilute solutions at room temperature, when the Raman lines of S_4N^- and S_3N^- are not observed, no Raman line is seen at 858 cm^{-1}. Several reasons could explain the absence of this line: the concentration of S_2N^- could be too small; the excitation line should instead be in the UV range; S_2N^- could also be a photosensitive species.

We consider now the interpretation of the temperature dependence of the Raman spectrum with the 647.1-nm excitation line.[3] It was observed that the intensity of the S_4N^- lines increases when the temperature decreases, while the intensity of the S_3^- line at 535 cm^{-1} decreases.[3] The S_3N^- Raman lines were not observed with the 647.1-nm excitation line. It was previously suggested that the increase of the S_4N^- lines intensity results from the decrease of the solution absorbance induced by the dimerization of S_3^- into S_6^{2-} when the temperature decreases. The new results reported above with the 514.5-nm line lead us to give now a more satisfactory explanation of the observations with the 647.1-nm line. Indeed the photosensitive property of S_4N^- explains also the increase of the intensity of the Raman lines for this species. The decrease of the S_4N^- concentration at low temperature under laser irradiation allows the increase of the S_4N^- lines intensity, because the absorbance of the solution is decreased. It must also be noted that the S_3N^- Raman lines have never been observed with the 647.1-nm line, even when the S_3N^- concentration is strongly increased relative to that of S_4N^- under the influence of the alkali-metal amide addition.[13] This is a consequence of the location of the 647.1-nm line outside the absorption band of S_3N^- at 460 nm.

It has been shown above that in the low-temperature Raman spectra of sulfur–ammonia solutions, S_3N^- is formed from S_4N^-. The confirmation of the results obtained by Raman spectroscopy will now be demonstrated by the study of the absorption spectrum at room temperature and at 200 K after white-light illumination.

Photosensitivity of Sulfur–Ammonia Solutions: Influence of the Absorption Spectrum. The absorption spectrum of sulfur–ammonia solutions in the equilibrium state is concentration dependent.[3] When the concentration is increased from 10^{-3} to 10^{-2} M, several modifications are observed. An absorption band in the visible range is shifted from 460 to 420 nm because the relative absorbance of S_3N^- decreases, while the UV absorbance near 300 nm assigned mainly to S_{am} increases relative to the S_4N^- absorbance at 580 nm. The S_3^- absorption band at 610 nm and that of S_6^{2-} near 440 nm are masked by the absorption bands of S_4N^- and S_3N^-, respectively.

After illumination with white light, the absorption spectrum is drastically changed as shown in Figure 2. Whatever the temperature of the solution for the illumination with white light,

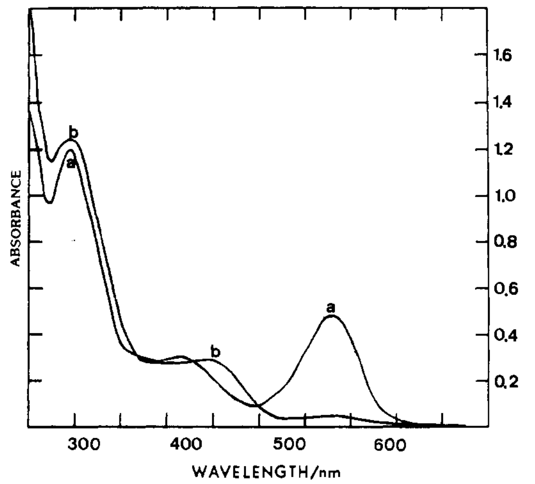

Figure 2. Absorption spectra of a sulfur–ammonia solution (10^{-2} M): (a) absorption spectrum of the solution in the equilibrium state at 200 K; (b) absorption spectrum of the solution after white-light illumination at 200 K (30 min). Optical path length: 1 mm.

the absorbance of S_4N^- at 580 nm decreases, but other variations of the spectrum are observed that are temperature dependent. At 200 K the absorbance is increased at 460 nm and in the UV range. At 460 nm, the increase of absorbance is larger for concentrated solutions. At 300 nm, the increase of absorbance is smaller for dilute solutions (10^{-3} M).

At room temperature the modifications of the absorption spectrum after illumination with white light depend on the concentration of the solution. For concentrated solutions (10^{-2} M) the absorbance decreases at 580 nm and increases at 420 and 300 nm, without modification at ca. 460 nm. For dilute solutions (10^{-3} M) the modifications depend on the time of illumination. For a short time of illumination (5 min with a slide projector with a 150-W lamp), the absorbance decreases at 580 nm and increases at 460 nm, as observed at 200 K. However after about 30 min of illumination, the maxima of absorbance are located near 420 nm and at 610 nm. For the same concentration and the same time of illumination, the increase of absorbance at 300 nm is larger at room temperature than at 200 K.

After illumination, the absorption spectrum of the solution returns gradually toward the initial absorption spectrum associated with the equilibrium state.[4] The absorption spectra are not modified during the time required to record a spectrum. At 200 K, when dilute solutions have been kept in the dark several hours after the illumination, the absorbance decreases at 300 nm and increases at 460 and 580 nm. It has been found that the variations of the absorption spectrum after illumination and the time required to recover the equilibrium state spectrum (several days) are quite similar to those observed during the initial solubilization process of sulfur in liquid ammonia.

