A Reinvestigation of One-Bond Deuterium Isotope Effects on Nitrogen and on Proton Nuclear Shielding for the Ammonium Ion[§]

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One-bond deuterium isotope effects on ^{14}N and ^{15}N nuclear shielding,[1]$\Delta^{14,15}$N(D), and two-bond isotope effects on ^{1}H nuclear shielding, $^{2}\Delta H(D)$, of the ammonium ion are reinvestigated. A series of ammonium salts, NH_4X ($X = NO_3^-$, ClO_4^-, SO_4^{2-}, Cl^-, Br^-, I^- and I_3^-), are investigated. [1]$\Delta N(D)$ at 2 molar concentration increases in the series $NO_3^- > SO_4^{2-} \sim ClO_4^- > \cdots Cl^- > Br^- > I^- \sim I_3^-$. It is furthermore shown that [1]$\Delta N(D)$ and $^{2}\Delta H(D)$ depend both on concentration and on added counter ion. The effects of a mixture of ammonium salts depend on the ratio of anions. Non-additivity of [1]$\Delta N(D)$ and $^{2}\Delta H(D)$ is observed. In the latter case the heavier isotopomers show the larger non-additivity. Both nature and concentration of counter ion play a role in the isotope effects. Evidence that hydrogen-bonding is responsible for the negative $^{2}\Delta H(D)$ is found.

The study of isotope effects thus leads to a model for the solvation around the ammonium ion in which the counter ions partially exclude water from the inner solvation sphere and in which water forms non-directional hydrogen bonds to the N-H bonds. In addition, proton isotope effects on ^{2}H nuclear shielding, $^{2}\Delta D(H)$, are investigated in order to support the above-mentioned results.

The deuterium isotope effects on ^{14}N and ^{15}N nuclear shielding of ammonium ion have attracted much interest recently.[1-9] This interest is based upon the high symmetry of the species, its well documented physical properties, such as vibrational pattern, energy levels etc., and the small molecular weight that enable exact theoretical calculations. The ammonium ion may also serve as a model for those alkali ions, viz. K^+ and Cs^+, which are difficult to observe by means of NMR. Furthermore, a structural relationship exists between NH_4^+ and H_3O^+.[10] A comparison of isotope effects of ammonia[11] and ammonium ions can shed further light on the basic mechanisms of isotope effects.[3,7,9] However, the published experimental results vary quite a lot, which makes it difficult to draw any conclusions. Several factors could be responsible for this variation, as the experimental conditions are rather different. The reported experiments were performed with different field strengths, temperatures, pH and anions, and both isotopes, ^{14}N and ^{15}N, have been studied. Furthermore, inadequate resolution due to the use of a very low field strength may also complicate the issue. We have reinvestigated the deuterium isotope effects on nuclear shielding of ^{14}N and ^{15}N, looking carefully into these possibilities. In addition, ^{1}H NMR spectra of the same solutions have been recorded, since the original investigation was made at very low field.[12]

The deuterium isotope effects observed for the ammonium ion display many interesting features. The negative $^{2}\Delta H(D)$ for the ammonium ion in contrast to the positive value for ammonia[11,13] is unusual. The relative smallness of [1]$\Delta N(D)$ compared to that for ammonia[2,3,4,9,11] is likewise intriguing. A comparison of the ammonium ion with other less symmetrical ions is also revealing.[3] The discussion has so far evolved around the high symmetry of the molecule,[2,5] the presence of a lone-pair in ammonia and not in the ammonium ion,[2,7] and the solvent and thereto related pH effects.[3]

The present paper investigates the factors affecting [1]ΔN(D) and $^{2}\Delta H(D)$ in the ammonium ion in order to explain the experimental results already published, but also to establish more definitely the factors which determines these isotope effects. This is achieved mainly by comparison of the one-bond deuterium isotope effects on ^{14}N nuclear shielding,[1]$\Delta N(D)$, with ^{14}N nuclear shielding in a series of compounds and by a study of the effects of salt concentration and of the nature of the counter ion. ^{15}N nuclear shielding in ammonium salts has previously been studied,[14,15] and much work has been done to understand the effects of concentration, nature of anion, etc., of the related alkali ions.[16,17]

The following series of compounds has been investigated: NH_4NO_3, $(NH_4)_2SO_4$, NH_4ClO_4, NH_4Cl, NH_4Br, NH_4I and NH_4I_3.

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Results

$^1\Delta^{14}N(D)$ and $^1\Delta^{15}N(D)$. The ^{14}N as well as the ^{15}N spectra of the ammonium salts usually consist of well-resolved resonances when measured at 18.07 and 25.35 MHz, respectively, at a H:D ratio of 2:3, as illustrated in Fig. 1. Individual isotope effects for the species NH_3D^+, $NH_2D_2^+$, NHD_3^+, ND_4^+ can be measured, as illustrated for selected samples in Table 1, but generally only the total effects are quoted (Table 2). The effects for the $ND_{4-x}H_x^+$ species

show the mass dependence pointed out by Wasylishen and Friedrich.[2] Throughout this study we have used a correct mass dependence as a means of quality control of the data. $^1J(N,H)$ and $^1J(N,D)$ can furthermore be measured.[1] $J(N,H)$ values are also given for selected examples in Table 1. Most of the experiments have been performed at 18.07 MHz, while some of the measurements have also been repeated at a lower field which corresponds to 7.195 MHz, and no field dependence for $^1\Delta N(D)$ is observed.
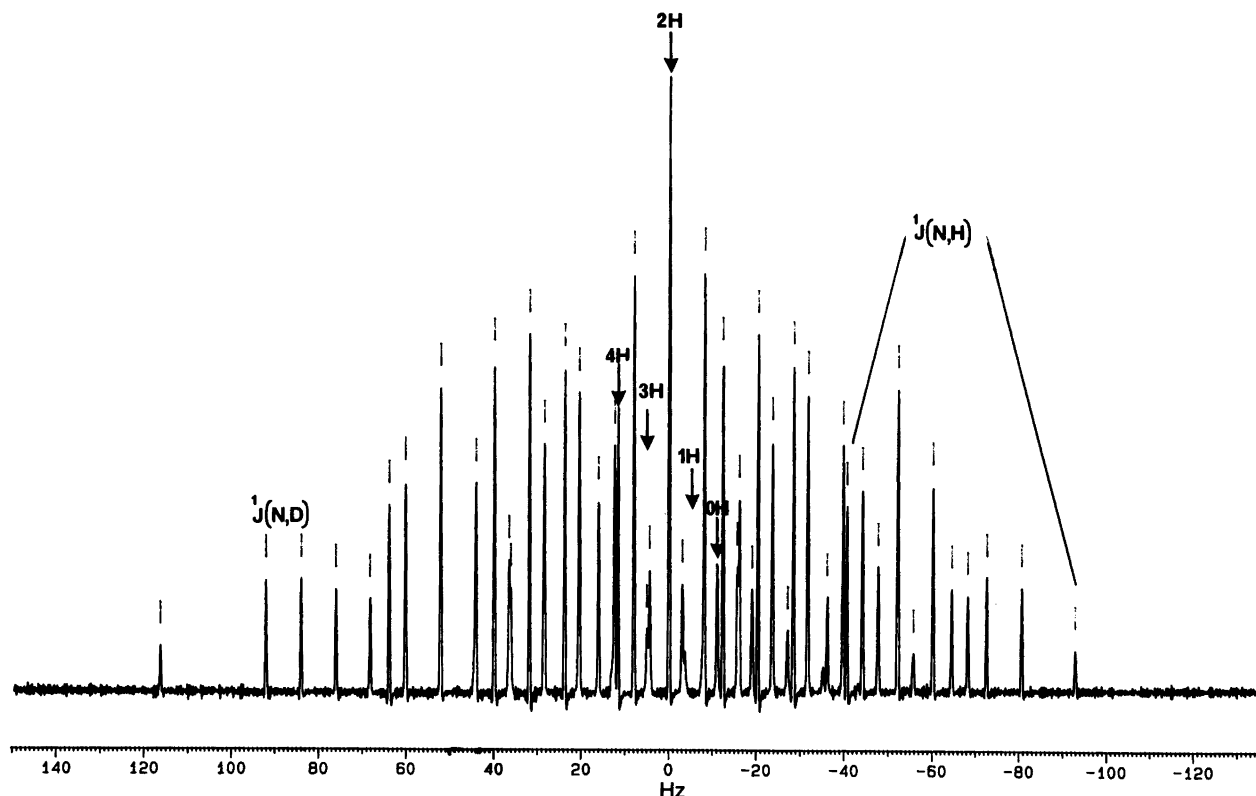

