# Microwave Spectrum, Structure, and Quadrupole Coupling Constants of *N*-Chloro-*N*-methylmethamine

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**Abstract:** The microwave spectra of *N*-chloro-*N*-methylmethamine (dimethylchloramine), $(CH_3)_2N^{35}Cl$ and $(CH_3)_2N^{37}Cl$, as well as four of the isotopic deuterium species, $(CH_3)(CD_3)N^{35}Cl$, $(CH_3)(CD_3)N^{37}Cl$, $(CD_3)_2N^{35}Cl$, and $(CD_3)_2N^{37}Cl$, have been investigated from 18.5 to 39 GHz. The *a*-type R-branch transitions have been identified and assigned on the basis of the rigid rotor model. A diagnostic least-squares adjustment was utilized to fit the 18 ground-vibrational-state rotational constants to obtain the following $r_0$ structural parameters: $r$(N-Cl) = 1.749 ± 0.001 Å, $r$(C-N) = 1.470 ± 0.001 Å, $r$(C-H) = 1.094 ± 0.002 Å, ∠ClNC = 108.04 ± 0.05°, ∠HCH = 110.13 ± 0.04°, and a methyl tilt angle toward the nonbonded electron pair of 4.12 ± 0.46°. The quadrupole coupling constants have been obtained, and from the values of −91.50 MHz for the $^{35}Cl$ species and −72.12 MHz for $^{37}Cl$, the nitrogen-chlorine bond is estimated to have 16% ionic character. These quantities are compared to similar quantities in some related molecules.

There have been relatively few determinations of the chlorine-nitrogen bond distance in the gas phase for small molecules which contain such bonds. However, for the few that have been determined, it is clear that there is a large variation in their value. For example, the N-Cl bond distances in nitrosyl chloride[1] (NOCl) and nitryl chloride[2] ($NO_2Cl$) are 1.9734 ± 0.0017 and 1.840 ± 0.002 Å, respectively. These values are significantly larger than the sum of the covalent radii of 1.73 Å for nitrogen and chlorine.[3] However, there have been several chlorine-nitrogen bond distances determined which have values more nearly the sum of the covalent radii. For example, the values for this distance in trichloroamine[4] and chloroamine[5] are 1.759 ± 0.002 and 1.7480 ± 0.0001 Å, respectively. Similarly, the chlorine-nitrogen bond distance in *N*-chloromethylamine[6] is 1.750 ± 0.003 Å which is essentially the same as that for chloroamine. This result is somewhat surprising since the comparison of the carbon-chlorine bond distances in the corresponding carbon analogues shows that the bond is elongated by 0.007 Å with the replacement of a hydrogen atom by a methyl group.[7-9] The N-Cl bond distance[10] of 1.703 ± 0.011 Å in chlorine isocyanate, ClNCO, is even shorter than the sum of the covalent radii. From an early electron diffraction study,[11] values of 1.74 ± 0.02 and 1.77 ± 0.02 Å were obtained for the N-Cl bond distances in $CH_3NCl_2$ and $(CH_3)_2NCl$, respectively. Although there are large uncertainties associated with these N-Cl distances, the values are consistent with the values expected for a covalent nitrogen-chlorine bond. However, because of the uncertainties in the bond distances, it is not possible to ascertain whether there is an elongation of the N-Cl bond when the hydrogen of $CH_3NHCl$ is replaced with a methyl group in $(CH_3)_2NCl$.

As one might expect from these variations in N-Cl bond lengths, there are also large variations reported for the chlorine quadrupolar coupling constants in these compounds. In nitrosyl chloride[12] and nitryl chloride,[2] the $^{35}Cl$ coupling constants have values of −57.20 and −94.28 MHz, respectively, whereas for *N*-chloromethamine a value of approximately −100 MHz is estimated from the microwave data.[6,13] The NQR spectra of *N*-chloro-*N*-methylmethamine and *N*-chloropiperidine have been measured at 77 K by Schempp[14] and Kashiwagi et al.,[15] respectively. From the single-resonance frequency for the $^{35}Cl$ nucleus at approximately 44 MHz in both compounds, a value of 88 MHz was reported for the quadrupolar coupling constants for the $^{35}Cl$ species. However, the quadrupolar coupling constant for the $^{37}Cl$ nucleus was not determined for either of these compounds. Therefore, in order to obtain the quadrupolar coupling constants for both the $^{35}Cl$ and $^{37}Cl$ nuclei in the gaseous state of *N*-chloro-*N*-methylmethamine, as well as to better determine the molecular structural parameters of this molecule, we have recorded and analyzed the microwave spectrum of the normal isotopic species as well as four of the deuterium-substituted molecules, $(CH_3)(CD_3)N^{35}Cl$, $(CH_3)(CD_3)N^{37}Cl$, $(CD_3)_2N^{35}Cl$, and $(CD_3)_2N^{37}Cl$. The results of these studies are reported herein.

## Experimental Section

The $(CH_3)_2NCl$ sample was prepared by condensing dimethylamine (Matheson) in vacuum at boiling liquid nitrogen temperature into a frozen mixture of a 5.25% aqueous solution of NaOCl saturated with NaCl to which some dibutyl ether was added to facilitate the removal of the product. The mixture was slowly warmed to room temperature, and the evolved chlorinated amine was first separated by trap-to-trap distillation at −20 and −77 °C, respectively, and finally purified by using a low-temperature vacuum-fractionating column. Samples of $(CH_3)(CD_3)NH$ and $(CD_3)_2NH$ (Merck) were used in the preparation of the $(CH_3)(CD_3)NCl$ and $(CD_3)_2NCl$ compounds, respectively. The purified products were stored in evacuated sample tubes at dry ice temperature.

The microwave spectra of the six isotopic species of *N*-chloro-*N*-methylmethamine were recorded in the region 20-39 GHz by using a Hewlett-Packard Model 8460A MRR spectrometer with 33.3 kHz Stark modulation. In order to reduce thermal decomposition of the materials and increase the population of the low rotational and vibrational states during the measurement of the spectra, the wave guide was cooled with a packing of dry ice. The vapor pressure of the sample in the wave guide was maintained at 15-20 μm. The measured frequencies are reliable within ±0.05 MHz.

