The Ground State Microwave Spectrum and Dipole Moment of 2-Isocyano-Propane

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The ground state rotational spectrum of 2-isocyano-propane is assigned. The rotational constants and the quartic centrifugal distortion constants are determined by Microwave Fourier Transform (MWFT) Spectroscopy. The analysis of the Stark effect leads to a total dipole moment of 4.055(1) D.

Alkyl-isocyanides are much less studied by experimental techniques than the isomeric alkyl-cyanides, although there has been a permanent interest of theoreticians in the structure and bonding of the isocyano group [1, 2]. We now report the assignment of the rotational spectrum and the determination of the dipole moment of 2-isocyano-propane.

Experimental

The title compound ($CH_3CH(NC)CH_3$) was prepared by the method of Casanova et al. [3] by dehydration of N-isopropyl-formamide with tosylchloride in quinoline and used after destillation (Figure 1).

Conventional Stark spectra in the K-band (18 to 26.5 GHz) were recorded with square wave voltage modulation and phase sensitive amplification. A Hewlett Packard 8340 B synthesized sweeper served as the microwave source, the K-band waveguide was tapered to the 3 m Stark cell with 10×47 mm cross section.

Zero-field MWFT spectra were recorded as described previously [4–6].

The X-band MWFT Stark spectrometer has been detailed in [7]. The cell was calibrated with the $J' \leftarrow J = 1 \leftarrow 0$ transition of carbonyl sulfide, using a dipole moment of 0.715196(10) D [8].

K-band MWFT Stark spectra were obtained with a bridge spectrometer described in [9]. The calibration was accomplished with the $J' \leftarrow J = 2 \leftarrow 1$ transition of carbonyl sulfide, using the above dipole moment.

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All MWFT spectra were recorded in a temperature region from 220 to 250 K and at a pressure ranging from 0.1 to 0.5 Pa (0.8 to 4.0 mTorr).

Assignment

The isocyano group has been shown to be linear within experimental error [10]. A structure of 2-isocyano-propane was assumed on a structural basis of the related compounds $CH_3CHClCH_3$ [11], $CH_3CH(CN)CH_3$ [12], and CH_3NC [13]. This led to the observation of five $J' \leftarrow J = 3 \leftarrow 2$ a-type transitions ($\Delta K_- = 0$, $\Delta K_+ = 1$) by conventional K-band Stark spectroscopy. Identification of the absorption signals was confirmed by comparison of the Stark components with estimates from second order perturbation theory [14].

All subsequent measurements were carried out with our MWFT spectrometers. Using the preliminary rotational constants from Stark spectroscopy, seven $J' \leftarrow J = 4 \leftarrow 3$ a-type transitions ($\Delta K_- = 0$, $\Delta K_+ = 1$) in the V-band (26.5 to 40 GHz) were recorded to high accuracy. With an iterative fit and measurement procedure, other transitions could be found in a straightforward manner. A list of observed a- and c-type transitions is given in Table 1, the derived rotational and quartic centrifugal distortion constants according to Watson's A reduction [15, 16] are listed in Table 2.

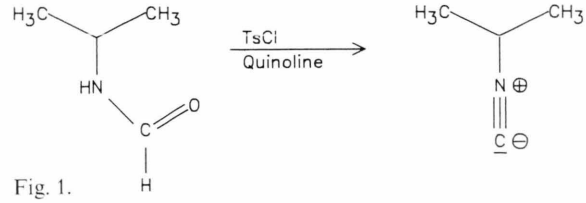

Fig. 1.

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Table 1. Transitions used for determination of rotational constants and centrifugal distortion analysis. ν: measured frequency (MHz), δ: difference between observed and calculated frequency (kHz).

