Acetyl Cyanide
III. Vibrational Spectrum and Vibrational Analysis

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The infrared spectrum of gaseous acetyl cyanide, CH_3COCN, has been recorded from 90–3200 cm^{-1}. The Raman spectrum of the liquid phase has been measured between 100 and 500 cm^{-1}. The eighteen fundamental vibrations have been assigned, mainly on the basis of the infrared band contours, and a normal coordinate analysis has been made.

I. Introduction

In order to support the rotation-torsion-vibration (RTV) interaction analysis of the rotational spectrum of acetyl cyanide, which is reported in Part II[1], we became interested in the vibrational level distribution of this molecule.

Recently vibrational spectra of acetyl cyanide have been reported by Sugiè and Kuchitsu[2]. The assignment of the eighteen fundamental vibrations was based on infrared and Raman studies of the liquid phase. A normal coordinate analysis, using a Urey-Bradley force field, was also made to calculate mean amplitudes and vibration corrections for use in an electron diffraction structure determination.

Our attention in the vibrational spectrum of this molecule was focussed at the fundamental far infrared vibrations in connection with the application of a RTV model[1]. Since the microwave analysis was performed for the vapour phase and, on the other hand, shifts of vibrational frequencies occur going from liquid to vapour phase, it appeared necessary for the consistency of the data to record the far infrared spectra of the vapour phase. Furthermore we remeasured the liquid phase Raman spectra between 100 and 500 cm^{-1} to determine depolarization ratios for the low frequency lines. As discrepancies were found with respect to the assignment of Ref.[2], we extended our studies of the vapour phase up to 3200 cm^{-1}. Finally we repeated the normal coordinate analysis using our data.

II. Experimental

A commercial sample of CH_3COCN from Fluka GmbH, Neu-Ulm, Germany, was distilled under vacuum, dried over P_2O_5, and then used for the experiments.

The far infrared spectra were run from 70–470 cm^{-1} with a Beckman FS 720 Michelson interferometer, equiped with a 3 m absorption cell[3]. The measurements were made at room temperature and at different pressures from 2 to 20 Torr. Each spectrum was calculated from six one-sided interferograms consisting of 1024 or 2048 points obtained with a sampling distance of 8 μ. The far infrared spectrum at two pressures is shown in Figure 1 d. Below ≈ 100 cm^{-1} the spectrum becomes increasingly unreliable due to noise.

The infrared spectra were recorded from 200 to 3200 cm^{-1} with a Perkin-Elmer 325 spectrometer at room temperature. The absorption cell was a multipass cell with chosen path lengths of 1.25 or 2.50 m. Figure 1 a – c presents some of the infrared spectra recorded. The liquid phase Raman spectra were measured at room temperature between 100 and 500 cm^{-1} with a Cary 82 spectrometer (Ar-laser: $\lambda = 4880$ Å, ≈ 1 W). The accuracies in the measurements are estimated to be ± 0.5 cm^{-1} for the gas phase and ± 1 cm^{-1} for the liquid phase.

III. Analysis of the Spectra and Results

The analysis presented in this paper is based on a r_0-structure[4] and C_s molecular symmetry. According to this symmetry the eighteen fundamental vibrations are classified as $12\,A' + 6\,A''$. The A' vibrations may exhibit more or less mixed A/B-type contours whereas the A'' vibrations are of C-type. The Raman bands of the latter species are expected to be depolarized.

The assignment of the fundamental vibrations was mainly based on the band contours, their inten-

