Rotation-Torsion-Vibration Interaction in Acetyl Cyanide: Normal and ^{15}N Isotopic Species

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The rotation — torsion — vibration interaction in the normal and ^{15}N isotopic species of Acetyl Cyanide is studied in the rotational spectrum of ground, first excited state of methyl torsion and first excited state of CCN in plane bending vibration. With respect to a previous work [1] a more detailed check of a model with five degrees of freedom, comprising three for the overall rotation and two for the two lowest vibrations was possible.

Potential parameters were fitted simultaneously to the splittings of the rotational transitions in the ground, excited torsional and excited vibrational states for the normal and ^{15}N isotopic species of the molecule. The coefficients V_3 and V_6 of the Fourier expansion of the hindering potential for the torsion and two interaction constants V_{3c}' and V_{3c}'' for the torsion and in plane CCN bending vibration were determined, apart from the harmonic force constant k_{2q} for the vibration, which is obtained from the measured infrared data of the normal species. Using these results, the (E-A) splittings of the rotational transitions could be nicely reproduced but not the absolute frequencies of the rotational transitions.

I. Introduction

In the analysis of the microwave spectrum of molecules containing an internally rotating top, one usually uses a model with three rotational degrees of freedom, and one torsional degree of freedom for the top [2]. This is essentially a rigid frame-rigid top (RF-RT) model. However, in the case of molecules possessing a vibrational mode with frequency comparable to the torsional frequency of the top, remarkable departures from the predictions of the RF-RT model are observed. Specifically, the RF-RT model does not consider vibrations. If vibrations are not influenced by torsion the rotational splittings of vibrational excited states should be that of the torsional ground state. For the case of the present $CH_3COC^{15}N$ molecule, as with its normal species [1] and with a number of other molecules too [3–7], the rotational splittings in the excited vibrational state have been found to differ significantly from those observed in the ground state. This clearly shows the limitation of the RF-RT model for such cases and demanded the consideration of an interaction between rotation — torsion — and other vibrations. In principle this is possible and adequate molecular models have been developed by Kirtman [8] and Quade [9], in which the interaction between rotation torsion and all other vibrations are considered. Such a theoretical interpretation, though complete in itself, is not practical for use due to the following two reasons. Firstly it needs the experimental data for the rotational spectra of the molecule in all the excited vibrational states and probably also in the excited combination states, which is very rarely possible to get. Secondly, the amount of computer time needed for such an analysis becomes unreasonably large as the effect of more and more vibrations is included. For this reason Dreizler and coworker [10, 11] developed a model *, in which, apart from the three rotational and one torsional (methyl) degree of freedom, only one more vibrational degree of freedom is added, which lies closest to the torsion in energy. For the present molecule, this is the in plane CCN bending vibration observed at ~ 176 cm^{-1}. In what follows, we present the observation of the rotational spectra of $CH_3COC^{15}N$ molecule in the first excited torsional (v_α, $v_q = 1{,}0$) and first excited CCN in plane bending vibrational (v_α, $v_q = 0{,}1$) states and its interpretation in terms of the RTV model. The spectra in the corresponding ground state and its interpretation in terms of the RF-RT model have previously been reported [12].

We have also included in this publication, the interpretation of the data for the normal species of the molecule for two reasons. Firstly, in the work of Ref. [1], a small mistake was found in the input data for the structural parameters of the molecule as borrowed from the work of Krisher and Wilson

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* Henceforth to be referred as RTV model.

[13]. It was thought desirable to correct it. Secondly, as a critical check of the theory and analysis of this kind, it could be of some interest to see how reasonably one can reproduce the internal rotation splittings for both the isotopic species of the molecule with the same set of potential parameters, as was done for CH_3CH_2CN [4].

II. Experimental

The experimental details concerning the preparation of the sample and other conditions have already been given in a previous publication [12]. For the unambigeous assignment of the E-lines of the torsional excited state spectrum, which are split from their corresponding A-lines from 15 MHz to as large as 180 MHz, frequent use was made of the radio frequency — microwave double resonance (RF-MW-DR) and microwave-microwave double resonance (MW-MW-DR) experiments. The corresponding instruments have been described elsewhere [14, 15].

III. Excited State Spectra

Most of the ground state transitions were found to be accompanied by satellite doublets (within about ± 150 MHz) occuring due to the transitions in the excited states of the molecule. Figure 1 shows a typical example furnished by the $2_{02}-1_{01}$ transition. The two most intense satellite spectra should correspond to the transitions in the two lowest frequency vibrational states of the molecule. The recent infrared and Raman findings on the normal species of this molecule and the subsequent normal coordinate analysis made it clear that these vibrations should be methyl torsion, and in plane bending of the CCN group. Assignment of the satellite spectrum to the proper vibrational state is based upon the following considerations.

