

# Studies of Membrane Processes. I. The $\text{NH}_4^+$ , $\text{ND}_4^+$ , $\text{ND}_3\text{H}^+$ , and $\text{CH}_3\text{ND}_3^+$ Ions in Equilibrium with an Oriented Electrical Double Layer

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**Abstract:**  $\text{NH}_4^+$ ,  $\text{ND}_4^+$ ,  $\text{ND}_3\text{H}^+$ , and  $\text{CH}_3\text{ND}_3^+$  ions are oriented in a lyotropic medium corresponding to the middle soap regions. They participate in an electrical double layer as mobile components exchanging with interstitial water. The proton and deuterium magnetic resonance spectra in both acidified aqueous solution and acidified nematic phases have been observed and explained. The degree of orientation of  $C_3$  axes in all ions has been determined and compared. The degree of orientation for the  $\text{CH}_3\text{ND}_3^+$  ion is about twice as large and of opposite sign to  $\text{ND}_4^+$ . The deuterium nuclear quadrupole coupling constant " $Q_D$ " for  $\text{CH}_3\text{ND}_3^+$  is determined along the N-D bond assuming  $\eta = 0$ . Assuming that the  $Q_D$  is positive for  $\text{ND}_4^+$ , we can estimate the approximate distortion in the tetrahedral angles of the ion and the sign of this distortion. It is also assumed that all distortions are in  $C_{3v}$  symmetry. A general method is developed for the study of complex ions involved in membrane equilibria and should be of considerable use in formulating models of biological processes.

We have recently shown<sup>2</sup> that complex ions are ordered in lyotropic middle phases<sup>3</sup> and that the techniques for preparing the appropriate phase are quite general. The nuclear magnetic resonance (nmr) spectra of these ions contain all the information with respect to partially averaged dipole-dipole coupling constants<sup>4</sup> and present for the first time a method for discovering nuclear positions in ions in aqueous solution. The mechanism of ordering is an exchange process involving the mobile component of an electrical double layer at a membrane interface.<sup>2,5</sup>

In this report the study of certain aspects of the proton and deuterium magnetic resonance signals in the ions  $\text{ND}_4^+$ ,  $\text{ND}_3\text{H}^+$ ,  $\text{NH}_4^+$ , and  $\text{CH}_3\text{ND}_3^+$  are investigated. The symmetry of a strictly tetrahedral ion is such that dipole-dipole coupling constants should average to zero. Snyder and Meiboom<sup>6</sup> have reported the small ordering of tetramethylsilane and neopentane in a thermotropic nematic solvent. The values of  $D_{\text{HH}}$  recorded were of the order 2-4 Hz depending on temperature. The explanation of the ordering centered around imposed distortions of the tetrahedral molecule by the nematic solvent. These distortions were shown to be of the order  $+0.1^\circ$  in the Si-C-H bond angle or bond length changes in the region 1 part in  $10^3$ . There has been no subsequent report of the ordering of highly symmetric molecules except  $\text{CH}_3\text{D}$  which has almost

the same structure as  $\text{CH}_4$ .<sup>7</sup> The spectrum of  $\text{CH}_3\text{D}$  in the proton region is a broadened 1:2:1 triplet with a measured degree of orientation  $|S|$  of  $6.7 \times 10^{-4}$ . It is shown by an argument, in which the sign of the scalar coupling is assumed, that  $S < 0$ .

The degree of ordering depends to a very small extent on the replacement of hydrogen by deuterium in molecules in thermotropic solvents.<sup>8</sup> Such differences can be determined by making the solute a mixture of the proton and deuterium containing compound in the same nematic solution.

This work is part of a series in which we study ions participating in an equilibrium involving the interface region of an electrical double layer at a membrane surface and a relatively free state in interstitial water. The structure of the ions can be determined since they are partially oriented, but exchange processes at membrane surfaces can also be investigated.

## Experimental Section

Proton magnetic resonances were observed on a Varian HA100 spectrometer with a probe temperature of  $30.3 \pm 0.05^\circ$ . Deuterium magnetic resonance was observed at 7.95 MHz using a Varian HR60 spectrometer. The side band technique was used to calibrate spectra on the HR60. Audio frequencies were counted with a Hewlett-Packard 522B electronic counter. Nematic middle phases were prepared with the following compositions according to the procedures described previously for positive complex ions:<sup>2</sup> (a) deuterated ammonium decyl sulfate 33.8 wt %, decanol-*O-d* 5.4%, anhydrous sodium sulfate 5.4%, methanol 1.8%, and  $\text{D}_2\text{O}$  (pH 1.3) 53.1%; (b) ammonium decyl sulfate 33.8 wt %, decanol 5.4%, methanol 1.8%, sodium sulfate 5.4% and water 53.6%; (c) 1,1,1-trideuteriomethylammonium decyl sulfate 33.2 wt %, decanol-*O-d* 5.0%, sodium sulfate 5.3%, and  $\text{D}_2\text{O}$  (pH 1.3) 56.5%.