## Results

The microwave spectra of $(CH_3)_2NCl$, $(CH_3)(CD_3)NCl$, and $(CD_3)_2NCl$ are typically those of asymmetric near-prolate rotors. Each compound showed the rotational bands for both $^{35}Cl$ and $^{37}Cl$ isotopic species. Only the strong *a*-type R-branch transitions were measured, although *c*-type transitions are also predicted for $(CH_3)_2NCl$ and $(CD_3)_2NCl$ and *b*-type transitions are predicted for $(CH_3)(CD_3)NCl$.

Under high resolution each transition was resolved into several components. Usually, up to four strong components were observed, which are originating from the interaction between the molecular

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**Table I.** Ground-State Rotational Transitions and Quadrupole Hyperfine Splittings (MHz) for $(CH_3)_2N^{35}Cl$, $(CH_3)(CD_3)N^{35}Cl$, and $(CD_3)_2N^{35}Cl$

| | | $(CH_3)_2N^{35}Cl$ | | $(CH_3)(CD_3)N^{35}Cl$ | | $(CD_3)_2N^{35}Cl$ | |
|---|---|---|---|---|---|---|---|
| transition | $F' \leftarrow F''$ | $\nu_{obsd}$ | $\Delta\nu^a$ | $\nu_{obsd}$ | $\Delta\nu^a$ | $\nu_{obsd}$ | $\Delta\nu^a$ |
| $3_{13} \leftarrow 2_{12}$ | 9/2 ← 7/2 | | | 21 027.90 | 0.09 | | |
| | 7/2 ← 5/2 | | | 21 023.10 | -0.08 | | |
| $3_{22} \leftarrow 2_{21}$ | 9/2 ← 7/2 | 25 328.25 | -0.14 | | | | |
| | 7/2 ← 5/2 | 25 308.07 | 0.14 | | | | |
| | 5/2 ← 3/2 | 25 322.79 | 0.23 | | | | |
| $3_{21} \leftarrow 2_{20}$ | 9/2 ← 7/2 | 26 601.02 | -0.04 | | | | |
| | 7/2 ← 5/2 | 26 579.45 | 0.06 | | | | |
| | 5/2 ← 3/2 | 26 594.12 | -0.19 | | | | |
| $3_{12} \leftarrow 2_{11}$ | 9/2 ← 7/2 | 27 319.08 | 0.09 | 25 198.31 | -0.03 | 23 565.97 | -0.03 |
| | 7/2 ← 5/2 | 27 314.65 | 0.35 | 25 193.92 | -0.01 | 23 561.70 | -0.09 |
| | 5/2 ← 3/2 | 27 313.75 | 0.09 | 25 193.40 | 0.24 | 23 561.00 | 0.07 |
| $4_{14} \leftarrow 3_{13}$ | 11/2 ← 9/2 | 30 214.65 | -0.06 | 27 724.48 | 0.06 | | |
| | 9/2 ← 7/2 | 30 212.90 | -0.09 | 27 722.81 | -0.01 | | |
| | 7/2 ← 5/2 | 30 212.10 | 0.11 | 27 721.90 | 0.05 | | |
| | 5/2 ← 3/2 | | | 27 723.31 | -0.31 | | |
| $4_{04} \leftarrow 3_{03}$ | 11/2 ← 9/2 | 31 055.31 | -0.29 | 28 375.73 | 0.04 | | |
| | 9/2 ← 7/2 | 31 056.11 | -0.33 | 28 376.93 | 0.35 | | |
| | 7/2 ← 5/2 | 31 053.65 | 0.38 | 28 374.09 | 0.19 | | |
| | 5/2 ← 3/2 | 31 052.82 | 0.37 | 28 373.38 | 0.01 | | |
| $4_{23} \leftarrow 3_{22}$ | 11/2 ← 9/2 | 33 494.60 | -0.16 | 30 843.29 | 0.03 | 28 734.30 | -0.19 |
| | 9/2 ← 7/2 | 33 486.65 | -0.18 | 30 835.66 | 0.04 | 28 726.70 | -0.16 |
| | 7/2 ← 5/2 | 33 489.50 | -0.12 | 30 838.38 | 0.07 | 28 729.45 | -0.09 |
| | 5/2 ← 3/2 | 33 497.47 | -0.06 | 30 845.97 | 0.04 | 28 737.25 | 0.09 |