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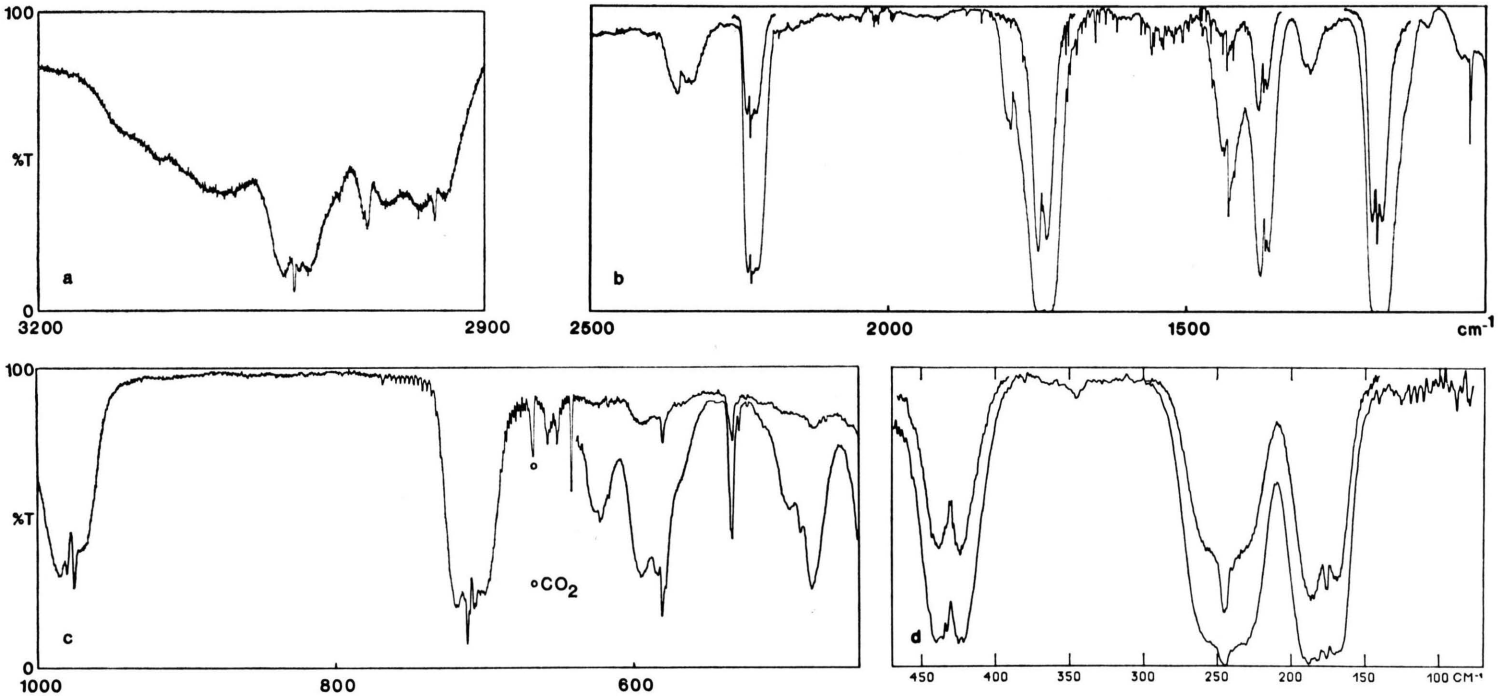

Fig. 1. Infrared spectra of gaseous CH_3COCN at room temperature. a) Pressure (p) $\sim$20 Torr, path length (l) $=$2.5 m, spectral slit width (Δ) $\sim$1 cm^{-1}. b) p $\sim$20 Torr and less, l=1.25 m, Δ=1.5$-$1 cm^{-1}. c) $p\sim$20 Torr and less, l=1.25 m, Δ=1$-$2 cm^{-1}. d) $p\sim$30 and = 2.0 Torr, l=3 m, Δ=1.2 and 0.6 cm^{-1}. The % transmission scale of the inserts is diplaced with respect to the main spectrum.

sities and comparison with similar compounds [5, 8]. Most of the fundamentals were assigned without difficulties since they are rather well predicted by group frequency arguments. Discrepancies with respect to the assignment of Ref. [2] exist in the region of the CH_3-stretching and in that of the lowest vibrational modes. A brief discussion particularly aimed at these points will follow.

In the CH_3-stretching region three bands are to be expected, two of A' and one of A'' symmetry. The A-type bands at 3027 cm^{-1} and 2932.5 cm^{-1} were assigned to the antisymmetric and symmetric methyl stretching respectively, whereas the C-type band at 2975.5 cm^{-1} was assigned to the other antisymmetric CH_3-stretching in accordance with the corresponding situation in acetone-d_3 [5]. The assignment of other fundamental vibrations above 600 cm^{-1} was rather straightforward and in agreement to that proposed by Sugiè and Kuchitsu [2]. Small differences in the frequencies are due to phase shifts.

Table 1. Observed vibrational frequencies, in cm^{-1}, for CH_3COCN in the vapour phase.

