ISOTOPE EFFECTS ON PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS IN THE AMMONIUM IONS $^{15,14}NH_{4-n}D_n^+$

Jeremy K.M. SANDERS
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Brian K. HUNTER
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Cynthia J. JAMESON
Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680, USA

and

Giovanni ROMEO
University of Messina, 98100 Messina, Italy

Received 13 October 1987; in final form 17 November 1987

The proton NMR spectra of ^{14}N- and ^{15}N-ammonium ions have been recorded in H_2O/D_2O mixtures under (acidic) conditions of slow proton exchange. Successive deuterium substitutions lead to unusual downfield shifts of about 20 ppb/D at the residual protons, but the effect is not additive; the increment increases by about 10% per deuterium. $^1J_{NH}$ is reduced by a secondary deuterium isotope effect and ^{15}N induces an upfield ^1H shift of 1.5 ppb. The magnitudes of the isotope shifts are consistent with the theoretical shielding derivatives. We believe that the unusual sign and the large deviations from additivity of the deuteration shifts are due to intermolecular effects.

1. Introduction

Experimentally measured isotope effects on NMR chemical shifts and coupling constants are important tests of theoretical predictions. They also play an increasingly important role in mechanistic investigations of chemical and biological processes [1]. We report here the ^1H spectrum of $^{15,14}NH_{4-n}D_n^+$, a molecule small enough to be the subject of theoretical calculations, and which is isoelectronic with $^{13,12}CH_{4-n}D_n$, also of fundamental interest. A large basis set calculation of the shielding surface and the coupling constant surface of CH_4 has been carried out [2], and rovibrational averaging on this surface will yield ab initio values of primary and secondary isotope effects on shielding and on coupling constants. However, experimental values of some of these quantities are not yet available for $^{13,12}CH_{4-n}D_n$. On the other hand, the ^{14}N spectrum of $^{14}NH_{4-n}D_n^+$ has been observed by Wasylishen and Friedrich [3]; and the ^{15}N spectrum (which has also been observed) provides essentially the same information [4]. The ^1H spectrum of $^{15,14}NH_{4-n}D_n^+$ reported here yields non-additive D-induced ^1H isotope shifts as well as isotope effects on the NH coupling constants.

2. Experimental

^{15}N-ammonium chloride was obtained from Prochem. ^{14}N- and ^{15}N-ammonium chloride were dissolved, separately or together, to a total concentration of 0.4–1 M, in H_2O/D_2O mixtures. For simultaneous measurements on all four H/D species the H:D ratio

0 009-2614/88/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

Table 1
Proton chemical shifts in $^{15,14}NH_{4-n}D_n^+$ [a]

Ion	^{14}N		^{15}N		$^1\Delta{}^1H(^{15/14}N)$
	δ	$^2\Delta{}^1H(^{2/1}H)$	δ	$^2\Delta{}^1H(^{2/1}H)$	
NH_4^+	0	+18.1	−1.4	+18.0	−1.4
NH_3D^+	+18.1	+20.0	+16.6	+19.9	−1.5
$NH_2D_2^+$	+38.1	+21.9	+36.5	+21.8	−1.5
NHD_3^+	+60.0		+58.3		−1.7

[a] In parts per billion (±0.3) relative to $^{14}NH_4^+$; positive shifts are downfield.

was generally in the range 1:3 to 1:4. Sufficient acid (concentrated HCl) was added to give a well-resolved, slow exchange spectrum.

All NMR spectra were obtained in Cambridge on a Bruker WH400 instrument. Initially, water suppression was achieved by continuous irradiation from the decoupler. Subsequently (4 years later!), most of the experiments were repeated using the 1,1 hard pulse suppression sequence [5] to ensure that the earlier results were not affected by Bloch–Siegert or other effects from the decoupler. No measurable differences were found.

2048 data points were acquired over a spectral width of 200 Hz. Following Gaussian resolution enhancement and zero filling (twice), the final digital resolution was 0.05 Hz/point. The quoted results are averaged over each line in a deuterium-coupled multiplet (triplet for NH_3D^+, quintet for $NH_2D_2^+$, septet for NHD_3^+). All individual results are consistent, within the digital resolution, across several samples examined over a period of 4 years. The results in tables 1 and 2 are probably reliable to better than ±0.1 Hz (0.3 ppb).

