A Nuclear Magnetic Relaxation Study of the Dynamics of NO_3^- and SCN^- Ions in Liquid Ammonia

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A nuclear magnetic relaxation study of the rotational dynamics of nitrate and thiocyanate anions in 1 M solutions of liquid ammonia is presented. For both anions $D_\perp$ was determined and shown to be larger than observed in aqueous solution. The rotational anisotropy of the nitrate ion was found to be temperature dependent (233—303 K). Thiocyanate ion ^{13}C relaxation was found to be dominated by the spin rotation mechanism. The overall dynamics of both ions is shown to be less restricted in liquid ammonia compared to their dynamics in aqueous solutions.

For the past two decades, single-molecule reorientational dynamics in the liquid phase has been a topic of interest. Nuclear magnetic relaxation (NMR) proved to be an excellent tool in the study of the physical state of these molecules. Our understanding of the translational dynamics of ions and neutral molecules has greatly increased over the last two decades through the development of theories and their experimental verification. However, the rotational dynamics of small anions in condensed phases has not received much attention.1) Aqueous solutions of $NaNO_3$ and NaSCN, among other salts, have been studied with NMR in our laboratory to obtain information about the reorientational anisotropy.2) The separation of different effects such as ion-pairing and ion-hydration to the observed relaxation rate is not straightforward2) but information on the reorientational anisotropy is easier to obtain.

In an attempt to reduce the ion-solvent interactions, NMR experiments were performed on nitrate and thiocyanate ions in liquid ammonia. It is known that ammonia can be described as a powerful hydrogen-bond acceptor but not as a donor.3) At any given temperature between 298 and 373 K, the dielectric constant of liquid ammonia is much smaller than that of water,4,5) consequently enhancing the possibility of ion-pairing in liquid ammonia compared to water.6) A change in these interactions will likely reflect itself in a change in the reorientational anisotropy of the anions.

^{14}N, ^{17}O, and ^{13}C NMR spectroscopy is used here to obtain the motional dynamics and anisotropy of the nitrate and thiocyanate ions. For the thiocyanate ion we were able to obtain an estimate of the angular velocity correlation time. Our results indicate that the dynamics of both nitrate and thiocyanate ions in liquid ammonia differ from that in water.

Theory

The relaxation of the ^{14}N and ^{17}O nuclear spin is governed by the intramolecular quadrupole mechanism. Rotational motion of these ions causes modulation of the electric field gradient (EFG) and can be observed by magnetic relaxation. In the extreme narrowing limit, the relaxation rate of a quadrupole nucleous of spin I is given by7)

$$R_1 = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(\frac{eQ}{\hbar}\right)^2 J(0), \tag{1}$$

where eQ is the nuclear quadrupole moment and $J(0)$ the spectral density of the reorientational motion at zero frequency. The spectral density is the Fourier transform of the EFG auto correlation function $G_m(\tau)$.

$$J_m(\omega) = \int_0^\infty \mathrm{d}t G_m(\tau) e^{i\omega\tau} \tag{2}$$

$$G_m(\tau) = < B_m^{(2)}(0) B_m^{(2)*}(\tau) >_{\mathrm{Lab}} \tag{3}$$

The $B_m^{(2)}$'s transform as second rank spherical tensors and are given in the principal axis frame by: $B_0^{(2)} = \frac{1}{2}eq$, $B_{\pm1}^{(2)} = 0$, $B_{\pm2}^{(2)} = \frac{1}{2\sqrt{6}}\eta eq$.8) The EFG asymmetry is represented by η. The calculation of $G_m(\tau)$ involved two transformations into the laboratory frame, one of which introduces the time dependence.