Assign.	Obs.		$P-Q$ [a]	$Q-R$ [b]
ν_1	3027	A, C_1	9.5	7.5
	3023.1	Q_2		
ν_{13}	2975.5	C, Q_1		
	2980.5	Q_2		
ν_2	2932.5	A, Q	6.5	10
$2\nu_7$	2345	B, min?	15	9
ν_3	2229	A, Q_1	10	6
	2225	Q_2		
ν_4	1740	A/B, Q	7.5	7
ν_5	1431.5	B, min?	overlapping	
ν_{14}	1428	C, Q		
ν_6	1368	A/B, Q	6	9
ν_7	1178	A, Q_1	8.5	8
	1181	Q_2		
ν_{15}	1026	C, Q_1		
	1024	Q_2		
	980	Q_2	~6	~9
ν_8	975.5	A, Q_1		
ν_9	712	A, Q_1	10.5	7.5
	707.5	Q_2		
—	658	C, Q		
—	651.5	C, Q		
—	642	C, Q		
—	623	C, Q		
ν_{10}	588.5	B, min?		6.5
—	581	C, Q_1		
	578	Q_2		
	537	Q_3		
	536	Q_2		
ν_{16}	535	C, Q_1		
	531	Q_4		
$2\nu_{17}$	489	A/B, Q	8.5	8.5
ν_{11}	431	B, min?	6	7
ν_{17}	245	C, Q		
ν_{12}	176	A/B, Q	6	10
ν_{18}	—			

[a] $P-Q$ is the frequency difference, in cm^{-1}, between the maximum of the P branch and the band center.

[b] $Q-R$ is defined analogously as above.

A quite different assignment results for the vibrations in the lowest region. The location of the CO-wagging is somewhat doubtful with the present information. The prediction from the normal coordinate calculation and intensity considerations pointed to the C-type band at 535 cm^{-1}. Further the C-type band at 245 cm^{-1} was assigned to the out-of-plane CCN-bending, while the B-type band at 176 cm^{-1} was unambigously attributed to the in-plane CCN-bending. The non-existing near degeneracy between these two bands appears clearly from the vapour phase spectrum of Fig. 1 d and from the liquid phase Raman spectrum considering the depolarization value ($\varrho = 0.75$) for the band at 253 cm^{-1}. The bands at 191 cm^{-1} and 253 cm^{-1} in the liquid phase correspond to those at 176 cm^{-1} and 245 cm^{-1} respectively in the vapour phase. The extremely weak series of bands around 120 cm^{-1} are probably due to transitions from levels of the CH_3-torsion. The complete assignment is given in Table 1.

To help the description of the normal vibrations, the prediction of frequencies, and the investigation of Ref. [1] a normal coordinate analysis was made, based on a simplified valence force field. The calculations were carried out following the Wilson FG matrix method [6]. Computer programs by Schachtschneider et al. [7] were used for the calculation of the *G*-matrix, solution of the vibrational secular equation, and least squares refinement of the force constants to the observed frequencies. No anharmonicity correction was made of the measured frequencies. The vibrational secular equation was factorized by the use of symmetry coordinates, see Table 2 and Figure 2. The *G*-matrix elements were calculated from the r_0-structure [4].

Several preliminary calculations were carried out with trial changes in the starting set of force constants, which were first estimated from ethyl cyanide [8], acetone [5], and other related molecules, Finally, by refining twelve force constants the experimental frequencies were reproduced with a standard deviation of 4.5 cm^{-1} or 0.8%. The final force constants are listed in Table 3, the experimental and

Table 2. Symmetry coordinates for CH_3COCN and their classification according to the C_s group. See also Figure 2.

A′	CH_3-antisym. stretch	$S_1 = 6^{-1/2}(2\,\Delta r_1 - \Delta r_2 - \Delta r_3)$
	CH_3-sym. stretch	$S_2 = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$
	CN-stretch	$S_3 = \Delta CN$
	CO-stretch	$S_4 = \Delta CO$
	CH_3-antisym. bend	$S_5 = 6^{-1/2}(2\,\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$
	CH_3-sym. bend	$S_6 = 6^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$
	C_1C_2-stretch	$S_7 = \Delta R$
	C_2C_3-stretch	$S_8 = \Delta R'$
	CH_3-in-plane rock	$S_9 = 6^{-1/2}(2\,\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$
	CCO-bend	$S_{10} = 2^{-1/2}(\Delta\delta_1 - \Delta\delta_2)$
	CCC-bend	$S_{11} = \Delta\omega$
	CCN-in-plane bend	$S_{12} = \Delta\Phi$
	Redundancy	$S_{13} = 6^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)$
	Redundancy	$S_{14} = 2^{-1/2}(\Delta\delta_1 + \Delta\delta_2)$
A″	CH_3-antisym. stretch	$S_{15} = 2^{-1/2}(\Delta r_2 - \Delta r_3)$
	CH_3-antisym. bend	$S_{16} = 2^{-1/2}(\Delta\alpha_2 - \Delta\alpha_3)$
	CH_3-out-of-plane rock	$S_{17} = 2^{-1/2}(\Delta\beta_2 - \Delta\beta_3)$
	CO-out-of-plane wag	$S_{18} = \Delta\Theta$
	CCN-out-of-plane bend	$S_{19} = \Delta\Phi'$
	CH_3-torsion	$S_{20} = \Delta\tau$

