Proton Magnetic Resonance Study of Molecular Motion in Solid Silver Sulfate Tetrammine, $Ag_2SO_4 \cdot 4NH_3$

Norbert Kummer, John L. Ragle *, Norbert Weiden, and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III,
Technische Hochschule Darmstadt

Z. Naturforsch. **34a**, 333–339 (1979); received December 8, 1978

The spin lattice relaxation time T_1 and the second moment of the proton magnetic resonance were studied on polycrystalline samples of $Ag_2SO_4 \cdot 4NH_3$. The wideline NMR measurements show a rapid reorientation of the NH_3 groups around their threefold axes in the temperature range 250 K $\leqq T \leqq$ 380 K. Below $T \approx 250$ K, the rotation of the NH_3 starts freezing-in. From T_1 measurements an activation energy of 27.5 kJ mol^{-1} for the rotation was found for temperatures above 210 K. Around 330 K a phase transition has been observed by T_1 measurements which is not recognized by wideline NMR measurements in the range 77 K $\leqq T \leqq$ 375 K. The results are discussed and compared with other NMR studies on solids containing NH_3 groups.

I. Introduction

The molecular motions of the NH_3 group in transition metal ammine complexes have occasioned considerable interest. By measurements of the second moment of ^{1}H-NMR Murray and Waugh [1] studied a series of hexammine complexes with different central ions and varying symmetry. They observed two types of motions: Rotational vibrations of the NH_3 around the pseudo-trigonal axes, which are determined by the metal-nitrogen bond and reorientational motions of the whole octahedral or pseudo-octahedral complexes $[Me(NH_3)_6]^{x\oplus}$. It was found that the motions of the individual NH_3 groups are maintained down to 77 K whereas the overall motions of the complex ions freeze in at some temperature above 77 K. The influence of crystallographically different sites of the individual ammine groups within the solid complexes on the motions of the NH_3 groups was studied by several authors [2–4] and different freezing-in temperatures were observed. Also, the crystallographic influences on the overall tumbling of the complex ions were studied [1, 4–6]. In octahedral or pseudo-octahedral ions $[Me(NH_3)_6]^{x\oplus}$, the resolution of wideline NMR techniques is in most cases too low to separate the individual spectra of each inequivalent NH_3 molecule within the solid. Linear diammine complexes offer a good chance to gain more detailed information on the molecular motions of $[Me(NH_3)_2]^{x\oplus}$ since tumbling of the whole quasi-linear ion is quite unfavorable. Such linear or almost linear ions $[Me(NH_3)_2]^{x\oplus}$ are found in the subgroups Ib and IIb of the periodic system of elements and have been often proposed for silver ammine complexes. The crystal structure of bis(diamminesilver)sulfate, $[Ag(NH_3)_2]_2SO_4$, is known [7, 8] and it seemed to be worthwhile to study both, the ^{1}H-NMR spectrum and the ^{1}H-NMR relaxation. The results of this study are reported here.

For another diamminesilver compound, the diamminesilver dinitroargentate $[Ag(NH_3)_2]Ag(NO_2)_2$, the crystal structure was determined recently [9]. Wideline ^{1}H-NMR and measurements of $T_1(^1H)$ [10] show high and low temperature phases. Further information about the molecular motions in this solid has been gained by ^{2}H-NMR measurements on $[Ag(ND_3)_2]Ag(NO_2)_2$ [25].

II. Experimental

Bisdiamminesilver sulfate was prepared following the method described by Corey and Wyckoff [7]. A saturated solution of silver sulfate in concentrated ammonia is slowly cooled down to room temperature whereby $[Ag(NH_3)_2]_2SO_4$ precipitates forming colorless tetragonal prisms. The substance decomposes in air within a few hours into Ag_2SO_4 and NH_3. The crystals are stable when kept in the dark and in contact with gaseous NH_3. The chemical analysis of the substance was satisfactory (calc/exp): Ag (56.78%/56.77%), NH_3 (17.9%/17.7%). The substance was also checked by X-ray powder diffraction techniques for phase purity. The lattice

* Alexander von Humboldt-Awardee 1977, on leave of absence from the Department of Chemistry, University of Massachussets, Amherst, Massachusetts 01002, USA.

