Research Article

Deuterium Isotope Effects on $^{14,15}\text{N}$ Chemical Shifts of Ammonium Ions: A Solid State NMR Study

Poul Erik Hansen

Department of Science, Systems and Models, Roskilde University, P.O. Box 260, 4000 Roskilde, Denmark

Correspondence should be addressed to Poul Erik Hansen, poulerik@ruc.dk

Received 10 August 2011; Revised 10 October 2011; Accepted 14 October 2011

Academic Editor: Rabindranath Mukherjee

Copyright © 2011 Poul Erik Hansen. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Deuterium isotope effects on $^{14,15}\text{N}$ chemical shifts are measured in ammonium halides in the solid state using both enriched ^{15}N salts and ^{14}N natural abundance materials. The effects are correlated to ^{15}N chemical shifts and to $\text{N} \cdots \text{X}$ distances. The deuterium isotope effects on $^{14,15}\text{N}$ chemical shifts in the solid state are discussed in relation to effects observed in solution. No NH couplings are seen due to fast rotation in the solid, which leads to self-decoupling, whereas ND couplings are present.

1. Introduction

Ammonium ions both in solution and in the solid state show extraordinary properties as expressed by a very fast rotation in solution [1] and in the solid by unusual structures both of the ammonium salts themselves [2] but also of the deuterated species [3].

The ammonium chloride, bromide, and iodide exist as CsCl structures at ambient temperature [4]. The nitrogen to halide distances are given in a couple of reference papers [5, 6].

Isotope effects of ammonium salts in solution show counter ion-dependent chemical shifts both on ^1H and $^{14,15}\text{N}$ chemical shifts [7]. The smallest effects for different salts were found in very dilute solutions [7]. Studies of ammonium ions in crown ethers and cryptands showed for ions fully embedded in a cryptand no counter ion dependence [8]. Theoretical calculations on ammonium ions surrounded by water or ammonia showed a dependence on heavy atom distance for deuterium isotope effects on nitrogen or hydrogen chemical shifts [8, 9]. Deuterium isotope effects in the solid state have been demonstrated for ammonium chloride [10]. Recent advances in solid state NMR have made it possible to measure ^{14}N solid state spectra of ammonium salts [11, 12].

The present study investigates deuterium isotope effects on nitrogen chemical shifts in order to elucidate the dependence on the heavy atom distance and direction to get a

firmer basis for interpretation of deuterium isotope effects on nitrogen chemical shifts also in solution.

2. Results

The primary goal has been to measure deuterium isotope effects on nitrogen chemical shifts of ammonium salts in the solid. The experiments have been done using fully deuterated compounds mixed with the nondeuterated species. In order to measure the isotope effects, a number of experiments have been done on ^{14}N or ^{15}N ammonium salts using both proton decoupling and no proton decoupling.

The signal from the fully deuterated species is a nonet. The chemical shift is that of the highest centre peak (marked on Figures 1(a) and 1(b)). The full deuterium isotope effect on the chemical shift is given as the difference between the chemical shift of the NH_4 and the ND_4 peaks.

2.1. ^{15}N Spectra. For the ^{15}N observation, spectra were typically recorded with a spinning speed of 12000 Hz in order to achieve good resolution. The line widths for the NH_4^+ peak 18 Hz and for the ND_4^+ species slightly better (see Figure 1(a)). A common feature for all proton-coupled spectra is a lack of observation of NH couplings.

2.2. ^{14}N Spectra. Magic angle spinning spectra without proton decoupling of ammonium chloride show sharp

FIGURE 1: (a) Solid state ^{15}N spectrum of a 1 : 1 mixture of NH_4Cl and ND_4Cl . The six highest peaks have the frequencies 0 ppm (NH_4^+) and -1.555 , -1.330 , -1.506 , -1.694 , and -1.870 ppm (ND_4^+). (b) Solid state ^{14}N spectrum of a 1 : 1 mixture of NH_4Br and ND_4Br (with a small amount of ND_3HBr). For the five highest peaks, the frequencies are 2.227 ppm (NH_4^+) 0.977, 0.783, 0.607, and 0.432 ppm (ND_4^+).