Fig. 1 shows part of the 400 MHz ^1H spectrum of ^{14}N-ammonium chloride in a strongly acidified water–D_2O mixture ($H:D \approx 1:4$). The characteristic 1:1:1 triplet of NH_4^+ is accompanied, at successively lower fields, by signals from NH_3D^+, $NH_2D_2^+$, and NHD_3^+. The signals of the deuterated species are further split by HD coupling ($J \approx 1.7$ Hz) into triplets (NH_3D^+), quintets ($NH_2D_2^+$) or septets (NHD_3^+). A total of 48 lines is resolved in this spectrum. The corresponding spectrum of the ^{15}N species yields only a doublet which is further shifted and split by deuterium. The spectrum of the $^{14}N/^{15}N$ mixture contains many overlapping signals, but a sufficient number of these are resolved to allow measurements of the differential shifts.

Table 2
N–H coupling constants in $^{15,14}NH_{4-n}D_n^+$ [a]

Ion	^{14}N		^{15}N this work
	ref. [4]	this work	
NH_4^+	52.52	52.38	73.47
NH_3D^+	52.47	52.28	73.40
$NH_2D_2^+$	52.41	52.21	73.34
NHD_3^+	52.37	52.19	73.27

[a] In Hz (±0.1).

Tables 1 and 2 list all the chemical shifts and coupling constants measured from these spectra. The results may be summarized as follows:

(i) $^2\Delta{}^1H(^{2/1}H)$, the secondary isotope shift induced by deuterium at the residual protons, is $\approx +20$ ppb/deuterium (i.e. ^1H is less shielded in the heavier isotopomer) but is strongly non-additive: the increment for the first deuterium is +18 ppb, while for the third deuterium it is +22 ppb. The overall magnitude of $^2\Delta$ is comparable to that observed (−16 ppb) in $CH_{4-n}D_n$ [6]. However, the sign is unusual and the deviation from additivity, around 10% of $^2\Delta$, is much larger than that observed for $^1\Delta{}^{15}N(^{2/1}H)$ in the same system [3]. These results have been confirmed in several samples over a period of 4 years.

(ii) $^1\Delta{}^1H(^{15/14}N)$, the N-induced isotope shift on ^1H shielding, is −1.5 ppb. This is as expected.

(iii) A secondary isotope effect on $^1J_{NH}$ is observed. The effect is small but real: -0.07 ± 0.1 Hz/D in the ^{15}N series and −0.05 to −0.06 Hz/D in the ^{14}N.