Reprint requests to Prof. Dr. A. Weiss, Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Petersenstr. 20, D-6100 Darmstadt.

0340-4811 / 79 / 0300-0333 $ 01.00/0

constants found are in agreement with the literature data [8]. For the NMR investigations the polycrystalline samples were sealed in dark brown glass tubes.

The ^{1}H wideline NMR measurements were carried out with a Robinson-type oscillator at a constant frequency of (12.5530 ± 0.0003) MHz by slowly varying the magnetic induction B_0 within a range of $\Delta B = \pm 30 \cdot 10^{-4}$ T. A conventional lock-in and signal averaging technique (1024 channel averager) was applied. The RF level was held as low as possible, nevertheless saturation effects occurred below 110 K. Constant sample temperatures in the range $110\ \mathrm{K} \leqq T \leqq 375\ \mathrm{K}$ were achieved by a temperature controlled N_2 gas stream and measured with a copper constantan thermocouple attached to the sample tube. The temperature stability was ± 0.1 K and the error in its measurement ± 0.7 K.

The second moments of the absorption spectra were calculated numerically and corrected for finite modulation amplitude [11]. Using a 90°–90° pulse sequence the proton spin lattice relaxation times T_1 have been determined at 28.75 MHz, using a signal-averaging technique. For each temperature, T_1 was found by a least squares fit of the heights of the second free induction decay, FID. Below $T = 179$ K no T_1 studies were done since the relaxation time became fairly long ($\gtrsim 5$ sec).

III. Results

1. ^{1}H-Wideline Measurements

The ^{1}H NMR spectra recorded by the CW technique in the temperature range $110\ \mathrm{K} \leqq T \leqq 375\ \mathrm{K}$ show half-widths and second moments which are practically constant from 375 K down to about 250 K. Both properties increase in the range $250\ \mathrm{K} \geqq T \geqq 160$ K. No further change is observed from $T = 160$ K down to 110 K. In Fig. 1 the second moment $\langle \Delta B^2 \rangle$ is shown as a function of temperature. From the slope of $\langle \Delta B^2 \rangle = f(T)$, $170\ \mathrm{K} \leqq T \leqq 250$ K, an activation energy for the line narrowing process was determined. $\langle \Delta B^2 \rangle$ at the temperature T, its maximum value $\langle \Delta B^2 \rangle_{\max}$, and its minimum value $\langle \Delta B^2 \rangle_{\min}$ are related to the activation energy E_a and a frequency factor τ_0 of the process by the equation [12]

$$\frac{\langle \Delta B^2 \rangle - \langle \Delta B^2 \rangle_{\min}}{\langle \Delta B^2 \rangle_{\max} - \langle \Delta B^2 \rangle_{\min}} = \frac{2}{\pi} \tan^{-1}\left[\frac{2\mu}{\hbar} \langle \Delta B^2 \rangle^{1/2} \cdot \tau_0 \exp\left(\frac{E_A}{RT}\right)\right] \tag{1a}$$

with μ = magnetic moment of the proton. A logarithmic plot of the experimental values according to

$$\ln\left\{\frac{\hbar}{2\mu \langle \Delta B^2 \rangle^{1/2}} \tan\left[\frac{\pi}{2} \frac{\langle \Delta B^2 \rangle - \langle \Delta B^2 \rangle_{\min}}{\langle \Delta B^2 \rangle_{\max} - \langle \Delta B^2 \rangle_{\min}}\right]\right\} = \ln \tau_0 + \frac{E_a}{R} \frac{1}{T} \tag{1b}$$

is shown in Figure 2. $E_a = 19.5$ kJ mol^{-1} and a frequency factor $\tau_0 = 3.2 \cdot 10^{-13}$ are found for the line-narrowing process.