| $4_{32} \leftarrow 3_{31}$ | 11/2 ← 9/2 | 34 331.40 | 0.05 | 31 724.41 | 0.08 | | |
| | 9/2 ← 7/2 | 34 313.30 | 0.69 | 31 707.03 | 1.06 | | |
| | 7/2 ← 5/2 | 34 322.28 | 0.16 | 31 715.80 | 0.53 | | |
| | 5/2 ← 3/2 | 34 339.55 | -1.31 | 31 733.60 | -0.01 | | |
| $4_{31} \leftarrow 3_{30}$ | 11/2 ← 9/2 | 34 627.47 | -0.19 | 32 082.14 | -0.18 | | |
| | 9/2 ← 7/2 | 34 608.27 | -0.20 | 32 063.29 | -0.05 | | |
| | 7/2 ← 5/2 | 34 618.16 | 0.03 | 32 072.78 | -0.05 | | |
| | 5/2 ← 3/2 | 34 637.55 | 0.23 | 32 091.25 | -0.51 | | |
| $4_{13} \leftarrow 3_{12}$ | 11/2 ← 9/2 | | | 33 010.65 | -0.07 | | |
| | 9/2 ← 7/2 | | | 33 009.61 | -0.15 | | |
| | 7/2 ← 5/2 | | | 33 008.17 | -0.09 | | |
| | 5/2 ← 3/2 | | | 33 009.20 | -0.01 | | |
| $4_{22} \leftarrow 3_{21}$ | 11/2 ← 9/2 | 36 197.10 | 0.02 | 33 591.62 | -0.06 | 31 730.10 | -0.06 |
| | 9/2 ← 7/2 | 36 188.38 | 0.06 | 33 583.23 | 0.05 | 31 721.95 | 0.09 |
| | 7/2 ← 5/2 | 36 191.15 | 0.02 | 33 585.91 | 0.07 | 31 724.40 | 0.03 |
| | 5/2 ← 3/2 | 36 199.96 | 0.09 | 33 594.35 | 0.02 | 31 732.75 | 0.09 |
| $5_{15} \leftarrow 4_{14}$ | 13/2 ← 11/2 | 37 390.80 | 0.03 | 34 279.04 | 0.05 | 31 639.50 | -0.06 |
| | 11/2 ← 9/2 | 37 390.01 | -0.03 | 34 278.32 | 0.02 | 31 638.95 | 0.03 |
| | 9/2 ← 7/2 | 37 389.25 | 0.07 | 34 277.50 | 0.02 | 31 638.05 | -0.03 |
| | 7/2 ← 5/2 | | | | | 31 638.61 | -0.10 |
| $5_{05} \leftarrow 4_{04}$ | 13/2 ← 11/2 | 37 865.17 | 0.03 | 34 611.45 | 0.07 | 31 829.64 | -0.00 |
| | 11/2 ← 9/2 | 37 865.50 | -0.01 | | | 31 829.90 | 0.14 |
| | 9/2 ← 7/2 | | | 34 610.40 | -0.10 | 31 828.84 | 0.22 |
| | 7/2 ← 5/2 | 37 863.87 | 0.01 | 34 609.78 | -0.40 | 31 828.55 | 0.04 |
| $5_{24} \leftarrow 4_{23}$ | 13/2 ← 11/2 | | | 38 102.36 | 0.01 | 35 383.97 | 0.04 |
| | 11/2 ← 9/2 | | | 38 098.82 | -0.03 | 35 380.48 | -0.05 |
| | 9/2 ← 7/2 | | | 38 099.29 | -0.03 | 35 380.86 | -0.11 |
| | 7/2 ← 5/2 | | | 38 102.85 | 0.04 | 35 384.41 | 0.05 |
| $5_{14} \leftarrow 4_{13}$ | 13/2 ← 11/2 | | | | | 37 073.92 | -0.01 |
| | 11/2 ← 9/2 | | | | | 37 074.75 | 0.01 |
| | 9/2 ← 7/2 | | | | | 37 073.40 | -0.00 |
| | 7/2 ← 5/2 | | | | | 37 072.62 | 0.02 |
| $5_{33} \leftarrow 4_{32}$ | 13/2 ← 11/2 | | | | | 37 161.50 | -0.05 |
| | 11/2 ← 9/2 | | | | | 37 152.52 | 0.06 |
| | 9/2 ← 7/2 | | | | | 37 155.47 | 0.02 |
| | 7/2 ← 5/2 | | | | | 37 164.60 | 0.07 |
| $6_{16} \leftarrow 5_{15}$ | 15/2 ← 13/2 | | | | | 37 573.08 | -0.09 |
| | 13/2 ← 11/2 | | | | | 37 572.76 | -0.08 |
| $6_{06} \leftarrow 5_{05}$ | 15/2 ← 13/2 | | | | | 37 643.93 | 0.20 |
| | 13/2 ← 11/2 | | | | | 37 643.58 | -0.05 |
| | 11/2 ← 9/2 | | | | | 37 642.78 | -0.13 |
| | 9/2 ← 7/2 | | | | | 37 643.16 | -0.13 |