The ammonium decyl sulfates were prepared as described previously<sup>2b</sup> by ion-exchange methods from sodium decyl sulfate. The salts were deuterated in N-H positions by successive solution in  $\text{D}_2\text{O}$  with intervening evaporations to dryness. The final deuterated products were recrystallized from anhydrous acetone. Methanol was included in samples (a) and (b) above to monitor the ordering of solutes by the middle phase from observation of the 1:2:1 triplet derived from the  $\text{CH}_3$  group protons. The outer transitions are very sensitive to the homogeneity of ordering of the

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(2) (a) L. W. Reeves, A. S. Tracey, and M. M. Tracey, *J. Amer. Chem. Soc.*, **95**, 3799 (1973); (b) L. W. Reeves, J. S. de Cara, M. Suzuki, and A. S. Tracey, *Mol. Phys.*, **25**, 1481 (1973).

(3) G. H. Brown, J. W. Doane, and W. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.

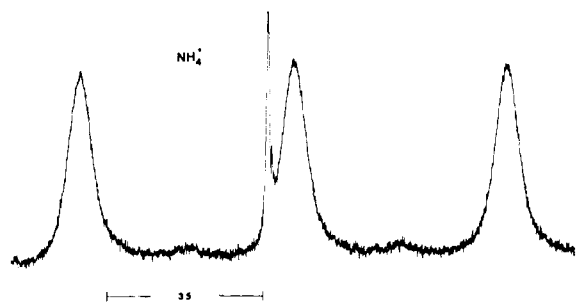
(4) P. Deihl and C. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, Springer-Verlag, New York, N. Y., 1969, p 1.

(5) D. M. Chen and L. W. Reeves, *J. Amer. Chem. Soc.*, **94**, 4384 (1972).

(6) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **44**, 4057 (1966).

(7) C. Yannoni, *J. Chem. Phys.*, **51**, 1682 (1969).

(8) P. Deihl and C. L. Khetrapal, *Can. J. Chem.*, **47**, 1411 (1969).



**Figure 1.** The proton magnetic resonance spectrum of acidified ammonium ion (pH  $\approx$  1.3) in a nematic middle soap phase; cf. phase (b) described in the Experimental Section. A calibration scale of 35 Hz is shown in the diagram. The sharp transition in the low-field side (left-hand direction) is that of oriented methanol in the same phase. This sharp transition is the low-field one of a 1:2:1 triplet derived from intramethyl dipole-dipole coupling. The line width of less than 1 Hz for this peak defines a high homogeneity of order for the phase. The separation of the 1:1:1 broad  $\text{NH}_4^+$  triplet gives  $(J + D)$  for the  $^{14}\text{N}$ - $^1\text{H}$  coupling.

phase and should ideally have line widths less than 1 Hz. We shall show that in the present work a high homogeneity of the degree of orientation was achieved.

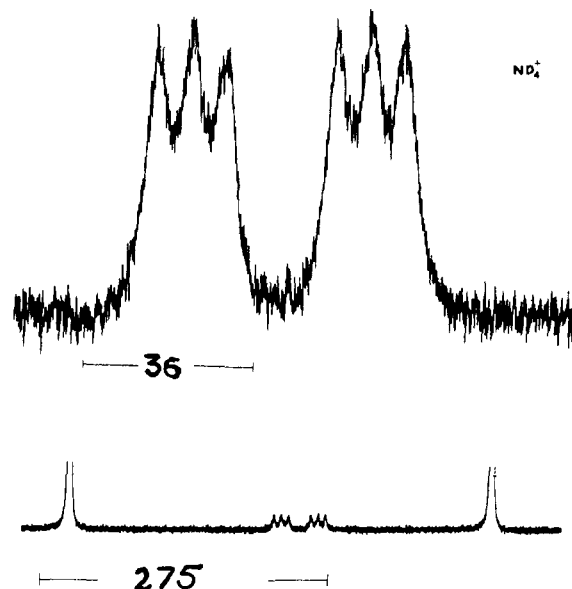
Trideuteriomethylammonium decyl sulfate was prepared from the methylammonium decyl sulfate by recrystallization and exchange with  $\text{D}_2\text{O}$ . The methylammonium decyl sulfate was made by ion-exchange methods as described previously<sup>2</sup> from sodium decyl sulfate.