2. Proton T_1 Measurements

Figure 3 shows a plot of log T_1 versus $1/T$. T_1 has a value of 4.8 s at 180 K. With increasing temperature T_1 decreases and reaches its minimum

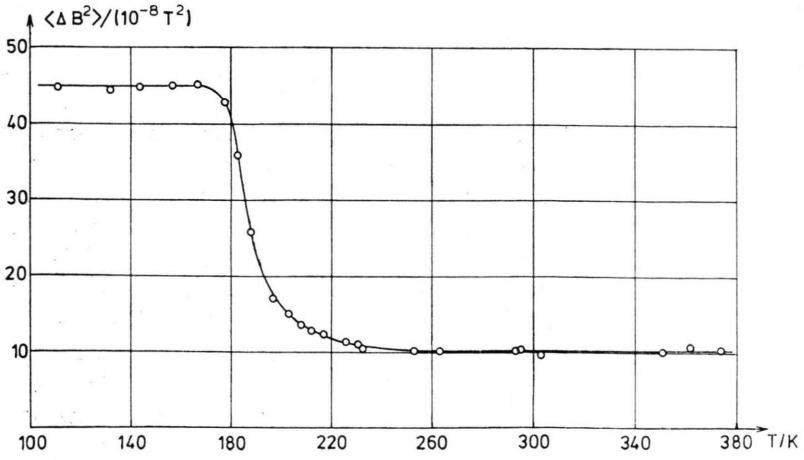

Fig. 1. Second moment $\langle \Delta B^2 \rangle$ of the proton magnetic resonance spectrum of $[Ag(NH_3)_2]_2SO_4$ as a function of temperature. $B_0 = 0.33917$ Tesla.

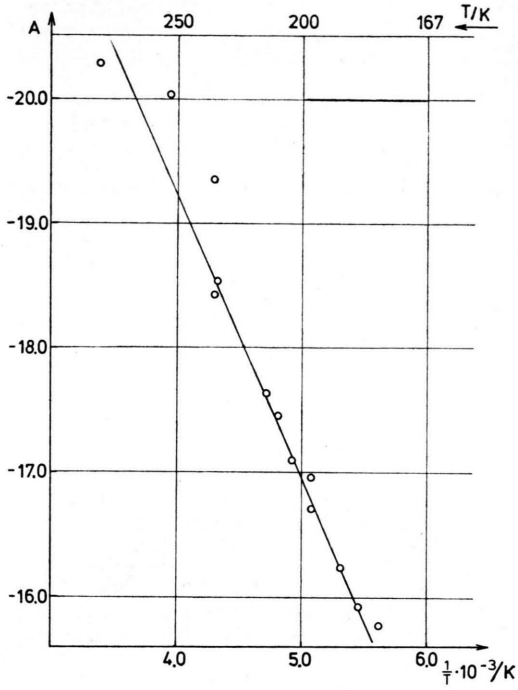

Fig. 2. Plot of

$$A = \ln\left\{\frac{\hbar}{2\mu\langle\Delta B^2\rangle^{1/2}}\tan\left[\frac{\pi}{2}\,\frac{\langle\Delta B^2\rangle - \langle\Delta B^2\rangle_{\min}}{\langle\Delta B^2\rangle_{\max} - \langle\Delta B^2\rangle_{\min}}\right]\right\}$$

versus $1/T$.

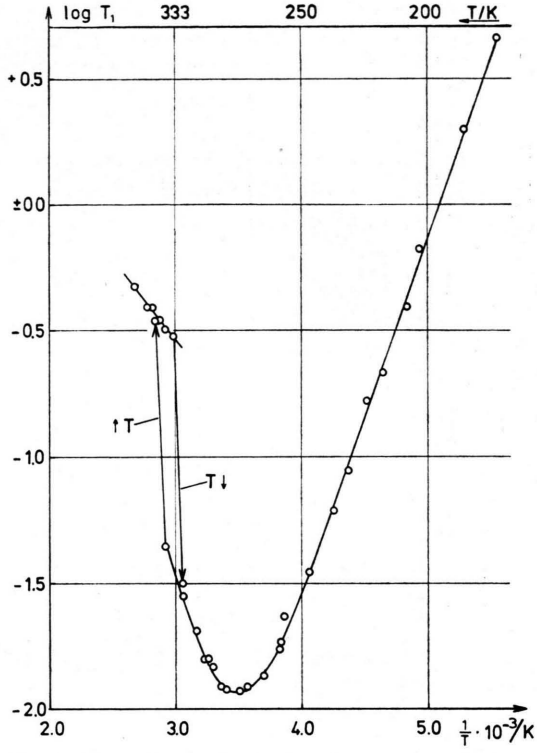

Fig. 3. Logarithm of the longitudinal relaxation time, $\log T_1(^1\mathrm{H})$, versus $1/T$ at constant frequency $\nu = 28.75$ MHz for $[Ag(NH_3)_2]_2SO_4$. The hysteresis in the phase transformation is marked by arrows.