[a] Observed minus calculated.

rotation and the chlorine quadrupole nuclei. For a few transitions, a secondary splitting was observed which produced a weaker satellite to each of the four components. This secondary splitting is thought to originate from the interaction with the $^{14}N$ quadrupole nucleus. No attempt was made to analyze this effect because only a few lines showed such splittings which were less than 1 MHz. Preliminary assignments were made from a comparison of the observed frequencies of the strongest component of each transition with those calculated from rotational constants derived from the structural parameters for $(CH_3)_2NCl$ reported from an electron diffraction study.[4] From the assignment of the observed transition frequencies, confirmed by a fit with the rigid rotor model, a set of rotational constants was determined for each of the six isotopic species. These rotational constants were used

**Table II.** Ground-State Rotational Transitions and Quadrupole Hyperfine Splittings (MHz) for $(CH_3)_2N^{37}Cl$, $(CH_3)(CD_3)N^{37}Cl$, and $(CD_3)_2N^{37}Cl$

| | | $(CH_3)_2N^{37}Cl$ | | $CH_3(CD_3)N^{37}Cl$ | | $(CD_3)_2N^{37}Cl$ | |
|---|---|---|---|---|---|---|---|
| transition | F′ ← F″ | $\nu_{obsd}$ | $\Delta\nu$[a] | $\nu_{obsd}$ | $\Delta\nu$[a] | $\nu_{obsd}$ | $\Delta\nu$[a] |
| $3_{12} \leftarrow 2_{11}$ | 9/2 ← 7/2 | 26 660.05 | −0.03 | | | | |
| | 7/2 ← 5/2 | 26 656.47 | 0.03 | | | | |
| | 3/2 ← 1/2 | 26 658.80 | −0.78 | | | | |
| $4_{14} \leftarrow 3_{13}$ | 11/2 ← 9/2 | 29 617.94 | 0.01 | 27 183.52 | 0.05 | | |
| | 9/2 ← 7/2 | 29 616.50 | −0.06 | 27 182.16 | −0.04 | | |
| | 7/2 ← 5/2 | 29 615.80 | 0.04 | 27 181.52 | 0.08 | | |
| | 5/2 ← 3/2 | 29 617.15 | 0.01 | 27 182.69 | −0.02 | | |
| $4_{04} \leftarrow 3_{03}$ | 11/2 ← 9/2 | 30 497.56 | 0.07 | 27 875.79 | 0.07 | | |
| | 9/2 ← 7/2 | 30 498.01 | −0.16 | 27 876.26 | −0.16 | | |
| | 7/2 ← 5/2 | 30 496.20 | −0.05 | 27 874.57 | −0.01 | | |
| | 5/2 ← 3/2 | 30 495.62 | 0.03 | 27 873.91 | 0.03 | | |
| $4_{23} \leftarrow 3_{22}$ | 11/2 ← 9/2 | 32 740.85 | −0.06 | | | | |
| | 9/2 ← 7/2 | 32 734.55 | −0.08 | | | | |
| | 7/2 ← 5/2 | 32 736.82 | −0.01 | | | | |
| | 5/2 ← 3/2 | 32 742.90 | −0.10 | | | | |
| $4_{31} \leftarrow 3_{30}$ | 11/2 ← 9/2 | 33 746.22 | 0.11 | | | | |
| | 9/2 ← 7/2 | 33 731.02 | −0.03 | | | | |
| | 7/2 ← 5/2 | 33 738.95 | 0.31 | | | | |
| $4_{13} \leftarrow 3_{12}$ | 11/2 ← 9/2 | 35 077.50 | −0.15 | 32 277.52 | −0.09 | 30 025.55 | 0.00 |
| | 9/2 ← 7/2 | 35 076.80 | 0.05 | 32 276.68 | −0.08 | 30 025.03 | 0.05 |
| | 7/2 ← 5/2 | 35 075.85 | 0.32 | 32 275.67 | 0.06 | 30 023.90 | 0.16 |
| | 5/2 ← 3/2 | | | | | 30 024.30 | −0.00 |
| $4_{22} \leftarrow 3_{21}$ | 11/2 ← 9/2 | 35 220.90 | −0.00 | | | 30 867.45 | 0.07 |
| | 9/2 ← 7/2 | 35 213.88 | −0.12 | | | 30 860.78 | 0.04 |
| | 7/2 ← 5/2 | 35 216.25 | 0.03 | | | 30 862.75 | −0.02 |
| | 5/2 ← 3/2 | 35 222.98 | −0.15 | | | 30 869.55 | 0.14 |
| $5_{15} \leftarrow 4_{14}$ | 13/2 ← 11/2 | 36 672.51 | −0.02 | 33 629.10 | −0.10 | 31 051.95 | −0.11 |
| | 11/2 ← 9/2 | 36 672.20 | 0.25 | 33 628.77 | −0.10 | 31 051.51 | 0.01 |
| | 9/2 ← 7/2 | 36 671.28 | 0.02 | 33 628.02 | 0.00 | | |
| | 7/2 ← 5/2 | 36 671.90 | 0.05 | 33 628.46 | −0.08 | | |
| $5_{05} \leftarrow 4_{04}$ | 13/2 ← 11/2 | 37 192.98 | −0.04 | 34 001.60 | 0.02 | 31 274.29 | 0.09 |
| | 11/2 ← 9/2 | 37 193.29 | −0.05 | | | | |
| | 9/2 ← 7/2 | 37 192.30 | −0.01 | 34 000.81 | 0.07 | 31 273.52 | 0.10 |
| | 7/2 ← 5/2 | 37 192.02 | 0.03 | | | | |
| $5_{24} \leftarrow 4_{23}$ | 13/2 ← 11/2 | | | 37 287.23 | −0.01 | 34 641.60 | 0.02 |
| | 11/2 ← 9/2 | | | 37 284.41 | −0.02 | 34 639.15 | −0.06 |
| | 9/2 ← 7/2 | | | 37 284.79 | −0.02 | | |
| | 7/2 ← 5/2 | | | 37 287.64 | 0.03 | | |
| $5_{33} \leftarrow 4_{32}$ | 13/2 ← 11/2 | | | | | 36 260.85 | −1.03 |
| | 11/2 ← 9/2 | | | | | 36 254.78 | 0.09 |
| | 9/2 ← 7/2 | | | | | 36 257.85 | 0.76 |
| | 7/2 ← 5/2 | | | | | 36 264.12 | 0.12 |
| $5_{14} \leftarrow 4_{13}$ | 13/2 ← 11/2 | | | | | 36 393.69 | −0.14 |
| | 11/2 ← 9/2 | | | | | 36 394.45 | 0.11 |
| $6_{16} \leftarrow 5_{15}$ | 15/2 ← 13/2 | | | | | 36 886.40 | 0.08 |
| $6_{06} \leftarrow 5_{05}$ | 15/2 ← 13/2 | | | | | 36 974.08 | 0.12 |
| | 13/2 ← 11/2 | | | | | 36 973.70 | −0.21 |
| $5_{23} \leftarrow 4_{22}$ | 13/2 ← 11/2 | | | | | 38 782.33 | 0.10 |
| | 11/2 ← 9/2 | | | | | 38 779.52 | 0.01 |

[a] Observed minus calculated.

in a computer program to calculate the quadrupole hyperfine splittings of the transition frequencies and the band centers, with both first- and second-order quadrupole corrections, from the values of the quadrupole coupling tensors in the quadrupole principal axis system. It was assumed that the electric field on the chlorine nucleus is axially symmetric about the N–Cl bond. If $z$ is chosen as the symmetry axis ($\chi_{xx} = \chi_{yy} = -{}^{1}/_{2}\chi_{zz}$), the following relationships are obtained between $\chi_{zz}$ and the quadrupole coupling constants in the inertial axis system

$$\chi_{aa} = (0.25 + 0.75 \cos 2\beta)\chi_{zz}$$

$$\chi_{bb} = -0.5\chi_{zz}$$

$$\chi_{cc} = (0.25 - 0.75 \cos 2\beta)\chi_{zz}$$

$$\chi_{ac} = 0.75 \sin 2\beta\chi_{zz}$$

$$\chi_{ab} = \chi_{bc} = 0$$

where $\beta$ is the angle between the bond axis and the $a$ inertial axis. Initially, for $^{35}Cl$ a value[8] of −88 MHz was chosen for $\chi_{zz}$ which was subsequently varied. The best fit with the observed hyperfine splittings was obtained with $\chi_{zz} = -91.50$ MHz. A similar procedure gives a value of $\chi_{zz} = -72.12$ MHz for $^{37}Cl$.

In Tables I and II the values of the observed and calculated hyperfine transition frequencies of the $^{35}Cl$ and $^{37}Cl$ isotopic species are listed, respectively, for both the normal and deuterated molecules. In Table III are listed the values of the quadrupole coupling constants in the principal axis system from which the hyperfine splittings were calculated.

## Molecular Structure

The values of the hypothetical rotational transition frequencies (band centers) for the six isotopic species of *N*-chloro-*N*-methylmethamine are listed in Table IV. In Table V are listed the effective rotational constants, centrifugal distortion constants, and moments of inertia of all six compounds. Because the measured transitions are relatively insensitive to the $A$ rotational constants, the accuracies of the $A$ rotational constants are poorer than those of $B$ and $C$.