## Results

The spectrum in isotropic aqueous solutions of the  $\text{NH}_4^+$  ion (acidified ammonium chloride), apart from a higher precision in measurement of the  $J_{\text{N-H}}$  coupling from HA100 spectra, differed in no regard from the results reported some time ago by Ogg and Ray.<sup>9</sup> The concentrations of ammonium chloride used were the same as in the middle phase. The acidity was adjusted similarly with sulfuric acid to pH  $\approx$  1.3. The spectrum is a 1:1:1 triplet with separation  $J_{\text{N-H}} = 52.24 \pm 0.05$  Hz.

The proton magnetic resonance spectrum of phase (b) described in the Experimental Section consists of the strong  $\text{H}_2\text{O}$  resonance and a 1:1:1 triplet from the  $\text{NH}_4^+$  ion. The methanol is clearly oriented by the phase and appears as a 1:2:1 triplet with all transitions of half-widths less than 1 Hz. The components of the ammonium 1:1:1 triplet are noticeably broadened ( $\sim$ 7 Hz half-width) in the nematic phase compared to isotropic solution. The peak separations are also different. If we assume that the  $\text{NH}_4^+$  ion is partly ordered then a value  $|J_{\text{N-H}} + D_{\text{N-H}}| = 48.47 \pm 0.05$  Hz can be measured from adjacent peak separations. The broadening of components of the 1:1:1 triplet may be a result of increased spin-spin relaxation or unresolved dipole-dipole coupling from the intraionic proton-proton interactions. The spectrum in Figure 1 shows the spectrum of the  $\text{NH}_4^+$  ion in the middle phase with an outer transition of the oriented methanol, which happens to fall in the same region. The value  $D_{\text{HH}}$  for the intramethyl dipole-dipole coupling in methanol from this phase was measured as  $234.7 \pm 0.2$  Hz. The separation of components in the methanol triplet is  $\frac{3}{2}D_{\text{HH}}$ .<sup>10</sup>

The deuterium spectrum of the  $\text{ND}_4^+$  ion in phase (a)



**Figure 2.** The deuterium magnetic resonance spectrum of  $\text{ND}_4^+$  and  $\text{D}_2\text{O}$  in phase (a) described in the Experimental Section. The lower spectrum with scale 275 Hz superimposed shows the doublet for  $\text{D}_2\text{O}$  derived from a partially averaged nuclear quadrupole coupling constant. The peaks are relatively intense and are cut off for convenience of presentation. In the base line of the lower spectrum is the spectrum of  $\text{ND}_4^+$ . The center of two 1:1:1 triplets is chemically shifted to high field with respect to the  $\text{D}_2\text{O}$  peaks. On an expanded scale above (36 Hz indicated) the spectrum of the  $\text{ND}_4^+$  reveals a nuclear quadrupole coupling (the doublet) and a combination of scalar and dipole-dipole coupling between the D and  $^{14}\text{N}$  nuclei in the ion (the triplets).

is represented as Figure 2. The principal doublet in the spectrum is assigned to the  $\text{D}_2\text{O}$  signal, which has been reported earlier for similar phases<sup>11</sup> while the doublet of triplets of low intensity derives from the  $\text{ND}_4^+$  ion. The doublet feature in the  $\text{ND}_4^+$  spectrum can be assigned to a partially averaged quadrupole coupling constant because of a small ordering of the ion in the phase. The separation in the 1:1:1 triplet components gives  $|J + D|$  for  $^{14}\text{N}$ -D. The  $\text{D}_2\text{O}$  doublet has a separation  $356 \pm 0.1$  Hz. The  $\text{ND}_4^+$  triplets have separations of their components by  $7.1 \pm 0.2$  Hz while the quadrupole derived splitting is  $38.02 \pm 0.2$  Hz. Line widths of the  $\text{D}_2\text{O}$  spectrum are  $\sim$ 3 Hz and those of  $\text{ND}_4^+$   $\sim$ 5 Hz. In the proton spectrum of phase (a), the methanol  $\text{CH}_3$  dipole-dipole coupling can be derived from the separation of the sharp triplet components (0.7 Hz line width) as  $183.6 \pm 0.05$  Hz. This, considerably smaller dipole-dipole coupling for methanol (cf. phase (b)), has no significance other than the happenstance of a slightly different composition leading to an overall lower degree of order for the phase. It was possible to examine in the proton spectrum the signal of oriented  $\text{ND}_3\text{H}^+$  which was also a 1:1:1 triplet with  $|J + D|$  between  $^{14}\text{N}$  and  $^1\text{H}$  of  $49.69 \pm 0.05$  Hz.

The  $\text{ND}_4^+$  ion was examined in isotropic acidified aqueous solution made up to the same concentration of deuterioammonium chloride. The value of  $J_{\text{ND}}/J_{\text{NH}}$  was exactly in the ratio of the gyromagnetic ratios and gives a value  $J_{\text{ND}} = 8.02 \pm 0.05$  Hz. The magnitude of geminal  $J_{\text{H-N-D}}$  was measured as  $1.78 \pm 0.05$  Hz which

(9) R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **26**, 1339 (1957).