value of (11.9 ± 0.5) ms at 285 K. Around 343 K the T_1 data show a discontinuity. With increasing temperature the low temperature phase exists up to 348 K, at which temperature it transforms rapidly to a high temperature phase in less than 10 min. With decreasing T the high temperature phase is stable down to about 333 K; then a somewhat slow transformation to the low temperature phase occurs, taking more than an hour to be complete. The sample was held in the high temperature phase at around 338 K for several hours without transformation. The entire cycle from low to high temperature and returning to low temperature was repeated several times with no indication of any irreversibility. The sample was heated up to about 373 K and cooled to room temperature without any effect upon the room temperature NMR signal.

IV. Discussion

The crystal structure of $Ag_2SO_4 \cdot 4NH_3$ is built up from linear groups $[Ag(NH_3)_2]^{\oplus}$ and tetrahedral ions $[SO_4]^{2\ominus}$. According to Corey and Wyckoff [7] the space group is D_{2d}^4-$P\bar{4}2_1c$ with two formula units in the unit cell. Except for the hydrogen atoms, the positions of all atoms within the unit cell are known. The distance Ag-N found is considerably shorter than in all other substances reported in the literature [9]. From the point of view of NMR, the three protons within one NH_3 molecule can be regarded in first approximation as an isolated group, since their next nearest neighbors are the nitrogen atom of the NH_3 group considered and three oxygen atoms. The respective nuclei have no or only very small magnetic moments. For this reason the theoretical treatment of Andrew and Bersohn [13] for an isolated regular triangle of identical nuclei is applicable to the calculation of the NMR line shape of the ^{1}H-NMR in $Ag_2SO_4 \cdot 4NH_3$. Thereby a direct calculation is possible of the two limiting cases a) rigid triangels, and b) freely rotating triangles. The influence of dipolar broadening on the line shape due to intermolecular interactions between the neighboring NH_3 groups is

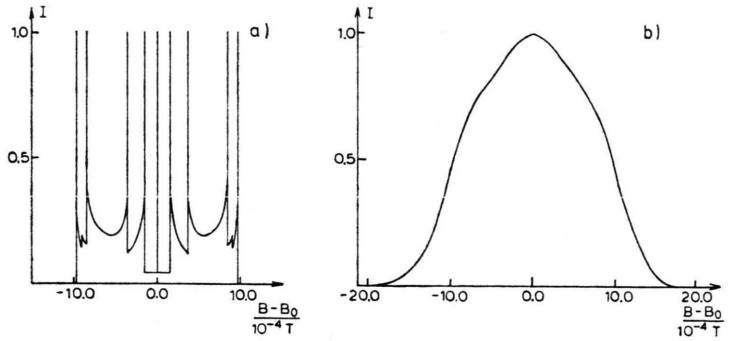

Fig. 4. Calculated NMR spectrum for three protons arranged in a rigid, regular triangle; the triangles are statistically oriented in space with respect to B_0; $d_{H-H} = 1.67$ Å. I is the normalized intensity. a) Isolated three proton system. b) Dipolar broadening included ($\beta = 3.1 \cdot 10^{-4}$ Tesla).

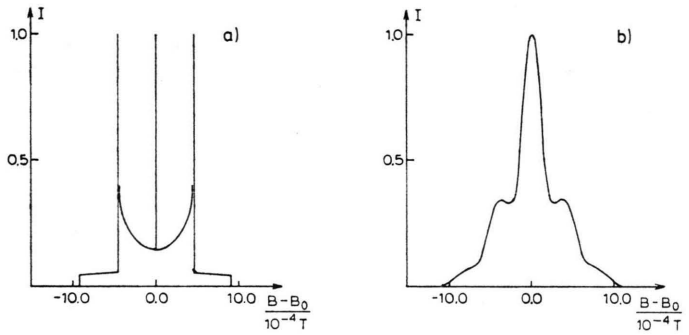

Fig. 5. Calculated NMR spectrum for three protons arranged in a regular triangle, rotating around its threefold axis; the triangles are statistically oriented in space with respect to B_0; $d_{H-H} = 1.67$ Å. I is the normalized intensity. a) Isolated three proton system, b) Dipolar broadening included ($\beta = 1.5 \cdot 10^{-4}$ Tesla).

