

Ab Initio Calculations of Deuterium Isotope Effects on Hydrogen and Nitrogen Nuclear Magnetic Shielding in the Hydrated Ammonium Ion*

Marianne Munch,^{a,†} Aage E. Hansen,^a Poul Erik Hansen^b and Thomas D. Bouman^{c,§}

^aChemical Laboratory IV, Department of Chemistry, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark,

^bInstitute of Life Sciences and Chemistry, University of Roskilde, PO Box 260, DK-4000 Roskilde, Denmark and ^cDepartment of Chemistry, Southern Illinois University, Edwardsville, IL 62026, USA

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¹H and ¹⁴N nuclear shieldings of the ammonium ion and of its mono- and tetra-hydrated species in directional as well as non-directional coordinations are calculated *ab initio* using the localized orbital/local origin (LORG) method; counterpoise calculations are included to test for basis set superposition effects. The variation of the ¹H and ¹⁴N shieldings with N–H distance is essentially linear in the bonding region, while the large-scale variations illustrate the transition from solvated ammonium to ammoniated hydroxonium complexes. The deuterium isotope effects for these systems are evaluated in a static approximation, and for the directionally coordinated NH₄⁺(H₂O)₄ ion the computed two-bond deuterium isotope effect on ¹H correctly reproduces the unusual (i.e. negatively signed) experimental result, while the bare ion and non-directionally coordinated NH₄⁺(H₂O)₄ yield positively signed effects. The decisive factor for the sign inversion is found to be the directional solvation of the deuterium atom, with an ammonium–water distance not exceeding ca. 3 Å, and the effect can be traced to a difference in the distance variation of the shielding perpendicular and parallel to the N–H bond. For the ¹⁴N nuclear shielding again the results obtained for directionally coordinated NH₄⁺(H₂O)₄ are in better agreement with experiments than the results obtained for the bare ion or for non-directional solvation.

Ab initio calculations of nuclear magnetic shielding have reached a level of accuracy where computations can complement experiments very effectively in studies of structural effects on shielding properties.¹ We present here an *ab initio* study of the isotope effects on the nuclear shielding in the ammonium ion with special emphasis on the influence of solvation (hydration).

The deuterium isotope effect on the shielding of a given magnetic nucleus X can be defined by² eqn. (1), where *n* is

$$n\Delta X(D) \equiv \sigma X(D) - \sigma X(H) = \delta X(H) - \delta X(D) \quad (1)$$

the number of bonds between X and the deuterium atom. $\sigma X(D)$ is the absolute shielding of X in the deuterated molecule, $\delta X(D)$ is the corresponding chemical shift, and $\sigma X(H)$ and $\delta X(H)$ refer similarly to the unsubstituted species. In the Born–Oppenheimer approximation the potential energy curves for nuclear motion are independent of

nuclear mass. However, in the presence of anharmonicity, the result is an effectively shortened X–D bond compared to the corresponding X–H bond, and although accurate studies require averaging over nuclear motion,³ estimates of deuterium effects can be based on signs and magnitudes of the derivatives of the shielding with respect to bond extension,^{4,5} or by a static approximation in which an appropriately shortened X–D bond is used in the electronic calculations;⁶ see Ref. 7 and 8 for similar studies of the electronic circular dichroism of isotopically chiral molecules.

Ab initio calculations^{4,5} of shielding derivatives in hydrides of first- and second-row atoms suggest that ${}^n\Delta H(D)$, for *n* equal to zero and two, is generally positive for these systems, the effect for *n*=2 being about an order of magnitude smaller than for *n*=0. For the heavy atoms in these hydrides the calculations suggest that ${}^1\Delta X(D)$ changes sign between the third and fourth column of the Periodic Table, being positive on the right-hand side of the Table. Representative values² for the experimental one- and two-bond deuterium effects in neutral ammonia, ${}^1\Delta N(D) = 0.65$ ppm/D⁶ and ${}^2\Delta H(D) = 0.029$ ppm/D,^{9,10} are in accord with the above expectation. For the ammonium ion in aqueous solution the experimental deuterium effects^{10–13} are quite

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[†] Present address: Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark.