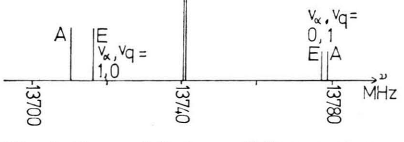

Fig. 1. General feature of the spectrum of the molecule in the ground, first excited torsional (v_α, $v_q = 1{,}0$) and first excited vibrational (v_α, $v_q = 0{,}1$) state as demonstrated by the $2_{02}-1_{01}$ transition of the ^{15}N isotopic species.

i) Measurement of the relative intensity in some favourable cases. This should approximately correspond to the measured infrared frequencies.

ii) Change of the observed inertia defect with respect to the corresponding ground state value. Herschbach and Laurie [16] have shown that for a molecule with a plane of symmetry, the inertia defect for an inplane excited vibrational state should increase as compared to that for the ground state. The reverse should, however, be the case for an out of plane excited vibrational state.

iii) Consideration of E-A splittings: Our past experience shows that the E-A splittings of the rotational transitions increases by at least an order of magnitude in the excited torsional state, whereas that in other excited vibrational states, it remains of the same order of magnitude.

a) CH_3 Torsion Spectrum

The lines of the strongest satellite spectra were assigned to the excited CH_3 torsion, as this was the lowest fundamental vibration in the molecule. Relative intensity measurements of the rotational lines (in some preferable cases) agree with this assignment. Also, the decrease in the inertia defect, compared to that in the ground state is in agreement with the conclusions of Herschbach and Laurie [16] for an out of plane vibration. Further support comes from the reasonable reproducibility of the spectrum in terms of the RTV model.

The rotational spectrum consists of E-A doublets, whose splittings range from 15 MHz to sometimes as 180 MHz. The correct assignment of the A transitions was established by a rigid rotor fit. Later, while assigning the corresponding E transitions, these were also confirmed by MW-MW-DR experiments. The assignment of E transitions pre-

Pump	Signal
$4_{13}-4_{04}$	$4_{13}-3_{12}$
	$4_{04}-3_{13}$
	$4_{04}-3_{03}$
	$5_{14}-4_{13}$
	$5_{15}-4_{04}$*
	$5_{05}-4_{04}$
$2_{02}-1_{01}$	$3_{13}-2_{02}$
$3_{03}-2_{12}$	$4_{14}-3_{03}$

Table 1. Details of the microwave — microwave double resonance connections used for the assignment of the excited torsional and excited CCN in plane bending vibrational state spectra (both A and E transitions).

* This double resonance experiment was performed only for the excited torsional state spectrum (A and E species).

Table 2. Observed and calculated rotational transitions for the excited torsional state spectrum (v_α, $v_q = 1, 0$). All frequencies are in MHz.

Transition $J_{K_-' K_+} - J'_{K_-' K_+'}$	Torsional species	Observed frequency	Calculated* frequency	Deviation (cal.-obs.)
$2_{12} - 1_{01}$	A	18942.21	18942.110	− 0.100
	E	18926.34		
$2_{12} - 1_{11}$	A	12765.07	12765.976	+ 0.906
	E	—[a]		
$2_{02} - 1_{01}$	A	13710.90[b]	13710.812	− 0.088
	E	13716.55[b]		
$3_{12} - 3_{03}$	A	10474.02	10473.942	− 0.078
	E	10610.71		
$3_{21} - 2_{20}$	A	21258.37	21258.493	+ 0.123
	E	—[a]		
$3_{22} - 2_{21}$	A	20758.10	20758.198	+ 0.098
	E	—[a]		
$3_{13} - 2_{12}$	A	19073.22	19073.237	+ 0.017
	E	19107.49		
$3_{13} - 2_{02}$	A	24304.71[b]	24304.535	− 0.175
	E	24316.41[b]		
$3_{03} - 2_{12}$	A	15026.63[b]	15026.605	− 0.025
	E	15062.76[b]		
$3_{03} - 2_{02}$	A	20257.95	20257.903	− 0.047
	E	20271.80		
$4_{22} - 4_{13}$	A	16856.87	16856.876	+ 0.006
	E	—[a]		
$4_{13} - 4_{04}$	A	13516.20[b]	13516.181	− 0.019
	E	13668.63[b]		
$4_{13} - 3_{12}$	A	29536.48[b]	29536.433	− 0.047
	E	29572.61[b]		
$4_{14} - 3_{13}$	A	25302.34	25302.349	+ 0.009
	E	25325.31		
$4_{14} - 3_{03}$	A	29349.10[b]	29348.981	− 0.119
	E	29369.81[b]		
$4_{04} - 3_{13}$	A	22447.62[b]	22447.561	− 0.059
	E	22470.02[b]		
$4_{04} - 3_{03}$	A	26494.18	26494.193	+ 0.013
	E	26514.53		
$5_{23} - 5_{14}$	A	16697.52	16697.754	+ 0.234
	E	—[a]		
$5_{14} - 5_{05}$	A	17680.03	17679.985	− 0.045
	E	17850.58		
$5_{14} - 4_{13}$	A	36614.08[b]	36614.043	− 0.037
	E	36654.43[b]		
$5_{15} - 4_{14}$	A	31446.11	31446.146	+ 0.036
	E	31466.09		
$5_{15} - 4_{04}$	A	34301.03[b]	34300.935	− 0.095
	E	34321.36[b]		
$5_{05} - 4_{14}$	A	29595.40	29595.452	0.052
	E	29617.33		
$5_{05} - 4_{04}$	A	32450.32[b]	32450.240	− 0.080
	E	32472.60[b]		
			RMS Deviation	0.204