taken into account by convoluting the theoretical line shape for an ensemble of statistically oriented triangles H_3 with a Gaussian function of the form

$$g(B - B_0) = \exp(-(B - B_0)^2/2\beta^2). \qquad (2)$$

B is the magnetic field and B_0 the resonance field of the protons. β reflects the intermolecular dipolar broadening. Figures (4a, b) and (5a, b) show spectra calculated for the two limiting cases with and without dipolar broadening.

In order to compare the second moments of the theoretical and the experimental spectra, β has to be estimated, which can be done by restriction to one molecule NH_3. The rest of the NH_3 within the unit cell is found by application of the symmetry operations valid to the space group $P\bar{4}2_1c$. According to the crystal structure the distance N-O in $[Ag(NH_3)_2]_2SO_4$ is 2.95 ± 0.02 Å and the angles included by the three vectors N→O (next nearest neighbors) are 107.1°, 104.0°, and 108.0° respectively. These angles are close to the angle H-N-H for the free NH_3 molecule (107°). Therefore it is reasonable to locate the hydrogen atoms on the bond N-O and to assume linear hydrogen bonds for a distance H...O of less than 2 Å. Furthermore the distance H-H in $[Ag(NH_3)_2]_2SO_4$ should not differ from the average value of 1.67 Å found in NH_3 and other ammines.

With these assumptions the point positions of the hydrogen atoms can be calculated. By application of (2) that part of β which is due to the intermolecular proton-proton dipolar broadening can be determined. For a rigid lattice of $[Ag(NH_3)_2]_2SO_4$, $\beta \approx 3.1 \cdot 10^{-4}$ T was found. With d(H-H) = 1.67 Å and $\beta = 3.1 \cdot 10^{-4}$ T a value of $46.6 \cdot 10^{-8}$ T² for the second moment of an ensemble of rigid proton triangles results, which is close to the experimental low temperature value of $46.3 \cdot 10^{-8}$ T². In Fig. (6a, b) the first derivative of the theoretical and of the experimental spectra at low temperatures are shown.

In the high temperature range the rigid lattice value of β is not very well suited for the comparison of theory and experiment. In contrast to a rigid lattice, a straightforward calculation of β is not possible. With different values of β ranging from 0.8 to $3.0 \cdot 10^{-4}$ T line shapes and second moments have been calculated and compared with the experimental data. Good agreement has been found for $\beta = 1.3 \cdot 10^{-4}$ T, from which $\langle \Delta B^2 \rangle_{calc} = 10.8 \cdot 10^{-8}$ T² results. This should be compared with the experimental high temperature value $\langle B^2 \rangle_{exp}$