For the nitrate ion, with an axially symmetric diffusion tensor, the theory developed by Versmold can be used.8)

$$G_m(\tau) = \frac{1}{5}\sum_{m=-2}^{2}\sum_{j'=-2}^{2}\left|D_{j,n}^{(2)}(\alpha,\beta,0)B_{j'}^{(2)}\right|^2 e^{-(6D_\perp + n^2(D_\| - D_\perp))\tau}. \tag{4}$$

$D_{j,n}^{(2)}$ $(\alpha, \beta, 0)$ represent the Wigner rotation matrix elements of which the angles α and β are determined by the orientation of the EFG principal component in the frame of the diffusion tensor of the anion. Due to the axial symmetry of the nitrate ion, only two diffusion coefficients, $D_\|$ and $D_\perp$ are required to fully describe the rotational reorientation. Performing the

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summation in Eq. 4 results in

$$G_m(\tau)\,|_{n=0}= \frac{1}{20}(eq)^2\left[\frac{1}{4}(3\cos^2\beta-1)^2 + \frac{1}{2}\eta\sin^2\beta(3\cos^2\beta-1)\cos 2\alpha+\frac{1}{4}\eta^2\sin^4\beta\cos^2\alpha\right]e^{-\frac{\tau}{\tau_0}} \quad (5)$$

$$G_m(\tau)\,|_{n=\pm 1} = \frac{1}{20}(eq)^2\left[\frac{3}{4}\sin^2 2\beta + \frac{1}{3}\eta^2\left(\sin^2\beta\left[\sin^2 2\alpha+\cos^2\beta\cos^2\alpha\right]\right) - 2\eta\cos^2\beta\sin^2\beta\cos 2\alpha\right]e^{-\frac{\tau}{\tau_{\pm 1}}} \quad (6)$$

$$G_m(\tau)\,|_{n=\pm 2}=\frac{1}{20}(eq)^2\left[\frac{3}{4}\sin^4\beta+\frac{1}{3}\eta^2(\cos^2\beta\sin^2 2\alpha + \frac{1}{4}\cos^2 2\alpha(1+\cos^2\beta)^2) + \frac{1}{2}\eta\sin^2\beta\cos 2\alpha(1+\cos^2\beta)\right]e^{-\frac{\tau}{\tau_{\pm 2}}} \quad (7)$$

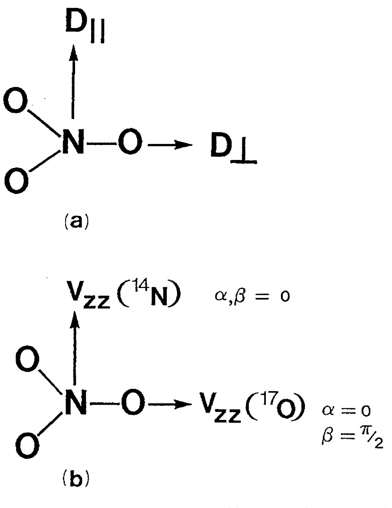
In the Eq. 5 through Eq. 7, the following time constants have been defined:

$$\tau_0 = \frac{1}{6D_\perp} \quad (8)$$

$$\tau_{\pm 1} = \frac{1}{5D_\perp + D_\parallel} \quad (9)$$

$$\tau_{\pm 2} = \frac{1}{2D_\perp + 4D_\parallel}. \quad (10)$$

Note that the interpretation of the correlation times τ_n in terms of the diffusion constants $D_\parallel$ and $D_\perp$ is only valid in the case of small angle diffusion. Figure 1 shows the orientation of the EFG principal axis frame for both the ^{14}N (spin I=1) and ^{17}O (spin $I=\frac{5}{2}$) nuclei with respect to the diffusion frame. Using the geometry of the EFG tensors with respect to the diffusion frame, one finally obtains the Eqs. 11 and 12 for the relaxation of the ^{17}O and ^{14}N nuclei in the nitrate anion respectively.