[§] It is with great sorrow that we advise that Professor Thomas D. Bouman died on April 12, 1992.

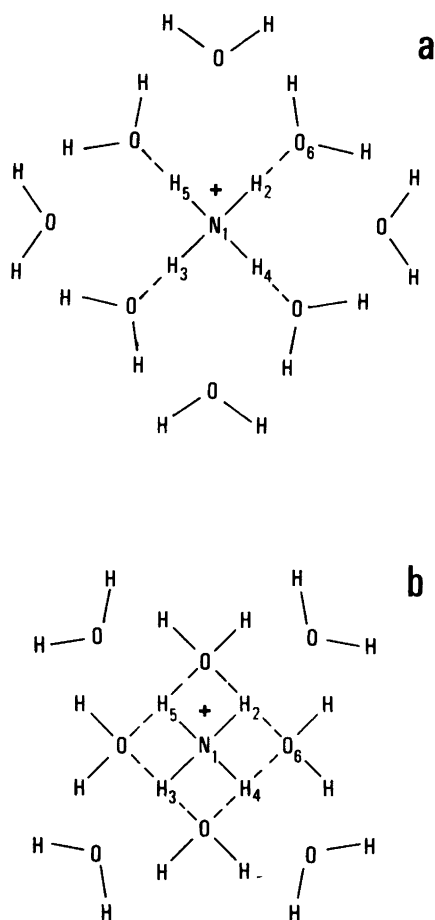


Fig. 1. Schematic coordination structures of hydrated ammonium: (a) with directional bonds, (b) with non-directional bonds. (See text for actual structures and distances.)

sensitive to concentration and to the nature of the counterions. By extrapolation to infinite dilution, Hansen and Lycka¹³ obtained approximately additive values of ${}^1\Delta N(D) = 0.36$ ppm/D and ${}^2\Delta H(D) = -0.017$ ppm/D, heavier isotopomers showing the largest non-additivity.

The two-bond deuterium effect on the proton shielding in the ammonium ion is hence inverted relative to the general trend in hydrides and to the effect in ammonia in particular; ${}^2\Delta H(D)$ in fact becomes increasingly more negative at low concentrations.¹³ In addition, the one-bond deuterium effect on the nitrogen shielding is notably smaller in the ammonium ion than in ammonia, and a similar reduction has been observed for less symmetrical compounds.^{10,12} The decrease in ${}^1\Delta N(D)$ upon protonation of ammonia is in accord with the calculated derivatives for the isolated species.⁴ However, although the calculations also indicate a similar decrease in ${}^2\Delta H(D)$ for the isolated species, the observed sign inversion suggests the importance of hydrogen bonding to water.^{11,13,14} The solvation sphere has been predicted¹⁵ to contain water molecules with directional as well as non-directional hydrogen bonds (Fig. 1), and Hansen and Lycka¹³ speculated that non-directional bonds (Fig. 1b) are the most important for inversion of the deuterium effect.

The present *ab initio* calculations of the shieldings are based on the localized orbital/local origin (LORG) method.¹⁶⁻¹⁸ The effect of isotopic substitution is simulated by the use of an appropriately shortened bond to the deuterium atom as discussed above, while the effect of solvation is simulated by treating the ion and selected water molecules as a supermolecule, and we include the results of counterpoise calculations to test for basis set superposition effects (see e.g. Ref. 19 and references therein).

Methods and calculations

The LORG method¹⁶⁻¹⁸ for the calculation of nuclear magnetic shielding is a distributed-gauge variant of coupled Hartree-Fock (CHF) theory,^{1,16,20-22} in which local gauge origins are defined relative to localized (occupied) molecular orbitals. The CHF level is expectedly adequate for nitrogen and hydrogen shieldings in the present bonding situations, since it appears that electron correlation beyond the CHF level becomes important specifically for the magnetic shielding properties of multiply bonded nuclei carrying lone-pair electrons.²³⁻²⁶ The actual LORG calculations of the shieldings were carried out with our RPAC Molecular Properties Package, version 8.2,²⁷ and the SCF results required for the LORG calculations were obtained with the GAUSSIAN 86 program system.²⁸ The geometry optimizations mentioned below were carried out with the Gaussian 80 program system utilizing the built-in 6-31G* basis sets.²⁹

