Microwave Spectrum and Barrier to Internal Rotation in $CH_3COC^{15}N$

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The ground state rotational spectra of the ^{15}N isotopic species of acetyl cyanide have been measured in the region from 8 to 40 GHz. The rotational and centrifugal distortion constants have been determined by a least squares fit to about 38 transition frequencies with $J \leqq 14$. The potential barrier parameter V_3 and the angle α between the top axis and the '*a*-axis' have been determined by a least squares of the (A-E) splittings of about 27 transitions. The methyl top moment of inertia was fixed at 3.14 amu Å^2.

Introduction

The first microwave spectroscopic studies of acetyl cyanide were done by Krisher and Wilson[1] and by Nelson and Pierce[2]. Recently, interest in this molecule has revived with an aim of testing the applicability of the rigid frame-rigid top (RF-RT) model to describe the rotational spectra of the molecule in the excited torsional and vibrational states. Scappini et al.[3–5] have presented an analysis of the rotational spectrum of the normal species of the molecule in the ground, first excited torsional and first excited vibrational (CCN in plane bending) state. They concluded that while the RF-RT model can successfully explain the spectrum in the ground state, it fails completely to account for the observed spectra simultaneously in the ground and two above mentioned excited states. The main reason of the failure of the RF-RT model is an interaction between the torsional and the vibrational levels, which depends partly on their energy difference. An extension to the RTV (Rotation-Torsion-Vibration interaction) model, which differs from the RF-RT model by including one additional vibrational degree of freedom (nearest to the torsion in energy; in this case the CCN in plane bending) was found to be adequate in describing the three spectra of the molecule simultaneously.

The present ground state study of the $CH_3COC^{15}N$ was undertaken with the following points in mind.

i) To prepare the basis for the study of excited torsional and vibrational state spectra of the molecule. This, in coordination with the excited torsional and vibrational state spectra of the normal species of the molecule[4] could be used to check more critically the validity of the RTV model. [Hamiltonian (2) of Reference [3].]

ii) To get the rotational constants of one more isotopic species of the molecule, which along with the previously determined ones[1, 3] could be used to derive a more reliable structure of the molecule.

Experimental

The microwave spectrum was recorded with a conventional 33 kHz Stark modulation spectograph employing phase stabilized BWO's as radiation sources and an automatic system of recording the frequency markers[6]. The spectrograph is equipped with an eight meter absorption cell and is operating in the range from 8 to 40 GHz. The measurements were carried out at a temperature of about -50 °C and at a pressure of $1-5$ mTorr. The frequency measurements are believed to be accurate within ±30 kHz. For the quick assignment of the spectra, use was also made of a radio frequency-microwave double resonance (RF-MW-DR) spectrograph, described in detail elsewhere[7, 8].

The ^{15}N species of acetyl cyanide was prepared[9] by adding acetyl bromide to dry $CuC^{15}N$ contained in an ice cooled ampul. Sufficient dry cyclohexane was added to wet all the cuprous cyanide and the ampul was sealed off. After standing for three days at room temperature, the content was distilled in vacuum.

Ground State Spectrum

The ground state spectrum was readily assigned with the help of RF-MW-DR experiments. For setting the approximate pump frequency and the approximate region, where the signal should be

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searched, use was also made of the 'r_0-structure' of the molecule, which was calculated with the help of the rotational constants of the previously studied isotopic species of the molecule. It had been the general experience that for predicting the spectrum of a new isotopic species of the molecule, 'r_0-structure' is the better choice. The assigned lines were later also confirmed by their characteristic Stark patterns. Table 1 gives the details of the RF-MW-DR experiments performed. It must be mentioned that because of the influence of the linear term in the coupling of overall and internal rotation angular momenta, the values of the pump frequencies were sometimes appreciably different for the A and E states of a transition. Therefore, for the E transitions, both the pump and the signal frequencies had to be located by a double search procedure.

Pump	Signal
$4_{31}-4_{32}$ (69.2 MHz for A and 97.6 MHz for E transition)	$5_{32}-4_{31}$
	$5_{33}-4_{32}$
	$4_{31}-4_{22}$
	$4_{32}-4_{23}$
	$4_{31}-3_{30}$
	$4_{32}-3_{31}$
$3_{30}-3_{31}$ (10.0 MHz for A and 69.8 MHz for E transition)	$4_{31}-3_{30}$
	$4_{32}-3_{31}$
	$3_{30}-3_{21}$
	$3_{31}-3_{22}$

Table 1. Radio frequency — microwave double resonance connections used for the assignment of the ground state spectra.