(a)

(b)

Fig. 1. a) Orientation of the diffusion frame with respect to the molecular frame of the nitrate ion. b) Orientation of the largest component of the EFG tensor relative to the diffusion frame. The Euler angles define the orientation (see text).

$$R_1(^{17}O)=\frac{24}{250}\pi^2<\chi^2>_O\frac{1}{3D_\perp(D_\perp+2D_\parallel)}\left[(1-\eta)^2D_\parallel+(4+(1+\eta)^2)D_\perp\right] \quad (11)$$

$$R_1(^{14}N)=\frac{3}{2}\pi^2<\chi^2>_N\frac{1}{6D_\perp}, \quad (12)$$

with χ representing the quadrupolar coupling constant. An expression for the relaxation rate of the ^{14}N nucleus in the thiocyanate ion can also be obtained from this theory. The thiocyanate ion has $C_{\infty v}$ symmetry and the largest component of the ^{14}N EFG tensor coincides with this axis on grounds of symmetry. From this information it follows that the thiocyanate ^{14}N relaxation can also be described by Eq. 12.

Experimental

All the NMR experiments were performed on a Nicolet 360 NB spectrometer. A broadband variable temperature probe with 50 μs $\frac{\pi}{2}$ pulse lengths was used for ^{17}O and ^{14}N measurements. For the ^{13}C measurements, a dedicated probe with 25 μs $\frac{\pi}{2}$ pulse lengths was used. Spin-lattice relaxation rates for ^{14}N were measured by an inversion recovery technique using phase cycling of the pulses. Typically, fourteen or more time delays were measured, Fourier transformed and fitted to a three parameter, single exponential expression.[7)] The inversion of magnetization was 90% or better. The ^{17}O relaxation rates were obtained from line width measurements as these were performed on natural abundant $N^{17}O_3^-$. The relaxation of this nucleus is in the extreme narrowing limit[9)] allowing this procedure. ^{13}C relaxation rates of thiocyanate were measured by means of a saturation recovery technique.[10)] The amplitudes of the frequency spectra were fitted to a two parameter, single exponential.[11)] The temperature in the probe was regulated with cold nitrogen gas and a heater build into the probes.

The nitrate and thiocyanate solutions were prepared by condensing dried ammonia gas into a well defined volume of a thick wall NMR tube containing the salt. Traces of water were removed by previously drying the salts under vacuum and drying the liquid ammonia over sodium. A final concentration of 1.0±0.1 mol L^{-1} was obtained this way. The NMR tubes were sealed under vacuum after freezing the sample in liquid nitrogen.

Results and Discussion

1. The Nitrate Ion. The temperature dependence of the ^{14}N and ^{17}O relaxation rates are shown in Fig. 2. Due to the low natural abundance of ^{17}O, 3.7×10^{-2} %, only a few spin–spin relaxation rates were measured. For the ^{17}O nuclei in the nitrate ion a quadrupolar coupling constant of χ=12.57 MHz and an EFG asymmetry of η=0.747 has been reported for solid $NaNO_3$.[12)] For ^{14}N, in NO_3^-, a χ of 745 kHz and an η of 0 has been reported.[13)] From the ^{14}N relaxation data $D_\perp$ can be calculated with the use of Eq. 12. These values were then used to calculate $D_\parallel$ from the ^{17}O relaxation data which in turn was used to calculate the reorientational anisotropy $\frac{D_\parallel}{D_\perp}$. In Table 1 anisotropy data of the nitrate ion are given for different temperatures.