For the shielding calculations, experimentation with basis sets showed, not unexpectedly, that the variation of the absolute shieldings with choice of basis set is rather non-trivial compared to the magnitude of the isotope effects. However, the differences that provide chemical shifts and isotope effects are quite stable at the level of triple-zeta polarized bases and beyond. The shielding results reported here were obtained with [3s3p1d] contracted GTOs for nitrogen and oxygen, and [2s1p] contracted GTOs for the hydrogen atoms in the ammonium ion, using basis B of Ref. 16 except that the 1d functions are now 50-50 contractions of two primitive Gaussians ($\alpha_N = 0.950$ and 0.240 , $\alpha_O = 1.0094$ and 0.2550), and the 1p function is a 50-50 contraction of two primitive Gaussians with $\alpha = 1.500$ and 0.400 . We have found that such contractions for the polarization functions simulate the effect of uncontracted sets of the corresponding primitive functions quite well. The hydrogen atoms in the water molecules are not involved in bonding to the NH_4^+ ion, and are described by [2s] contracted GTOs as in basis A of Ref. 16. For the largest system considered here, $NH_4^+(H_2O)_4$, this generates a total of 121 contracted basis functions, and the same basis functions are used in the counterpoise calculations.¹⁹ The latter simply amount to NH_4^+ calculations in which the basis functions of the water molecules are retained at the (ghost) positions of the water nuclei. In the RPAC 8.2 program package,²⁷ and effective iterative procedure¹⁷ is used to solve the CHF equations, which for the present systems encompass up to 2400 singly excited configurations and

Table 1. Overall LORG results for the nuclear shielding and deuterium isotope effects (in ppm) for the non-hydrated and hydrated ammonium ion.

Compound	$\sigma(\text{N})$	$\sigma(\text{H})$	${}^1\Delta\text{N}(\text{D})$	${}^0\Delta\text{H}(\text{D})$	${}^2\Delta\text{H}(\text{D})$
NH ₄ ⁺ (free)	243.07 243.1 ^a	25.94 27.48 ^a	0.667 0.376 ^a	0.36 0.22 ^a	0.006 0.005 ^b
NH ₄ ⁺ , (H ₂ O) ₄ (Fig. 1a)	240.58 239.77 ^c	24.38 25.94 ^c	0.59 0.67 ^c	0.43 0.36 ^c	-0.005 0.010 ^c
NH ₄ ⁺ , (H ₂ O) ₄ (Fig. 1b) ^d	221.44	25.68	0.81	0.36	0.005 ^d 0.010 ^e
NH ₄ ⁺ , (H ₂ O) ^{f,g} (Fig. 1a)	239.29 244.45 ^h	26.57 27.09 ^h	0.33 0.20 ^h	0.47 0.18 ^h	-0.012 -0.011 ^h
NH ₄ ⁺ , (H ₂ O) ^{f,i} (Fig. 1a)	239.29 244.45 ^h	20.97 21.83 ^h	0.75 0.80 ^h	0.42 0.37 ^h	0.005 0.009 ^h
NH ₄ ⁺ , (H ₂ O) ^{f,j} (Fig. 1b)	233.46	25.12 26.28 ^k	0.72	0.37	0.000 0.005 ^k
NH ₄ ⁺ (aq), exptl.	223.8 ^l		0.36 ^m		-0.017 ^m

^aDerived from the GIAO results of Ref. 5, see text. ^bDerived from the GIAO result of Ref. 4, see text. ^cCounterpoise calculations, see text. ^dDeuteration at H₂; ²ΔH(D) refers to H₄. ^eDeuteration at H₂; ²ΔH(D) refers to H₃. ^fThe water molecule retained is the O₆ containing unit in the respective structure in Fig. 1. ^gDeuteration at H₂; $\sigma(\text{H})$ and ²ΔH(D) refer to H₅. ^hNegative point charge at oxygen position (O₆), see text. ⁱDeuteration at H₅; $\sigma(\text{H})$ and ²ΔH(D) refer to H₂. ^jDeuteration at H₄; $\sigma(\text{H})$ and ²ΔH(D) refer to H₂. ^k $\sigma(\text{H})$ and ²ΔH(D) refer to H₃. ^lRef. 32. ^mRef. 13.

hence implicitly up to about 1.4×10^6 doubly excited configurations.