(10) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

(11) K. D. Lawson and T. J. Flautt, *J. Amer. Chem. Soc.*, **89**, 5489 (1967).

implies a  $J_{\text{H-N-H}}$  of 11.60 Hz. Considerable care was taken to reproduce as closely as possible the concentrations of  $\text{NH}_4^+$  and  $\text{ND}_4^+$  in aqueous solution as was used in the phases. This care proved to be unnecessary as an investigation of  $J_{\text{N-H}}$  in the  $\text{NH}_4^+$  over a five-fold range of concentration of the ion covering the phase concentration revealed no change to a precision of  $\pm 0.05$  Hz.

Middle phase (c) made from methylammonium- $d_3$  decyl sulfate was examined in the proton and deuterium resonance region. The proton resonance spectrum of the  $\text{CH}_3\text{ND}_3^+$  ion is a 1:2:1 triplet corresponding to a dipole-dipole coupling in the  $\text{CH}_3$  group of  $-326.9 \pm 0.1$  Hz.<sup>12</sup> Each component of this triplet was further split into five transitions with intensity ratios approximately 1:2:3:2:1. These small couplings derive from scalar and dipolar coupling between the  $\text{ND}_3$  deuterons and the  $\text{CH}_3$  protons. This gives no information in a single resonance experiment that cannot be obtained from the  $\text{CH}_3\text{NH}_3^+$  ion which will be discussed elsewhere.<sup>12</sup> The deuteron magnetic resonance spectrum had a doublet structure for the  $\text{ND}_3^+$  group in addition to the usual  $\text{D}_2\text{O}$  doublet. The complex multiplet structure on each  $\text{ND}_3^+$  doublet was not resolved but arises because of the coupling to other heterospins in the ion. The separation of the  $\text{ND}_3^+$  group peaks was measured as  $|1315 \pm 1 \text{ Hz}|$ .

## Discussion

**Orientation of the  $\text{ND}_4^+$  and  $\text{NH}_4^+$  Ions.** The observed  $J_{\text{NH}}$  (scalar coupling constant) from the isotropically reorienting  $\text{NH}_4^+$  ion of  $52.23 \pm 0.05$  Hz can be used to find  $D_{\text{NH}}$  (dipole-dipole coupling constant) for the partially oriented ion. From phase (b) the value of  $|J_{\text{NH}} + D_{\text{NH}}|$  is  $48.26 \pm 0.05$  Hz. We assign the value of  $J_{\text{NH}}$  as absolutely positive, similar to  $J_{\text{CH}}$ ,<sup>13</sup> noting that the magnetogyric ratio of the nitrogen-14 nucleus is also positive. This being the case we have two possible values for  $D_{\text{NH}}$  in phase (b), either  $-100.49$  or  $-3.97$  Hz. For a tetrahedral ion the proton-proton coupling constants of the dipole type are not observable,<sup>4</sup> but small distortions of the tetrahedron make nonzero values possible.

The oriented  $\text{ND}_4^+$  has a  $|J_{\text{ND}} + D_{\text{ND}}| = 7.10 \pm 0.2$  Hz with  $J_{\text{ND}}$  from the isotropic  $\text{ND}_4^+$  spectrum equal to  $+8.02$  Hz. The values of  $D_{\text{ND}}$  possible are  $-0.92$  or  $-15.12$  Hz. We note immediately that the values  $D_{\text{ND}} = -15.12$  Hz and  $D_{\text{NH}} = -100.47$  Hz are much closer to the ratio of the magnetogyric ratios of deuterium to proton. We expect small deviations from the strict ratio of the  $\gamma$ 's because of differing degrees of orientation in phases (a) and (b) for the  $\text{ND}_4^+$  and  $\text{NH}_4^+$ , respectively. These small differences in orientation are not sufficient to allow the values  $D_{\text{ND}} = -0.92$  Hz and  $D_{\text{NH}} = -3.97$  Hz. Ultimately, this indirect argument is not needed, but it is a necessary check on our interpretation of these spectra.

The spectrum of  $\text{ND}_3\text{H}^+$  in the same phase (a) allows another check on the calculations. For this ion, the value of  $J_{\text{NH}}$  from isotropic solutions is also 52.23 Hz

(no isotope effect on  $J_{\text{NH}}$ ) but  $|D_{\text{NH}} + J_{\text{NH}}|$  from the proton spectrum in phase (a) is 49.69 Hz. This gives  $D_{\text{NH}} = -2.54$  or  $-101.92$  Hz. The value  $D_{\text{NH}} = -101.92$  is much closer to the ratio  $\gamma_{\text{D}}/\gamma_{\text{H}} = 0.153$  for  $D_{\text{NH}}$  and  $D_{\text{ND}}$  derived from  $\text{ND}_3\text{H}^+$  and  $\text{ND}_4^+$  in the same phase than is the value  $-2.54$ . Small differences in orientation deriving from isotopic substitution have been reported.<sup>7</sup> The absolute sign and magnitude of  $D_{\text{NH}}$  and  $D_{\text{ND}}$  in the ions  $\text{ND}_4^+$ ,  $\text{ND}_3\text{H}^+$ , and  $\text{NH}_4^+$  oriented in phases (a) and (b) have thus been determined.