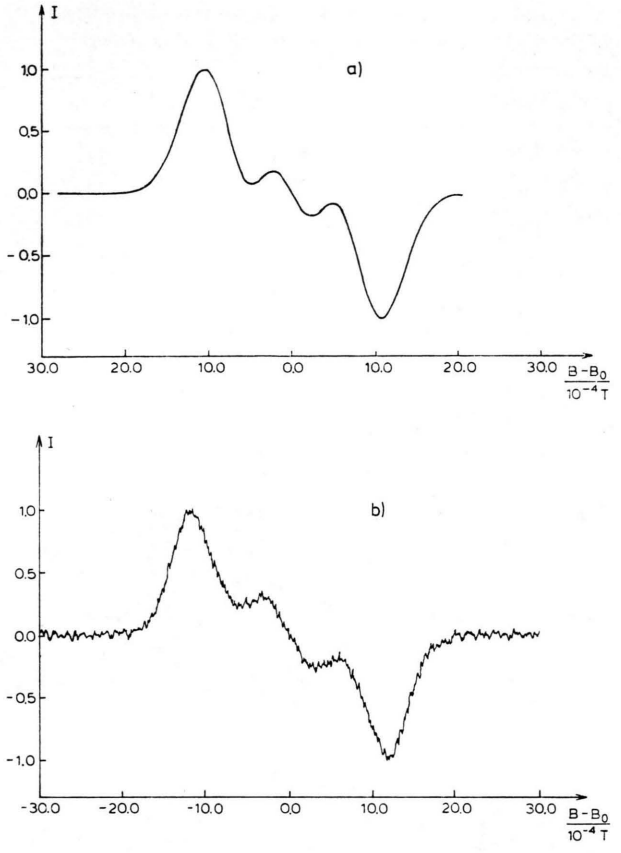

Fig. 6. First derivative of the ^{1}H-NMR spectrum. The intensity I is normalized. a) Calculated for rigid triangles, $d_{H-H} = 1.6$ Å; $\beta = 3.1 \cdot 10^{-4}$ Tesla. b) Experimental spectrum of $[Ag(NH_3)_2]_2SO_4$ at $T = 144$ K; $B_0 = 0.33917$ Tesla.

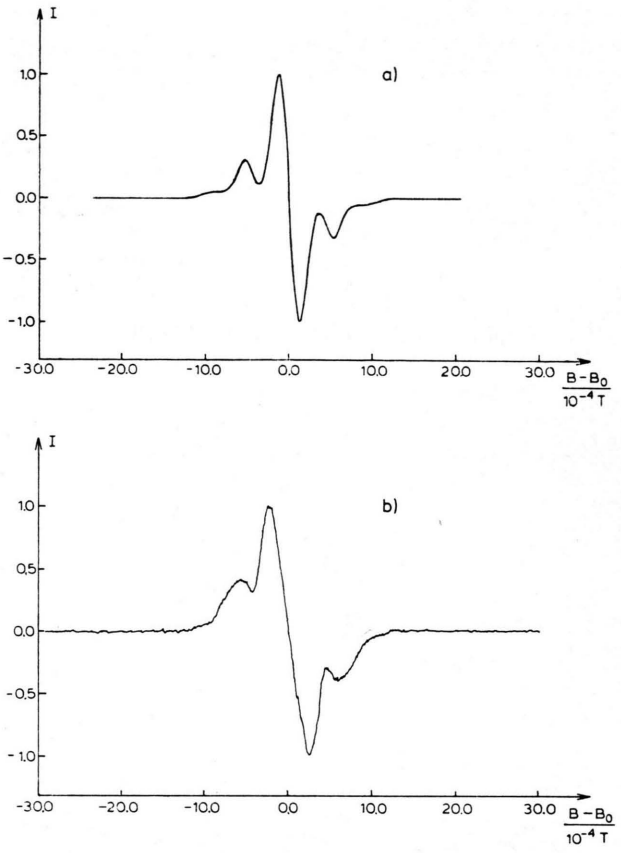

Fig. 7. First derivative of the ^{1}H-NMR spectrum. The intensity I is normalized. a) Calculated for rotating regular triangles, $d_{H-H} = 1.67$ Å; $\beta = 1.3 \cdot 10^{-4}$ Tesla. b) Experimental spectrum of $[Ag(NH_3)_2]_2SO_4$ at $T = 375$ K; $B_0 = 0.33917$ Tesla.

$= 10.2 \cdot 10^{-8}\,T^2$ (Figures 7a, b). The difference of $\sim 0.6^{-8}\,T^2$ and the slight differences between experiment and calculation found for the line shape may be due to motions of the NH_3 group in addition to the free rotation around its trigonal axis. A smaller value in β leads to better agreement between $\langle \Delta B^2 \rangle_{calc}$ and $\langle \Delta B^2 \rangle_{exp}$, but then the line shapes differ more. The comparison of theoretical and experimental line shapes and second moment data leads clearly to the following model: At room temperature the NH_3 groups rotate nearly freely around their threefold axes. A gradual freezing-in of the rotation occurs in the range 160 K $\leqq T \leqq$ 250 K, and below 160 K the NH_3 are rigidly fixed.