For the isolated NH₄⁺ ion, MP2/6-31G* optimization²⁹ gave an N–H distance of 1.029 Å, which is close to the experimental bond length.³⁰ This value was used as the ‘equilibrium’ N–H bond length also in the solvated structures, and the perfect tetrahedral symmetry of the isolated ammonium ion was enforced in all the hydrated structures considered here. We have selected two specific structures for the ammonium ion hydrated by four water molecules, NH₄⁺(H₂O)₄, one with directional (linear) hydrogen bonds (Fig. 1a), the other with non-directional bonds where each hydrogen on the ammonium ion is coordinated to two oxygen atoms (Fig. 1b). Other possibilities and higher coordinations exist;³¹ however, the actual nuclear shieldings are averages over a number of conformations, and the one- and two-coordinated structures selected here probably dominate the hydrogen bonding effects.

With directional hydrogen bonds to four water molecules (Fig. 1a) the energy optimized geometry (with the above-mentioned constraints) is of *D*_{2d} symmetry and the resulting N–O distance is 2.9113 Å, while for non-directional hydrogen bonds between the ammonium ion and four water molecules (Fig. 1b) the optimized geometry has *C*_{2v} symmetry with an N–O distance of 2.8580 Å. The *C*₂ axis of the structure in Fig. 1b bisects the H₂–N–H₃ and the H₄–N–H₅ angles, and the same sets of atoms define the symmetry planes. We shall also report results for monohydrated am-

monium ions, NH₄⁺(H₂O). With a single directionally bound water molecule (as in Fig. 1a) the optimized geometry has *C*_s symmetry and an N–O distance of 2.7290 Å, whereas the optimized *C*_{2v} structure with a single non-directionally bound water molecule (as in Fig. 1b) has an N–O distance of 2.6766 Å. In all cases the effect of deuteration is simulated by shortening the bond by 0.01 Å to an N–D distance of 1.019 Å, while the respective N–O distances and other structural parameters are kept unchanged. The implied neglect of relaxation is of course unrealistic; however, short of a full dynamic study we see no way to simulate relaxations faithfully, and have hence preferred to single out the effect of bond shortening in the present investigation.

Results

The overall results are presented in Table 1. For the free ammonium ion we include for comparison ⁿΔX(D) values obtained from the results reported by Chesnut⁴ and Chesnut and Wright,⁵ using eqn. (1) to derive the isotope effects corresponding to the present N–D bond length from their shielding derivatives. The calculations of Chesnut and Wright^{4,5} are based on the gauge-including atomic orbital (GIAO) approach,^{1,21} using the basis sets of the Gaussian program packages,^{28,29} and the agreement between the LORG and the GIAO results is within the variation expected from differences in method and basis sets. We note in particular that we agree in sign and magnitude for ²ΔH(D) in the isolated ion.

For the two tetrahydrated solvation models, NH₄⁺(H₂O)₄, the results for the directional structure (Fig. 1a) in fact show a reduction in ¹ΔN(D) and sign inversion of ²ΔH(D) relative to the free ion, and the counterpoise results show that neither feature is a result of basis set extension. On the other hand, the results for the non-directional structure (Fig. 1b) do not reflect the experimental trends. In the non-directional arrangement the values 0.005 and 0.010 reported for ²ΔH(D) correspond to the two-bond effect for hydrogens coordinated, respectively, to the same water molecule and to different water molecules. In more general terms the results for the four coordinated arrangements show that the proton shielding in the non-directional structure resembles the shielding in the free ion quite closely, presumably indicating relatively loose hydrogen bonding in this arrangement. For the nitrogen shielding the closer resemblance is, however, between the directionally coordinated structure and the free ion, whereas the shielding in the non-directional structure is shifted downfield by almost 20 ppm. The latter effect is found to be caused entirely by an increase in the magnitude of the paramagnetic contribution to the shielding.