Following Saupe<sup>4,14</sup> the dipole-dipole coupling constant  $D_{ij}$  between nuclei  $i$  and  $j$  is given by

$$D_{ij} = -\frac{1}{2} \frac{h\gamma_i\gamma_j}{\pi^2 r_{ij}^3} S_{ij} \quad (1)$$

where  $i$  and  $j$  belong to the same rigid part of the molecule. The factor  $-1/2$  rather than  $-1/4$  in the equation differs from ref 4 (p 9) because of the definition of  $D_{ij}$ .<sup>10</sup> Thus, evaluating  $D_{ij}$  for proton-proton couplings

$$D_{ij} = \frac{-240,134}{r_{ij}^3} (\text{Hz } \text{\AA}^3) S_{ij} \quad (2)$$

This relationship can be converted to cases of other coupled spins by multiplying by appropriate ratios of gyromagnetic ratios of the nuclei involved. For the ions studied here,  $\text{NH}_4^+$ ,  $\text{ND}_3\text{H}^+$ , and  $\text{ND}_4^+$ , we shall choose  $S_{ij}$  along one of the  $C_3$  axes. In this case, the direct dipole-dipole coupling NH and ND is directed along this axis, and no transformation to off-axis internuclear vectors is required. In the  $\text{ND}_4^+$  ion

$$D_{\text{ND}} = \frac{-2,663.5}{r_{\text{ND}}^3} S_{C_3} (\text{Hz}) \quad (3)$$

The bond lengths in the ammonium ions are reliably known<sup>15</sup> and  $r_{\text{ND}}$  is 1.030  $\text{\AA}$ . Substituting into the equation for the two possible values of  $D_{\text{ND}} = -0.92$  and  $-15.12$  Hz gives  $S_{C_3} = +3.77 \times 10^{-4}$  or  $S_{C_3} = +6.20 \times 10^{-3}$ , respectively. Although we have already shown that  $D_{\text{ND}} = -15.12$  Hz, it is interesting to pursue the two theoretically possible values of  $D_{\text{ND}}$  to check against the data for nuclear quadrupole coupling constants. If the value  $D_{\text{NH}} = -101.92$  Hz for the  $\text{ND}_3\text{H}^+$  ion in the same phase is used in an analogous manner with a modified bond length  $r_{\text{NH}} = 1.035$   $\text{\AA}$ <sup>15</sup> (the NH bond is slightly longer), then the order parameter  $S_{C_3}$  becomes  $6.29 \times 10^{-3}$ . This indicates a negligible change in the orientation parameter between  $\text{ND}_4^+$  and  $\text{ND}_3\text{H}^+$  in the same phase.

In phase (b) the order parameter of  $S_{C_3}$  for the  $\text{NH}_4^+$  ion may be computed from  $D_{\text{NH}} = -100.49$  Hz to give  $S_{C_3} = +6.42 \times 10^{-3}$ . The three degrees of orientation in phase (a) for the  $\text{NH}_4^+$  ion and in phase (b) for the  $\text{ND}_4^+$  and  $\text{ND}_3\text{H}^+$  ions are very similar. The methanol in phases (a) and (b) may be characterized by the degree of orientation of the  $C_3$  axis of the  $\text{CH}_3$  group. This  $C_3$  axis is perpendicular to the proton-proton vectors in the methyl group so that

$$D_{\text{HH}} = \frac{-240,134}{\gamma_{\text{HH}}^3} \left( -\frac{1}{2} \right) S_{C_3} \quad (4)$$

If we assume that  $r_{\text{HH}}$  for methanol from reliable data<sup>16</sup>

(12) L. W. Reeves and A. S. Tracey, paper in preparation describing the structure of the  $\text{CH}_3\text{NH}_3^+$  ion and justifying the signs used for couplings.

(13) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 682.

(14) A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968).

(15) L. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958).

(16) P. Deihl and C. L. Khetrapal, *Can. J. Chem.*, **47**, 1411 (1969).

is 1.795 Å, then  $|S_{C_3}|$  for the methyl  $C_3$  axis in methanol becomes  $8.84 \times 10^{-3}$  in phase (a) and  $1.13 \times 10^{-2}$  in phase (b). In this case, we have no way of determining the sign of  $S_{C_3}$ .