Fig. 1. ^{14}N spectrum of 4 M ammonium chloride in 2 M HCl with an H_2O/D_2O ratio of 40:60. The magnitudes of $^1J(N,H)$ and $^1J(N,D)$ are indicated as well as the chemical shifts for the different isotopomers.

Table 1. Deuterium isotope effects on ^{14}N nuclear shielding, $^1\Delta^{14}N(D)$, and one-bond hydrogen-nitrogen coupling constants, $^1J(N,H)$, for ammonium nitrate.

Entry	1		2		3		4		5		6	
	Δ^a	J^b	Δ^a	J^b	Δ^a	J^b	Δ^a	J^b	Δ^a	J^b	Δ^a	J^b
$(NH_4)^+$	0.0	52.55	0.0	52.73	0.0	53.02	0.0	52.40	0.0	52.59	0.0	53.01
$(NH_3D)^+$	0.288	52.49	0.287	52.68	0.276	52.96	0.289	52.34	0.289	52.54	0.278	52.96
$(NH_2D_2)^+$	0.566	52.45	0.562	52.63	0.544	52.93	0.575	52.30	0.567	52.50	0.547	52.89
$(NHD_3)^+$	0.835	52.40	0.826	52.60	0.802	52.88	0.848	52.29	0.834	52.46	0.807	52.87
$(ND_4)^+$	1.095	–	1.082	–	1.054	–	1.092	–	1.094	–	1.059	–
δN	-359.3^c		-354.9^c		-348.0^c		-358.0^c		-358.9^c		-346.7^c	
NH_4NO_3/g	3.2		3.2		3.2		0.8		0.8		0.8	
D_2O/ml	5.5		5.0		3.0		5.5		5.5		2.9	
H_2O/ml	3.5		1.6		–		3.5		3.5		0.1	
$NaNO_3/g$	–		–		–		–		2.5		–	
65 % HNO_3/ml	1.2		3.6		7.2		1.2		1.2		7.2	

$^a\Delta = {}^1\Delta^{14}N(D) = \delta^{14}N(H) - \delta^{14}N(D)$ (given in ppm). $^bJ = {}^1J(^{14}NH)$. $^c\delta(^{14}N) = \delta(^{14}NO_3)$.

Table 2. Deuterium isotope effects on ^{14}N nuclear shielding, $^{1}\Delta N(D)$,[a,b] and one-bond hydrogen-nitrogen coupling constants, $^{1}J(N,H)$[a].

Entry	Salt (NH₄X)	$^{1}\Delta N$ (D)[a,b]	$\delta^{14}N^d$	$^{1}J(N,H)^c$	g NH₄X	ml HX	g KX	ml D₂O	ml H₂O
7	NH₄I	1.67	9.20	52.52	0.91	1.80^g	–	1.75	0
8	NH₄I	1.56	7.68	52.44	1.81	0.83	–	1.75	1.00
9	NH₄I	1.56	7.16	52.50	0.91	1.30	–	1.75	0.5
10	NH₄I	1.46	5.51	52.41	0.90	0.83	–	1.75	1.00
11	NH₄I	1.39	4.27	– ^{l}	0.45	0.83	–	1.75	1.00
12	NH₄I₃	1.56	7.46	52.44	1.81	0.83^e	–	1.75	1.00
13	NH₄Br	1.40^f	4.44	52.45	0.90	0.75	–	1.75	1.00
14	NH₄Br	1.53	6.59	52.53	0.62	1.75^h	–	1.75	0
15	NH₄Br	1.45	5.92	52.45	0.62	0.75	0.83	1.75	1.00
16	NH₄Br	1.43	5.39	52.45	1.25	0.75	–	1.75	1.00
17	NH₄Br	1.43	5.07	52.44	1.25	0.75	–	1.00	1.75
18	NH₄Br	1.43	4.87	52.51	0.62	1.2	–	2.30	0
19	NH₄Br	1.42	5.25	52.44	0.98	0.62	–	1.75	1.00
20	NH₄Br	1.41	4.96	52.44	0.68	0.75	0.42	1.75	1.00
21	NH₄Br	1.35	3.81	– ^{l}	0.62	0.75	–	1.75	1.00
22	NH₄Br	1.33	2.90	52.40	0.31	0.75	–	1.75	1.00
23	NH₄Br	1.31	2.99	52.19	0.62	0.40^j	–	2.1	1.00
24	NH₄Cl	1.34	3.52	52.41	0.54	0.40^j	–	1.4	0.8
25	NH₄Cl	1.24	1.73	52.30	0.165	0.50	–	1.75	1.00
26	NH₄Cl	1.28	2.32	52.32	0.33	0.50	–	1.75	1.00
27	NH₄Cl	1.31	2.94	52.40	0.50	0.50	–	1.75	1.00
28	NH₄Cl	1.24	2.01	52.33	0.33	0.25	–	1.70	1.30
29	NH₄Cl	1.36	3.53	52.42	0.33	1.00	–	1.75	0.50
30	NH₄Cl	1.26	2.35	52.47	0.69	0.50^j	–	1.75	1.00
31	NH₄NO₃	1.19	1.04	52.50	0.53	0.53^j	–	1.75	1.00
32	NH₄NO₃	1.17	1.09	52.53	1.06	0.53^j	–	1.75	1.00
33	NH₄NO₃^k	1.09	0	52.60	1.12	0.40^j	–	1.20	0.80
34	^{15}NH₄NO₃^o	1.10	–	73.70^p	0.80	0.30	–	1.40	1.00
34a	^{15}NH₄NO₃^q	1.10	–	73.67^r	0.80	0.30	–	1.40	1.00
34b	^{15}NH₄NO₃^s	1.09	–	– ^{t}	0.80	0.30	–	1.40	1.00
35	(NH₄)₂SO₄	1.11	0.19	– ^{t}	0.71	0.24^t	–	1.40	0.80
36	NH₄ClO₄^n	1.11	–0.14	52.62	– ^{n}	0.60	–	1.75	1.00

