# Rotational Spectroscopy and the Nature of the Trimethylammonium Chloride Molecule in the Vapour Phase: Hydrogen-bonded Dimer or Ion Pair?

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Spectroscopic constants have been determined from the ground-state rotational spectrum of the dimer [$(CH_3)_3{}^{14}N,H^{35}Cl$] in the vapour phase above solid trimethylammonium chloride and are interpreted to provide evidence about the nature of the associated species; there is probably greater proton transfer than in the corresponding ($NH_3,HCl$) complex.

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We have established recently[1,2] by means of a detailed analysis of the ground-state rotational spectrum of ammonium chloride vapour that the dimer ($NH_3,HCl$) can be described as predominantly a hydrogen-bonded species $H_3N \cdots HCl$ rather than as an ion pair $H_3\overset{+}{N}H\ Cl^-$. A question of chemical significance concerns the nature of the associated species [$(CH_3)_3N,HCl$] in trimethylammonium chloride vapour. Given that the methyl group has a $+I$ effect relative to hydrogen, methylation of ammonia is expected to enhance the stability of the ion pair $(CH_3)_3NH^+\ Cl^-$ compared with $H_3\overset{+}{N}H\ Cl^-$. Recent *ab initio* calculations[3] suggest a progressive transfer of the proton from Cl to N in $R_{3-n}H_nN \cdots HCl$ as $NH_3$ is methylated. We have now examined the ground-state rotational spectrum exhibited by the associated species [$(CH_3)_3N,HCl$] in trimethylammonium chloride vapour in an attempt to provide an experimental answer to the above question.

The spectrum was detected in the frequency range 7—15 GHz by using the technique of pulsed-nozzle, Fourier-transform microwave spectroscopy,[4] the vapour of trimethylammonium chloride being produced by heating the solid within the nozzle.[2] The rotational transitions were characteristic of those of a symmetric-top molecule and exhibited a complicated nuclear quadrupole hyperfine structure of exactly the form expected if the $^{14}N$ and Cl nuclei lie on the symmetry axis. Analysis of the $J = 2 \leftarrow 1$, $3 \leftarrow 2$, and $4 \leftarrow 3$ transitions by the usual methods[2] led to the rotational constant $B_0$, the centrifugal distortion constants $D_J$ and $D_{JK}$, and the nuclear quadrupole coupling constants $\chi(^{14}N)$ and $\chi(^{35}Cl)$ for the isotopomer [$(CH_3)_3{}^{14}N,H^{35}Cl$] given in Table 1.

Some preliminary conclusions about the nature of the observed dimer are available from the spectroscopic constants in Table 1. Although detailed isotopic substitution is in progress to establish the order of the nuclei, it seems likely on

**Table 1.** Observed ground-state spectroscopic constants of trimethylammonium chloride $[(CH_3)_3{}^{14}N,H^{35}Cl]$.

| $B_0$/MHz | $D_J$/kHz | $D_{JK}$/kHz | $\chi(^{14}N)$/MHz | $\chi(^{35}Cl)$/MHz |
|---|---|---|---|---|
| 1800.4605(3) | 0.321(13) | 13.60(13) | −3.504(6) | −21.627(6) |

chemical grounds that the order is as shown in Figure 1, with the proton lying on the $C_3$ axis somewhere between the $^{14}N$ and $^{35}Cl$ nuclei. The possibilities for the proton position are illustrated in Figure 1 and range from the hydrogen-bonded species (I) in which there is no proton transfer, through the continuum of intermediate forms (II) involving partial proton transfer, to the ion pair (III) for which proton transfer is complete.

The magnitude of the nuclear quadrupole coupling constant $\chi(^{35}Cl)$ provides the first evidence of partial proton transfer. For axially symmetric molecules, $\chi(^{35}Cl)$ is proportional to the electric field gradient $F_{zz}$ at the $^{35}Cl$ nucleus along the symmetry axis $z$. The values[5,2,6] of $\chi(^{35}Cl)$ for free $H^{35}Cl$, the hydrogen-bonded dimer $H_3N\cdots H^{35}Cl$, the ion pair $Na^+Cl^-$, and the free ion $^{35}Cl^-$ are compared with that of the dimer $[(CH_3)_3{}^{14}N,H^{35}Cl]$ in Table 2. In the free ion $Cl^-$, $F_{zz}$ is necessarily zero but in the ion pair $Na^+Cl^-$ the presence of $Na^+$ polarizes the electronic charge distribution of $Cl^-$ leading to a small value of $F_{zz}$ and, hence, of $\chi(^{35}Cl)$. We note from Table 2 that $\chi(^{35}Cl)$ for the trimethylammonium chloride molecule is small in magnitude and lies closer to that of $Na^+Cl^-$ than it does to the free $H^{35}Cl$ value. On the other hand, $\chi(^{35}Cl)$ of $H_3N\cdots HCl$ lies closer to the free $H^{35}Cl$ value than it does to that of $Na^+Cl^-$. Qualitatively, this suggests that proton transfer is more significant in trimethylammonium chloride than in ammonium chloride.