The results given in Table 1 for the monohydrated species, NH₄⁺(H₂O), in a directionally coordinated structure (Fig. 1a) show that the important part of the mechanism for ²ΔH(D) sign inversion is associated with structures where the deuterium substitution takes place in the hydrogen

Table 2. Proton and nitrogen shieldings and isotope effects (in ppm) for $\text{NH}_4^+(\text{H}_2\text{O})^a$ as a function of $R(\text{N}-\text{O}_6)$.

$R(\text{N}-\text{O}_6)/\text{\AA}$	${}^2\Delta\text{H}(\text{D})$	$\sigma(\text{H}_2)$	$\sigma(\text{H}_3)$	$\sigma(\text{N})$	${}^1\Delta\text{N}(\text{D})$
2.72	-0.012	20.97	26.57	239.29	0.37
3.02	-0.003	23.41	26.32	240.64	0.48
3.52	0.005	24.89	26.11	241.49	0.56
4.02	0.005	25.37	26.02	241.58	0.60
∞^b	0.006	25.94	25.94	243.07	0.67

^aAs in Fig. 1a with the O_6 water molecule retained. ^bFree ammonium ion.

bond, whereas hydrogen bonding involving the proton is quite important for the magnitude of the absolute shielding, but does not in itself produce a sign inversion of the isotope effect. In addition, the sign inversion is quite insensitive to solvent rotamers; the value ${}^2\Delta\text{H}(\text{D}) = -0.012$ ppm reported in Table 1 for deuteration in the hydrogen bond of the singly solvated species is stable to within ± 0.002 ppm with respect to rotation of the water molecule along the direction of the hydrogen bond. The results superscripted (*h*) in Table 1 are obtained when the water molecule in this monohydrated directionally coordinated structure is replaced by a negative point charge of unit magnitude (in atomic units) located at the position of the oxygen atom. The trends in $\sigma(\text{H})$, ${}^2\Delta\text{H}(\text{D})$ and ${}^1\Delta\text{N}(\text{D})$ going from the free ion to the hydrated species are mimicked quite well by this point charge model, while the change in $\sigma(\text{N})$ clearly requires the presence of a real water molecule.

The results reported in Table 1 for the monohydrated directional structure (Fig. 1a) essentially reproduce the features of the corresponding tetrahydrated species, except that the downfield shift of the nitrogen atom is not fully realized in the singly solvated ion.

The monohydrated species, $\text{NH}_4^+(\text{H}_2\text{O})$, in the directionally coordinated configuration therefore exhibits most of the characteristic features of the solvation effect for the present purpose, and the shielding properties of this system are studied in more detail in Table 2 and in Figs. 2 and 3. Table 2 presents the variation of the shielding properties as a function of distance between the ion and the solvent molecule, converging towards the properties of the free ion. The variations are monotonic; however, we note that the sign inversion of ${}^2\Delta\text{H}(\text{D})$ occurs only for solvent molecules inside a sphere of ca. 3 Å from the nitrogen atom. Fig. 2 then illustrates the variations in the Hartree–Fock energy and shieldings as a function of the hydrogen-bonded N–H₂ (N–D) distance (Fig. 1a) when the N–O distance and the remaining N–H distances are kept fixed at 2.7290 and 1.029 Å, respectively. The figure reveals two distinct regions, which can be ascribed to the characteristics of the complexes $\text{NH}_4^+-\text{OH}_2$ and $\text{NH}_3-\text{OH}_3^+$, respectively, although the potential energy curve shown in Fig. 2a exhibits only a single minimum located in the region corresponding to the solvated ammonium ion. The position of this mini-

mum is quite close to the N–H distance of 1.029 Å assumed for the equilibrium distance (see previous section); this distance is indicated by the vertical line in the figure. For internal consistency in the figure, the Hartree–Fock potential energy curve is shown for the atomic basis set used also in the shielding calculations. The energies found in the 6-31G** Hartree–Fock calculations used in the optimizations, as described in the previous section, are ca. 0.02 a.u. higher than those shown in Fig. 2a, while MP2 calculations lead to a lowering of the energy curve by ca. 0.40 a.u., but in neither case is a second minimum introduced in the potential energy curve.