* Calculated with the help of rotational constants of Table 3.

[a] Could not be unambigeously assigned. Not measured.

[b] Confirmed by MW-MW-DR experiments.

Table 3. Rotational constants for the excited torsional state (v_α, $v_q = 1, 0$) spectra, A species, derived from a rigid rotor model.

A (MHz)	10172.244
B (MHz)	3996.111
C (MHz)	2923.288
I_a (amu Å^2)[a]	49.68186
I_b (amu Å^2)[a]	126.4670
I_c (amu Å^2)[a]	172.8793
$I_c - I_a - I_b$ (amu Å^2)	− 3.26956
RMS Deviation (MHz)	0.204

[a] Conversion factor $5.05376 \cdot 10^5$ MHz · amu Å^2, Mass scale ^{12}C.

sented difficulty, because within the expected splitting range many candidate lines were often found. Their assignment on the basis of Stark effect was difficult as the E transitions in the excited torsional state are expected to show a different Stark behaviour (strong linear contribution to the Stark effect). However, they were quickly assigned with the help of MW-MW-DR experiments. For this purpose, both the signal and the pump frequencies had to be located by a double search procedure. For getting an idea of the correct direction of change for the pump, the asymmetric shape of the signal transition was also of much help [17]. Table 1 gives the details of the MW-MW-DR experiments performed. The measured transitions, including those in which the *E* components of the doublet could not be unambigeously assigned are listed in Table 2. The effective values of the rotational constants are determined by fitting the observed frequencies (A species) to a rigid rotor model. The rotational constants, moments of inertia and the inertia defect are given in Table 3.

b) *CCN in Plane Bending Spectrum*

The second most intense satellite spectrum was assigned to the excited CCN in plane bending vibrational state. The relative intensities of the rotational transitions as compared to those in the ground vibrational state confirm its frequency to be ~ 176 cm^{-1}, as observed in the vapour phase infrared measurements for the normal species. The increase in the inertia defect as compared to that in the ground state also confirm that it corresponds to an excited in plane vibrational state. The rotational spectrum shows E-A doublets, whose seperations are different (sometimes up to 80%) from the corresponding ones in the ground state. The assignment of the A transitions was confirmed by a rigid rotor fit. Although all the A transitions were accompanied

Table 4. Observed and calculated rotational transitions for the excited CCN in plane bending vibrational state spectrum (v_α, $v_q = 0, 1$). All frequencies are in MHz.