In the low temperature region, as can be seen from Fig. 2,

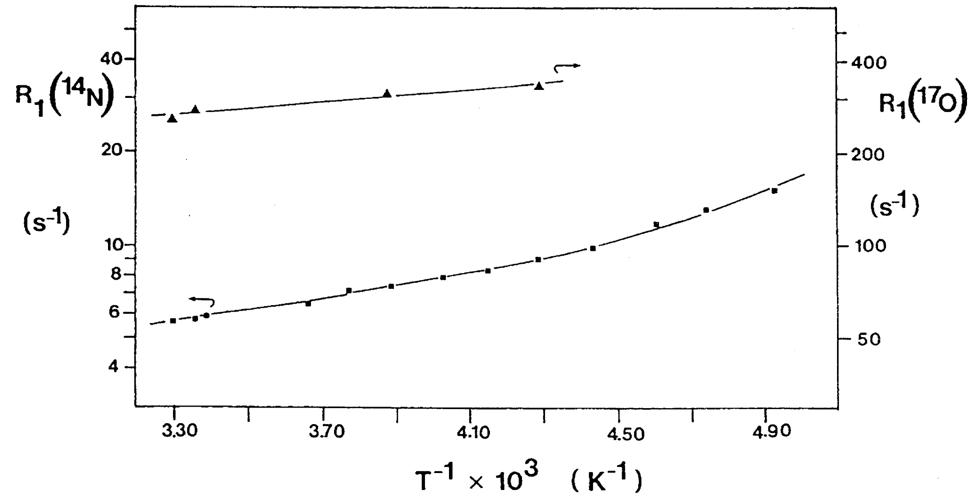


Fig. 2. Temperature dependence of the ^{14}N (■) and ^{17}O (▲) relaxation rates of the nitrate ion in 1.0±0.1 M $NaNO_3$ in liquid ammonia.

Table 1. Diffusion Constants and Rotational Anisotropy of the Nitrate Ion in Liquid Ammonia

$\frac{T}{\mathrm{K}}$	$\frac{D_{\perp}\times 10^{-11}}{\mathrm{s}^{-1}}$	$\frac{D_{\parallel}\times 10^{-10}}{\mathrm{s}^{-1}}$	$\frac{D_{\parallel}}{D_{\perp}}$
303	2.4	5.1	0.21
298	2.3	4.3	0.19
258	1.9	4.6	0.24
233	1.5	5.9	0.39

the ^{14}N relaxation rate exhibits a deviation from linearity as a function of the reciprocal temperature. A similar deviation from linearity has also been observed for aqueous solutions of nitrate ions[1,2] and, for instance, also in the ^{1}H relaxation rate of pure water.[14,15] This non-Arrhenius behavior is not well understood but has to be related to changes in the ion–water and/or water–water interactions upon changes in temperature. To determine whether this non-Arrhenius behavior could also be observed for NH_3 in the 1 M $NaNO_3$ in liquid ammonia solution (1 M=1 mol dm^{-3}), the ^{14}N relaxation of ammonia was measured. No deviation from linearity could be observed over a temperature region of $231<T<272$ K. The apparent activation energy for the $^{14}NH_3$ relaxation rate was 9.0±0.2 kJ mol^{-1}. This value is somewhat larger than obtained by Atkins et al. (7.9±0.2 kJ mol^{-1})[16] for pure liquid ammonia. This indicates that the out-of-plane reorientation of the NH_3 molecules in the nitrate sample is slightly deactivated as compared to the pure ammonia.