In Fig. 2b the shielding of the spectator proton at position 5 increases uniformly with increasing distance between nitrogen and the proton (or deuterium) in the hydrogen bond, in accord with a negative value for ${}^2\Delta\text{H}(\text{D})$, while the shielding of the proton in the hydrogen bond (Fig. 2c) as well as the shielding of the nitrogen nucleus (Fig. 2d) go through a minimum in the transition range between the two complexes. For the hydrogen-bonded proton the variation reflects a change from predominantly N–H to predom-

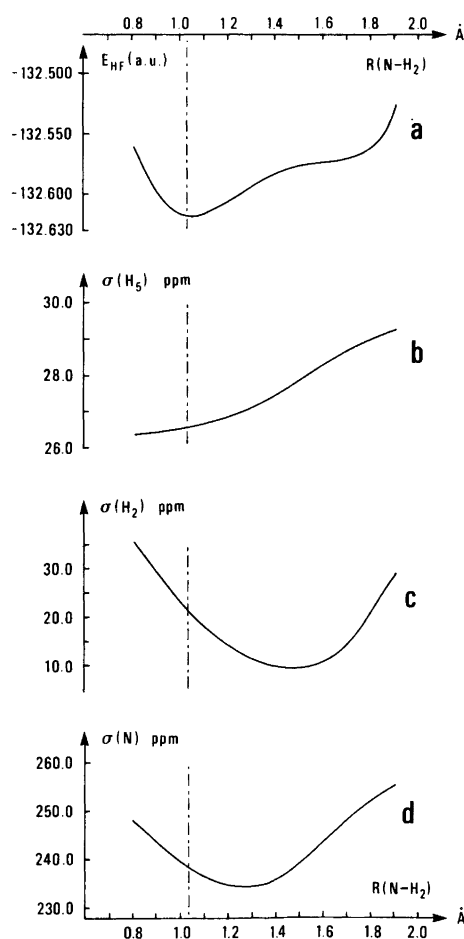


Fig. 2. Calculated total Hartree–Fock energy and shieldings as function of the N–H₂ distance in the monohydrated ammonium ion in directional coordination (Fig. 1a retaining only the O_6 containing water moiety) for a fixed N– O_6 distance. The vertical line indicates the assumed equilibrium distance, $R(\text{N}-\text{H}) = 1.029$ Å (see text).

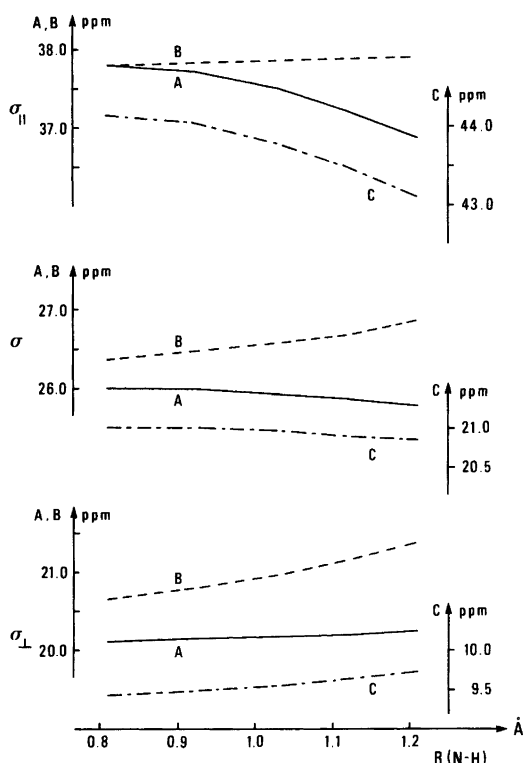


Fig. 3. Calculated shielding components for one proton as function of the distance between N and one of the other protons for free and monohydrated (O_6) ammonium (Fig. 1a): (A) free NH_4^+ , (B) shielding of H_5 as function of $R(\text{N}-\text{H}_2)$; (C) shielding of H_2 as function of $R(\text{N}-\text{H}_5)$.