Wideline measurements can aid in the interpretation of the results of the T_1 measurements. For a random reorientation of molecular groups the spin lattice relaxation time T_1 of the protons is given by [14]

$$T_1^{-1} = \frac{C}{\omega_0}\left[\frac{\omega_0 \tau_c}{1+\omega_0^2 \tau_c^2} + \frac{4\,\omega_0 \tau_c}{1+4\,\omega_0^2 \tau_c^2}\right] \qquad (3)$$

with $\omega_0 = \gamma B_0$. τ_c is the correlation time of the motion, and C is a measure of the strength of the relaxation interaction. For a regular triangle of identical nuclei rotating about the threefold axis C is [15]

$$C = \frac{9}{20}\frac{\gamma^4 \hbar^2}{r^6} \qquad (4)$$

with $r =$ internuclear distance within the triangle. From the accepted value $r = 1.67$ Å, $C = 1.8 \cdot 10^{10}$ sec^{-2} results. The wideline measurements and the minimum value of $T_1 = f(T)$ found at room temperature confirm that the rotation about the three-

fold axis dominates $T_1 = f(T)$ between 180 K and 380 K and that this rotation is thermally activated. For thermally activated rotation τ_c can be described by an Arrhenius equation

$$\tau_c = \tau_0 \exp\{E_a/kT\}, \quad (5)$$

where τ_0 is constant (frequency factor) and E_a the activation energy of the motion.

For the temperature region below 250 K, in which the correlation time τ_c is proportional to T_1, an activation energy of 27.5 kJ mol^{-1} and a frequency factor $\tau_0 \cong 10^{-15}$ s is obtained from Equations (3—5). The results for the activation energy and the frequency factor found from second moment measurements and from the determination of the spin lattice relaxation time differ considerably:

$$E_a(M_2) = 19.5 \pm 1.5 \text{ kJ mol}^{-1};$$
$$\tau_0 = 3 \cdot 10^{-13} \text{ s};$$
$$E_a(T_1) = 27.54 \pm 0.26 \text{ kJ mol}^{-1};$$
$$\tau_0(T_1) = 1 \cdot 10^{-15} \text{ s}.$$

The differences in E_a and τ_0 are due to two facts: a) the error in determining $\langle \Delta B^2 \rangle$ is larger than that for T_1; b) $E_a\langle \Delta B^2 \rangle$ and $\tau_0\langle \Delta B^2 \rangle$ have been found from Eq. (1), which is valid only for strictly Gaussian type lines. Therefore, a quantitative discussion of E_a relies mainly on

$$E_a(T_1) = 27.5 \text{ kJ mol}^{-1}.$$

The high activation energy and the fact that the correlation time τ_c at room temperature is only about 10^{-8} s ($\omega_0\tau_0 \approx 1/\sqrt{2}$) indicate that the NH_3 groups are rather strongly hindered in their rotation. This supports the assumption of hydrogen bonding as proposed by the estimate of β in Equation (2). Activation energies of similar magnitude to the E_a determined here were observed by ^1H spin-lattice relaxation time measurements in amino acids. In $[Ag(NH_3)_2]Ag(NO_2)_2$ [10] and in cobalt ammine complexes, E_a is lower by a factor of 2—3, where no indication of marked hydrogen bonding is found in these substances (Table 1). The high activation energy found for $[Ag(NH_3)_2]_2SO_4$ is comparable to that of the substituted ammonium compounds shown in Table 1. The line width at low temperatures approaches that of a rigid lattice. This observation supports the assumption of rather strong hydrogen bonds in the compound. The discontinuity in the T_1 data around 343 K marks a structural phase transition but one which requires an internal stress field in the crystal to proceed with a rapid rate. This phase transition has also been observed by Caulder et al. [16] by thermal analysis.

Table 1. Activation energies for NH_3, $(NH_3)^+$, respectively, group rotation in different compounds ([a] this paper).