resonances (line width 42 Hz), but no splittings due to NH couplings. Proton decoupling led to a sharpening of the resonances (line width 17 Hz). This holds true for a spinning speed range between 7000 and 12000 Hz. For the corresponding perdeuterated compounds primarily ND_4^+ with a small amount of ND_3H^+ showed resolved ND couplings at spinning speeds above 10000 Hz. Isotope effects were typically measured in 1 : 1 mixtures of NH_4 and ND_4 salts (Figures 1(a) and 1(b)). For ammonium chloride, the ^{14}ND coupling constant is 7.6 ± 0.8 Hz and the $^1\Delta\text{N}(\text{D})_4$ isotope effect is measured as 1.61 ppm. For ammonium bromide, the isotope effect is measured as 1.62 ppm and the coupling constant is 7.6 ± 0.8 Hz, whereas the ammonium iodide gave $^1\Delta\text{N}(\text{D})_4 = 1.81$ ppm, no resolved couplings could be seen.

2.3. Nitrogen Chemical Shifts. The nitrogen chemical shifts are -26 , 0 , 2.3 , and 15.9 ppm for the F^- , Cl^- , Br^- , and I^- , respectively, as reported earlier [14]. ^{14}N spectra of ammonium chloride cooled to -44°C showed a slight change in chemical shifts at -30°C in line with a phase transition at this temperature [4].

3. Discussion

The finding that no NH couplings could be seen is due to fast rotation of the ammonium ion in the solid leading to self-decoupling as seen for adamantane [15]. In support of such a suggestion is the finding that the spectra become sharper at high spinning speeds and become very complex

at low spinning speeds. Chemical exchange can be excluded as no major changes are seen as a function of cooling to temperatures as low as -44°C . The reason that ND couplings are seen but not those of NH can be ascribed to the fact that homonuclear couplings are much smaller for DD than for HH. The importance of homonuclear couplings were demonstrated for adamantane for which the NH couplings could be reestablished by quenching of the self-decoupling by means of strong off-resonance rf-irradiation of the protons [15].

The isotope effects in the solid are seen to increase in the series $\text{ND}_4\text{Cl} \sim \text{ND}_4\text{Br} < \text{ND}_4\text{I}$. If we furthermore include the data for the cryptand SC-24 [8], we find a decent correlation between $^1\Delta\text{N}(\text{D})_4$ and the ^{15}N chemical shifts (Figure 2). Knowing the chemical shifts of NH_4F [14] we can now estimate $^1\Delta\text{N}(\text{D})_4$ to 1.16 ppm. Using the nitrogen to acceptor distances, acceptor being either halide or N (for SC-24), we see again a decent correlation (Figure 3), but slightly different for the solid state halide data and those of SC-24 and for ammonium ions solvated by water (the latter two marked by triangles). The water distance is obtained from [16–18]. This distance is a matter of debate, but, whether one is using 2.78 or 3.08 Å, we see that water is more effective in reducing $^1\Delta\text{N}(\text{D})_4$ than halide ions.

The slope $^1\Delta\text{N}(\text{D})_4/\delta\text{N}$ is 0.017 ppm/Å (Figure 2). This can be compared with solution in which it is 0.06 [7]. This indicates a quite different origin of the isotope effects in the liquid and solid state. In the solid state, the isotope effects decrease as the heavy atom distance is shortened (Figure 3). This is also supported by calculations [9, 19]. The heavy atom

FIGURE 2: Plot of $^{14,15}\text{N}$ chemical shifts versus $^1\Delta N(D)_4$. Data for SC-24 from [8].

FIGURE 3: Plot of $R_{N...X}$ versus $^1\Delta N(D)_4$. The distance for SC-24 is given as an average of the distances found in [13].

distance is clearly important but most likely in an indirect way as the nitrogen chemical shift has been shown to depend much more strongly on the NH bond length than on the heavy atom distance [14]. However, indirectly, the heavy atom distance will determine the interaction potential and the NH bond length.