inantly O-H shielding, while the variation for nitrogen reflects a difference between N-H and lone-pair contributions to the shielding. However, all three shieldings in Fig. 2 vary nearly linearly in a range around the assumed equilibrium value of 1.029 Å for the N-H₂ distance (indicated by a vertical line in the figure). Note that the order-of-magnitude difference between $^0\Delta\text{H}(\text{D})$ and $^2\Delta\text{H}(\text{D})$ found for the solvated as well as the free ion (see Table 1 and Ref. 4) is apparent from the large difference in slopes in Figs. 2c and 2b.

A more detailed view of the solvent effect in the inversion of $^2\Delta\text{H}(\text{D})$ can be gleaned from Fig. 3, which shows the isotropic shielding (σ) of one of the protons, and the shielding components parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the bond between nitrogen and this proton, as a function of the distance between N and one of the other protons. These shielding contributions are related through eqn. (2), while the anisotropy of the shielding is defined by eqn. (3).

$$\sigma = \frac{1}{3} \sigma_{\parallel} + \frac{2}{3} \sigma_{\perp} \quad (2)$$

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} \quad (3)$$

Curves A represent the situation in free NH_4^+ , curves B show the shielding of a proton at position H_5 in Fig. 1a as a function of the N-H₂ distance, and curves C show the shielding of a proton at position H_2 as a function of the

N-H₅ distance. Curve b for the isotropic shielding in Fig. 3 is therefore an enlarged segment of Fig. 2b, and the positive slope of this curve, generating the negative two-bond deuterium isotope effect, is now seen to arise from a relatively strong increase in the perpendicular shielding component, while the corresponding parallel component is almost constant within this distance region. On the other hand, the negative slopes of curves A and C for the isotropic shielding, generating the corresponding positive two-bond deuterium isotope effects, are dominated by a strong decrease in the parallel shielding, overriding a moderate increase in the perpendicular components.

A side result of the shieldings displayed in Fig. 3 is an illustration of the fact that the anisotropy is much larger for the proton in the hydrogen bond ($\Delta\sigma \approx 35$ ppm for curves C) than for the non-coordinated protons ($\Delta\sigma \approx 15$ –20 ppm for curves A and B). Similar effects of hydrogen bonding on the shielding anisotropy of protons have been observed in other theoretical^{33,34} as well as experimental studies.^{35,36}

Discussion and comparison with earlier work

The isotope effects discussed in this paper are minute. However, the small positive and negative numbers reported in Table 1 for the calculated isotope effects are not the result of computational fluctuations, but reflect well developed trends for the shieldings, as evidenced by the slopes of the distance variations shown in Fig. 2 and 3. In fact, the various shieldings exhibit almost linear variation with the appropriate N-H distance in the range between 0.9 and 1.1 Å, justifying in part the use of the static approximation for the simulation of the deuterium isotope effects, and demonstrating that the computed values for these isotope effects are relatively insensitive to the exact choice of the proton equilibrium distance (the vertical line in Fig. 2). Also, as emphasized above, the counterpoise calculations show that the computed changes in isotope effects upon solvation can not be blamed on the basis set expansion going from the free ion to the solvated supermolecule.

The calculations and measurements by Heinzinger *et al.*^{15,37} indicate that the NH_4^+ ions have eight water molecules in the first solvation sphere and that four of these are directional and four are non-directional (combine Figs. 1a and 1b) with approximately the same N-O distance. The results of Table 1 strongly suggest that the negative two-bond isotope effects can be accounted for by the directionally bonded water molecules, whereas non-directionally coordinated water has little effect. Perrin and Gipe³⁸ proposed that the fast rotation of the ammonium ion could be accounted for by non-directional solvation of one N-H bond by two water molecules, leading to five coordination. However, non-directional water molecules are not likely to generate negative $^2\Delta\text{H}(\text{D})$ isotope effects as just discussed. Fraenkel *et al.*³⁹ suggested that the unusual sign of $^2\Delta\text{H}(\text{D})$ was due to a stronger hydrogen bond, i.e. a shorter N-O distance, as a result of deuteration. The present calculations have kept the N-O distance the same, regardless of