It is interesting to compare the ^{14}N and ^{17}O NO_3^- relaxation data for the liquid ammonia and aqueous samples. At room temperature, the ^{14}N relaxation rate in aqueous solution[2] is approximately twice as large as that for the nitrate ions in liquid ammonia. As a result, $D_{\perp}$ of the NO_3^- ion is approximately twice as large in liquid ammonia as in water. On the other hand, the ^{17}O relaxation times of nitrate ions in aqueous solution and in liquid ammonia do also differ; 2.5 ms[2] and 3.6 ms respectively. At 295 K, $D_{\parallel}$ for NO_3^- in water is reported to be 5.12×10^{10} s^{-1}. This value is very close to that observed in liquid ammonia (see Table 1). That the observed values for $D_{\parallel}$ in the two systems are close is due to the insensitivity of Eq. 11 to small changes in $D_{\parallel}$. For approximately $D_{\perp}\geq D_{\parallel}$, changes in $D_{\perp}$ dominate the relaxation rate. As a result the rotational anisotropy, $\frac{D_{\parallel}}{D_{\perp}}$, for the NO_3^- ion at 295 K in liquid ammonia should be higher by approximately a factor 2 compared to the anisotropy observed in water. Apparently the effect of liquid ammonia, as compared to water as solvent, is to enhance the end-over-end rotations ($D_{\perp}$) of the NO_3^- ion. These results clearly indicate that the $D_{\perp}$ motion of the nitrate ion is less hindered in liquid ammonia and that the reorientational anisotropy in liquid ammonia is different from that in water. In aqueous solution, the rotational anisotropy, $\frac{D_{\parallel}}{D_{\perp}}$, seems to be temperature independent with an average value of 0.45 over a temperature region of $295<T<353$ K.[2] In liquid ammonia, a slightly temperature dependent rotational anisotropy of the nitrate ion (0.2 to 0.4), as listed in Table 1, was observed. One should realize that the relative error in the measured anisotropy of Table 1 could be as large as 30% due to the relatively large uncertainty in the ^{17}O relaxation rates. However, the observed rotational anisotropy of the nitrate ions is larger in liquid ammonia than in water.

For the ^{14}N relaxation of the nitrate ion in liquid ammonia an activation energy of 4.1±0.2 kJ mol^{-1} was obtained for $233<T<303$ K and a value of 7.0±0.2 kJ mol^{-1} in the temperature region of $203<T<225$ K. The activation energy for $D_{\perp}$ of aqueous NO_3^- ions has been reported to be much higher than observed for NO_3^- ions dissolved in liquid ammonia, 19.3 kJ mol^{-1} for $273<T<298$ K.[2] Together with the increase in $D_{\perp}$, these results are in line with the general view of a weakening of the hydrogen-bonding network.[2] Using the Arrhenius expression for the $D_{\perp}$ (NO_3^-); $D_{\perp}=D_{\perp}^{0}\exp\left(-\frac{E_a}{RT}\right)$, it can be shown that $D_{\perp}^{0}$ for the aqueous solution is about 200 times larger than $D_{\perp}^{0}$ in liquid ammonia. Such a difference indicates differences in microscopic structure of the two solutions. Our results also show that ion-pairing is likely not enhanced. If this would be the case one would expect a higher value for the reorientational anisotropy. Formation of aqua-ions or NH_3-ions complexes results in the formation of larger, more spherical, complexes which show less rotational anisotropy. These complexes must also slow down the end-over-end rotations of the NO_3^- ions. Comparing liquid ammonia and water, a change in ion-pairing interactions is likely to reflect itself in a change in the activation energy ratio for the two temperature regions. This, however, is not observed for the NO_3^- ion.

2. The Thiocyanate Ion. Apart from ^{14}N relaxation measurements, additional ^{13}C relaxation measurements were performed on the thiocyanate ion. For the ^{13}C (spin $I=\frac{1}{2}$) magnetization, more than one relaxation mechanism is active. The closely related spin-rotation (SR) and chemical shielding anisotropy (CSA) interactions dominate the thiocyanate ^{13}C relaxation. Intermolecular ^1H–^{13}C dipolar interactions with solvent protons can be excluded as no NOE[17] was observed for the thiocyanate ^{13}C resonance at 299 K.

The SR interaction describes the coupling of molecular angular momentum with the nuclear spin. The SR contribution to the observed ^{13}C relaxation of the thiocyanate ion is given by[18]

$$R_1(^{13}\mathrm{C})_{\mathrm{SR}} = \frac{3}{4}\frac{k_\mathrm{B}T}{\hbar^2} I_\perp C_\perp^2 \tau_J. \tag{13}$$

The angular velocity correlation time is resembled by τ_J and the SR constant by $C_\perp$. In the appendix, the SR constant for the thiocyanate ion is calculated. The contribution of the CSA to the observed ^{13}C relaxation rate is given by[11,23]

$$R_1(^{13}\mathrm{C})_{\mathrm{CSA}} = \frac{2}{15}\omega^2(\Delta\sigma)^2\tau_2. \tag{14}$$

