The Microwave Spectrum, Structure, and Nuclear Quadrupole Coupling Constants of Chlorine Isocyanate, ClNCO

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Summary The structure and nuclear quadrupole coupling constants of chlorine isocyanate have been determined from its microwave spectrum.

THE product of the pyrolysis of trichloroisocyanuric acid has been identified as chlorine isocyanate, ClNCO.[1] This molecule is isoelectronic with silyl isocyanate, SiH_3NCO, which, unlike most isocyanates, has a linear heavy atom chain,[2] a feature which has been attributed to $(d\text{-}p)\pi$ bonding between silicon and nitrogen. We have begun a study of the chlorine derivative to decide whether it is similarly linear, and to determine its structural parameters.

The spectrum of the ground vibrational state has been found, however, to be that of a slightly asymmetric prolate rotor having components of its dipole moment along the *a*- and *b*-principal inertial axes. Rotational transitions of both $^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ and $^{37}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ have been measured. Each transition was clearly resolved to several components by nuclear quadrupole coupling of chlorine, and some further resolved by that of nitrogen; while all the coupling constants of chlorine were calculated, only a value for χ_{aa} for nitrogen in $^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ has thus far been obtainable. In addition, significant centrifugal distortion was evident. Since we have insufficient data thus far to obtain all possible asymmetric rotor distortion constants, the spectrum was fitted using the centrifugal distortion expression $E_{cd} = -D_J J^2(J+1)^2 - D_{JK} J(J+1)\langle P_a{}^2\rangle$ in essentially the symmetric rotor limit. At present these distortion constants are effectively fitting parameters, and have simply been used to obtain improved rotational constants. The distortion constant D_K, which is probably a few MHz, could not be separated from our derived value of A, and introduces uncertainty into its value. Rotational transitions could be reproduced with r.m.s. deviations of 0·20 and 0·21 MHz for $^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ and $^{37}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ respectively. All the derived constants are given in the Table.

Rotational constants, centrifugal distortion constants, principal moments of inertia, and nuclear quadrupole coupling constants of chlorine isocyanate

	$^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ (Ground state)	$^{37}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ (Ground state)	$^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ (Excited state)
A(MHz)	51561·0	51241·5	53500
B(MHz)	3130·68	3057·70	3147·4
C(MHz)	2945·17	2879·48	2953·6
D_J(kHz)	2·7	2·8	—
D_{JK}(kHz)	−277·5	−270·1	−294·3
I_a(Amu-Å^2)	9·801	9·863	9·45
I_b(Amu-Å^2)	161·427	165·279	160·57
I_c(Amu-Å^2)	171·594	175·509	171·10
Δ(Amu-Å^2)†	0·366	0·367	1·08
χ_{aa}(Cl) (MHz)	−70·8 ± 0·6	−56·6 ± 0·9	−70·9 ± 1·2
η(Cl)	0·603 ± 0·012	0·589 ± 0·021	—
χ_{aa}(N) (MHz)	3·5 ± 1	—	—

† $\Delta = I_c - I_b - I_a$.

We have also measured some *a*-type transitions of $^{35}\mathrm{Cl}^{14}\mathrm{N}^{12}\mathrm{C}^{16}\mathrm{O}$ in an excited vibrational state. Preliminary values for the rotational constants, and the chlorine quadrupole coupling constant χ_{aa} are also given in the Table. From the relative intensities of the spectra of the ground and excited vibrational states the vibration frequency was deduced to be 200 ± 60 cm^{-1}.

Since the spectrum of chlorine isocyanate is that of an asymmetric rotor, the molecule is evidently not linear, in contrast with silyl isocyanate. The small positive inertial defects, however, which do not vary with isotopic substitution, show it to be planar. Furthermore, the small positive value of χ_{aa} for nitrogen suggests that it is indeed the isocyanate, with chlorine bonded to nitrogen; were it the cyanate a small negative value would be expected.[3] It is likely that the molecule has a linear N–C–O chain, with chlorine off this axis. If the chlorine atom is located by the substitution method,[4] and the N–C–O chain assumed to be the same as that in HNCO,[5] one obtains r(Cl–N) = 1·688 ± 0·02 Å and ∠(Cl–N–C) = 123° 43′ ± 1°. The Cl–N length is slightly smaller than, though very near to, the sum of the single-bond radii[6] possibly suggesting only slight π-bonding. This conclusion is tentative, however, for though the structure fits the rotational constants rather well, it depends on the significant assumption of the N–C–O parameters.

With one principal axis of the chlorine quadrupole coupling tensor assumed to coincide with the Cl–N bond the chlorine coupling constants were transformed from the inertial axis system to the bond axis system (z parallel to the Cl–N bond, y perpendicular to the molecular plane). Principal values of the ^{35}Cl quadrupole coupling tensor obtained are $\chi_{xx} = 61{\cdot}6$ MHz, $\chi_{yy} = 56{\cdot}7$ MHz, $\chi_{zz} = -118{\cdot}3$ MHz. Though the value of χ_{zz} is large, indeed slightly greater than that for a $3p$ electron deficit (−109·6 MHz), it is not unreasonable. Chlorine and nitrogen are customarily assigned the same electronegativity, so that such a large value is expected if the Cl–N bond is essentially covalent. χ_{xx} and χ_{yy} are nearly equal, suggesting only slight asymmetry of the Cl–N bond. The quadrupole coupling is thus consistent with the suggestion of only slight π-bonding. This deduction is also tentative, however, since the derived principal values are sensitive functions of the internuclear parameters, and definite conclusions must await a more refined structural determination.

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