deuteration, while still obtaining the unusual sign. On the other hand, it is evident from Table 1 that solvation involving the deuterium atom is much more important than solvation of the protons, and in addition Table 2 shows that a shortening of the N–O distance indeed is expected to enhance the effect. In more detail Fig. 3 shows that the single most important consequence of solvation at the deuterium atom is that the parallel component of the shielding of the protons is almost invariant with respect to the location of the deuterium atom (curve B for σ_{\parallel}), making the unusual sign of ${}^2\Delta H(D)$ a result of the positive slope of the corresponding variation of the perpendicular shielding component (curve B for σ_{\perp}).

Solvation also has an effect on the one-bond deuterium isotope effect on the nitrogen shielding. The ${}^1\Delta N(D)$ results for directionally hydrated ammonium ions in Table 1, in particular, show some interesting features, since monohydration at the deuterated position leads to a significant decrease in ${}^1\Delta N(D)$, whereas hydration at a non-deuterated position yields a small increase, compared to the bare ion. For the tetra-hydrated ion the resulting slight decrease in the ${}^1\Delta N(D)$ isotope effect relative to the bare ion then appears essentially as the sum of the effects observed in the monohydrated cases.

In search of a mechanism, Shporer and Loewenstein¹⁴ have discussed the unusual sign of ${}^2\Delta N(D)$ for ammonium ions in terms of electric field effects due to different charges on H and D as described by Gutowsky.⁴⁰ This is at variance with the present demonstration of the importance of solvation, and with the calculations reported here and by Chesnut⁴ showing that deuteration of the bare ammonium ion (Table 1) on its own leads to the normal sign for ${}^2\Delta H(D)$. On the other hand, an electric field effect due to the negative charge on the oxygen atom in the water molecules is suggested by the point charge results (Table 1) and by the stability of the isotope effects with respect to rotation of the solvent molecules. In fact it is found that the shieldings obtained with the point charge simulation of a solvent molecule reproduce the pertinent distance variations (i.e. the slopes of curves B and C in Fig. 3) quite well, while underestimating the anisotropy of curves C.

The calculations involving point charges are also relevant in estimation of the effect of negative counterions, at least for counterions without back-donating p and d orbitals. Counterions like NO_3^- have a very small effect on ${}^1\Delta N(D)$ and ${}^2\Delta H(D)$.¹³ As little back-bonding is expected from a small and hard ion of a first row element, this can be taken as evidence for a small charge effect, indicating that the hard counterions on the average are a rather long distance away from the ammonium ions. On the other hand, large, soft ions like I^- are known to increase both ${}^1\Delta N(D)$ and ${}^2\Delta H(D)$,¹³ whereas the calculations of the effect of a negative charge show that the isotope effects should decrease with increasing presence of negative charge. Hence the effect of soft ions is probably dominated by back-bonding effects.⁴¹

Conclusion

The primary conclusions of these *ab initio* studies are that hydration indeed plays a decisive role in the experimentally observed unusual (i.e. negative) sign of the two-bond deuterium isotope effect, ${}^2\Delta H(D)$, in aqueous ammonium solutions, and that the important components of the solvation sphere are the directionally coordinated water molecules (Fig. 1a), while the non-directionally coordinated water molecules (Fig. 1b) do not seem to affect the shielding properties of the ammonium protons significantly. In addition, the study of the monosolvated species shows that the sign inversion is associated with hydration of the deuterium atom, whereas hydration of the proton for which ${}^2\Delta H(D)$ is being studied in itself is of little importance. Finally, the calculations suggest that this inversion effect requires ammonium–water distances less than ca. 3 Å, the effect in fact increasing with decreasing distance. The latter prediction is presently being tested in a study of deuterated ammonium ions included in crown ethers and cryptands.⁴²

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