**Nuclear Quadrupole Coupling Constants.** The partially averaged quadrupole coupling constant<sup>18</sup> of deuterium nuclei in molecules partially oriented by some means has been treated in several previous papers.<sup>16-25</sup> We shall assume that distortions from tetrahedral symmetry, with the small degree of orientation observed, are small and derive the conclusion that the asymmetry parameter  $\eta \cong 0$ . In this case for an axis  $zz$  in the ion with respect to the magnetic field

$$\Delta\nu = \frac{3}{2} Q_D \frac{1}{2} (3 \cos^2 \gamma - 1) S_{zz} \quad (5)$$

$\Delta\nu$  is the observed doublet separation (hertz) in the deuterium nmr spectrum.  $Q_D$  is the deuterium quadrupole coupling constant resolved along the axis  $zz$ .  $S_{zz}$  is the degree of orientation of the chosen axis.  $\gamma$  is the angle between the orientation axis  $zz$  and the principal axis of the nuclear quadrupole coupling tensor. For the  $ND_4^+$  ion a  $C_3$  axis will be chosen as the  $zz$  axis and in this case the observed doublet separation  $\Delta\nu$  will be a weighted average of the  $Q_D$  in the ND bond of the  $C_3$  axis and three  $Q_D$ 's resolved along this axis from the other three ND bonds. As usual we assume the principal axis of the coupling tensor is along the ND bond.

The observed  $\Delta\nu$  for the  $ND_4^+$  ion becomes

$$\Delta\nu = \frac{1}{4} \left[ \frac{3}{2} Q_D S_{C_3} \right] + \frac{3}{4} \left[ \frac{3}{2} Q_D \frac{1}{2} (3 \cos^2 \gamma - 1) S_{C_3} \right] \quad (6)$$

where  $\gamma$  is now the angle between the  $C_3$  axis and the off-axis N-D bonds.

If the  $ND_4^+$  ion is in an isotropic medium, it is, on average, over all internal motions a truly tetrahedral ion. It can be seen from eq 6 that the multiplier of the common factor on the right  $\{0.25 + 0.375(3 \cos^2 \gamma - 1)\}$  is identically zero for  $\gamma = (180^\circ - 109^\circ 28')$ . A nonzero  $\Delta\nu$  for the quadrupole coupling constant must therefore arise from slight distortions from the tetrahedral angle.

We take the point of view here that the orientation at the electrical double layer of the  $ND_4^+$  ion is such as to induce  $C_{3v}$  symmetry on the tetrahedron, *i.e.*, that one deuterium for instance is pointing at the interface and perhaps forms transient hydrogen bonds with the sulfate anion groups. The assumption that all distortions of the tetrahedral ion induce  $C_{3v}$  symmetry on the ion is necessarily a considerable simplification of the actual situation. It is expected to lead to exaggeration of the computed distortions in this one symmetry. The actual

(17) M. H. Cohen and F. Reif, *Solid State Phys., Suppl.*, **5**, 321 (1962).

(18) J. C. Powell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

(19) W. J. Caspary, F. Millett, M. Reichbach, and B. P. Dailey, *J. Chem. Phys.*, **51**, 623 (1969).

(20) D. Gill, M. P. Klein, and G. Kotowycz, *J. Amer. Chem. Soc.*, **90**, 6870 (1968).

(21) M. P. Klein, D. Gill, and G. Kotowycz, *Chem. Phys. Lett.*, **2**, 677 (1968).

(22) B. M. Fung and I. Y. Wei, *J. Amer. Chem. Soc.*, **92**, 1497 (1970).

(23) M. J. Gerace and B. M. Fung, *J. Chem. Phys.*, **53**, 2984 (1970).

(24) F. S. Millett and B. P. Dailey, *J. Chem. Phys.*, **56**, 3249 (1972).

(25) C. W. Hilbers, J. Biemond, and C. Maclean, invited lectures presented at the 14th International Symposium on Magnetic Resonance, 1971, D. Fiat, Ed., IUPAC, Butterworths, London, 1972, p 197.

nmr spectrum derives from all distortions of the tetrahedron of all possible symmetries, which divide up the distortion into smaller displacements of nuclear positions and angles. Since this small distortion over all internal motions of the ion is not available to compute  $Q_D$ , then we shall refer to previously measured values for the  $ND_4^+$  ion to estimate the distortion entailed in the bond angles. The choice of a  $C_3$  axis to estimate the distortion is equally good if the  $ND_4^+$  is oriented in the reverse sense with three D atoms attached to the membrane interface, but all choices are arbitrary. This reverse orientation has analogies with the  $CH_3-ND_3^+$  ion where the  $C_3$  axis is also chosen, but in this case the lower overall symmetry of the ion is sufficient in itself to lead to quadrupole coupling.