In order to determine the $r_0$ structure, the structural parameters which best fit the 18 effective rotational constants of the 6 isotopic species were determined by using the method of diagnostic least squares described by Curl[16] and modified by Groner et al.[17] The

**Table III.** $^{35}$Cl and $^{37}$Cl Quadrupole Coupling Constants (MHz) for the Isotopic Species of *N*-Chloro-*N*-methylmethamine

| molecule | $\chi_{zz}$ | $\chi_{aa}$ | $\chi_{bb}$ | $\chi_{cc}$ | $\chi_{ac}$ | orientation of *x*, *y*, and *z* axes |
|---|---|---|---|---|---|---|
| $(CH_3)_2N^{35}Cl$ | -91.5 | -81.86 | 45.75 | 36.11 | 35.08 | *z* along N-Cl bond; ∠ between *a* and *z* 15.37°; *x* in plane of symmetry |
| $(CD_3)_2N^{35}Cl$ | -91.5 | -80.90 | 45.75 | 35.15 | 36.64 | *z* along N-Cl bond; ∠ between *a* and *z* 16.13°; *x* in plane of symmetry |
| $(CH_3)(CD_3)N^{35}Cl$ | -91.5 | -79.77 | 45.75 | 34.02 | 38.46 | *z* along N-Cl bond; ∠ between *a* and *z* 17.00° |
| $(CH_3)_2N^{37}Cl$ | -72.12 | -64.58 | 36.06 | 28.52 | 27.55 | *z* along N-Cl bond; ∠ between *a* and *z* 15.31°; *x* in plane of symmetry |
| $(CD_3)_2N^{37}Cl$ | -72.12 | -63.83 | 36.06 | 27.77 | 28.78 | *z* along N-Cl bond; ∠ between *a* and *z* 16.08°; *x* in plane of symmetry |
| $(CH_3)(CD_3)N^{37}Cl$ | -72.12 | -63.02 | 36.06 | 26.96 | 30.03 | *z* along N-Cl bond; ∠ between *a* and *z* 16.86° |

**Table IV.** Hypothetical Rotational Transitional Frequencies (MHz) for $(CH_3)_2N^{35}Cl$, $(CH_3)(CD_3)N^{35}Cl$, $(CD_3)_2N^{35}Cl$, $(CH_3)_2N^{37}Cl$, $(CH_3)(CD_3)N^{37}Cl$, and $(CD_3)_2N^{37}Cl$

| | $(CH_3)_2N^{35}Cl$ | | $(CH_3)(CD_3)N^{35}Cl$ | | $(CD_3)_2N^{35}Cl$ | | $(CH_3)_2N^{37}Cl$ | | $(CH_3)(CD_3)N^{37}Cl$ | | $(CD_3)_2N^{37}Cl$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| transition | $\nu_0$(exptl) | $\Delta\nu^a$ | $\nu_0$(exptl) | $\Delta\nu^a$ | $\nu_0$(exptl) | $\Delta\nu^a$ | $\nu_0$(exptl) | $\Delta\nu^a$ | $\nu_0$(exptl) | $\Delta\nu^a$ | $\nu_0$(exptl) | $\Delta\nu^a$ |
| $3_{13} \leftarrow 2_{12}$ | | | 21025.86 | 0.01 | | | | | | | | |
| $3_{22} \leftarrow 2_{21}$ | 25322.62 | 0.08 | | | | | | | | | | |
| $3_{21} \leftarrow 2_{20}$ | 26594.70 | -0.06 | | | | | | | | | | |
| $3_{12} \leftarrow 2_{11}$ | 27316.89 | -0.01 | 25196.39 | 0.06 | 23564.04 | 0.04 | 26658.45 | 0.04 | | | | |
| $4_{14} \leftarrow 3_{13}$ | 30213.65 | -0.01 | 27723.41 | -0.03 | | | 29617.10 | 0.00 | 27182.71 | -0.05 | | |
| $4_{04} \leftarrow 3_{03}$ | 31055.01 | 0.34 | 28375.50 | 0.05 | | | 30497.25 | -0.06 | 27875.54 | -0.08 | | |
| $4_{23} \leftarrow 3_{22}$ | 33491.75 | -0.13 | 30840.48 | 0.05 | 28731.63 | 0.11 | 32738.54 | -0.09 | | | | |
| $4_{32} \leftarrow 3_{31}$ | 34325.35 | 0.06 | 31718.48 | 0.09 | | | | | | | | |
| $4_{31} \leftarrow 3_{30}$ | 34621.41 | -0.03 | 32076.07 | -0.09 | | | 33741.28 | 0.04 | | | | |
| $4_{13} \leftarrow 3_{12}$ | | | 33009.81 | -0.08 | | | 35076.93 | 0.05 | 32276.93 | 0.02 | 30024.98 | -0.01 |
| $4_{22} \leftarrow 3_{21}$ | 36193.87 | 0.05 | 33588.53 | 0.02 | 31727.08 | -0.08 | 35218.28 | -0.06 | | | 30864.94 | -0.00 |
| $5_{15} \leftarrow 4_{14}$ | 37390.19 | 0.03 | 34278.44 | 0.00 | 31639.00 | 0.17 | 36672.12 | 0.07 | 33628.73 | 0.03 | 31051.50 | -0.04 |
| $5_{05} \leftarrow 4_{04}$ | 37864.93 | 0.01 | 34611.16 | -0.01 | 31829.44 | 0.28 | 37192.84 | -0.02 | 34001.44 | 0.07 | 31274.08 | 0.16 |
| $5_{24} \leftarrow 4_{23}$ | | | 38100.82 | -0.03 | 35382.44 | 0.01 | | | 37286.03 | -0.02 | 34640.35 | 0.06 |
| $5_{14} \leftarrow 4_{13}$ | | | | | 37073.91 | -0.08 | | | | | 36393.73 | -0.01 |
| $5_{33} \leftarrow 4_{32}$ | | | | | 37158.21 | 0.03 | | | | | 36259.18 | 0.26 |
| $6_{16} \leftarrow 5_{15}$ | | | | | 37572.73 | -0.25 | | | | | 36886.11 | -0.20 |
| $6_{06} \leftarrow 5_{05}$ | | | | | 37643.48 | -0.13 | | | | | 36973.86 | 0.02 |
| $5_{23} \leftarrow 4_{22}$ | | | | | | | | | | | 38781.00 | -0.19 |

[a] $\nu_{obsd} - \nu_{calcd}$.