[a]Defined as $^{1}\Delta^{14}N(D)$ = δNH_4 – δND_4. Temperature 300° (given in ppm). [b]Individual values for other isotopomers are given in Table 1 for selected cases. [c]$^{1}J(N,H)$ for NH₄⁺. The coupling constants for the other isotopomers are usually 0.05 Hz less per deuterium, as shown for some examples in Table 1 and in Table 3. $^{1}J(N,D)$ can also be measured. [d]Nuclear shielding relative to ^{14}NH₄NO₃. [e]1.1 g I₂ added. Also repeated with 2.2 g I₂ added, with almost identical results. [f]At 295° and at 300° very similar results were obtained, but the ND₄⁺ signal is hidden. At 310° very poor spectra are obtained. [g]HI (57 %) zur analyse. [h]HBr (density 1.46–1.49) (Analar). [i]Fuming HCl (37 %) zur analyse. [j]Concentrated HNO₃ (65 %; density 1.40) zur analyse. [k]For other NH₄NO₃ salts, see Table 1. [l]Concentrated H₂SO₄ (95–97 %) zur analyse. [m]Concentrated HClO₄ (70 %; density 1.67 g cm⁻³). [n]Saturated solution. [o]^{15}N enriched. ^{15}N resonance observed. Temperature 300°. [p]$^{1}J(^{15}N,H)$. [q]^{15}N enriched. ^{15}N resonance observed. Temperature 294°. [r]^{1}J ($^{15}N,H$). [s]^{15}N enriched. ^{15}N resonance observed. Temperature 311°. [t]Cannot be determined accurately because of overlapping resonances.

The data of Table 2 demonstrate that $^{1}\Delta^{15}N(D)$ for ammonium nitrate is very insensitive to temperature changes (entries 34, 34a and 34b), and that $^{1}\Delta^{14}N(D)$ and $^{1}\Delta^{15}(D)$ are very similar. The latter finding is contrary to the result of Tarasov et al.[4] Tables 1 and 2 show, furthermore, that $^{1}\Delta^{14}N(D)$ for NH₄NO₃ in the pH range investigated is rather insensitive to changes in pH. $^{1}\Delta^{14}N(D)$ for NH₄NO₃ is also insensitive to changes in concentration. These features are illustrated in Figs. 2 and 3. On the other hand, Table 2 and Fig. 2 show that $^{1}\Delta^{14}N(D)$ values for chlorides, bromides and iodides depend on concentration, the latter most strongly. $^{1}\Delta N(D)$ also depends strongly on the nature of the counter ion.

At concentrations of about 2 M, $^{1}\Delta N(D)$ decreases in the series $NO_3^-<SO_4^{2-}\sim ClO_4^-<Cl^-<Br^-<I^-\sim I_3^-$. Measurements on NH₄ClO₄ could only be made on a solution less than 1 M, but as the effect is rather concentration-inde-

pendent for NO_3^- and as ClO_4^- is similar to NO_3^-, the lower concentration is of no consequence. Tarasov et al.[4] have previously claimed that $^{1}\Delta^{15}N(D)$ is independent of the counter ion and solvent type in the concentration range 0.01–2 M (pH 2–3). We have attempted to measure $^{1}\Delta^{14}N$ (D) for ammonium chloride at pH 1.85 but failed, as only a broad, unresolved resonance was observed.

Fig. 3 and Table 2 show that $^{1}\Delta N(D)$ depends strongly on the concentration of the counterion. Again, the order is $I^->Br^->Cl^->NO_3^-$. The dependence for the NO_3^- salt is opposite to those observed for the halides. Table 2 and Fig. 3 also demonstrate that it does not matter very much whether the extra anions are added as HX or MeX (Me = alkali metal ion). From Figs. 2 and 3, extrapolations in two steps, i.e. first extrapolation to zero NH₄X concentration but fixed HX concentration and then extrapolation of the obtained value to zero HX concentration, yields
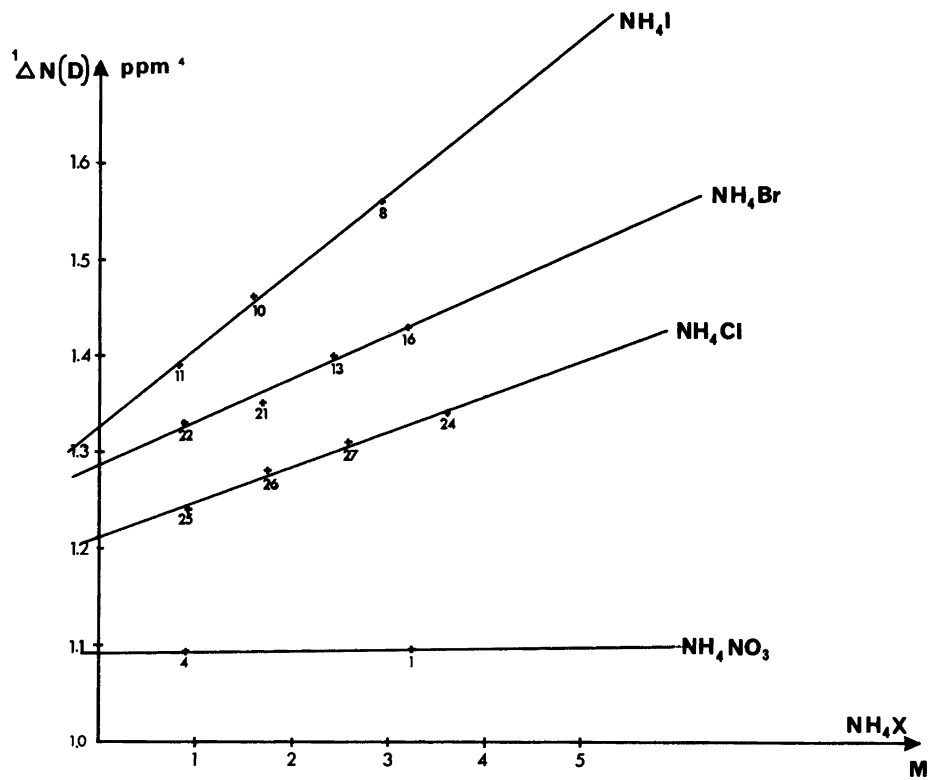
Fig. 2. Dependence of $^1\Delta^{14}N(D)$ on HX concentration at constant concentration of NH_4X (~1.7 M). $^1\Delta N(D) = \delta NH_4 - \delta ND_4$.
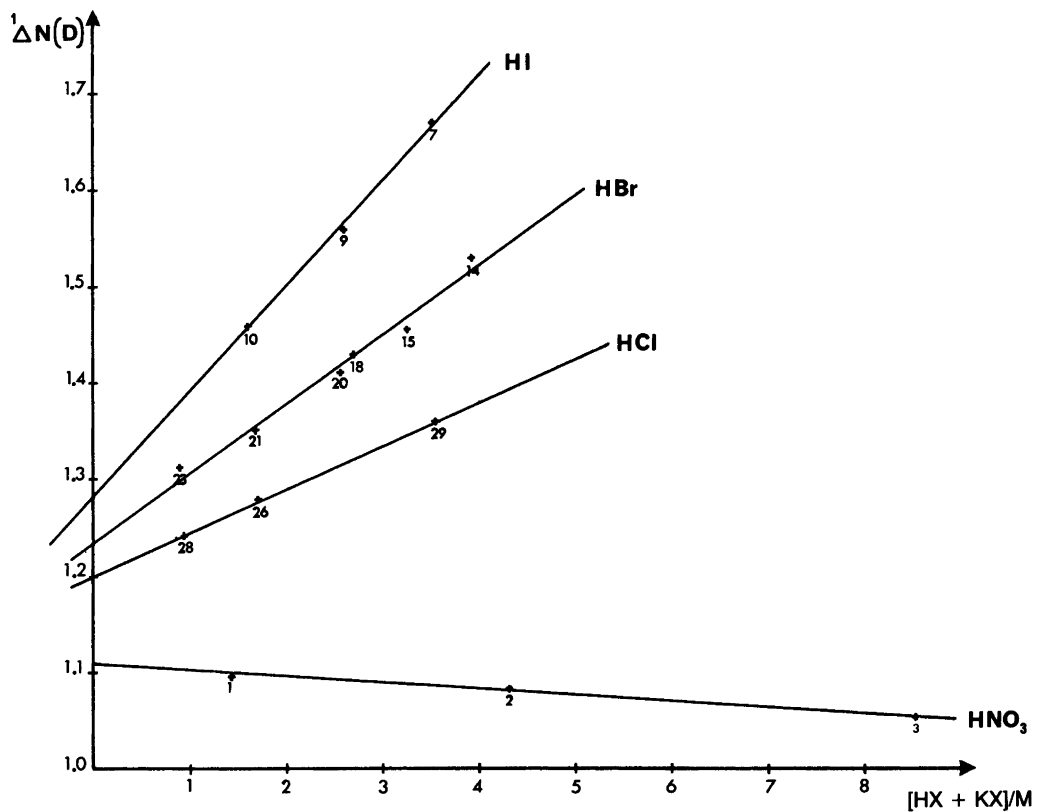