The most puzzling aspects of these results are the

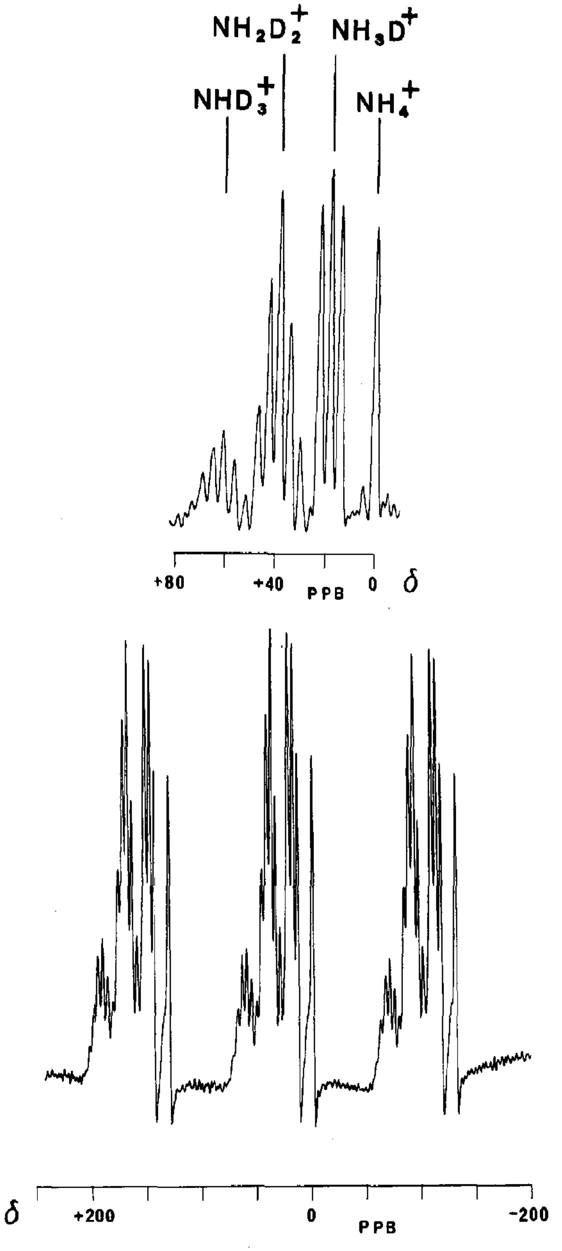

Fig. 1.

sign and deviation from additivity of D-induced ^{1}H isotope shifts.

3. Discussion

The observed secondary isotope effect on J_{NH} is not measured with great precision (≈ -0.07 Hz/D for ^{15}N, -0.05 Hz/D for ^{14}N); however, when expressed in the reduced form of the coupling constant, these values (-0.17×10^{20} cm^3) are comparable to the value in $CH_{4-n}D_n$: $-(0.26\pm0.07)\times10^{20}$ cm^3 [7,8]. The primary N-induced isotope effect on $^1J(NH)$, $|^1J(^{15}NH)| - |^1J(^{14}NH) \times \gamma_{^{15}N}/\gamma_{^{14}N}|$, is too small to be observed, as expected, for it should be 1/105 times the size of $|^1J(^{14}ND)\gamma_H/\gamma_D| - |^1J(^{14}NH)| = +0.18\pm0.20$ Hz [3]. The secondary isotope effect on $^2J(HD)$ is also too small to detect. $^2J(HD)$ is the same (≈ 1.7 Hz) for NH_3D^+, $NH_2D_2^+$, and NHD_3^+ within the digital resolution of our experiments.

The two-bond isotope shifts observed here can be compared to the one-bond shifts in the same molecule, $^2\Delta{}^1H(^{2/1}H)$ and $^1\Delta{}^{14}N(^{2/1}H)$ in $NH_{4-n}D_n^+$ are ≈ 20 ppb and -307 ppb per D [3]; in the isoelectronic $CH_{4-n}D_n$ molecules they are $^2\Delta{}^1H(^{2/1}H) = -16$ ppb [5], $^1\Delta{}^{13}C(^{2/1}H) = -192$ ppb [6]. The ratios are nearly the same, i.e. the magnitudes of the D-induced ^{1}H isotope shifts reported here are not unexpected. However, the sign and large deviations from additivity need explanations.

Vibrational contributions to two-bond isotope shifts are nearly additive [9,10] according to our earlier theoretical analysis, which makes use of only the first shielding derivatives with respect to bond length and which neglects shielding derivatives with respect to bond angle (in CH_4) and second and higher shielding derivatives. At this level of approximation, the magnitudes of the isotope shifts can be calculated. Although dynamic calculations have not been carried out for the NH_4^+ ion, the mean bond displacements for CH_4 and its isotopomers have been calculated using a good anharmonic force field. Replacement of H by D reduces the average bond length by 5.53×10^{-3} Å and the adjacent CH bond length by 1.6×10^{-4} Å; replacement of ^{12}C by ^{13}C reduces the average bond length by 6.2×10^{-5} Å [10]. Adopting these values directly for NH_4^+ isotopomers, except that $^{15/14}$N substitution would involve a mass factor which is 0.75 times that for $^{13/12}$C substitution, gives a change of 4.6×10^{-5} Å in the average NH bond length. The changes in ^{1}H and N or C shielding with bond extension have been calculated for CH_4 and NH_4^+. In ppm Å^{-1}, the shielding derivatives are [11]:

$$(\partial\sigma^{N}/\partial r_{NH})_e = -67.9\,, \quad (\partial\sigma^{C}/\partial r_{CH})_e = -51.1\,,$$

$$(\partial\sigma^{H}/\partial r_{NH})_e = -37.1\,, \quad (\partial\sigma^{H}/\partial r_{CH})_e = -25.4\,,$$

$$(\partial\sigma^{H}/\partial r_{NH'})_e = -0.54\,, \quad (\partial\sigma^{H}/\partial r_{CH'})_e = -2.6\,,$$

where the last two involve the stretching of a remote bond. We estimate the isotope shifts using the above data:

$$\begin{aligned} &{}^{1}\Delta^{15}N({}^{2/1}H) \approx (\partial\sigma^{N}/\partial r_{NH})_e(\langle \Delta r_{NH}\rangle - \langle \Delta r_{ND}\rangle) \\ &\quad \approx -67.9\times 5.53\times 10^{-3} \approx -375\ \text{ppb} \\ &\quad (\text{obs.} -307\ \text{ppb})\,, \qquad (1) \end{aligned}$$

which is comparable to the ^{13}C shift in CH_4 (−192 ppb),

$$\begin{aligned} &{}^{2}\Delta^{1}H({}^{2/1}H) \\ &\quad \approx (\partial\sigma^{H}/\partial r_{NH})_e(\langle \Delta r_{NH}\rangle_{NH_4^+} + \langle \Delta r_{NH}\rangle_{NH_3D^+}) \\ &\quad + (\partial\sigma^{H}/\partial r_{NH'})_e(\langle \Delta r_{NH}\rangle - \langle \Delta r_{ND}\rangle) \\ &\quad \approx -37.1\times 1.6\times 10^{-4} - 0.54\times 5.5\times 10^{-3} \\ &\quad \approx -9\ \text{ppb} \quad (\text{obs.} +18\ \text{ppb!})\,. \qquad (2) \end{aligned}$$

This may be compared with CH_4:

$$\begin{aligned} &{}^{2}\Delta^{1}H({}^{2/1}H) \\ &\quad \approx -25.4\times 1.6\times 10^{-4} - 2.1\times 5.53\times 10^{-3} \\ &\quad \approx -18.4\ \text{ppb} \quad (\text{obs.} -16\ \text{ppb})\,. \qquad (3) \end{aligned}$$

The ^{15}N-induced ^{1}H isotope shift can also be estimated:

$$\begin{aligned} &{}^{1}\Delta^{1}H({}^{15/14}N) \approx -37.1\times 4.6\times 10^{-5} \approx -1.7\ \text{ppb} \\ &\quad (\text{obs.} -1.5\ \text{ppb})\,, \qquad (4) \end{aligned}$$

which may be compared with CH_4:

$$\begin{aligned} &{}^{1}\Delta^{1}H({}^{13/12}C) \approx -25.4\times 6.2\times 10^{-5} \approx -1.6\ \text{ppb} \\ &\quad (\text{obs.} -2.4\ \text{ppb})\,. \qquad (5) \end{aligned}$$

Most magnitudes and signs of the six different types of isotope shifts in the NH_4^+ and CH_4 systems are consistent with the theoretical shielding derivatives and the mean bond displacements. The exceptions are the sign and the relatively large deviations from additivity of the D-induced ^{1}H shifts in NH_4^+(aq). In the discussion which follows, we show that the unusual sign of the D-induced ^{1}H isotope shift in NH_4^+ compared to two-bond isotope shifts in general, and CH_4 in particular, may be attributed to intermolecular effects. The deviations from additivity also appear to have an intermolecular origin.

In a series of isotopomers related by substitution at equivalent positions, the isotope shift is generally observed to be additive [12]. That is not the case in these ions. The ^{1}H isotope shifts observed here tend to be about 10% larger in magnitude than strict additivity. ^{14}N isotope shifts in the same system show small deviations from additivity but only of the order of 2% and of opposite sign to that observed here, i.e. the D-induced ^{14}N shifts tend to be slightly smaller in magnitude than dictated by strict additivity as more deuterons replace protons [3]. Although such small deviations from additivity can be expected on the basis of the present rovibrational theory of isotope shifts, deviations as large as 10% are not anticipated [10]. We consider several possible mechanisms for these deviations.