Transition $J_{K_- K_+} - J'_{K_-' K_+'}$	Torsional species	Observed frequency	Calculated frequency*	Deviation (cal.-obs.)
$2_{11} - 1_{10}$	A	15014.88	15014.881	+ 0.001
	E	15012.91		
$2_{02} - 1_{01}$	A	13778.71[a]	13778.628	− 0.082
	E	13777.58[a]		
$3_{12} - 3_{03}$	A	10554.83	10554.479	− 0.351
	E	10552.08		
$3_{21} - 2_{20}$	A	21399.26	21399.610	+ 0.350
	E	21392.73		
$3_{22} - 2_{21}$	A	20870.74	20871.052	+ 0.312
	E	20872.31		
$3_{13} - 2_{02}$	A	24302.85[a]	24302.401	− 0.449
	E	24302.31[a]		
$3_{03} - 2_{12}$	A	15180.37[a]	15179.882	− 0.448
	E	15179.63[a]		
$3_{03} - 2_{02}$	A	20342.59	20342.495	− 0.095
	E	20341.30		
$4_{22} - 4_{13}$	A	16730.61	16730.192	− 0.418
	E	—[b]		
$4_{13} - 4_{04}$	A	13698.22[a]	13698.051	− 0.169
	E	13693.30[a]		
$4_{13} - 3_{12}$	A	29725.19[a]	29725.241	+ 0.051
	E	29721.82[a]		
$4_{04} - 3_{12}$	A	22621.68[a]	22621.762	+ 0.082
	E	22619.54[a]		
$4_{04} - 3_{03}$	A	26581.75[a]	26581.669	− 0.081
	E	26580.55[a]		
$5_{23} - 5_{14}$	A	16629.71	16629.921	+ 0.211
	E	16628.61		
$5_{14} - 5_{05}$	A	17993.75	17993.801	+ 0.051
	E	17985.96		
$5_{14} - 4_{13}$	A	36829.97[a]	36830.160	+ 0.190
	E	36826.15[a]		
$5_{05} - 4_{04}$	A	32534.39[a]	32534.410	+ 0.020
	E	32533.60[a]		
			RMS Deviation 0.254	

* Calculated with the help of the rotational constants of Table 5.

[a] Confirmed by MW-MW-DR experiments.

[b] Unresolved.

by the corresponding E lines at a seperation of 1 to 8 MHz, and could readily be assigned, we preferred to confirm them by MW-MW-DR experiments. A list of the measured doublets are given in Table 4. The effective values of the rotational constants are determined by fitting the observed frequencies (A species) to a rigid rotor. The rotational constants, moments of inertia and the inertia defect are given in Table 5.

Table 5. Rotational constants for the excited CCN in plane bending vibrational state ($v_\alpha, v_q = 0, 1$) spectra, A species derived from a rigid rotor model.

A (MHz)	10156.983
B (MHz)	4028.932
C (MHz)	2928.086
I_a (amu Å^2)[a]	49.75651
I_b (amu Å^2)[a]	125.4367
I_c (amu Å^2)[a]	172.5960
$I_c - I_a - I_b$ (amu Å^2)	− 2.59719
RMS Deviation (MHz)	0.254

[a] Conversion factor $5.05376 \cdot 10^5$ MHz · amu Å^2, Mass scale ^{12}C.

IV. Hamiltonian

The basic Hamiltonian of the RTV model has been formulated with the following simplifying conditions.

i) The internal rotor (top) has at least C_3 symmetry about its axis of rotation.

ii) The configuration of the internal rotor is not affected by the vibration, i.e. it is considered to be rigid.

iii) The molecule has a plane of symmetry (designated as y-z plane), which remains unchanged during the vibration.

iv) For formulating the Hamiltonian, a molecule fixed coordinate system, obeying the Eckart condition [18] is used. With this choice of the axes system no net angular momentum is produced by the vibration and the explicit Coriolis interaction between rotation and vibration is transferred to other terms.

With these assumptions the Hamiltonian operator can be written as:

$$H = H_\mathrm{R} + H_\mathrm{T} + H_\mathrm{V} + H_\mathrm{RT} + H_\mathrm{TV} + H_\mathrm{RV} + H_\mathrm{RTV} \,. \tag{1}$$

The details are given in Ref. [1] (formula 2). The explicit expression for the potential energy in (1) is

$$\begin{aligned} V(\alpha, q) = {} & (1/2)\, V_3 (1 - \cos 3\alpha) \\ & + (1/2)\, V_6 (1 - \cos 6\alpha) \\ & + (1/2)\, k_{2q} q^2 + (1/2)\, k_{3q} q^3 + (1/2)\, k_{4q} q^4 \\ & + V_{3c}' q (1 - \cos 3\alpha) + V_{3c}'' q^2 (1 - \cos 3\alpha) \,. \end{aligned} \tag{2}$$

It contains a three and a six fold term for the pure torsion (V_3, V_6), harmonic, cubic and quartic force constants for the vibration (k_{2q}, k_{3q}, k_{4q}) and two potential coupling terms (V_{3c}' and V_{3c}'') for the potential interaction between the torsion and vibration. The potential coupling terms represent cubic and quartic force constants in the limit of small amplitudes of the torsional angle.

A word should be added here about the three simplifying assumptions mentioned in the beginning of this section, as to their validity for the present molecules.