Fig. 3. Dependence of $^1\Delta^{14}N(D)$ on HX concentration at constant concentration of NH_4X (~1.7 M). $^1\Delta N(D) = \delta NH_4 - \delta ND_4$.

Table 3. $^1\Delta^{14}N(D)$ isotope effects measured in two-tube experiments.[a]

X	$^1\Delta^{14}N(D)$
Cl^-	1.17
NO_3^-	1.20
$(ND_4)_2SO_4$	1.19

[a]Concentration 1 M. The deuterated solution was placed in the outer tube.

effectively extrapolation to zero concentration. A concentration-independent value of 1.15 ± 0.02 ppm is found. The results measured by means of the two-tube method are given in Table 3. These compare quite well with the results arrived at from the one-tube measurements extrapolated to infinite dilution. The concentration dependence for the NO_3^- salt is low and so is that for $(NH_4)_2SO_4$ probably also. The concentration dependence for NH_4Cl is slightly greater, as seen in Fig. 2. Judging from Fig. 2, an increase of ca. 0.04 ppm relative to the infinite dilution value is expected. The value for NH_4NO_3 is less easily explained.

Furthermore, the reason that the two-tube method are different from those published earlier is basically that the earlier values were obtained using solutions containing NH_4X dissolved in D_2O.[3] In the present study ND_4X salts in D_2O were used. From the data of Table 2 it can be deduced that a mixture of counter ions yields a $^1\Delta N(D)_{mix}$ as follows:

$$^1\Delta N(D)_{mix} = x \; {}^1\Delta N(D)_A + (1-x) \; {}^1\Delta N(D)_B \tag{1}$$

in which x is the mole fraction and $^1\Delta N(D)_{A,B}$ are the one-bond isotope effects for the anions A and B, in our case Cl^- and NO_3^-. The results published by Wasylishen and Friedrich[2] are fully accounted for, as they investigated a solution of NH_4NO_3 in HCl.

^{14}N chemical shifts in Table 2 are given relative to the chemical shifts for the NH_4^+ ion of NH_4NO_3, in most cases determined by measuring the spectrum offset. This approach has been chosen since the chemical shift of the NO_3^- ion, which is customarily used, is pH dependent.[15] However, for comparison the shifts are referenced to NO_3^- of NH_4NO_3 in Table 1. ^{15}N chemical shifts for ammonium salts have previously been investigated by Briggs and Randall.[14] Our results show the same trends, and it is important to notice that the shifts go to low field with increasing concentration of the counter ion. A correlation between $\delta(N)$ (relative to NH_4NO_3) and $^1\Delta N(D)$ is illustrated in Fig. 4.

The results obtained for a mixture of I^- and I_2 show no great difference from those for the I^- solution. The composition of the mixture is not fully known; it contains to a large extent I_3^- and I^-, but also higher complexes such as I_5^- cannot be excluded.[18]

$^1J(N,H)$ varies as observed by Wasylishen and Friedrich[2] for the different isotopomers, as seen in Table 1. The variation from NH_4^+ to NHD_3^+ is 0.13 Hz. Furthermore, $^1J(N,H)$ varies from salt to salt and with the concentration of the salt and the counter ion concentration, but there seems to be no correlation between $^1\Delta N(D)$ and $^1J(N,H)$. The larger $^1J(N,H)$ appears for the solutions with high anion concentrations, but no anion specificity is observed.

Fig. 4. Dependence of $\delta^{14}N$ (relative to δ for NH_4NO_3) on $^1\Delta^{14}N(D)$.

¹H NMR spectra. The deuterium isotope effects on ^1H nuclear shielding are defined as $^2\Delta H(D)_{tot}$ = $\delta NH_4 - \delta NHD_3$. The individual contributions associated with each isotopomer are denoted $^2\Delta H(D)_1$ = $\delta NH_4 - \delta NH_3D$, $^2\Delta H(D)_2 = \delta NH_4 - \delta NH_2D_2$ and $^2\Delta H(D)_3$ = $\delta NH_4 - \delta NHD_3$. Unless otherwise stated, $^2\Delta H(D)$ is intended to mean the total isotope effect over two bonds, or in other words $^2\Delta H(D)_3$. The isotope effects are negative, as previously reported.[12] Furthermore, the present data reveal, as seen in Table 4, that the individual effects are non-additive, in contrast to the previous report.[12] The individual isotope effects, $^2\Delta H(D)_i$, in Hz (at 250 MHz) can be represented as:

$$^2\Delta H(D)_2 = 2 \times {}^2\Delta H(D)_1 + 0.5 \text{ Hz} \qquad (2)$$
$$^2\Delta H(D)_3 = 3 \times {}^2\Delta H(D)_1 + 1 \text{ Hz} \qquad (3)$$

The fact that $^2\Delta H(D)_x/D$ increases with increasing deuterium substitution is in contrast to the situation observed for ammonia.[11]

The $^2\Delta H(D)$'s are also seen to vary with the nature of the counter ion and with the counter ion concentration. The hard ions[19] ClO_4^- and SO_4^{2-} give the numerically larger effects, whereas the soft ions I^- and Br^- give numerically smaller values. A plot of $^2\Delta H(D)_1$ vs. total counter ion concentration does not give a very good correlation. However, a plot of $^2\Delta H(D)_1$ vs. NH_4X concentration with HX concentration held constant (~ 1.7 M), or a plot of $^2\Delta H(D)_1$ vs. HX concentration at constant NH_4X concentration (~ 1.7 M) yields well correlated plots, as seen in Figs. 5 and 6. We have chosen to plot $^2\Delta H(D)_1$ rather $^2\Delta H(D)_{total}$, as the former can be determined more accurately. An extrapolation to infinite dilution in two steps, as described previ-

Table 4. $^2\Delta H(D)^a$ and $^1J(^{14}N,H)^b$ for ammonium salts.