Calculated rotational and vibrational contributions to two-bond isotope shifts [9,10] are very nearly additive. In addition to the additive 18.4 ppb per D in eq. (3) there are smaller not-quite-additive terms which have been estimated for ^{1}H shielding in $CH_{4-n}D_n$: +0.278, +0.236, and +0.232 ppb increments with each successive deuteration [9]. Their contributions to non-additivity are small: only 0.04 and 0.09 ppb.

Chemical shifts due to intermolecular interactions depend on the separation between the nucleus and the collision partner, which is different from the separation between the centres of mass of the molecules. A "nuclear site effect" model takes these differences into account by a multiplicative factor (site factor) which depends on the characteristic distance parameter r_0 of the intermolecular potential and the distance d of the observed nucleus from the centre of mass [13]. The eccentricity of the solvation shift has been derived both for the binary collision gas model and for a "cage" of nearest-neighbor solvent molecules, resulting in nearly the same functional dependence on d/r_0 for both [13]. The more "exposed" nuclei suffer larger solvent shifts. This site effect model has been used [14] to calculate the observed density dependence of the isotope shift in the D_2–HD system [15]. As the $NH_{4-n}D_n^+$ ion is rotating in solution, the ^{1}H sites in NH_3D^+ are more exposed than the ^{1}H sites in NH_4^+, and so on in the series, as the centre of mass moves further away from the ^{1}H nucleus when more deuteriums are added. Thus, the ^{1}H solvation shifts should increase in magnitude in the series

$$NH_4^+ < NH_3D^+ < NH_2D_2^+ < NHD_3^+ \ .$$

In neutral molecules ^{1}H solvation shifts are generally deshielding, i.e. the resonance frequencies would tend to increase in the order shown above, which is the same order as in fig. 1. For $CH_{4-n}D_n$ these differences in ^{1}H site factors have been calculated and are found to be smaller than strictly additive [14]. The calculated site factors arising from the eccentricity of the ^{1}H nuclei lead to

$$\sigma(CH_4, \text{soln}) = \sigma(CH_4, \text{free}) + \sigma_{\text{sol}} \ ,$$

$$\sigma(CH_3D, \text{soln}) = \sigma(CH_3D, \text{free}) + 1.0446\sigma_{\text{sol}} \ .$$

The site factors are 1.0833 and 1.1171 for CH_2D_2 and CHD_3, and $\sigma_{\text{sol}} \approx -266$ to -781 ppb for ^{1}H in CH_4 in non-aromatic solvents [16]. As a first approximation let us simply transfer these calculated eccentricity factors and the calculated smaller terms in $CH_{4-n}D_n$ to $NH_{4-n}D_n^+$. Neglecting the effects of the counter ions,

$$\sigma(NH_4^+, \text{free}) = x \text{ ppb} \ ,$$

$$\sigma(NH_4^+, \text{aq}) = x + \sigma_{\text{sol}} \ ,$$

$$\sigma(NH_3D^+, \text{aq}) = x + \sigma_D + 0.278 + 1.0446\sigma_{\text{sol}} \ ,$$

$$\sigma(NH_2D_2^+, \text{aq}) = x + 2\sigma_D + 0.278 + 0.236 + 1.0833\sigma_{\text{sol}} \ ,$$

$$\sigma(NHD_3^+, \text{aq}) = x + 3\sigma_D + 0.278 + 0.236 + 0.232 + 1.1171\sigma_{\text{sol}} \ .$$

If we assume the additive part of the ^{1}H two-bond isotope shift to be the calculated value, $\sigma_D \approx +9$ ppb per deuterium and the solvation contribution to the shielding to be $\sigma_{\text{sol}} \approx -612$ ppb (such as would be appropriate for an intermolecular effect of -1.5 ppb amagat^{-1} and the density of pure liquid H_2O at room temperature, 403 amagat), then we calculate the following chemical shifts: $\delta(NH_{4-n}D_n^+, \text{aq}) = 0, +18.0, +32.5, +43.9$ ppb for $n = 0$ to 3. The signs and magnitudes are about right but the estimated deviations from additivity are in the wrong direction compared to our experimental values (0, +18.1, +38.1, +60.0 ppb, respectively). However, these estimates are close to the values for ^{1}H observed for NH_4Br in H_2SO_4–D_2SO_4 solution: 0, +17, +32, +43 ppb [17] [#1].