Our recent structure determination work [19] shows a small asymmetry for the methyl top ($C-H_{sym}$ and $C-H_{asym}$ bond lengths differ by 0.008 Å and $\sphericalangle H_{asym}-C-H_{asym}$ and $\sphericalangle H_{sym}-C-H_{asym}$ differ by 6°) both differences are beyond the corresponding errors projected from the uncertainty of measurements. The effect of such a small asymmetry on the internal rotation splitting of the rotational transitions in the ground and excited vibrational states is not precisely known. However, we feel that this asymmetry is small enough to be neglected. Hence all calculations will be done with the structural parameters of Ref. [19] (Table 9 column γ) with the modification to obtain a C_3 symmetric methyl group, viz. by taking $C-H = 1.086$ Å and $\sphericalangle C-C-H = 110.2°$. With this structure the moment of inertia of the top agrees with that obtained for the asymmetric methyl group ($I_\alpha = 3.1407$ amu Å^2).

ii) The infrared and Raman measurements of Heise et al. [20] and the corresponding normal coordinate analysis shows that after the torsion, the lowest energy vibrational mode, in which the hydrogen atoms are involved is ν_8 (CH_3 in plane rock), which lies at about 975 cm^{-1}. As this is considerably higher than the low frequency vibrations considered here, the methyl group can, within our approximations be treated as effectively rigid.

iii) The structure determination does show that the molecule has a plane of symmetry. Also, as the considered low frequency vibration is a mixture of two in plane bending motions (CCN and CCC bending), the symmetry plane is unchanged during the vibration.

V. Analysis of the Spectrum

The interpretation of the spectrum follows with a computer program* in which the Hamiltonian operator (1) is handled in a way detailed in Ref. [1].

As the available experimental information is not sufficient to determine all the molecular constants of Hamiltonian (1), we fixed the constants of the kinetic part as described in Section VI. In the potential part of (1), some of the potential parameters were determined from the infrared spectra and the others were fitted to reproduce the observed spectra (see Section VII). Possible inaccuracies in the numerical handling of the Hamiltonian were eliminated or reduced to a reasonable extent throughout the calculations. The number of the basis functions in the different steps of diagonalization procedure was established by successive truncation of the matrices. In the present case the following number of functions have been found to be sufficient to give the desired accuracy of 10 kHz for the calculation of E-A splitting of the rotational transitions:

24 $U_m(\alpha)$
6 $U_{v_\alpha\sigma}(\alpha)$
5 $H_{v_p}(q)$
18 $\Phi_{v_\alpha\sigma,\, v_q}(\alpha, q)$.

VI. Kinetic Coefficients

For the numerical treatment of the problem, the q dependent coefficients of the kinetic part of the Hamiltonian are expanded in power series of q up to the second order

$$Y = Y_0 + Y' q + Y'' q^2 \qquad (3)$$

where Y stands for A, B, C, D_{yz}, Q_y, Q_z, F, M, and W (see Ref. [1]). These expansion coefficients are molecular constants, depending upon atomic masses, molecular structure and the nature of the vibrational mode.

For calculating these kinetic coefficients of the Hamiltonian, a computer program ANMA5.F4 (Author: U. Andresen and H. Mäder) was available, which needed the following informations as the input parameters

i) r_e-structure of the molecule,
ii) complete description of the mode of considered vibration,
iii) maximum vibrational displacement q_{max} to be used for the determination of the Y', Y'' parameters of Equation (3).

In place of r_e-structure, we have used the r_s-structure of the molecule recently determined by us [19]. This structure was slightly modified as described before.

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* Programs MRTVD1.F4 and MRTVD4.F4 written by H. Mäder.

To determine the mode of the considered vibration, we have borrowed information from the infrared and Raman studies of the normal species of the molecule [20] and its subsequent normal coordinate analysis in the harmonic approximation. From this study it was concluded that the considered vibration at ~ 176 cm^{-1} is mainly a mixture of CCN and CCC angle deformation in the ratio 10 : 1 and with the same phase (see Fig. 2, Ref. [1]). The vibrational coordinate q was thus chosen to be the deviation of the $\sphericalangle$ CCN from equilibrium (180°) and it is defined to be positive for a displacement of the N atom towards the methyl group.

The maximum vibrational displacement $q_{\max}$ was taken to be the same as in Ref. [1] (12°).

With the input parameters chosen in the above mentioned way, the components of the generalized tensor of inertia [Eq. (17) of Ref. [11]] and the coefficients of the kinetic part of Hamiltonian (1) were calculated for eleven values of q varying from $q_{\max} = 12°$ to $-q_{\max} = -12°$ in steps of 2.4° and fitted to a fifth order polynomial. The expansion coefficients up to the second order are mentioned in Table 6 for the CH_3COCN and $CH_3COC^{15}N$ molecules.