Entry	Compound	$^2\Delta H(D)$					$^1J(^{14}N,H)^d$			
		$^2\Delta H(D)_3^a$	diff.^{c}	$^2\Delta H(D)_2$	diff.^{c}	$^2\Delta H(D)_1$	NH$_4$	NH$_3$D	NH$_2$D$_2$	NHD$_3$
7	NH$_4$I	−53.96	−19.96	−34.00	−17.96	−16.04	52.51	52.47	52.42	52.38
8	NH$_4$I	−55.08	−20.31	−34.77	−18.24	−16.53	52.46	52.41	52.37	52.33
9	NH$_4$I	−55.84	−20.60	−35.24	−18.60	−16.64	52.47	52.43	52.37	52.32
10	NH$_4$I	−57.44	−21.08	−36.36	−18.87	−17.49	52.43	52.38	52.33	52.31
11	NH$_4$I	−58.77	−21.67	−37.10	−19.11	−17.99	52.40	52.35	52.30	− ^{h}
11a^e	NH$_4$I	−55.95	−20.60	−35.35	−18.60	−16.75	52.45	52.40	52.34	52.28
11b^f	NH$_4$I	−57.92	−21.40	−36.52	−19.20	−17.32	52.41	52.37	52.32	52.30
12	NH$_4$I$_3$	−57.28	−20.88	−36.40	−19.16	−17.24	52.45	52.40	52.35	−
13	NH$_4$Br	−56.25	−20.47	−35.78	−18.87	−16.91	52.42	52.36	52.31	52.29
14	NH$_4$Br	−54.88	−20.12	−34.76	−18.24	−16.52	52.51	52.46	52.41	52.37
15	NH$_4$Br	−54.76	−20.16	−34.60	−18.20	−16.40	52.45	52.41	52.35	52.31
16	NH$_4$Br	−55.76	−20.48	−35.28	−18.56	−16.72	52.44	52.39	52.34	52.30
17	NH$_4$Br		− ^{h}	−35.36	−18.24	−17.12	52.44	52.39	52.34	− ^{h}
18a	NH$_4$Br	−56.16	−20.60	−35.56	−18.72	−16.84	52.46	52.41	52.36	52.31
18b^g	NH$_4$Br		− ^{h}	−36.98	−18.92	−17.06	52.45	52.41	52.34	−
19	NH$_4$Br	−55.84	−20.52	−35.32	−18.56	−16.76	52.44	52.39	52.34	52.30
20	NH$_4$Br	−56.24	−20.60	−35.64	−18.84	−16.80	52.45	52.40	52.34	52.30
21	NH$_4$Br	−57.64	−21.16	−36.48	−19.04	−17.44	52.42	52.37	52.31	52.25
22	NH$_4$Br	−58.40	−21.23	−37.17	−19.52	−17.65	52.40	52.35	52.30	−
23	NH$_4$Br	−58.28	−21.32	−36.96	−19.48	−17.48	52.40	52.35	52.30	52.26
24	NH$_4$Cl	−58.04	−21.16	−36.88	−19.44	−17.44	52.39	52.34	52.29	52.24
25	NH$_4$Cl		− ^{h}	−38.12	−19.92	−18.20	52.25	52.32	− ^{h}	− ^{h}
26	NH$_4$Cl	−59.31	−21.68	−37.63	−19.72	−17.91	52.37	52.32	52.27	52.24
27	NH$_4$Cl	−58.52	−21.24	−37.28	−19.57	−17.71	52.38	52.33	52.27	52.18
28	NH$_4$Cl	−59.40	−21.64	−37.76	−19.68	−18.08	52.35	52.31	52.25	52.23
29	NH$_4$Cl	−58.54	−21.29	−37.25	−19.57	−17.68	52.41	52.36	52.31	52.26
1	NH$_4$NO$_3$	−58.08	−21.20	−36.88	−19.16	−17.72	52.58	52.53	52.48	52.43
2	NH$_4$NO$_3$	−	− ^{h}	−	− ^{h}	−17.13	52.78	− ^{h}	− ^{h}	− ^{h}
4	NH$_4$NO$_3$	−59.80	−21.80	−38.00	−19.72	−18.28	52.50	52.44	52.37	− ^{h}
31	NH$_4$NO$_3$^{i}	−59.16	−21.64	−37.52	−19.68	−17.84	52.46	52.40	52.36	52.31
32	NH$_4$NO$_3$^{i}	−57.84	−21.16	−36.68	−19.24	−17.44	52.54	52.49	52.43	52.39
33	NH$_4$NO$_3$	−57.68	−20.96	−36.72	−19.24	−17.48	52.59	52.54	52.48	52.43
34	NH$_4$NO$_3$^{i}	−58.04	−21.28	−36.76	−19.28	−17.48	73.68^k	73.65^k	73.55^k	73.49^k
35	(NH$_4$)$_2$SO$_4$	−60.12	−21.88	−38.24	−19.92	−18.32	52.44	52.39	52.34	52.30
36	NH$_4$ClO$_4$	−60.69	−22.23	−38.46	−20.27	−18.19	52.66	52.59	52.55	52.50