Table 3. Ground state parameters derived from the semirigid model according to Watson [c].

A (MHz)	10183.659 ± 0.008
B (MHz)	4011.073 ± 0.002
C (MHz)	2925.282 ± 0.002
d_J (MHz)	$\{-0.2145 \pm 0.03\} \cdot 10^{-2}$
d_{JK} (MHz)	-0.1271 ± 0.006
d_K (MHz)	-0.2749 ± 0.01
d_{WJ} (MHz)	$\{+0.8450 \pm 0.08\} \cdot 10^{-3}$
d_{WK} (MHz)	$\{+0.4003 \pm 0.01\} \cdot 10^{-1}$
I_a (amu Å^2) [a]	49.64139
I_b (amu Å^2) [a]	126.0339
I_c (amu Å^2) [a]	172.8145
$I_a+I_b-I_c$ (amu Å^2)	2.86079
RMS deviation [b] (MHz)	0.035

[a] Conversion factor = $5.05531 \cdot 10^5$ MHz. amu Å^2 Mass scale ^{16}O.

[b] The RMS deviation to a least square fit of the observed transition frequencies to a rigid rotor is 1.718 MHz.

[c] In the fitting procedure, the parameters d_{JK}, d_{WK} and d_{WJ} were highly correlated. The highest correlation coefficient was 0.998 and the lowest 0.898.

The measured ground state rotational transitions are detailed in Table 2. The rotational constants are determined by fitting the observed frequencies (A species) to an eigth parameter centrifugal rotor according to Watson [10]. The formula for the energy eigenvalue for a rotational level is given by

$$W = W_0 - d_J J^2 (J+1)^2 - d_{KJ} J (J+1) \langle P_z^2 \rangle - d_K \langle P_z^4 \rangle - d_{WJ} W_0 J (J+1) - d_{WK} W_0 \langle P_z^2 \rangle ,$$

the symbols having their usual meanings. The rotational constants, centrifugal distortion constants and the moments of inertia are given in Table 3.

Table 4. Observed and calculated internal rotation splitting of the ground state transitions of $CH_3COC^{15}N$ molecule. All splittings are in MHz.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Observed splitting [a]	Calculated splitting [a, b]	Deviation
$2_{20}-2_{11}$	+ 2.79	+ 2.594	0.196
$2_{21}-2_{12}$	− 6.13	− 5.744	0.386
$2_{11}-2_{02}$	− 1.02	− 0.937	0.083
$2_{12}-1_{01}$	− 0.72 [c]	− 0.695	0.025
$2_{11}-1_{10}$	− 1.01	− 0.955	0.055
$2_{02}-1_{01}$	− 0.55 [c]	− 0.543	0.007
$3_{30}-3_{21}$	+26.41	+26.298	0.112
$3_{31}-3_{22}$	−31.51	−31.227	0.283
$3_{12}-3_{03}$	− 1.67	− 1.578	0.092
$3_{13}-2_{02}$	− 0.60 [c]	− 0.544	0.056
$3_{03}-2_{12}$	− 0.50 [c]	− 0.510	0.010
$3_{22}-2_{21}$	+ 2.19	+ 2.140	0.050
$3_{21}-2_{20}$	− 4.37	− 4.135	0.235
$3_{03}-2_{02}$	− 0.67 [c]	− 0.663	0.007
$4_{31}-4_{22}$	+11.28	+11.590	0.310
$4_{22}-4_{13}$	− 0.83 [c]	− 0.759	0.071
$4_{13}-4_{04}$	− 2.72	− 2.570	0.150
$4_{04}-3_{13}$	− 0.76 [c]	− 0.775	0.015
$4_{31}-3_{30}$	−17.13	−16.877	0.253
$4_{32}-3_{31}$	+14.35	+14.273	0.077
$4_{14}-3_{13}$	− 0.44 [c]	− 0.482	0.042
$5_{23}-5_{14}$	− 1.31	− 1.222	0.088
$5_{14}-5_{05}$	− 4.07	− 3.893	0.177
$5_{32}-4_{31}$	−11.72	−11.495	0.225
$6_{24}-6_{15}$	− 2.15	− 2.001	0.149
$6_{15}-6_{06}$	− 5.75	− 5.397	0.353
$6_{24}-5_{33}$	+ 2.56	+ 2.791	0.231
$7_{25}-7_{16}$	− 3.39	− 3.219	0.171
$7_{25}-6_{34}$	− 1.11	− 1.143	0.033
$8_{35}-8_{26}$	− 0.65 [c]	− 0.794	0.144
$8_{26}-8_{17}$	− 5.06	− 4.876	0.184
$8_{26}-8_{27}$	− 6.42	− 6.139	0.281
$9_{36}-9_{27}$	− 1.58	− 1.719	0.139
$9_{36}-8_{45}$	+ 3.94	+ 4.001	0.061
$10_{37}-10_{28}$	− 3.05	− 3.247	0.197
		RMS deviation =	0.170