J'	K'_-	K'_+	J	K_-	K_+	ν	δ
2	0	2	1	0	1	14 549.687	−1
2	0	2	1	1	0	9 675.450	13
2	1	1	1	0	1	20 913.214	−9
2	1	2	1	1	1	13 583.143	−4
2	2	1	2	1	1	10 938.918	−8
3	2	2	3	1	2	9 281.737	13
4	0	4	3	0	3	27 507.940	2
4	1	3	3	1	2	31 437.156	8
4	1	3	4	1	4	12 035.535	9
4	1	4	3	1	3	26 733.324	0
4	2	2	3	2	1	31 526.074	0
4	2	3	3	2	2	29 416.088	11
4	3	1	3	3	0	30 261.671	−12
4	3	2	3	3	1	30 053.966	−8
6	2	4	6	2	5	11 406.750	5
7	3	5	7	2	5	10 513.784	1
11	4	8	11	3	8	9 577.887	−2
13	5	8	13	5	9	9 257.987	−8
14	5	10	14	4	10	11 664.330	−5
16	6	10	16	6	11	11 176.794	−3
18	6	13	18	5	13	8 994.427	4
19	7	12	19	7	13	13 085.385	4

Dipole Moment

2-Isocyano-propane theoretically shows ^{14}N nuclear quadrupole coupling, although quadrupole coupling energies of isocyanides have been shown to be small [17–20]. ^{14}N nuclear quadrupole coupling could not be observed in the title compound to date, and the line shapes of the zero-field transitions used for Stark effect analysis also justify the assumption of negligible quadrupole coupling in these cases.

The strong field approximation [21], in which the Stark energies are much larger than the quadrupole coupling energies, is assumed to hold for the analysed transitions. Because the quadrupole coupling constants of 2-isocyano-propane are not yet known, quadrupole coupling is neglected in Stark effect analysis.

A list of the zero-field transition frequencies and experimental Stark splittings used in the determination of the dipole moment is given in Table 3. The splittings were refined by a line shape analysis [22]. Stark effect analysis was performed by diagonalizing

A	7963.0932 (30)	1.00						
B	4316.7602 (15)	0.62	1.00					
C	3088.8111 (15)	0.38	0.93	1.00				
Δ_J	1.228 (53)	0.45	0.92	0.91	1.00			
Δ_{JK}	10.96 (11)	0.03	−0.07	−0.01	−0.31	1.00		
Δ_K	−4.92 (40)	0.44	0.11	0.05	0.23	−0.76	1.00	
δ_J	0.3107 (73)	0.35	−0.01	−0.05	−0.27	0.88	−0.37	1.00
δ_K	6.593 (92)	0.20	0.04	0.03	0.30	0.96	0.55	−0.977
σ	9							
N	22							

Table 2. Rotational (MHz) and quartic (kHz) centrifugal distortion constants (including standard errors) according to Watson's A reduction with correlation matrix. σ: standard deviation of the fit (kHz), N: number of evaluated transitions.

J'	K'_-	K'_+	J	K_-	K_+	$\lvert M\rvert$	E	ν_0	$\nu_{St}-\nu_0$	δ
2	1	1	1	0	1	0	91.42	20 913.214	−0.786	−0.008
						0	103.92		−1.029	0.004
						1	103.92		1.056	0.007
						0	114.29		−1.235	−0.005
						1	114.29		1.281	0.005
						1	124.73		1.539	−0.007
						1	145.52		2.092	−0.008
						1	166.33		2.722	0.002
4	1	3	4	1	4	4	118.36	12 035.536	−0.808	0.001
						4	135.55		−1.068	0.011
						3	157.94		−0.786	−0.007
						4	157.94		−1.424	−0.011
						3	175.17		−0.975	−0.001
						4	175.17		−1.763	0.001
						2	192.63		−0.509	0.007
						3	192.63		−1.172	−0.004
						4	192.63		−2.137	0.008

Table 3. Transitions used for Stark effect analysis. E: Stark field strength (V/cm), ν_0: zero field frequency (MHz), $\nu_{St}-\nu_0$: Stark shift (MHz), δ: difference between observed and calculated shift (MHz).

the energy matrix [23]. The determined components are $|\mu_a| = 3.991(1)$ D and $|\mu_c| = 0.715(1)$ D, the overall moment being $\mu = 4.055(1)$ D.

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