^{a}In ppb; defined as $^2\Delta H(D)_x = NH_xD_{4-x}^+$. ^{b}Temperature 300°. $^2\Delta H(D)_3 = {}^2H(D)_{tot}$ which is usually called $^2\Delta H(D)$. $^2J(H,D) = 1.71 \pm 0.02$ Hz. Average values. ^{c}The difference refers to $^2\Delta H(D)_3 - {}^2\Delta H(D)_2$ and $^2\Delta H(D)_2 - {}^2\Delta H(D)_1$, respectively. ^{d}Obtained from the ^1H spectra. Selected values obtained from ^{14}N spectra are given in Table 1. ^{e}Solution composition: 1.35 NH$_4$I, 0.83 ml HI, 1.75 ml H$_2$O and 1.00 ml H$_2$O. ^{f}Solution composition: 0.67 g NH$_4$I, 0.83 ml HI, 1.75 ml D$_2$O and 1.00 ml H$_2$O. ^{g}Solution composition: 0.62 g NH$_4$Br, 1.2 ml HBr, 1.75 ml H$_2$O, 1.00 ml D$_2$O. ^{h}Could not be measured accurately. ^{i}Mixture of NO$_3^-$ and Cl$^-$ counter ions. For composition, see Table 2. ^{j}^{15}NH$_4$NO$_3$. ^{k}$^1J(^{15}N,H)$.
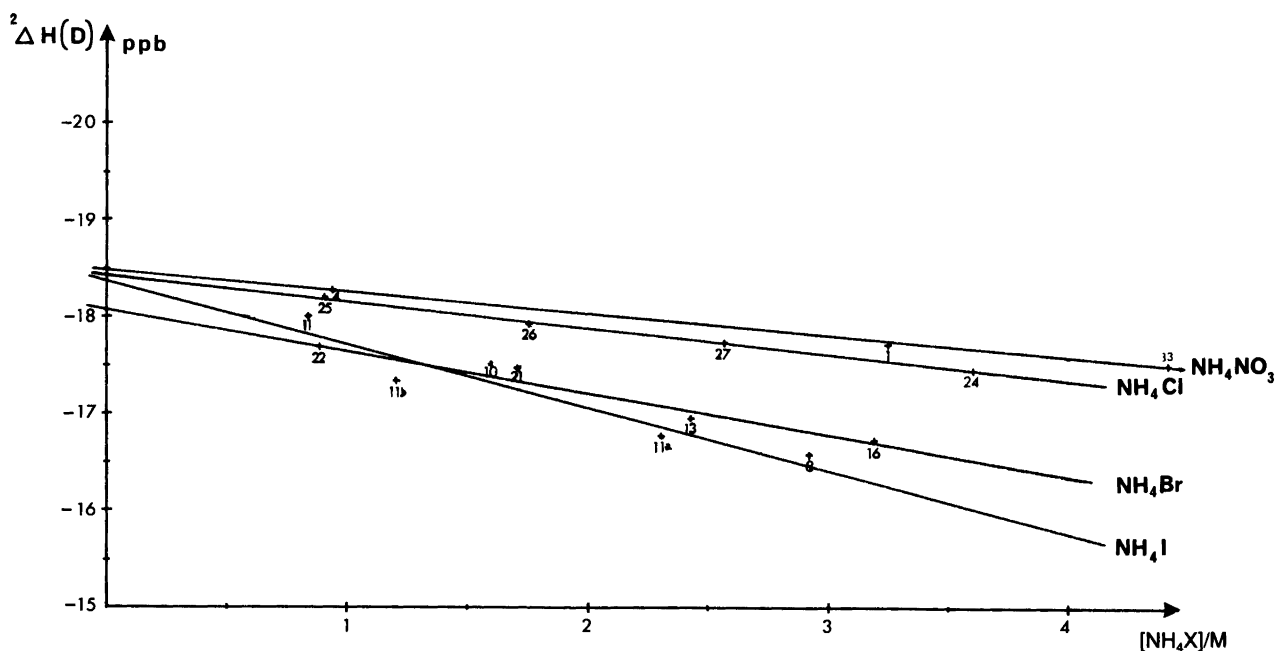
Fig. 5. Dependence of $^2\Delta H(D)_1$ on counter ion concentration at fixed HX concentration ($\sim$1.7 M) $^2\Delta H(D)_1$ = δNH_4 − δNH_3D. Similar plots can be produced for the other isotopomers.

ously, yields a value of -18.90 ± 0.15 ppb for $\Delta H(D)_1$. It is also found that the non-additivity is conserved at infinite dilution. By inspection of Figs. 5 and 6 we see that the slope for NH_4I is almost the same in Fig. 5 as in Fig. 6. The same holds true for NH_4Br etc. A change of 0.012 ppm M^{-1} can be calculated for NH_4X from Fig. 5, and 0.014 ppm M^{-1}

from Fig. 6. These values are a factor of 7 smaller than those observed in the ^{14}N spectra (Figs. 2 and 3). The ^1H chemical shift moves to low field (high frequencies) with increasing concentration at fixed HX concentration.

$^2J(H,D)$'s have also been measured from these spectra, and they show little variation (1.71 $\pm$ 0.05 Hz). The latter value is very close to that for the deuterated methanes,[20] but somewhat different from that for the deuterated ammonias (1.54 $\pm$ 0.12 Hz).[12]
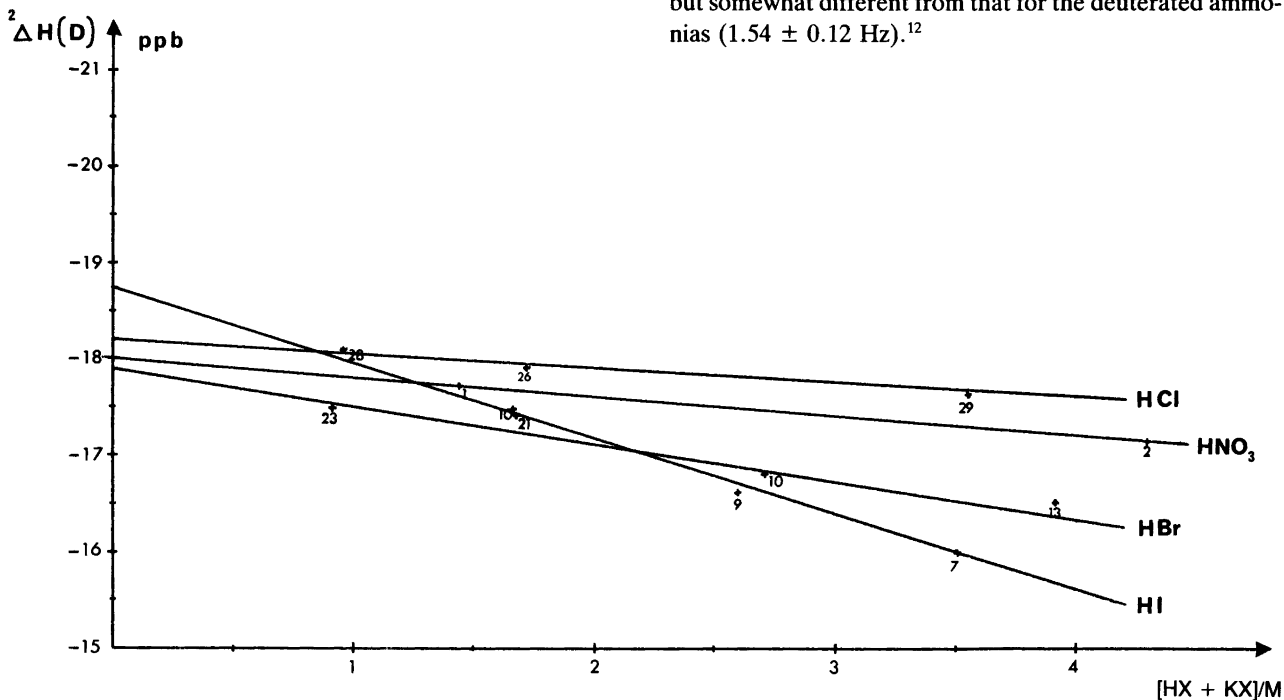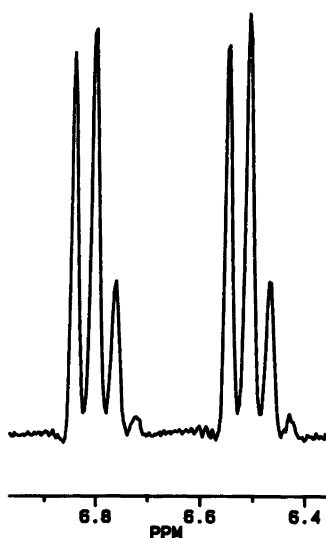

Fig. 6. Dependence of $^2\Delta H(D)_1$ on HX concentration of NH_4X ($\sim$1.7 M). $^2\Delta H(D)_1$ = δNH_4 − δNH_3D. Similar plots can be produced for the other isotopomers.