From studies of deuterated ammonium sulfate at 4.2°K Knispel, Petch, and Pintar<sup>26</sup> obtain a quadrupole coupling constant in the ammonium ion of 175 kHz with an asymmetry parameter  $\eta = 0.1$ . In principle this is probably an average for two crystallographically distinct ions which differ in quadrupole coupling constant by less than 20%. For deuterium atoms covalently bonded to carbon of all coordination numbers possible and for polar and nonpolar compounds alike, the quadrupole coupling constants do not exceed the range 165 to 200 kHz.<sup>24</sup> The asymmetry parameter of 0.1 reported<sup>26</sup> is assumed to be the result of distortions in the solid state of the  $ND_4^+$  in accommodating to hydrogen bonds N-D—O. In a tetrahedral ion which is tumbling in a lyotropic phase, a negligible asymmetry parameter is expected as indeed one observes in series of carbon compounds of varied symmetry.<sup>24</sup> Chiba<sup>27</sup> in measurements of a series of  $ND_4^+$  salts at more elevated temperatures finds quadrupole coupling constants of the order 2–4.2 kHz, also with high asymmetry parameters. These are partly averaged by motions in the solid state. It is also known that the quadrupole coupling constants of deuterium are dominantly determined by the nucleus and electrons of the bonded atom.<sup>28</sup> We shall assume in what follows that  $Q_D = +175$  kHz and  $\eta \cong 0$ . The positive sign appears to be common for all deuterium nuclear quadrupole coupling constants.<sup>24, 28</sup>

From eq 6, if  $\Delta\nu = 38.02$  Hz, and from  $D_{ND} = -0.92$  (this value can be neglected on grounds previously discussed, but we proceed to further test the consistency of our arguments) we have  $S_{C_3} = 3.77 \times 10^{-4}$  for the  $ND_4^+$  ion, to give  $\gamma = 47.7^\circ$ . This amount of distortion is unacceptable. If on the other hand  $\Delta\nu = -38.02$ ,  $\cos^2 \gamma < 0$ , and we have no solution for  $\gamma$ , it appears that the previous rejection of  $D_{ND} = -0.92$  Hz is further justified.

If  $D_{ND} = -15.12$  Hz, the degree of orientation of the  $C_3$  axis is  $6.20 \times 10^{-3}$  and with  $\Delta\nu = +38.02$  Hz the value of  $\gamma$  becomes  $72.5^\circ$ . The value of  $\gamma$  for a true tetrahedron is  $70.53^\circ$ . Repeating the calculation for  $\Delta\nu = -38.02$  the angle  $\gamma$  becomes  $68.7^\circ$ . Although these distortions in angle are exaggerated by the choice of a single symmetry to represent them, they are much more reasonable and lend further support to the selection  $D_{ND} = -15.12$  Hz. If the sign of  $Q_D$  is

(26) R. R. Knispel, H. E. Petch, and M. M. Pintar, *J. Chem. Phys.*, **56**, 676 (1972).

(27) T. Chiba, *J. Chem. Phys.*, **36**, 1122 (1962).

(28) R. Bersohn, *J. Chem. Phys.*, **32**, 85 (1960).

assumed to be unknown, this leads to uncertainty in the sign of the angle distortion.

We have separately studied, in detail, the structure of the methylammonium ion using the  $^{13}\text{C}$ - and  $^{15}\text{N}$ -substituted ion<sup>29</sup> and from the C-H bond as a standard derive " $r_{\text{HH}}$ ," the interproton distance in the methyl group, as 1.796 Å. Using now the value  $D_{\text{HH}} = -326.9 \pm 0.1$  Hz (the negative sign is also known to us) measured here from the proton spectrum of  $\text{CH}_3\text{ND}_3^+$ , the degree of orientation of the  $C_3$  axis  $S_{C_3}$  becomes  $-0.0158$ . If we assume  $\eta = 0$  then

$$\Delta\nu = \frac{3}{2}Q_{\text{D}}S_{C_3} \frac{1}{2}(3 \cos^2 \gamma - 1) \quad (7)$$

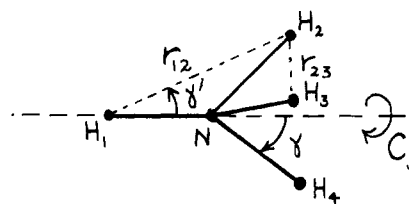
$\Delta\nu = 1315$  Hz, the doublet separation reported in the Experimental Section.  $\gamma$  has been determined by us<sup>29</sup> to be  $69.38^\circ$ . Substitution into (7) gives  $Q_{\text{D}} = +176.7$  kHz. This value agrees very well with that reported for  $\text{ND}_4^+$ .<sup>26</sup> The sign of  $\Delta\nu$  can be positive or negative but only the positive sign gives a positive quadrupole coupling constant. If the  $Q_{\text{D}}$  in the ion  $\text{ND}_4^+$  is also positive as expected,<sup>24,28</sup> we can conclude that the more correct angle  $\gamma$  in the distorted ammonium ion is  $72.5^\circ$ . In principle, these assignments of sign could be also determined by double resonance experiments using  $^{14}\text{N}$  and D. Such experiments would also determine the sign of the nitrogen quadrupole coupling constant, all compared to  $J_{\text{ND}}$  which is absolutely positive. The equipment to do such work is not available to us.