The contributions discussed above apply to CH_4, NH_4^+ and BH_4^-, with the solvation shift σ_{sol} depending on the composition of the solution. Two additional effects have to be considered in NH_4^+ and BH_4^-. These are the effects of the counter ions in solution and of hydrogen-bonding. The counter ions provide an outer cage around the $NH_4^+ \cdot (H_2O)_x$ moiety. For the purpose of eliciting an explanation of the large deviations from additivity, the effect of the counter ions can be combined with the solvent cage in the σ_{sol} terms, the nature of which has not been specified and could include electrostatic and dispersion contributions, even hydrogen-bonding. Counter ions apparently have an effect. With the Cl^- counter ion (this work) the isotope shifts are larger than strictly additive, whereas with Br^- and SO_4^{2-} the shifts are smaller than strictly additive. The effects of counter ions have also been observed in the $BH_{4-n}D_n^-$ system; the larger the counter ion (Li^+, Na^+, or K^+) the larger the observed isotope shifts [19]. Nevertheless, these ^{1}H isotope shifts were all normal sign and additive, unlike the ^{1}H isotope shifts in the $NH_{4-n}D_n^+$ system.

So far our model is that of a thermal average cage of solvent molecules (and counter ions further out) surrounding a freely or nearly freely rotating $NH_{4-n}D_n^+$, BH_4^- or CH_4 having a different centre of mass for different n. Finally, we consider a contribution which is not present in CH_4 or BH_4^-, the differential hydrogen-bonding of H and D to the oxygen of H_2O [20]. A simple model for this is a static structure consisting of $NH_{4-n}D_n^+$ with n N–D...O bonds and $4-n$ N–H...O bonds to specific H_2O or D_2O solvent molecules which form an asymmetric cage around the ion. The cage is asymmetric due to the different hydrogen-bond strengths of N–H...O and N–D...O leading to different average N–O distances. In this limiting case, the proton electronic environment is modified by changing n, and the chemical shift with n is not necessarily additive.

Thus we have two factors which lead to an unusual sign in NH_4^+ but not in CH_4 or BH_4^- and to a rel-

---

[#1] Data obtained at lower fields were less precise [18].

atively large deviation from additivity in NH_4^+ but not in CH_4 or BH_4^-. These are (a) the much smaller shielding derivative $(\partial\sigma^{H_1}/\partial r_{MH_2})_e$ in NH_4^+ compared to CH_4 or BH_4^- [11], leading to a much smaller isotope shift in the free NH_4^+ ion and (b) hydrogen-bonding in NH_4^+, but not in CH_4 or BH_4^-, would tend to make σ_{sol} larger for NH_4^+ so that the (opposite sign) intermolecular effects could dominate over the usual sign intrinsic isotope shifts in NH_4^+, leading to an unusual sign for the ^1H isotope shift in NH_4^+. Furthermore, the differential hydrogen-bonding in N–H...O compared to N–D...O could lead to secondary changes in the electronic environment at ^1H depending on n in $NH_{4-n}D_n^+$ but not in $BH_{4-n}D_n^-$. The model of a nearly freely rotating $NH_{4-n}D_n^+$ ion in a thermal average cage of H_2O molecules gives ^1H chemical shift estimates of 0, +8, +32.5, +43.9 ppb for $n=0$ to 3. Calculations for the other model of a $NH_{4-n}D_n^+$ ion hydrogen-bonded to its cage, the asymmetry of the cage depending on n, have not been carried out. It is possible, though not obvious, that the differential hydrogen-bonding alone could give rise to a contribution to $^2\Delta^1H$ which has an unusual sign and is greater than n-additive. If so, there should be concomitant effects on the ^{14}N or ^{15}N isotope shifts in the same system. These have not been observed.