Fig. 7. ^{2}H spectrum of ^{15}NH$_4$NO$_3$; 0.8 g is dissolved in 1.7 ml D$_2$O + 0.5 ml H$_2$O + 0.3 ml HNO$_3$.

^{2}H NMR spectra. The deuterium NMR spectra of ^{15}ND$_{4-x}$H$_x$NO$_3$ show reasonably sharp resonances, as seen in Fig. 7. The resonance belonging to the ND$_4^+$ isotopomer is observed at lowest field (highest frequency). ^1J(N,D) is equal to 11.29 Hz, which is equivalent to a ^1J(N,H) value of 74.50 Hz. This value is slightly larger than that found in the ^{15}N spectra. ^2J(H,D) is the same as found in the ^{1}H spectra. ^{2}ΔD(H) can be measured to be close to 0.65 Hz (16.93 ppb/D). A slight variation in magnitude for the various isotopomers is observed, but the accuracy is insufficient to fully substantiate this. It is, however, noticeable that the effect is smaller than that observed for ^{2}ΔH(D).

Discussion

^{1}ΔN(D). From a brief overview of the literature data a dependence of ΔN(D) on pH appeared to be a possibility.[3] The pH dependence and the dependence on concentration of counter ion are linked together, since pH has to be maintained at a low value. From Figs. 1 and 2 it is evident that ^{1}ΔN(D) depends both on concentration and on the nature of the counter ion. From Fig. 2, a dependence on the amount of HX added is clearly demonstrated for HI, HBr and HNO$_3$. No such effects were reported using a two-tube method[3] because of the much lower concentrations used, and ^{1}ΔN(D) was also claimed to be independent of counter ion in one-tube experiments.[4]

^{1}ΔN(D) increases in the series NO$_3^-$ < SO$_4^{2-}$~ClO$_4^-$ < Cl$^-$ < Br$^-$ < I$^-$ I$_3^-$, as seen from Fig. 1 and Table 2. This order is very similar to that found for δ^{14}N.[14] ^{1}ΔN(D) and δ^{14}N are proportional, as seen from the plot in Fig. 4, which has a slope of 0.059 and a correlation coefficient of 0.99. We can thus expect ^{1}ΔN(D) to behave very much like δ^{15}N and δ^{14}N. Templeman and van Geet[17] found a downfield shift for Na$^+$ ions with increasing X$^-$ concentration,

and they ascribed this to back-bonding into the 3p orbital. Using the observation by Jameson[5–8] that ^{1}ΔN(D) is proportional to the shielding of N, one thus expects a larger isotope effect at high X$^-$ concentrations.

The experiments in the present work were performed at an acid concentration of 1.8 M in order to lower the exchange rates of the N-H protons and thereby obtain sharp resonances. ^{1}ΔN(D) depends, however, on the concentration of the acid HX, as demonstrated in Fig. 3. This figure shows, furthermore, that addition of an equivalent amount of the salt KX leads to almost the same increase. ^{1}ΔN(D) thus depends not on the concentration of H$^+$, but only on the concentration of the counter ion. This finding is also supported by the experiments made using a mixture of NH$_4$Cl and HNO$_3$ (*vide infra*). The dependence on X$^-$ follows very much the same trends as found for the concentration dependence, except that ^{1}ΔN(D) for NH$_4$NO$_3$ decreases with increasing NO$_3^-$ concentration. It is tempting to extrapolate the values obtained for ^{1}ΔN(D) to infinite dilution. This is difficult because of the rather high acid concentrations. However, an attempt to first extrapolate to zero concentration at fixed acid concentration, as demonstrated in Fig. 2, followed by an extrapolation to zero acid concentration at constant salt concentration, which is admittedly not zero, leads to a value at infinite dilution of 1.15 ± 0.02 ppm. This value is further supported by the two-tube experiments for 1 M solutions at pH 4.75, which in accordance with the quite low X$^-$ concentration yield values of 1.15–1.20 ppm (Table 3).

The variation in ^{1}ΔN(D) can thus be accounted for. It is, however, obvious that ^{1}ΔN(D) per D is much less than the effect observed for ammonia. The proportionality between ^{1}ΔN(D) and δN (Fig. 2) makes it possible to estimate ^{1}ΔN(D) for NH$_4$OH in the following way. Ammonium ions generally resemble potassium and rubidium ions, and, to a lesser extent, sodium ions. As very little NMR data exist for the former two ions, a comparison with sodium chemical shifts is useful.[16] The counter ion dependences of nuclear shielding are similar for Na$^+$ and for NH$_4^+$. The data for NaI and NaOH are available,[17] and the latter study shows that the OH$^-$ ion interacts more strongly with Na$^+$ than does I$^-$. If we assume that δNaI/δNaOH = δNH$_4$I/δNH$_4$OH = ^{1}ΔN(D)NH$_4$I/^{1}ΔN(D)NH$_4$OH we can then predict a value of 1.93 ppm for ^{1}ΔN(D), which is ~0.5 ppm/D. This value is much smaller than the effects observed for ammonia and similar compounds, 0.7 ppm/D.[1,11] One important difference between ammonia and the ammonium ion is the presence of lone-pairs in ammonia, as pointed out by Jameson and Osten.[7] The other is the different hydrogen bond pattern in the two compounds.[3] These two factors are likely to cause the difference.

The change in nuclear shielding caused by anions is explained by ion-ion interactions, and generally the order is: NO$_3^-$ < F$^-$ < Cl$^-$ < Br$^-$ < I$^-$.[16] In the Na$^+$ case the effect has been attributed to repulsion due to orbital overlap.[16,17] The NH$_4^+$ ion has the same ion-radius as K$^+$. The order just mentioned shows that the harder ions[19] such as NO$_3^-$,

ClO_4^- and SO_4^- overlap poorly. The same is found to hold for hydrogens (*vide infra*).

$^2\Delta H(D)$ and $^2\Delta D(H)$. The analysis of methane, another XH_4 system, has previously been investigated both experimentally and theoretically.[5,24] Additivity was found experimentally and also predicted theoretically. Furthermore, $^2\Delta H(D)$ is found to be positive for methane. A positive value is also found for ammonia.[11,13] The negative value observed for the ammonium ion must clearly be associated with features not found in methane or ammonia. Furthermore, the heavier isotopomers show the larger values per deuterium, as shown in eqns. (2) and (3). This feature means that the mass dependence is not a simple one (*vide infra*), as this should decrease with increasing number of deuterium atoms. Symmetry does not seem to play an important role either, in contrast to the situation for $^1\Delta N$ (D). As mentioned above, $^2\Delta H(D)$ for ammonia is positive and the value for $^2\Delta H(D)_1$ is larger than for $^2\Delta H(D)_2 - {}^2\Delta H(D)_1$, in agreement with a mass dependence. It is interesting to note that both the negative sign and the mass dependence for the ammonium ion is the opposite of that observed for ammonia and, furthermore, that the effect for ammonia is most negative in dilute solution, which means that an increased concentration of the counter ions causes a more positive effect. A possible model to explain these features is as follows: In pure water $^2\Delta H(D)$ consists of two contributions, i.e. an intrinsic isotope effect, $^2\Delta H(D)_{int}$ and a water-related effect. The intrinsic effect depends on counter ion concentration, is positive (as for ammonia) and depends on mass in a manner similar to that for ammonia. The observed mass dependence for the ammonium ion can now be understood, since $^2\Delta H(D)_{int\,1}$ according to the statement above is largest, which means that $^2\Delta H(D)_1$ becomes smallest. For the isotope effects observed in the deuterium spectra the same argument also leads to agreement with observation.