The above results related to the modifications of the absorption spectrum under illumination are in good agreement with our results of Raman spectroscopy. Both experimental techniques show the temperature dependence of the photosensitivity of sulfur–ammonia solutions. At low temperature, the increase of absorbance at 460 nm induced by illumination is assigned to the formation of S_3N^- described by eq 3. The concentration and temperature dependence of the absorbance at 460 nm confirms the photosensitivity of the S_3N^- species. The products of the photoinduced reaction of S_3N^- absorb in the UV range, and this suggests the formation of S_{am}. The slow rate of reversibility to the equilibrium state is also consistent with the formation of S_{am}. The weak absorbance near 610 nm after illumination at room temperature indicates that the S_3^- concentration has been decreased by illumination. This result is consistent with the increase of the S_{am} concentration induced by illumination and shows that the overall effect of illumination is the decrease of the disproportionation described by eq 1.

The illumination of $S_7NH–NH_3$ solutions[13] with white light at room temperature induces modifications of the absorption spectrum very similar to those observed for sulfur–ammonia solutions. After a short time of illumination, the S_4N^- absorbance at 580 nm decreases, while the absorbances of S_3N^- at 460 nm and S_{am} at ca. 300 nm increase and reach a maximum. For a longer time of illumination a small decrease of the absorbance at 300 nm is observed, and a new weak absorption band is found at 390 nm. The equilibrium state absorption spectrum is recovered after several days as for sulfur–ammonia solutions.

Our analysis of the photosensitivity of sulfur–ammonia solutions allows understanding of the photosensitivity of S_7NH–ammonia solutions. In both cases, the photosensitivity of S_4N^- and of S_3N^- is demonstrated. An interesting difference is the observation of a weak absorption band at 390 nm after illumination of a $S_7NH–NH_3$ solution. We suggest that this band at 390 nm results from the photosensitivity of S_3N^-, and we assign it tentatively to S_2N^-. The band at 390 nm was not observed after illumination of sulfur–ammonia solutions but the values of absorbance in the UV range are higher in sulfur–ammonia solutions than in S_7NH–ammonia solutions and could obscure the possible formation of S_2N^- in sulfur–ammonia solutions. However the formation of S_2N^- in sulfur–ammonia solutions at low temperature has been suggested from the Raman line observed at 858 cm^{-1} (Figure 1). Furthermore an absorption band was observed at 390 nm in sulfur–ammonia solutions under the addition of an alkali-metal amide after the absorbance of S_3N^- at 460 nm had reached a maximum.[13] Consequently it is suggested that the photoreaction of S_3N^- is similar to that of S_4N^- (eq 3): S_2N^- is produced from S_3N^- by the cleavage of a sulfur-sulfur bond. In such a case, S_2N^- would more likely be a symmetric species. It must be noted that theoretical studies of the S_2N^- ion with various conformations have been reported by Trsic and Laidlaw.[17]

Discussion and Conclusion

The photochemical effects can be compared to the solubilization process. In the solubilization process the initial step is the opening of the S_8 cycle leading to S_{am}; the formation of S_3N^- from S_{am} has been discussed;[4] this formation occurs through unidentified intermediate steps involving probably S_2N^-. It has been shown that the main oxidized species in the equilibrium state (i.e. S_4N^-) is formed from S_3N^-.[4] The photochemical effects described in this paper for $S_8–NH_3$ and $S_7NH–NH_3$ solutions display opposite variations. It is therefore understandable that the photochemical effects are reversible. However, the photochemical effects did not display any observation equivalent to the initial step of the solubilization process, but this would require an UV illumination. It must also be noted that both experimental observations (solubilization process and photochemical effects) have been found to be strongly temperature dependent.

Finally it must be emphasized that the photochemical observations reported here have a common feature: they are related to the cleavage of a S–S bond in a S_nN^- species and are therefore different from photosensitive properties reported for sulfur[14,15] and for sulfur (S_8) solutions.[16]

Acknowledgment. This research was supported by the CNRS (ATP Application de l'ēlectricitē ā la Chimie No. 249) and by the AFME (dēcision d'aide ā la Recherche No. 42139261). We are grateful to the Laboratoire de Spectroscopie Infrarouge et Raman de l'Universitē de Lille for the use of its Raman spectrometers. We thank Dr. Lorriaux for experimental assistance and Dr. Corset for helpful discussions.

Registry No. S_7NH, 293-42-5; S_4N^-, 51330-98-4; S_3N^-, 76468-83-2; S_2N^-, 91054-03-4; sulfur, 7704-34-9; ammonia, 7664-41-7.

---

(14) Spear, W. E.; Adams, A. R. In *Elemental Sulfur*; Meyer, B., Ed.; Interscience: New York, 1965; p 185.
(15) Meyer, B. *Sulfur, Energy and Environment*. Elsevier: Amsterdam, 1977.
(16) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149.
(17) Trsic, M.; Laidlaw, W. G. *J. Mol. Struct.* **1985**, *123*, 259.