[a] Splitting mentioned as $(\nu_E - \nu_A)$.

[b] Calculated with the help of the internal rotation parameters of Table 5.

[c] Observed splittings, which are less than 1 MHz are not included in the fitting procedure.

Table 2. Measured ground state rotational transitions of the $CH_3COC^{15}N$ molecule. All frequencies are in MHz.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Torsional species	Observed frequency	Calculated frequency [a]	Deviation	Centrifugal distortion correction
$2_{20}-2_{11}$	A	18648.62	18648.618	0.002	−0.168
	E	18651.41			
$2_{21}-2_{12}$	A	21774.84	21774.837	0.003	−0.294
	E	21768.71			
$2_{11}-2_{02}$	A	8474.99	8475.004	0.014	−0.192
	E	8473.97			
$2_{12}-1_{01}$	A	18959.46	18959.454	0.006	−0.050
	E	18958.73			
$2_{11}-1_{10}$	A	14958.38	14958.355	0.025	−0.145
	E	14957.37			
$2_{12}-1_{11}$	A	12786.81	12786.874	0.064	−0.044
	E	12786.81			
$2_{02}-1_{01}$	A	13741.69	13741.677	0.013	−0.004
	E	13741.14			
$3_{30}-3_{21}$	A	33021.32 [b]	33021.331	0.011	−0.584
	E	33047.73 [b]			
$3_{31}-3_{22}$	A	33654.17 [b]	33654.214	0.044	−0.676
	E	33622.66 [b]			
$3_{12}-3_{03}$	A	10527.92	10527.922	0.002	−0.427
	E	10526.25			
$3_{13}-2_{02}$	A	24320.63	24320.604	0.026	−0.114
	E	24320.03			
$3_{03}-2_{12}$	A	15079.36	15079.360	0.000	0.036
	E	15078.86			
$3_{22}-2_{21}$	A	20808.59	20808.563	0.027	−0.501
	E	20810.78			
$3_{21}-2_{20}$	A	21320.40	21320.404	0.004	−0.577
	E	21316.03			
$3_{13}-2_{12}$	A	19102.70	19102.827	0.127	−0.068
	E	19102.70			
$3_{03}-2_{02}$	A	20297.15	20297.137	0.013	−0.009
	E	20296.48			
$4_{31}-4_{22}$	A	32208.09 [b]	32208.010	0.080	−1.308
	E	32219.37 [b]			
$4_{22}-4_{13}$	A	16847.55	16847.539	0.011	−0.970
	E	16846.72			
$4_{13}-4_{04}$	A	13614.65	13614.669	0.019	−0.764
	E	13611.93			
$4_{04}-3_{13}$	A	22512.46	22512.401	0.059	0.070
	E	22511.69			
$4_{31}-3_{30}$	A	28037.91 [b]	28037.867	0.043	−1.564
	E	28020.60 [b]			
$4_{32}-3_{31}$	A	27978.66 [b]	27978.652	0.008	−1.541
	E	27993.01 [b]			
$4_{14}-3_{13}$	A	25338.95	25338.958	0.008	−0.104
	E	25338.51			
$5_{23}-5_{14}$	A	16709.09	16709.105	0.015	−1.572
	E	16707.78			
$5_{14}-5_{05}$	A	17837.05	17837.040	0.010	−1.193
	E	17832.98			
$5_{32}-4_{31}$	A	35238.13 [b]	35238.130	0.000	−2.038
	E	35226.41 [b]			
$6_{24}-6_{15}$	A	17508.59	17508.592	0.002	−2.303
	E	17506.44			
$6_{15}-6_{06}$	A	23104.24	23104.252	0.012	−1.710
	E	23098.49			
$6_{24}-5_{33}$	A	13748.90	13748.903	0.003	0.620
	E	13751.46			
$7_{25}-7_{16}$	A	19470.30	19470.264	0.036	−3.160
	E	19466.90			
$7_{25}-6_{34}$	A	23674.39	23674.408	0.018	1.119
	E	23673.28			
$8_{35}-8_{26}$	A	25903.35	25903.400	0.050	−5.914
	E	25902.70			
$8_{26}-8_{17}$	A	22739.10	22739.100	0.000	−4.136
	E	22734.04			
$8_{26}-8_{27}$	A	17327.43	17327.442	0.012	−2.392
	E	17321.01			
$9_{36}-9_{27}$	A	25293.34	25293.386	0.046	−7.354
	E	25291.76			
$9_{36}-8_{45}$	A	22905.96	22905.959	0.001	3.460
	E	22909.90			
$10_{37}-10_{28}$	A	25852.81	25852.758	0.052	−8.831
	E	25849.80			
$14_{4,10}-14_{4,11}$	A	15112.22	15112.225	0.005	−4.236
	E	— [c]			