In the liquid state, the largest isotope effects were found for high concentrations of iodide ions [7]. In contrast, the smallest $^1\Delta N(D)_4$ is found in very dilute solutions [7] as a function of the inner water solvation shell leading to short $\text{N} \cdots \text{O}$ distances. At higher concentration of halide ions, the waters will be partly displaced by halide ions but at a longer heavy atom distance leading to the observed increase in $^1\Delta N(D)_4$ both because of this and because halide ions are less effective in reducing the isotope effects (see earlier).

Ammonium ions are also a good model for positively charged lysine molecules. For hydrated lysines, a $^1\Delta N(D)_3$ of 1.05 ppm is found [20]. The isotope effects per deuterium are only slightly different for ammonium ions (0.30 ppm) and for lysines (0.35 ppm). Deuterium isotope effect on $^{14,15}\text{N}$ chemical shifts may be used to gauge the amount of solvation in biological systems.

4. Experimental

Ammonium salts were deuterated by repeated dissolution in D_2O followed by evaporation under reduced pressure.

The ^{15}N spectra were recorded on 90% ^{15}N enriched ammonium chloride purchased from Aldrich. All solid state

NMR spectra were measured on a Varian 600 Inova instrument using magic angle spinning.

The ^{14}N MAS NMR spectra were acquired at 14.1 T using a homebuilt 5 mm CP/MAS probe for 5 mm o.d. rotors, a spinning speed of $\nu_R = 12.0$ kHz, single-pulse excitation with a 90° pulse ($\gamma B_1/2\pi = 45$ kHz), a 4-s repetition delay, and 512 scans. Acquisition time is 0.2 s, spectral width 100000 Hz, and number of points 40000.

The ^{15}N MAS spectra were recorded without cross-polarization at 14.1 T ($\nu_R = 12.0$ kHz and $\gamma B_1/2\pi = 50$ kHz) using a homebuilt 4 mm CP/MAS probe for 4 mm o.d. rotors, a 30-s relaxation delay, and 64 scans. Acquisition time is 0.1 s, spectral width 100000 Hz, and number of points 20032. Acoustic ringing caused no significant problems in either of the experiments due to the narrow resonances observed in both spectra.

Acknowledgments

The author would very much like to thank Rigmor S. Johansen for her expert help in recording the spectra and Professors Hans Jørgen Jakobsen and Jørgen Skibsted for help and advice.

References

- [1] C. L. Perrin and R. K. Gipe, "Rotation and solvation of ammonium ion," *Science*, vol. 238, no. 4832, pp. 1393–1394, 1987.
- [2] R. Born, D. Hohlwein, and G. Eckold, "Orientational disorder in ammonium chloride: elastic diffuse neutron scattering with a new technique," *Journal of Applied Crystallography*, vol. 22, pp. 613–619, 1989.
- [3] R. Born and D. Hohlwein, "Lokale Gitterverzerrungen in ammoniumchlorid," 27. Diskussionstagung der Arbeitsgemeinschaft Kristallographie, 1982.
- [4] H. A. Levy and S. W. Peterson, "Neutron diffraction determination of the crystal structure of ammonium bromide in four phases," *Journal of the American Chemical Society*, vol. 75, no. 7, pp. 1536–1542, 1953.
- [5] M. Mascali, "A statistical analysis of halide...H-A (A = OR, NR₂, N⁺R₃) hydrogen bonding interactions in the solid state," *Journal of the Chemical Society*, no. 10, pp. 1999–2001, 1997.
- [6] T. Steiner, "Hydrogen-bond distances to halide ions in organic and organometallic crystal structures up-to-date database study," *Acta Crystallographica*, vol. B54, pp. 456–463, 1998.
- [7] P. E. Hansen and A. Lycka, "A reinvestigation of one-bond deuterium isotope effects on nitrogen and on proton nuclear shielding for the ammonium ion," *Acta Chemica Scandinavica*, vol. 43, pp. 222–232, 1989.
- [8] P. E. Hansen, A. E. Hansen, A. Lycka, and A. Buvári-Barcza, " $^2\Delta N(D)$ and $^1\Delta N(D)$ isotope effects on nuclear shielding of ammonium ions in complexes with crown ethers and cryptands," *Acta Chemica Scandinavica*, vol. 47, pp. 777–788, 1993.
- [9] M. Munch, A. E. Hansen, P. E. Hansen, and T. D. Bouman, "ab initio calculations of deuterium isotope effects on hydrogen and nitrogen nuclear magnetic shielding in the hydrated ammonium ions," *Acta Chemica Scandinavica*, vol. 46, pp. 1065–1071, 1992.
- [10] T. C. Stringfellow, G. Wu, and R. E. Wasylshen, "Experimental study of isotope effects on NMR parameters in the solid state,"