The CSA was reported to be $\Delta\sigma=321\pm7$ ppm[19] and the rotational correlation time τ_2 in Eq. 14, is the same as determined from ^{14}N relaxation measurements on the thiocyanate ion. For the ^{14}N thiocyanate quadrupolar interaction a coupling constant of 2.432 MHz and an $\eta=0$ was used.[20]

The thiocyanate ^{14}N and ^{13}C relaxation rates, as a function of the reciprocal temperature, are shown in the Figs. 3 and 4 respectively. A low boiling point of the sample restricted the ^{13}C relaxation rate measurements over a small temperature region. Observed ^{14}N relaxation rates were used to obtain the rotational correlation time τ_2. With these values the contribution of the CSA to the observed thiocyanate ^{13}C relaxation rate was obtained. From the calculated SR and CSA contributions to the observed ^{13}C relaxation rate, it is clear that the SR mechanism dominates the ^{13}C spin relaxation for $287<T<299$ K. For example, at 298 K, $R_1^{\mathrm{CSA}}(^{13}\mathrm{C})=5.8\times10^{-3}$ s^{-1} and $R_1^{\mathrm{SR}}(^{13}\mathrm{C})=130\times10^{-3}$ s^{-1}, while at 287 K, $R_1^{\mathrm{CSA}}(^{13}\mathrm{C})=6.7\times10^{-3}$ s^{-1} and $R_1^{\mathrm{SR}}(^{13}\mathrm{C})=24\times10^{-3}$ s^{-1}. Thus, even at 287 K the CSA mechanism is only responsible for approximately 28% of the observed ^{13}C relaxation rate.

The ^{14}N relaxation rates of thiocyanate in liquid ammonia can be described by an activation energy of 10.6 ± 0.4 kJ mol^{-1} in the region $243<T<299$ K and 11.5 ± 0.5 kJ mol^{-1} in the region of $203<T<233$ K. In aqueous solution a value of 17.1 kJ mol^{-1} for $273<T<298$ K has been reported.[2] Note that the activation energy for the end-

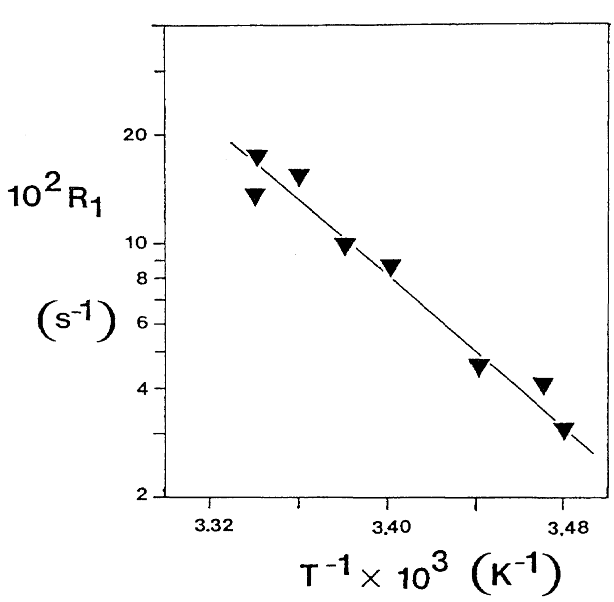


Fig. 4. Temperature dependence of the ^{13}C relaxation rate of the thiocyanate ion in 1.0 ± 0.1 M NaSCN in liquid ammonia.