Compound	E_a/kJ mol^{-1}	Ref.
$[Cd(NH_3)_6](BF_4)_2$	8.4	[17]
$[Co(NH_3)_6]J_3$	7.5	[18]
$[Co(NH_3)_4CO_3]_2SO_4$	8.0 18.0	[2]
$[Co(NH_3)_4CO_3]Br$	9.6	[19]
$[Co(NH_3)_5F]Cl_2$	7.5 13.0	[4]
Cis-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$	3.8	[3]
$(CH_3)_3CNH_3^{\oplus}Tr^{\ominus}$ Tr = $C_7H_6O_2$ (Tropolon)	30.2	[20]
CD_3NH_3Cl β-Phase γ-Phase	26.4 32.0	[21]
CH_3NH_3Cl β-Phase	23.8	
amino acids	27.8—51.7	[22, 23]
solid NH_3	9.6	[24]
$[Ag(NH_3)_2]Ag(NO_2)_2$	7.2 10.0	[10]
$[Ag(NH_3)_2]_2SO_4$	27.5 12.0	[a]

T_1 and hence the inverse correlation time increase by an order of magnitude during the phase transition and the high temperature phase has an activation energy of 12.0 kJ mol^{-1}, more than two times less than the low temperature phase. This phase transition could not be detected by the wide-line studies which indicates that the reorientation around the threefold axis is still the dominating process and no tumbling or flipping motion of the whole complex ion $[Ag(NH_3)_2]^{\oplus}$ is coming into play at higher temperatures, as was observed in some cobalthexammine salts [1]. Only the degree of hindrance decreases markedly in the high temperature phase probably because of less favorable hydrogen bonding.

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial support of this work.

One of us (J.L.R.) would like to express his gratitude for the generous support of the Alexander von Humboldt Foundation.

[1] G. R. Murray, Jr., and J. S. Waugh, J. Chem. Phys. **29**, 207 (1958).
[2] B. A. Dunnel, M. D. Pachal, and S. E. Ulrich, Cand. J. Chem. **51**, 1107 (1973).
[3] B. A. Dunnel, J. F. Nattrass, and S. E. Ulrich, Cand. J. Chem. **52**, 900 (1974).
[4] E. C. Reynhardt, A. Watton, and H. E. Petch, J. Chem. Phys. **66**, 1594 (1977).
[5] S. S. Dharmatti, V. Savaswati, and R. Vijayavaghavan, Proc. Colloq. Ampere, XIII, 133 (1964), publ. (1965).
[6] T. Ito and T. Chiba, Bull. Chem. Soc. Japan **42**, 108 (1969).
[7] R. B. Corey and R. W. G. Wyckoff, J. Kristallogr. **87**, 264 (1934).
[8] S. Haussühl, Z. Naturforsch. **15a**, 549 (1960).
[9] H. M. Maurer and Al. Weiss, Z. Kristallogr. **146**, 227 (1977).
[10] H. M. Maurer, J. L. Ragle, and Al. Weiss, Ber. Bunsenges. Physik. Chem. **82**, 602 (1978).
[11] E. R. Andrew, Phys. Rev. **91**, 425 (1953).
[12] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[13] E. R. Andrew and R. Bersohn, J. Chem. Phys. **18**, 159 (1950).
[14] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).
[15] D. E. O'Reilly and T. Tsang, Phys. Rev. **157**, 417 (1967).
[16] S. M. Caulder, K. H. Stern, and F. L. Carter, J. Inorg. Nucl. Chem. **36**, 234 (1974).
[17] N. Pislewski, J. Stankowski, and L. Larys, Phys. Stat. Sol. (a) **31**, 415 (1975).
[18] N. Pislewski, J. Stankowski, and M. Latanowicz, Acta Phys. Pol. A **50**, 555 (1976).
[19] M. Okabe, Y. Arata, A. Yamasari, and S. Fujiwava, J. Phys. Soc. Japan **28**, 935 (1970).
[20] C. A. McDowell, P. Raghunathan, and D. S. Williams, J. Magn. Res. **24**, 113 (1976).
[21] S. Albert and J. A. Ripmeester, J. Chem. Phys. **58**, 541 (1973).
[22] E. R. Andrew, W. S. Hinshow, M. G. Hutchins, and R. O. J. Sjöblom, Mol. Phys. **31**, 1479 (1976); Mol. Phys. **34**, 1695 (1977).
[23] E. R. Andrew, W. S. Hinshaw, M. G. Hutchins, R. O. J. Sjöblom, and P. C. Canepa, Mol. Phys. **32**, 795 (1976).
[24] J. L. Carolan and T. A. Scott, J. Magn. Res. **2**, 243 (1970).
[25] H. M. Maurer and Al. Weiss, J. Chem. Phys. **69**, 4046 (1978).