Gas-phase Infrared Spectroscopic Evidence for the Inversion and Non-planarity of Cyanamide

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Summary A vapour-phase i.r. spectroscopic study of cyanamide, NH_2CN, and its deuteriated equivalents gives values for the small moment of inertia and higher vibrational transitions associated with the inversion mode; from these data estimates are made of 43 ± 1·5° for the out-of-plane angle and 467 ± 30 cm^{-1} for the barrier to inversion.

THERE has been considerable discussion over the exact configuration of bonds about the amino nitrogen atom in cyanamide. Several i.r. studies of condensed phases[1] have been inconclusive, but vapour-phase microwave evidence[2,3] shows that the out-of-plane angle (between the H–N–H bisector and the N–C–N skeleton) is approximately 38°. However the large rotational constant which reflects the smallest moment of inertia was not measured, and no i.r. spectra of cyanamide vapour have been published. We have obtained such spectra for NH_2CN and ND_2CN with a resolution of about 1·0 cm^{-1}. The results are readily interpreted in terms of a non-planar molecule with an out-of-plane angle of 43 ± 1·5° and a barrier to inversion of 467 ± 30 cm^{-1}.

Many of the gas-phase fundamentals of cyanamide show a well-resolved inversion doubling effect. Analysis of the K-structure of bands due to the stretching vibrations $\nu_{as}(NH_2)$, $\nu_{as}(ND_2)$ and $\nu(NH)$ yielded A rotational constants for the 0^+ and 0^- levels of NH_2CN, ND_2CN and NHDCN respectively. This parameter is sensitive to both the out-of-plane angle and the H–N–H angle; the rest of the molecular geometry is accurately known from microwave measurements.[2,3] The H–N–H angle may be estimated from the vapour phase -NH_2 stretching frequencies using formulae given by Linnett.[4] By this means the angle is estimated to be 113° which is in good agreement with the measured H-N-H angle of aniline.[5,6] Aniline[7] and cyanamide have almost identical -NH_2 stretching frequencies in the vapour phase. Values of the out-of-plane angle which reproduce the observed moments of inertia are listed in Table 1.

TABLE 1

Out-of-plane angles of cyanamide and isotopic species

Molecule	Level	A constant (cm^{-1})	Out-of-plane angle
NH_2CN	0^+	10·37 ± 0·015	41·0 ± 0·2°
	0^-	10·16 ± 0·015	44·6 ± 0·2
ND_2CN	0^+	5·03 ± 0·01	42·4 ± 0·4
	0^-	5·01 ± 0·01	43·2 ± 0·4
NHDCN	0^+	6·84 ± 0·1	44·0 ± 2·5
	0^-		

Several transitions of the wagging–inversion mode of NH_2CN were observed at lower frequencies. Band origins were determined by analysis of the K-structure as follows:—

$0^+ \rightarrow 1^-$ 714·1 ± 0·4 cm^{-1}

$0^- \rightarrow 1^-$ 670 ± 10·0 cm^{-1} (a parallel-type band)

$0^- \rightarrow 1^+$ 364·3 ± 2·0 cm^{-1}

These transitions were fitted to a double minimum quartic–harmonic potential function, using tables kindly supplied by Lord and Laane.[8] The reduced mass was calculated from the formulae of Kasuya[9] to be 1·706 a.m.u. The best fit was obtained for V (cm^{-1}) = 1350·1 ($\zeta^4 - 1·18\zeta^2$), where ζ is the out-of-plane angle in radians. The minima of this potential correspond to an out-of-plane angle of 43·5°, in good agreement with the values calculated from the observed moments of inertia (Table 1); the potential itself is similar to that found for aniline.[5]

If it is assumed that this potential is unchanged on isotopic substitution, then the inversion transitions for ND_2CN can be calculated. Kasuya's formulae give an isotopic ratio of reduced masses, ($\mu_{D_2}:\mu_{H_2}$) of 1·75. The calculated energy levels are summarised in Table 2, and are in good agreement with microwave evidence[2,10] that the 0^+—0^- separations of NH_2CN and ND_2CN are approximately 50 cm^{-1} and 15 cm^{-1} respectively. Unfortunately ND_2CN vapour appears to be very weakly absorbing in the low-frequency region, so the predicted 0^+—1^- frequency for this species remains unconfirmed by experiment.

TABLE 2

Predicted and observed energy levels of the wagging–inversion vibration of cyanamide

	NH_2CN		ND_2CN
Energy level	Observed	Calculated (cm^{-1})	Calculated (cm^{-1})
0^+	0	0	0
0^-	44 ± 10[a]	49·3	14·7
1^+	408 ± 10[b]	413·8	293·8
1^-	714·1 ± 0·4	713·9	468·0

[a] From ($0^+ \rightarrow 1^-$) − ($0^- \rightarrow 1^-$), viz. 714·1 − 670 cm^{-1}, see text; [b] from ($0^- \rightarrow 1^+$) + ($0^+ \rightarrow 0^-$).

Expectation values for the A rotational constants of the 0^+ and 0^- levels of NH_2CN and ND_2CN were calculated as the quantum mechanical average of the A-constant over the inversion vibrational wave-functions. A model for the inversion path chosen in which the nitrogen bond angles vary from 120° for the planar molecule, to 90° for the 90° out-of-plane molecule. The "expectation" out-of-plane angles were found to account very well for the different values given in Table 1.

All spectra were taken at a pathlength of 16·5 m in a multireflection cell uniformly heated to 90°. Cyanamide, in a bulb held at 85°, was continuously streamed through the cell. Perkin–Elmer Models 125 and 621 i.r. spectrophotometers were used.

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