The finding that the slope for the harder ions NO_3^- and ClO_4^- is smaller than for the softer anions Br^- and I^- shows that the variation in the two types of isotope effects with the anions is similar, although hydrogen can be considered a hard center and nitrogen a soft one.

It has previously been suggested that the negative isotope effect over two bonds is linked to hydrogen-bonding.[13] The findings of this study support this suggestion, since the most negative value is found for dilute solutions. At infinite dilution the counter ion plays no role and water is free to form hydrogen-bonds. The fact that non-additivity is conserved at extrapolation to infinite dilution shows clearly that this feature is not caused by the counter ions, but it could be caused by the intrinsic effect or by water. Hydrogen-bonding can clearly cause a change in isotope effects.[22-24] According to theoretical calculations,[25] two types of hydrogen-bonds are possible, viz. directional and non-directional hydrogen bonds (Figs. 8a and b). It is difficult to envisage how directional hydrogen-bonds could alter the isotope effects so dramatically. A more likely explanation
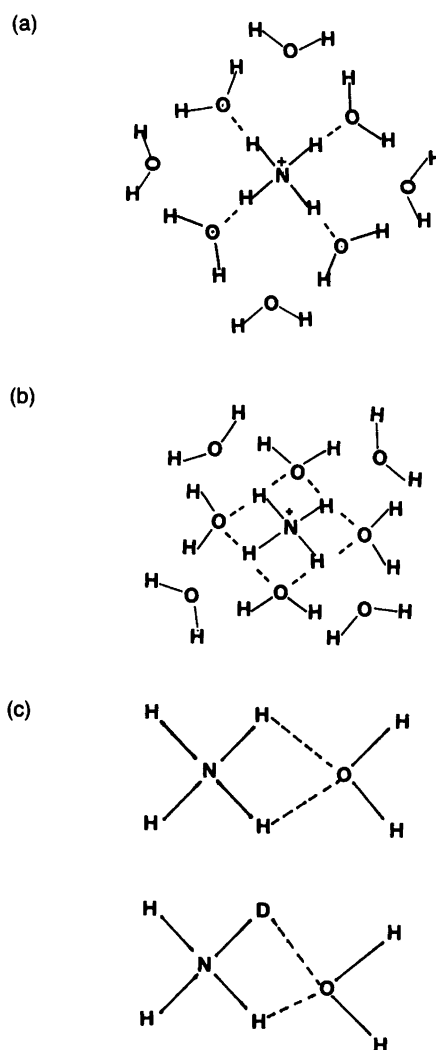

Fig. 8. Static picture of solvation. (a) With directional bonds. (b) With non-directional bonds. (c) The effect of deuteriation on bond length and symmetry.

is the presence of non-directional hydrogen-bonds. The situation is then as described in Fig. 8b, i.e. that the N-H or the N-D hydrogens (deuteriums) form hydrogen-bonds to the oxygens of the surrounding water molecules with bent hydrogen bonds. The negative $^2\Delta H(D)$ can be explained by assuming that the water molecules form stronger hydrogen bonds to an N-H hydrogen than to an N-D deuterium. That the hydrogen bonds involving deuterium can differ in strength from those involving hydrogens is clearly demonstrated in several systems.[22-25] This different hydrogen-bond strength could, in a deuteriated molecule with non-directional bonds, lead to an asymmetric situation in which hydrogen-bonding to the N-H hydrogen is stronger than in the corresponding diprotio species, as illlustrated in Fig. 8c. The situation depicted in Fig. 8c shows that the water molecule moves slightly towards the N-H group in order to maximise overlap with both the N-H and the N-D proton (deuteron). This leads to stronger hydrogen-bonding in this species compared to the diprotio species, and thus leads to

a low-field shift for the hydrogen and to a negative isotope effect. This will likewise result in a high-field shift for the deuteriated species in deuterium spectra, as also observed.

Solvation model

The solvent structure around the ammonium ion has been treated theoretically. Two different kinds of water were predicted.[26] The finding that the nuclear shielding of the heavier alkali ions varies strongly with the nature and concentration of the counter ions has been taken as evidence that the counter ion competes with water for the inner solvation sphere.[16] The finding that both δN and $^2\Delta N(D)$ also depend strongly on the counter ion concentration, paired with the fact that the softer counter ions give the strongest interactions with nitrogen and the weakest with hydrogen, suggests that this is also the case for the ammonium ion. The theoretical studies[26] predict also that the non-directional water molecules surrounding the ammonium ion have a high degree of motional freedom. If this average is altered by structure-breaking ions, a change in both the ^{15}N chemical shift and the isotope effects can be expected. The fact that both the I^- and the ClO_4^- ion are strongly structure-breaking but give rise to very different isotope and chemical shift effects seems, however, to disfavour such an explanation. The presence of non-directional hydrogen-bonds to water molecules can explain the negative $^2\Delta H(D)$ isotope effects. This does not, however, mean that water molecules with directional bonds are not present; they probably do not give rise to detectable contributions to the isotope effects. Non-directional hydrogen-bonds have been suggested by Perrin and Gipe[27] in order to explain the very short correlation time found for the ammonium ion. The model illustrated in Fig. 8b seems best able to explain the above-mentioned facts. Further calculations based on the observed isotope effects may be able to determine more accurately the distance of both types of water molecules to the nitrogen.[28] This model also accounts for the fact that no solvent isotope effects are observed in this case. The counter ions are not included, but are likely to penetrate the inner solvation sphere quite frequently.

Experimental

^{14}N NMR spectra were recorded at 7.195, 18.069 and 21.689 MHz on a JNM-Fx 100 JEOL, a Bruker AC 250 and a Bruker AM 300 NMR spectrometer, respectively. The temperature was 300 K unless otherwise stated. Preliminary studies were carried out using an FX 100 spectrometer. Typical acquisition parameters are given in Ref. 3. Typical acquisition parameters for the high-field instruments are as follows: spectral width 1000 Hz, 32 K of memory for the FID, 90° flip angle, no relaxation delay, zero filling to 64 K; line-narrowing by means of Gauss multiplication (LB = -1.5, GB = 0.3) was performed prior to Fourier transformation. Samples were prepared as described in Tables 1 and 2. The ^{15}N spectra were recorded on a Bruker AC 250

at 25.35 MHz in a similar manner to the ^{14}N spectra. ^1H NMR spectra were also recorded on the same instrument at 250 MHz and with the same samples. ^2H spectra were recorded at 38 MHz in the unlocked mode.

Note added in proof: Since this work was submitted a paper by Sanders *et al.*[29] has come to our attention. These authors confirm the non-additivity of the two-bond isotope effects. They also provide support for the idea that hydrogen-bonding may be partly responsible, but suggest in addition that eccentricity due to deuteriation could play a role, although the calculated effects show the wrong non-additivity.

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