VII. Potential Coefficients

The number of potential and potential coupling parameters are also too many to be all fitted to the measured spectra. Hence we used the following procedure. For the normal species of the molecule, the force constant k_{2q} is determined from the measured CCN in plane deformation frequency (176 cm^{-1}) by the relation

$$k_{2q} = \omega^2 / M_0 \tag{4}$$

where M_0 is part of Eq. (1) and is mentioned in Table 6. It has been seen that neither M', M'', F', F'', W' and W'' nor the potential coefficients V_{3c}', V_{3c}'' shift the energy of the vibrational level by more than 0.1 cm^{-1}, a value which is much less than the experimental uncertainty ($\pm$ 0.5 cm^{-1}). Thus Eq. (4) seems to be a good method for calculating k_{2q}.

For the ^{15}N species of the molecule, same value of k_{2q} was used. It has been concluded elsewhere [4] that this is correct within the experimental uncertainty of the measured vibrational frequencies.

Table 6. Components of generalized tensor of inertia [a] and kinetic coefficients of Hamiltonian (1) [b]. Conversion factor $5.05376 \cdot 10^5$ amu Å^2 · MHz, Mass scale ^{12}C.

Parameter	In units of	CH_3COCN [c]	$CH_3COC^{15}N$
I_{zz}^0	amu Å^2	49.378178	49.385719
I_{zz}'	amu Å^2 rad^{-1}	2.252366	2.253142
I_{zz}''	amu Å^2 rad^{-2}	3.897451	3.923403
I_{yy}^0	amu Å^2	121.743663	126.206235
I_{yy}'	amu Å^2 rad^{-1}	$-$ 3.669559	$-$ 3.765740
I_{yy}''	amu Å^2 rad^{-2}	$-$ 22.730985	$-$ 23.807047
I_{xx}^0	amu Å^2	167.981105	172.451218
I_{xx}'	amu Å^2 rad^{-1}	$-$ 1.417193	$-$ 1.512598
I_{xx}''	amu Å^2 rad^{-2}	$-$ 18.833535	$-$ 19.883644
I_{yz}'	amu Å^2 rad^{-1}	14.174940	14.674978
I_{yz}''	amu Å^2 rad^{-2}	$-$ 1.338679	$-$ 1.313774
λ_z^0		$-$ 0.487237	$-$ 0.485087
λ_z'	rad^{-1}	0.110965	0.135645
λ_z''	rad^{-2}	0.003727	0.004059
λ_y^0		$-$ 0.873270	$-$ 0.874466
λ_y'	rad^{-1}	$-$ 0.073071	$-$ 0.075246
λ_y''	rad^{-2}	0.010798	0.011506
$(G^{-1})^0$	amu Å^2 rad^{-2}	6.139548	6.311770
$(G^{-1})'$	amu Å^2 rad^{-3}	0.234030	0.253773
$(G^{-1})''$	amu Å^2 rad^{-4}	3.216138	3.448429
I_α	amu Å^2	3.1407	3.1407
A^0	GHz	10.394918	10.391769
A'	GHz rad^{-1}	$-$ 0.636224	$-$ 0.638341
A''	GHz rad^{-2}	$-$ 0.408273	$-$ 0.400535
B^0	GHz	4.235758	4.083251
B'	GHz rad^{-1}	0.116295	0.110822
B''	GHz rad^{-2}	0.964452	0.941812
C^0	GHz	3.008529	2.930545
C'	GHz rad^{-1}	0.025382	0.025704
C''	GHz rad^{-2}	0.337523	0.338119
D_{yz}^0	GHz	0.116392	0.111827
D_{yz}'	GHz rad^{-1}	$-$ 1.259297	$-$ 1.256514
D_{yz}''	GHz rad^{-2}	0.163136	0.156908
Q_z^0	GHz	$-$ 5.166436	$-$ 5.138705
Q_z'	GHz rad^{-1}	2.762560	2.809611
Q_z''	GHz rad^{-2}	0.105164	0.108517
Q_y^0	GHz	$-$ 3.755669	$-$ 3.624908
Q_y'	GHz rad^{-1}	0.217751	0.220531
Q_y''	GHz rad^{-2}	$-$ 1.048962	$-$ 1.031039
F^0	GHz	166.707031	166.572618
F'	GHz rad^{-1}	$-$ 1.938367	$-$ 1.980036
F''	GHz rad^{-2}	1.150856	1.150911
M^0	GHz rad^{-2}	164.629636	160.137554
M'	GHz rad	$-$ 6.275387	$-$ 6.438495
M''	GHz	$-$ 85.965758	$-$ 87.194716
W'	GHz rad^{-1}	6.097559	6.517151
W''	GHz rad^{-2}	95.333611	99.427113

[a] See Eq. (17) of Ref. [11].