Although all isotopomers can best be observed in solutions with H_2O/D_2O ratios of 1:3 to 1:4, the same isotope shifts were obtained for various H_2O/D_2O ratios. This indicates that changing the ratio of H/D in the solvent cage produces a negligible effect on the isotope shifts.

In conclusion, the observed ^1H isotope shifts in $NH_{4-n}D_n^+$ in solution can be attributed to several effects: (1) the intrinsic isotope shift in the free ion, which is very nearly additive and has the usual sign, (2) intermolecular effects which are opposite in sign and include both the effects of the eccentricity of the ^1H nuclei on the shifts, which make the intermolecular contributions not quite additive and hydrogen-bonding which make the intermolecular contributions larger than usual and also may be not quite additive. Counter ions contribute to the intermolecular effects. The deviations from additivity due to eccentricity effects on the medium shifts can be large enough to be observable under the following conditions: (a) Substituted nuclei have to be H; only hydrogen offers a large enough fractional mass change; (b) the central atom has to be light so that deuteration can shift the center of mass significantly; (c) the intermolecular interactions have to give large enough medium shifts so that differential medium shifts can be observed, as when hydrogen-bonding with the solvent is involved.

In summary, we report high-resolution experimental ^1H chemical shifts in isotopomers of NH_4^+ and provide an interpretation of their unusual sign and unusually large deviations from additivity.

References

[1] J.K.M. Sanders and B.K. Hunter, Modern NMR spectroscopy: a guide for chemists (Clarendon Press, Oxford, 1987).

[2] P.W. Fowler, M. Grayson, P. Lazzeretti, W.T. Raynes, A.J. Sadlej and R. Zanasi, paper presented at the International NMR Symposium, Cambridge, July 1985.

[3] R.E. Wasylishen and J.O. Friedrich, J. Chem. Phys. 80 (1984) 585.

[4] R.E. Wasylishen and J.O. Friedrich, private communications.

[5] P.J. Hore, J. Magn. Reson. 55 (1983) 283.

[6] R.A. Bernheim and B.J. Lavery, J. Chem. Phys. 42 (1965) 1464.

[7] M. Alei and W.E. Wageman, J. Chem. Phys. 68 (1978) 783.

[8] C.J. Jameson and H.J. Osten, J. Am. Chem. Soc. 108 (1986) 2497.

[9] C.J. Jameson and H.J. Osten, J. Chem. Phys. 81 (1984) 4293.

[10] H.J. Osten and C.J. Jameson, J. Chem. Phys. 81 (1984) 4288.

[11] D.B. Chesnut, Chem. Phys. 110 (1986) 415.

[12] H. Batiz-Hernandez and R.A. Bernheim, Progr. NMR Spectry. 3 (1967) 63.

[13] F.H.A. Rummens and H.J. Bernstein, J. Chem. Phys. 43 (1965) 2971;
F.H.A. Rummens, W.T. Raynes and H.J. Bernstein, J. Phys. Chem. 72 (1968) 2111.

[14] C.J. Jameson, A.K. Jameson and D. Oppusunggu, J. Chem. Phys. 81 (1984) 2313.

[15] J.R. Beckett and H.Y. Carr, Phys. Rev. A24 (1981) 144.

[16] F.H.A. Rummens and F.M. Mourits, Can. J. Chem. 55 (1977) 3021.

[17] W. McFarlane and R.R. Dean, J. Chem. Soc. A (1968) 1535.

[18] G. Fraenkel, Y. Asahi, H. Batiz-Hernandez and R.A. Bernheim, J. Chem. Phys. 44 (1966) 4647.

[19] I.A. Oxton, A.G. McInnes and J.A. Walter, Can. J. Chem. 57 (1979) 503;
B.D. James, B.E. Smith and R.H. Newman, J. Chem. Soc. Chem. Commun. (1974) 294.

[20] A.D. Buckingham and Liu Fan-Chen, Intern. Rev. Phys. Chem. 1 (1981) 253.