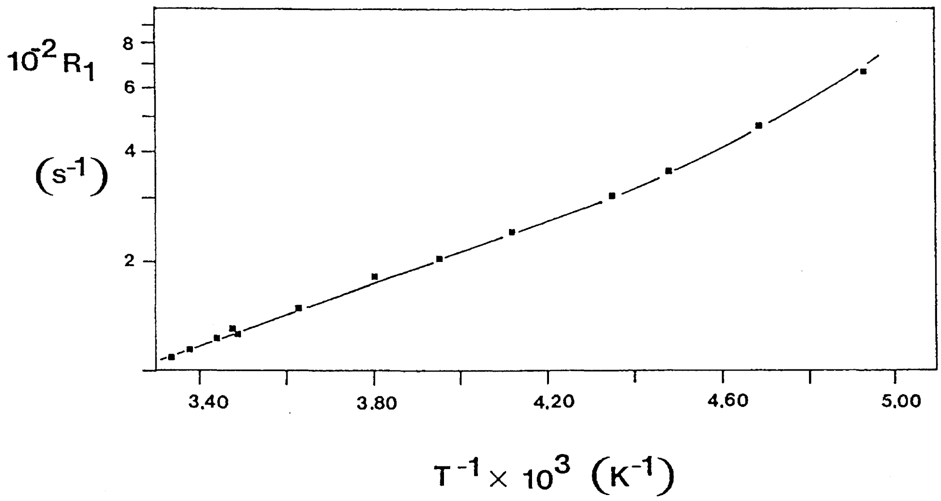


Fig. 3. Temperature dependence of the ^{14}N relaxation rate of the thiocyanate ion in 1.0 ± 0.1 M NaSCN in liquid ammonia.

over-end rotations of the SCN^- ion in the two solvents for $273<T<298$ K do not differ much. This is different for the NO_3^- ion where we observed a large change. It should be pointed out that the activation energy for the end-over-end rotational motion of the thiocyanate ion is less temperature dependent than the out-of-plane motion of the nitrate ion as reflected in the change in activation energy in the two temperature regions. Within the framework of small angle diffusion, $D_\perp$ of the SCN^- ion is observed to be approximately twice as large in liquid ammonia (Table 2) than at 298 K in aqueous solution.[2] As for the NO_3^- ion this change is likely due to a weakening of the hydrogen-bond network. Raman experiments in liquid ammonia indicate that the ion-pairing is more important in aqueous solution than in liquid ammonia in general.[6,21] These ion-pairing interactions also seem to be more intense in the thiocyanate solutions than in the nitrate solutions.[21] This indicates that the small change in ^{14}N activation energy as observed in Fig. 3, is likely to be due to small changes of the interaction in this temperature region. Apparently, ion-pairing interactions in the liquid ammonia–thiocyanate system do not show significant changes throughout the temperature region investigated. This is reflected in the small change in activation energy for the $D_\perp$ reorientational motion. The ratio of the activation energies in the two temperature regions is less in liquid ammonia than observed in water.[2]

With both τ_2 and τ_J of the thiocyanate end-over-end rotation available, one could, in principle, test theories describing the rotational dynamics of ions in solution. Unfortunately, no such theories are available and one could resort to a model developed to describe the dynamics of molecular fluids such as the Gordon's extended J-diffusion model.[22] Within this framework we can conclude that, in the small temperature region of $291<T<299$ K, the dynamics of the thiocyanate ion does not obey the Hubbard Limit, i.e., $\tau_2 \cdot \tau_J \neq \frac{1}{6}\frac{I}{k_BT}$. It should thus be noted that for $T>291$ K, the reorientational motion of the SCN^- ions is probably not accurately described by a small angle diffusion model. However, most of data was obtained for lower temperatures for which the small angle diffusion limit should apply.