[b] I^1 representation ($a - z$, $b - y$, $c - x$) has been used.

[c] The numbers mentioned here for $CH_3COC^{14}N$ differ from those of Ref. [2]. This is because a slightly different structure (as determined in Ref. [19]) has been used here.

The determination of higher order force constants, viz. k_{3q}, k_{4q} involve more infrared data than are presently available (from hot band and combination band measurements). Hence they could not be determined and set arbitrarily as zero. The remaining four potential parameters, viz. V_3, V_6, V_{3c}' and V_{3c}'' were fitted to the E-A splittings of the rota-

Table 7. Observed and calculated (E-A) splittings of the rotational transitions of $CH_3COC^{14}N$ in the ground, first excited torsional and first excited vibrational states.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	$(\nu_E-\nu_A)_{obs}$* (MHz)	$(\nu_E-\nu_A)_{calc}$** (MHz)	|Deviat.| (MHz)
Ground state $v_\alpha, v_q = 0, 0$			
$2_{21}-1_{10}$	− 5.76	− 5.78	0.02
$2_{12}-1_{01}$	− 0.62	− 0.69	0.07
$3_{21}-2_{20}$	− 4.13	− 4.24	0.11
$3_{22}-2_{21}$	1.92	1.89	0.03
$3_{13}-2_{12}$	− 0.43	− 0.45	0.02
$3_{03}-2_{02}$	− 0.66	− 0.74	0.08
$3_{13}-2_{02}$	− 0.48	− 0.51	0.03
$3_{30}-3_{21}$	26.66	26.97	0.31
$3_{31}-3_{22}$	32.00	− 31.59	0.41
$4_{31}-3_{30}$	− 18.67	− 18.67	0.00
$4_{32}-3_{31}$	15.89	15.64	0.25
$4_{13}-3_{12}$	− 1.83	− 1.90	0.07
$4_{04}-3_{03}$	− 0.63	− 0.71	0.08
$4_{04}-3_{13}$	− 0.82	− 0.94	0.12
$4_{31}-4_{22}$	10.17	10.75	0.58
$4_{32}-4_{23}$	− 15.37	− 15.13	0.24
$5_{14}-4_{23}$	− 1.66	− 2.01	0.35
First excited torsional state $v_\alpha, v_q = 1, 0$			
$2_{02}-1_{01}$	6.18	5.44	0.74
$2_{12}-1_{01}$	− 13.34	− 14.72	1.38
$2_{02}-1_{11}$	107.46	106.67	0.79
$2_{11}-2_{02}$	130.10	129.55	0.55
$3_{13}-2_{12}$	33.81	33.41	0.40
$3_{03}-2_{02}$	15.09	14.69	0.40
$3_{13}-2_{02}$	13.83	13.23	0.60
$3_{03}-2_{12}$	34.58	34.87	0.29
$3_{12}-3_{03}$	140.43	141.63	0.20
$4_{14}-3_{13}$	23.21	23.13	0.07
$4_{04}-3_{03}$	21.69	21.71	0.02
$4_{14}-3_{03}$	21.95	21.67	0.28
$4_{04}-3_{13}$	22.98	23.17	0.19
$5_{15}-4_{14}$	20.76	20.83	0.07
$5_{05}-4_{04}$	23.05	23.29	0.24
$5_{15}-4_{04}$	20.98	20.79	0.19
$5_{05}-4_{14}$	22.81	23.33	0.52
First excited vibrational state $v_\alpha, v_q = 0, 1$			
$2_{02}\quad 1_{01}$	− 1.13	− 0.99	0.14
$2_{12}-1_{01}$	− 0.90	− 0.90	0.00
$2_{11}-2_{02}$	− 1.11	− 1.37	0.26
$3_{12}-2_{11}$	− 3.07	− 2.43	0.64
$3_{13}-2_{12}$	− 0.88	− 0.71	0.17
$3_{03}-2_{02}$	− 1.43	− 1.16	0.27
$3_{13}-2_{02}$	− 0.53	− 0.61	0.08
$3_{03}-2_{12}$	− 1.76	− 1.26	0.50
$3_{12}-3_{03}$	− 2.98	− 2.64	0.34
$4_{14}-3_{13}$	− 1.02	− 0.85	0.17
$4_{04}-3_{03}$	− 1.31	− 1.08	0.23
$4_{04}-3_{13}$	− 2.17	− 1.63	0.54

* Observed (E-A) splittings are from Ref. [1].