**Table V.** Ground-State Rotational Constants[a] (MHz), Centrifugal Distortion Constants (kHz), and Principal Moments of Inertia ($U \cdot Å^2$)[b] for the Isotopic Species of *N*-Chloro-*N*-methylmethamine

| | $(CH_3)_2N^{35}Cl$ | $(CH_3)(CD_3)N^{35}Cl$ | $(CD_3)_2N^{35}Cl$ | $(CH_3)_2N^{37}Cl$ | $(CH_3)(CD_3)N^{37}Cl$ | $(CD_3)_2N^{37}Cl$ |
|---|---|---|---|---|---|---|
| *A* | 8992.50 ± 0.29 | 7851.11 ± 0.14 | 6817.64 ± 0.23 | 8990.60 ± 0.22 | 7848.93 ± 0.35 | 6817.05 ± 0.20 |
| *B* | 4967.38 ± 0.02 | 4597.07 ± 0.01 | 4331.21 ± 0.03 | 4836.42 ± 0.01 | 4476.12 ± 0.03 | 4215.86 ± 0.01 |
| *C* | 3473.52 ± 0.01 | 3186.01 ± 0.01 | 2939.65 ± 0.02 | 3409.07 ± 0.01 | 3127.25 ± 0.02 | 2886.10 ± 0.01 |
| $\Delta_{JK}$ | 6.66 ± 1.39 | 8.38 ± 1.19 | 6.49 ± 3.53 | 6.22 ± 1.77 | 8.03 ± 3.83 | (7.16)[c] |
| $I_A$ | 56.200 | 64.370 | 74.128 | 56.212 | 64.388 | 74.135 |
| $I_B$ | 101.740 | 109.935 | 116.683 | 104.495 | 112.906 | 119.876 |
| $I_C$ | 145.494 | 158.625 | 171.918 | 148.246 | 161.605 | 175.108 |
| $\kappa$ | -0.4586 | -0.3950 | -0.2823 | -0.4886 | -0.4287 | -0.3235 |

[a] Calculated from the transitions listed in Table IV. [b] Conversion factor: $505379 U \cdot Å^2$ MHz. [c] Fixed as the average value from the other five species.

structural parameters for two possible structures for $(CH_3)_2NCl$ have been listed in Table VI. For structure I, *r*(N-Cl), *r*(C-N), *r*(C-H), *r*(C-H′), *r*(C-H″), ∠ClNC, ∠NCH, ∠NCH′, and ∠NCH″ were taken as independent parameters. The dihedral angles among the NCH, NCH′, and NCH″ planes were fixed at 120°. For structure II, the $CH_3$ groups were assumed to have "local" $C_{3v}$ symmetry with equal CH distances and HCH angles, but the symmetry axes were allowed to deviate from the direction of the NC bonds. The tilt angle is measured between the methyl symmetry axis and the corresponding NC bond. The direction of the tilt is described by the dihedral angle for the tilt listed in Table VI. The independent parameters for structure II were therefore *r*(N-Cl), *r*(C-N), *r*(C-H), ∠ClNC, the angle between the methyl symmetry axis and the CH bonds, the tilt angle, and the dihedral angle for the tilt (Figure 1).

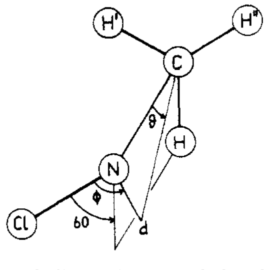

Figure 1. Definition of tilt angle, $\theta$, and dihedral angle for tilt, $\phi$. Dummy atom d is within the symmetry plane. The second methyl group is not shown for clarity.

## Discussion

The magnitude of the nuclear quadrupole coupling constant $\chi_{zz}$ for the $^{35}$Cl species (91.5 MHz) obtained in the present study of *N*-chloro-*N*-methylmethamine is approximately 4% greater than the solid-state value (88 MHz) determined by the NQR study.[14] This is not unexpected since a larger value of the quadrupole coupling constant in the gas phase, relative to the value in the solid, has been observed in a number of compounds.[18] The difference

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**Table VI.** Diagnostic Least-Squares Adjustment of the Structure of *N*-Chloro-*N*-methylmethamine and Calculated Rotational Constants (MHz)

| parameter | initial value | estd uncertainty | adjusted value for I | adjusted value for II |
|---|---|---|---|---|
| *r*(NCl), Å | 1.770 | ±0.020 | 1.742 ± 0.002 | 1.749 ± 0.001 |
| *r*(CN), Å | 1.470 | ±0.020 | 1.473 ± 0.001 | 1.470 ± 0.001 |
| *r*(CH), Å | 1.093 | ±0.020 | 1.116 ± 0.004 | 1.094 ± 0.002 |
| *r*(CH′), Å | 1.093 | ±0.020 | 1.091 ± 0.003 | 1.094 ± 0.002 |
| *r*(CH″), Å | 1.093 | ±0.020 | 1.083 ± 0.006 | 1.094 ± 0.002 |
| ∠ClNC, deg | 107.45 | ±2.0 | 108.41 ± 0.09 | 108.04 ± 0.05 |
| ∠NCH, deg | 109.47[a] | ±2.0 | 108.84 ± 1.62 | 112.63[c] |
| ∠NCH′, deg | 109.47[a] | ±2.0 | 109.66 ± 0.85 | 105.56[c] |
| ∠NCH″, deg | 109.47[a] | ±2.0 | 108.35 ± 0.60 | 108.14[c] |
| ∠HCH, deg | 109.47[b] | ±2.0 | 110.29[c] | 110.13 ± 0.04 |
| ∠HCH, deg | 109.47[b] | ±2.0 | 109.65[c] | 110.13 ± 0.04 |
| ∠HCH, deg | 109.47[b] | ±2.0 | 110.28[c] | 110.13 ± 0.04 |
| tilt angle, deg | 3.00[b] | ±2.0 | | 4.12 ± 0.46 |
| dihedral angle for tilt, deg | 60.00[b] | ±10.0 | | 81.4 ± 5.5 |