We have established elsewhere[2,7] that the reduction in the magnitude of $\chi(^{35}Cl)$ for $H_3N\cdots H^{35}Cl$ from its value in free $H^{35}Cl$ can be satisfactorily understood in terms of a hydrogen-bonded structure $H_3N\cdots HCl$ without the need to invoke proton transfer. In that analysis allowance was made for the additional electric field gradient at the Cl nucleus resulting from the effects of the nearby electric charge distribution of the $NH_3$ subunit and for the zero-point oscillations of the HCl subunit. Such a treatment is not yet possible for model (I) in Figure 1 because a detailed electric charge distribution for $(CH_3)_3N$ is not available, although *ab initio* calculations are in progress to rectify this.[8] Nevertheless, it seems unlikely that the observed reduction in magnitude of $\chi(^{35}Cl)$ can be explained entirely in this way, especially as the increased strength of binding in $[(CH_3)_3{}^{14}N,H^{35}Cl]$ compared with $H_3N\cdots HCl$ (see below and Table 2) will reduce the zero-point oscillation of the HCl subunit in the former and therefore tend to increase the magnitude of $\chi(^{35}Cl)$. Clearly, it is of great interest in the present context to predict $\chi(^{35}Cl)$ for the ionic model (III) of Figure 1 and this is also in hand.[8] Further evidence for a significant degree of proton transfer in trimethylammonium chloride comes from the value $\chi(^{14}N) = -3.504(6)$ MHz which is again greatly reduced in magnitude from the value, −5.502(3) MHz, for free trimethylamine.[9] Presumably, protonation of $(CH_3)_3N$ to give $(CH_3)_3\overset{+}{N}H$ will lead to a decreased $\chi(^{14}N)$.

Another indication that the associated species $[(CH_3)_3N,HCl]$ is somewhat different in nature from $H_3N\cdots HCl$ follows from the value of the intermolecular stretching force constant, $k_\sigma$, which can be estimated by the method of Millen[10] from the centrifugal distortion constant $D_J$ on the assumption of rigid subunits joined by a single weak bond. The value $k_\sigma$ = 84(3) N m$^{-1}$ determined in this way for trimethylammonium chloride is compared with similarly determined values[2,11] of $H_3N\cdots HCl$ and $Na^+Cl^-$ in Table 2. Clearly, the $k_\sigma$ value for trimethylammonium chloride is again closer to that expected in the ion-pair limit than in the hydrogen-bonded limit.

**Table 2.** Comparison of the $^{35}Cl$-nuclear quadrupole coupling constants $\chi(^{35}Cl)$ and intermolecular stretching force constants $k_\sigma$ for the vibrational ground-states of several molecules.

| Molecule | $\chi(^{35}Cl)$/MHz | $k_\sigma$/N m$^{-1}$ |
|---|---|---|
| $H^{35}Cl$ | −67.6189[a] | — |
| $H_3{}^{14}N\cdots H^{35}Cl$ | −47.607(9)[b] | 17.6(3)[b] |
| $[(CH_3)_3{}^{14}N,H^{35}Cl]$ | −21.627(6)[c] | 84(3)[c] |
| $^{23}Na^+\,{}^{35}Cl^-$ | −5.643(4)[d] | 108.6[e] |
| $^{35}Cl^-$ | 0 | — |

[a] Ref. 5. [b] Ref. 2. [c] This work. [d] Ref. 6. [e] Ref. 11.

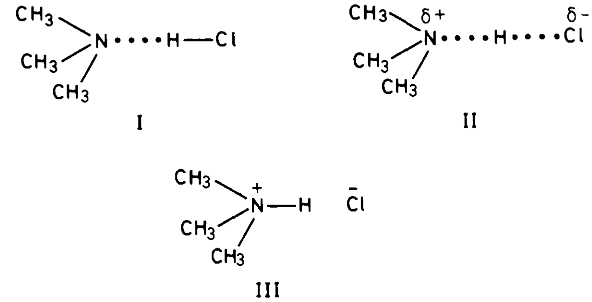

**Figure 1.** Possible models for the associated species $[(CH_3)_3N,HCl]$ observed in the vapour of trimethylammonium chloride: I, no proton transfer; II, partial proton transfer; III, complete proton transfer.

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