- Journal of Physical Chemistry B*, vol. 101, no. 46, pp. 9651–9656, 1997.
- [11] T. Giavani, H. Bildsøe, J. Skibsted, and H. J. Jakobsen, “ ^{14}N MAS NMR spectroscopy and quadrupole coupling data in characterization of the IV-III phase transition in ammonium nitrate,” *Journal of Physical Chemistry B*, vol. 106, no. 11, pp. 3026–3032, 2002.
- [12] H. J. Jakobsen, A. R. Hove, R. G. Hazell, H. Bildsøe, and J. Skibsted, “Solid-state ^{14}N MAS NMR of ammonium ions as a spy to structural insights for ammonium salts,” *Magnetic Resonance in Chemistry*, vol. 44, no. 3, pp. 348–356, 2006.
- [13] E. Graf, J. P. Kintzinger, J. M. Lehn, and J. LeMoigne, “Molecular recognition. Selective ammonium cryptates of synthetic receptor molecules possessing a tetrahedral recognition site,” *Journal of the American Chemical Society*, vol. 104, no. 6, pp. 1672–1678, 1982.
- [14] C. I. Ratcliffe, J. A. Ripmeester, and J. S. Tse, “ ^{15}N NMR chemical shifts in solid NH_4^+ salts,” *Chemical Physics Letters*, vol. 99, no. 2, pp. 177–180, 1983.
- [15] M. Ernst, A. Verhoeven, and B. H. Meier, “High-speed magic-angle spinning ^{13}C MAS NMR spectra of adamantane: self-decoupling of the heteronuclear scalar interaction and proton spin diffusion,” *Journal of Magnetic Resonance*, vol. 130, no. 2, pp. 176–185, 1998.
- [16] G. Pálkás, T. Radnai, G. I. Szász, and K. Heinzinger, “The structure of an aqueous ammonium chloride solution,” *The Journal of Chemical Physics*, vol. 74, no. 6, pp. 3522–3526, 1981.
- [17] Y. L. Zhao, M. Meot-Ner, and C. Gonzalez, “Ionic hydrogen-bond networks and ion solvation. 1. an efficient monte carlo/quantum mechanical method for structural search and energy computations: ammonium/water,” *Journal of Physical Chemistry A*, vol. 113, no. 12, pp. 2967–2974, 2009.
- [18] P. Intharathap, A. Tongraar, and K. Sagarik, “Structure and dynamics of hydrated NH_4^+ : an ab initio QM/MM molecular dynamics simulation,” *Journal of Computational Chemistry*, vol. 26, no. 13, pp. 1329–1338, 2005.
- [19] S. Ullah, T. Ishimoto, M. P. Williamson, and P. E. Hansen, “Ab initio calculations of deuterium isotope effects on chemical shifts of salt-bridged lysines,” *Journal of Physical Chemistry B*, vol. 115, no. 12, pp. 3208–3215, 2011.
- [20] J. H. Tomlinson, S. Ullah, P. E. Hansen, and M. P. Williamson, “Characterization of salt bridges to lysines in the protein G B1 domain,” *Journal of the American Chemical Society*, vol. 131, no. 13, pp. 4674–4684, 2009.