| molecule | rotational const | obsd | structure I calcd | structure I Δ, obsd − calcd | structure II calcd | structure II Δ, obsd − calcd |
|---|---|---|---|---|---|---|
| $(CH_3)_2N^{35}Cl$ | *A* | 8992.50 | 8991.70 | 0.80 | 8990.80 | −1.70 |
| | *B* | 4967.38 | 4967.37 | 0.01 | 4967.41 | −0.03 |
| | *C* | 3473.52 | 3473.53 | −0.01 | 3473.52 | 0.00 |
| $(CH_3)(CD_3)N^{35}Cl$ | *A* | 7851.11 | 7850.96 | 0.15 | 7851.50 | −0.39 |
| | *B* | 4597.07 | 4597.07 | 0.00 | 4597.08 | −0.01 |
| | *C* | 3186.01 | 3186.00 | 0.01 | 3186.04 | −0.03 |
| $(CD_3)_2N^{35}Cl$ | *A* | 6817.64 | 6817.44 | 0.20 | 6817.39 | 0.25 |
| | *B* | 4331.21 | 4331.22 | −0.01 | 4331.20 | 0.01 |
| | *C* | 2939.65 | 2939.74 | −0.09 | 2939.60 | 0.05 |
| $(CH_3)_2N^{37}Cl$ | *A* | 8990.60 | 8991.14 | −0.54 | 8990.23 | 0.37 |
| | *B* | 4836.42 | 4836.42 | 0.00 | 4836.40 | 0.02 |
| | *C* | 3409.07 | 3409.07 | 0.00 | 3409.03 | 0.04 |
| $(CH_3)(CD_3)N^{37}Cl$ | *A* | 7848.93 | 7849.05 | −0.12 | 7849.57 | −0.64 |
| | *B* | 4476.12 | 4476.09 | 0.03 | 4476.09 | 0.03 |
| | *C* | 3127.25 | 3127.25 | −0.00 | 3127.29 | −0.04 |
| $(CD_3)_2N^{37}Cl$ | *A* | 6817.05 | 6817.14 | −0.09 | 6817.06 | −0.01 |
| | *B* | 4215.86 | 4215.85 | 0.01 | 4215.86 | 0.00 |
| | *C* | 2886.10 | 2886.18 | −0.08 | 2886.07 | 0.03 |

[a] Initial value for structure I only. [b] Initial value for structure II only. [c] Calculated from other parameters for comparison.

**Table VII.** Comparison of the Molecular Structural Parameters on *N*-Chloro-*N*-methylmethamine with Those of Similar Molecules and Some of Their Carbon Analogues

| molecule | *r*(NCl) or *r*(CCl) | *r*(NC) | ∠ClNC/∠ClCC or ∠ClNH/∠ClCH | ∠ClNCl | ref |
|---|---|---|---|---|---|
| $NCl_3$ | 1.759 ± 0.002 | | | 107.1 ± 0.5 | 4 |
| $HNCl_2$ | 1.76 ± 0.02 | | | 106 | 26 |
| $H_2NCl$ | 1.7480 ± 0.0001 | | 103.67 ± 0.35 | | 5 |
| $CH_3NHCl$ | 1.750 ± 0.003 | 1.474 ± 0.005 | 109.43 ± 0.17<br>102.83 ± 0.17 | | 6 |
| $(CH_3)_2NCl$ | 1.749 ± 0.001 | 1.470 ± 0.001 | 108.04 ± 0.05 | | this study |
| $CH_3NCl_2$ | 1.74 ± 0.02 | | | | 11 |
| $H_3CCl$ | 1.7812 ± 0.0001 | | 108.4 ± 0.3 | | 7,8 |
| $CH_3CH_2Cl$ | 1.788 ± 0.002 | | 111.03 ± 0.13<br>106.4 | | 9 |
| $(CH_3)_2CHCl$ | 1.798 ± 0.004 | | 109.4 ± 0.4<br>105.3 ± 0.7 | | 27 |
| $(CH_3)_3CCl$ | 1.803 ± 0.002 | | 108.0 ± 0.1 | | 28 |

is partly explained by the lowering of the molecular symmetry in the crystalline environment which will also affect the axial symmetry of the electric field within the isolated molecule. It should however be noted that in our calculation of the hyperfine states we ignored the effect of the $^{14}N$ quadrupole nucleus because the hyperfine splittings due to the $^{14}N$ quadrupole nucleus could not be resolved in the microwave spectrum of $(CH_3)_2NCl$ or any of the deuterated species.

The values of the quadrupole coupling constants for $^{35}Cl$ (−91.50 MHz) and $^{37}Cl$ (−72.12 MHz) are in the same ratio as the nuclear quadrupole moments ($Q$) of $^{35}Cl$ and $^{37}Cl$ which are $-0.085 \times 10^{-24}$ and $-0.067 \times 10^{-24}$ cm$^2$, respectively. This indicates that the field gradient $q$ (which is positive at the Cl nucleus) remains unchanged in all the isotopic species.

Both the NQR[14] and present microwave study of $(CH_3)_2NCl$ give values of the nuclear quadrupole coupling constants $|(\chi_{zz})|$ for $^{35}Cl$ and $^{37}Cl$ which are smaller than those of $^{35}Cl$ and $^{37}Cl$ in the atomic state (109.74 and 86.51 MHz, respectively).[19] This is explained by assuming that the N–Cl bond is partly polarized in which the chlorine atom tends to be negative. By use of the quantity[20]

$$i_c = 1 - \frac{\chi_{zz}}{|eQq|_{\text{atomic}}}$$

as an index of the ionic character of the bond to chlorine, where Cl is negative, a value of 16.5% ionic character is obtained for the $N^+$–$Cl^-$ bond in *N*-chloro-*N*-methylmethamine. For comparison, the ionic character of related molecules is calculated by the same formula above which neglects corrections for partial

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double bond character. The values obtained are ClNO$^{12}$ 48%, ClNO$_2$$^2$ 14%, ClNH$_2$$^5$ 9%, ClNHCH$_3$$^6$ 9%, with the partial negative charge on chlorine. In contrast, a partial positive charge on chlorine is obtained for ClNCO$^{10}$ with an ionic character of 10%.