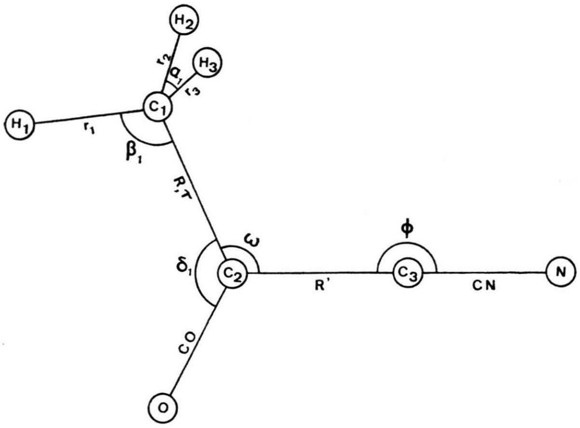

Fig. 2. Internal coordinates for CH_3COCN.

Table 3. Force constants for CH_3COCN obtained by the fit to the observed frequencies of Table 1. Quoted standard errors.

Force const. [a]	Int. cord. involved	
K_r	CH_1	5.00 ±0.02
K_r'	$CH_{2,3}$	4.75 [b]
K_R	C_1C_2	4.30 ±0.10
K_R'	C_2C_3	4.94 [c]
K_{CN}	CN	17.06 ±0.19
K_{CO}	CO	9.97 ±0.16
F_r	CH, CH	0.07 [d]
F_R	C_1C_2, C_2C_3	0.42 [d]
H_α	HCH	0.50 ±0.01
H_β	HCC	0.59 ±0.01
H_ω	CCC	1.37 ±0.10
H_δ	CCO	1.08 ±0.05
H_Φ	CCN	0.19 ±0.01
H_Θ	CO-wag	1.34 ±0.06
H_τ	CH_3 [e]	0.003 ±0.001
$F_{R\omega}$	CC, CCC	0.22 [d]
F_δ	C_1C_2O, C_3C_2O	0.28 [d]
F_β	HCC, HCC	−0.05 ±0.01
$F_{R\beta}$	CC, HCC	0.03 [d]

[a] Stretching force constants in mdyn·Å^{-1}, bending force constants in mdyn·Å·rad^{-2}, stretching-bending interaction force constants in mdyn·rad^{-1}.

[b] Held at a constant ratio of 0.95/1 with respect to K_r.

[c] Held at a constant ratio of 1.15/1 with respect to K_R.

[d] Held fixed.

[e] The torsional coordinate is defined as the sum of three trans torsions about the CC bond.

Table 4. Fundamental frequencies, in cm^{-1}, for CH_3COCN in the vapour phase and potential energy distribution. Frequencies are calculated with the force constants of Table 3.

Assign.		Obs.	Calc.	Approximate description [a]
A′	ν_1	3027	3036	100% CH_3-antisym. stretch
	ν_2	2932.5	2924	97% CH_3-sym. stretch
	ν_3	2229	2229	87% CN-stretch
	ν_4	1740	1740	75% CO-stretch
	ν_5	1431.5	1423	92% CH_3-antisym. bend
	ν_6	1368	1371	76% CH_3-sym. bend, 29% CC-stretch
	ν_7	1178	1173	44% CC-stretch, 24% CCO-bend, 23% CH_3-rock
	ν_8	975.5	974	67% CH_3-in-plane rock
	ν_9	712	716	65% CC-stretch
	ν_{10}	588.5	588	40% CCC-bend, 26% CCO-bend
	ν_{11}	431	434	92% CCO-bend
	ν_{12}	176	188	85% CCN-bend
A″	ν_{13}	2975.5	2968	100% CH_3-antisym. stretch
	ν_{14}	1428	1423	92% CH_3-antisym. bend
	ν_{15}	1026	1026	81% CH_3-rock
	ν_{16}	535	527	77% CO-wag
	ν_{17}	245	239	83% CCN-bend
	ν_{18}	—	120	97% CH_3-torsion

[a] Potential energy contributions below 15% are not reported.

calculated fundamental frequencies are presented in Table 4, together with the potential energy distribution associated to the symmetry coordinates.

In conclusion we think that the present work has provided an essential contribution to the RTV interaction analysis [1] and also a better understanding of the vibrational spectrum of acetyl cyanide. In this case the simplified valence force field has been a satisfactory basis for the calculation and description of the fundamental vibrations. A more complete study measuring frequencies of isotopic species is planned.

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