Conclusions

For both the nitrate and thiocyanate ion it was observed that the overall rotational dynamics is less restricted in liquid ammonia than in aqueous solution. Both the NO_3^- and SCN^- ions show, at room temperature, approximately a doubling of $D_\perp$ in liquid ammonia. This change was attributed to a weakening of the hydrogen-bond network in liquid ammonia as compared to water. Relaxation measurements of ^{14}N and ^{17}O magnetization show that the reorientation of the nitrate ion is still anisotropic in liquid ammonia as well as in aqueous solution. However, the rotational anisotropy of the nitrate ion in liquid ammonia is higher than obtained in water. This increase in anisotropy can also be related to a change in hydrogen-bonding of the solvent. The apparent dynamics of the nitrate and thiocyanate ions is less hindered in liquid ammonia due to the low hydrogen-bond donor capacity of ammonia. This low hydrogen-bond donor capacity weakens the hydrogen-bonding network. The small change in the ratio of the activation energy of the SCN^- ^{14}N relaxation rate in the two temperature regions indicates only minor changes in ion-pairing interactions. For the NO_3^- ion this ratio was found the same in liquid ammonia and water. Ion-pairing interactions are reported to be less important in liquid ammonia and more important for the NO_3^- than the SCN^- ion.[6,21] Apparently ion-pairing interactions in the liquid ammonia/thiocyanate sample present throughout the temperature region studied do not show any large change as a function of temperature. For the NO_3^- ion, ion-pairing interactions are likely to become important at lower temperatures in both liquid ammonia and aqueous systems.

Table 2. Rotational Correlation Times and Angular Velocity Correlation Times for the Thiocyanate Ion in Liquid Ammonia

T	$\tau_2 \times 10^{12}$	$\tau_J \times 10^{13}$
K	s	s
299	1.23	7.13
296	1.29	4.36
294	1.33	3.40
291	1.40	2.02
287	1.47	1.12

From the activation energies of the ^{14}N relaxation studies we determined no direct indication of a strong change in ion-pairing interactions as observed from the rotational dynamics of the thiocyanate ion in liquid ammonia. The activation energies of the $D_\perp$ reorientation of the nitrate ion in liquid ammonia show a similar ratio as observed in water.

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Appendix

In this section we calculate the SR constant of the thiocyanate ion. Using Ramsey's theory of chemical shielding,[23] the chemical shift tensor can be written as a sum of a diamagnetic and a paramagnetic part; σ^d and σ^p respectively.

$$\sigma = \sigma^d + \sigma^p \tag{15}$$

The diamagnetic part of the shielding depends only on the ground state electronic wave function and can in principle be calculated by means of MO theory or approximated by the theory of Flygare.[24] The isotropic part of the diamagnetic shielding is given by

$$<\sigma^d>=<\sigma^d(\text{freeatom})> + \frac{e^2}{3mc^2}\sum_N \frac{Z_N}{r_N}. \tag{16}$$

The paramagnetic part depends on the SR constant of the molecule. For linear molecules ($C_{\infty v}$ symmetry) the following relation holds,[23,24]

Table 3. Thiocyanate ^{13}C Shielding Data and Atomic Parameters[24)]

$\sigma_\perp$	−55.0 ppm
$\sigma_\parallel$	266.0 ppm
$\sigma_{\mathrm{iso}}=\frac{1}{3}[\sigma_\parallel+\sigma_\perp]$	52 ppm
$\sigma^{\mathrm{d}}_{\mathrm{av}}$(freeatom)	321.7 ppm
η_{CSA}	0
r_{SC}	1.649 Å
r_{CN}	1.176 Å
$I_\perp$	1.389×10^{-38} g cm^2

$$\sigma^{\mathrm{p}}_\perp = \frac{e}{3mhc}R_\perp I_\perp - \frac{e^2}{3mc^2}\sum_N \frac{Z_N}{r_N}, \qquad (17)$$

with $I_\perp$ the moment of inertia of a linear molecule. Note that $\sigma^{\mathrm{p}}_\parallel=0$ but that $\sigma^{\mathrm{d}}_\perp\neq0$. $R_\perp$ is given by

$$R_\perp = \frac{C_\perp h}{g_N \mu_N}. \qquad (18)$$

The other symbols have their usual meaning. The SR constant $C_\perp$ was calculated from experimentally obtained shielding values, listed in Table 3. For $C_\perp$ a value of 2895 Hz was calculated.

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