Structure I has unsymmetrical methyl groups in which the CH bond parallel to the plane of symmetry is longer than the other two CH bonds by 0.02 and 0.03 Å, respectively. A long CH bond has also been reported for isobutane$^{21}$ (1.10 Å) and trimethylamine$^{22}$ (1.109 Å). On the other hand, in structure II, the methyl groups are symmetric ($r$(CH) = 1.094 Å) and each has an upward tilt of 4.1° toward the lone pair. Similar methyl tilts have been reported for a number of molecules$^{23}$ including methylamine,$^{24}$ trimethylamine,$^{22}$ and *N*-chloromethamine.$^6$ In the last three instances, tilt angles of ~3°, 1.3°, and ~3.5°, respectively, have been determined.

No appreciable difference is observed in the C–N bond length in structures I and II, which are 1.473 and 1.470 Å, respectively. In CH$_3$NHCl$^6$ the C–N bond distance was found to be 1.474 ± 0.005 Å. In each case the length of the C–N bond obtained from microwave studies appears to be in good agreement with the value of 1.47 Å which was reported for (CH$_3$)$_2$NCl and CH$_3$NCl$_2$ from electron diffraction studies.$^{11}$ The calculated value of the CNC bond angle (110.7° in structure I and 111° in structure II) is considerably larger than 108° which was assumed for this angle in the electron diffraction work.$^{11}$ However, the CNC angle presently obtained is consistent with the values of 110.9° and 111.6° which have been reported$^{22,25}$ for this angle in (CH$_3$)$_3$N and (CH$_3$)$_2$NH, respectively.

Of special interest is the N–Cl bond length. The N–Cl bond distance in (CH$_3$)$_2$NCl reported in the electron diffraction study$^{11}$ is 1.77 Å which is 0.04 Å longer than the sum of the covalent radii of N and Cl (1.73 Å).$^3$ The N–Cl bond length obtained herein (1.742 Å in structure I and 1.749 Å in structure II) is smaller than the electron diffraction value and closer to the value predicted from the covalent radii of the two atoms. A comparison of this bond length with those reported for CH$_3$NCl$_2$ (1.74 Å)$^{11}$ and CH$_3$NHCl (1.750 Å)$^6$ shows that the N–Cl bond distance remains practically unchanged in this series of compounds. It should be noted, however, that the size of the ClNC angle in (CH$_3$)$_2$NCl (108.4° in structure I and 108.0° in structure II) is appreciably smaller than that reported$^6$ for CH$_3$NHCl (109.4°). The apparent contraction of the ClNC angle in (CH$_3$)$_2$NCl is to be expected considering the inductive effect due to the second methyl group in (CH$_3$)$_2$NCl which replaces the hydrogen atom in CH$_3$NHCl. The electron diffraction results$^{11}$ for the ClNC angles in (CH$_3$)$_2$NCl and CH$_3$NCl$_2$ are 107° ± 2° and 109° ± 2°, respectively. Despite the high degree of uncertainty in the electron diffraction measurements, these data correctly reflect the inductive effect of the methyl substituent.

It is interesting to note that the inductive effect of the methyl group on the corresponding carbon compounds results in a significant elongation of the carbon–chlorine bond length (see Table VII). For example, this distance in ethyl chloride$^9$ is 1.788 Å which is 0.007 Å longer than the corresponding distance in methyl chloride$^{7,8}$ but 0.010 Å shorter than the carbon–chlorine distance in isopropyl chloride.$^{27}$ Therefore, it is rather surprising that the nitrogen–chlorine distance remains so constant with the substitution of the methyl group for a hydrogen atom in the corresponding nitrogen compounds.

**Acknowledgment.** We gratefully acknowledge the financial support of this study by the National Science Foundation by Grant CHE-83-11279.

**Registry No.** Me$_2$N$^{35}$Cl, 104374-13-2; Me$_2$N$^{37}$Cl, 104374-14-3; Me(CD$_3$)N$^{35}$Cl, 104374-15-4; Me(CD$_3$)N$^{37}$Cl, 104374-16-5; (CD$_3$)$_2$N$^{35}$Cl, 104374-17-6; (CD$_3$)$_2$N$^{37}$Cl, 104374-18-7; Me$_2$NH, 124-40-3; MeNHCD$_3$, 20786-94-1; (CD$_3$)$_2$NH, 14802-36-9.

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# Luminescence from Nitrido Complexes of Osmium(VI). Evidence for a Nontotally Symmetric Excited-State Distortion

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**Abstract:** Vibronically resolved emission spectra have been obtained for the [Ph$_4$As][OsNX$_4$] (X = Cl, Br; $C_{4v}$ ground state) complexes. The observation of long ($\tau > 10$ μs) emission lifetimes and very weak absorptions, together with a large geometric distortion along the OsN coordinate, supports assignment of the excited state to B$_1$, B$_2$ ($^3$E) (($d_{xy}$)$^1$($d_{xz}$,$d_{yz}$)$^1$). Large distortions are also observed along a deformation vibrational coordinate of b$_1$ symmetry (ground-state vibrational frequency 151 cm$^{-1}$ (X = Cl), 112 cm$^{-1}$ (X = Br)) that is Jahn-Teller active. It is proposed that the $^3$E excited states are strongly distorted toward a $C_{2v}$ (equatorial nitrido) trigonal-bipyramidal geometry.

The electronic structures of high-valent transition-metal complexes containing multiple metal–ligand bonds have been the subject of numerous spectroscopic investigations.$^3$ Recent attention has been focused on 6-coordinate d$^2$ MO$_2^{n+}$ species, in part because of their solution luminescence properties.$^4$ One characteristic dynamic process of the emissive $^3$E$_g$ excited state of each of these d$^2$ complexes is a distortion from the ground-state structure along symmetric coordinates, with the metal–oxo bond undergoing a particularly large displacement.$^4$ We have continued our investigations of d$^2$ metal–ligand multiply bonded species, and included in the present report are emission spectroscopic results that

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