**The Dipole-Dipole Coupling Constants " $D_{\text{HH}}$ " in  $\text{NH}_4^+$ .** Earlier in the paper the question of the apparent line widths of the proton and deuterium resonance peaks was mentioned. These can derive from transverse relaxation in a single resonance or overlapping peaks of small splitting which cannot be resolved by the spectrometer. Since they are respectively  $\sim 5$  Hz for  $\text{ND}_4^+$  and  $\sim 7$  Hz for  $\text{NH}_4^+$  in a solution  $\text{pH} \cong 1.3$ , the line widths invite interpretation in terms of the maximum distortion of the tetrahedron allowed. In the strictly tetrahedral ions  $D_{\text{HH}}$  and  $D_{\text{DD}}$  are identically zero.

If we assume the bond length ( $r_{\text{NH}} = 1.035$  Å) remains the same in the anisotropic medium but distortions occur in the angles only, then it would be appropriate to compute the proton-proton dipole coupling in  $\text{NH}_4^+$ , resulting from the angular deviations derived earlier using the quadrupole coupling constant in  $\text{ND}_4^+$ .

In Figure 3 a  $C_3$  axis  $\text{NH}_1$  is chosen and distorted angles of interest are  $\gamma$  and  $\gamma'$  with this axis. The resulting changes in  $r_{\text{H}_1\text{H}_2}$  and  $r_{\text{H}_2\text{H}_3}$  are shown in Table I.

(29) L. W. Reeves and A. S. Tracey, submitted for publication.



**Figure 3.** Representation of distortions in the ammonium ion.  $\text{NH}_1$  is taken as a  $C_3$  axis in the distorted ion and values of distances and angles assuming  $r_{\text{NH}} = 1.035$  are given in Table I.

**Table I.** Distances  $r_{\text{H}_1\text{H}_2}$  and  $r_{\text{H}_2\text{H}_3}$  Referred to the Diagram in Figure 3\*

	$\gamma = 72.5^\circ$	$\gamma = 68.7^\circ$
$r_{\text{H}_1\text{H}_2}, \text{Å}$	1.672	1.707
$r_{\text{H}_2\text{H}_3}, \text{Å}$	1.708	1.673
$\gamma', \text{deg}$	36.25	34.35

\* From the measured quadrupole derived splitting in  $\text{ND}_4^+$ , the distortions of three ND bonds from the  $C_3$  axis become  $72.5^\circ$  or  $68.7^\circ$  rather than  $70.53^\circ$  for a tetrahedron. The resulting values of the interproton distances are tabulated together with the angle  $\gamma$  denoted in Figure 3.  $r_{\text{NH}} = 1.035$  Å is assumed and for the calculation  $S_{\text{NH}} = 6.42 \times 10^{-3} = S_{C_3}$ .

If  $\gamma = 72.5^\circ$   $D_{\text{HH}}$  becomes  $+1.5$  Hz and if  $\gamma = 68.7^\circ$   $D_{\text{HH}}$  becomes  $-1.7$  Hz. An observed line width of  $\sim 7$  Hz including inhomogeneity broadening is consistent with both calculations of  $D_{\text{HH}}$ . The spectrum of  $\text{NH}_4^+$  in aqueous solution at  $\text{pH} \sim 1.3$  has a line width some 2-3 Hz less than in the ordered solvent.

## Conclusion

Methods have been developed to study the effect on ions of participation in processes involving the electrical double layer. In the present case the double layer is that contained in a lyotropic nematic phase which models a biological membrane, free of protein material. The hydrophobic hydrocarbon chains and the water in the phase are separated by a negative ion static component of sulfate groups attached to the hydrocarbon chains and mobile small ions which exchange between the water and the double layer interface.

By using the ions  $\text{ND}_4^+$ ,  $\text{ND}_3\text{H}^+$ ,  $\text{NH}_4^+$ , and  $\text{CH}_3\text{-ND}_3^+$ , we can account for the proton and deuterium resonance spectra in terms of the degree of orientation of  $C_3$  axis in the ions, dipole-dipole coupling constants, nuclear quadrupole coupling constants, and indirect spin-spin coupling constants.

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