RMS deviation = 0.035 [d]

[a] Calculated with the help of rotational and centrifugal distortion parameters of Table 3.
[b] Confirmed and measured in RF-MW double resonance experiments.
[c] Not measured because of disturbing lines.
[d] The RMS deviation of a least square fit of the observed transition frequencies to a rigid rotor is 1.718 MHz.

Barrier to Internal Rotation in the Molecule

As has been concluded elsewhere[3], the internal rotation splittings (E-A) of the transitions in the ground state can successfully be interpreted in terms of the rotation-torsion interaction alone (RF-RT model). The vibration interaction term i. e. the non-rigidity of the frame shows observable effects only in the excited state spectra.

The effective Hamiltonian, which has been used to fit the internal rotation splittings can be expressed in the principal axes system as[11]

$$\begin{aligned} H_{v\sigma} &= A\,P_a^2 + B\,P_b^2 + C\,P_c^2 \\ &\quad + F\sum_{n=1}^{2} W_{v\sigma}^{(n)}\,\{\lambda_a (I_\alpha/I_{aa})\,P_a + \lambda_b (I_\alpha/I_{bb})\,P_b\}^n \end{aligned}$$

where

P_a, P_b, P_c are components of the total angular momentum operator (c-axis is perpendicular to the molecular symmetry plane),

$F = \hbar^2/(2\,r\,I_\alpha)$,

$r = 1 - \lambda_a^2 (I_\alpha/I_{aa}) - \lambda_b^2 (I_\alpha/I_{bb})$,

λ_a, λ_b are direction cosines between the symmetry axis of the top and the a and b principal axes respectively (in this case $\lambda_c = 0$),

$W_{v\sigma}^{(n)}$ are the nth order perturbation coefficients,

$s = 4\,V_3/(9\,F)$ is the reduced barrier parameter,

I_{aa}, I_{bb}, I_{cc} are the principal moments of inertia,

A, B, C are the rotational constants,

I_α is the moment of inertia of the top about its symmetry axis.

Table 4 presents the measured internal rotation splitting of the ground state transitions of the molecule. A computer program DIRMAT (Author H. Mäder) was available, which calculates the internal rotation splittings as a function of s and direction cosine λ_a. This program takes care of the first and second order perturbations and neglects the higher ones. This program in coordination with a general fitting program SPEFIT was used to extract the potential barrier parameter V_3 and the angle between the top axis and the a-axis by making a least squares fit to the observed splittings. The results are given in Table 5. In the fitting procedure I_α was fixed at 3.14 amu Å². The effect of I_α on the (E-A) splittings is correlated to that of V_3. Using a separate computer program SPLIKR (Author H. D. Rudolph), it was confirmed that the effect of the fourth order perturbation was within the experimental uncertainty (60 kHz) of the measured splittings.

Table 5. Internal rotation parameters.

F (GHz)	166.80
s	33.83 ± 0.07
λ_a	0.5079 ± 0.003
I_α (amu Å²)	3.14 [a]
V_3 (cal mol^{-1})	1210 ± 4
Tilt of the to axis	1.48° [b]

[a] Kept fixed as its variation is highly correlated to that of V_3. I_α value taken from structure (Reference [1]).
[b] Towards the C=O bond.

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