** Calculated by using model Hamiltonian (Eq. 1) and and the constants of Tables 6 and 9 (column III).

Table 8. Observed and calculated (E-A) splittings of the rotational transitions of $CH_3COC^{15}N$ in the ground, first excited torsional and first excited vibrational states.

Transition $J_{K_-K_+}-J'_{K_-'K_+'}$	$(\nu_E-\nu_A)_{obs}$ (MHz)	$(\nu_E-\nu_A)_{calc}$* (MHz)	|Deviat.| (MHz)
Ground state $v_\alpha, v_q = 0, 0$**			
$2_{11}-1_{10}$	− 1.01	− 1.04	0.03
$2_{02}-1_{01}$	− 0.55	− 0.58	0.03
$2_{12}-1_{01}$	− 0.72	− 0.68	0.04
$2_{20}-2_{11}$	2.79	3.00	0.21
$2_{21}-2_{12}$	− 6.13	− 6.04	0.09
$2_{11}-2_{02}$	− 1.02	− 0.96	0.06
$3_{21}-2_{20}$	− 4.37	− 4.48	0.11
$3_{22}-2_{21}$	2.20	2.32	0.12
$3_{03}-2_{02}$	− 0.67	− 0.71	0.04
$3_{13}-2_{02}$	− 0.60	− 0.51	0.09
$3_{03}-2_{12}$	− 0.50	− 0.61	0.11
$3_{12}-3_{03}$	− 1.67	− 1.67	0.00
$4_{14}-3_{13}$	− 0.44	− 0.51	0.07
$4_{04}-3_{13}$	− 0.76	− 0.89	0.13
$4_{22}-4_{13}$	− 0.83	− 0.63	0.20
$4_{13}-4_{04}$	− 2.71	− 2.75	0.04
$5_{23}-5_{14}$	− 1.31	− 1.14	0.17
$5_{14}-5_{05}$	− 4.07	− 4.20	0.13
First excited torsional state $v_\alpha, v_q = 1, 0$			
$2_{02}-1_{01}$	5.65	4.98	0.67
$3_{13}-2_{12}$	34.27	33.69	0.58
$3_{03}-2_{02}$	13.85	13.36	0.49
$3_{13}-2_{02}$	11.70	11.04	0.66
$3_{03}-2_{12}$	36.13	36.01	0.12
$3_{12}-3_{03}$	136.69	137.89	1.20
$4_{13}-3_{12}$	36.12	36.11	0.01
$4_{14}-3_{13}$	22.97	22.71	0.26
$4_{04}-3_{03}$	20.35	20.29	0.06
$4_{14}-3_{03}$	20.71	20.39	0.32
$4_{04}-3_{13}$	22.40	22.61	0.21
$4_{13}-4_{04}$	152.43	153.71	1.28
$5_{14}-4_{13}$	40.35	39.52	0.83
$5_{15}-4_{14}$	19.98	20.16	0.18
$5_{05}-4_{04}$	22.28	22.44	0.16
$5_{15}-4_{04}$	20.34	20.26	0.08
$5_{05}-4_{14}$	21.93	22.34	0.41
$5_{14}-5_{05}$	170.56	170.79	0.23
First excited vibrational state $v_\alpha, v_q = 0,1$			
$2_{11}-1_{10}$	− 1.97	− 1.60	0.37
$2_{02}-1_{01}$	− 1.13	− 0.90	0.23
$3_{21}-2_{20}$	− 6.52	− 7.18	0.61
$3_{03}-2_{02}$	− 1.29	− 1.07	0.22
$3_{13}-2_{02}$	− 0.54	− 0.58	0.04
$3_{03}-2_{12}$	− 0.74	− 1.12	0.38
$3_{12}-3_{03}$	− 2.75	− 2.36	0.39
$4_{13}-3_{12}$	− 3.37	− 2.74	0.37
$4_{04}-3_{03}$	− 2.14	− 2.02	0.12
$4_{14}-3_{03}$	− 1.21	− 1.29	0.08
$4_{13}-4_{04}$	− 4.93	− 4.08	0.85
$5_{14}-4_{13}$	− 3.82	− 3.14	0.68
$5_{05}-4_{04}$	− 0.79	− 0.86	0.07
$5_{23}-5_{14}$	− 1.10	− 1.29	0.19
$5_{14}-5_{05}$	− 7.80	− 6.36	1.44

* Calculated by using model Hamiltonian (Eq. (1)) and the constants of Tables 6 and 9 (column III).

** The ground state measured splittings are from Ref. [12].

Table 9. Potential parameters of Hamiltonian (1) determined by a least square fit of the observed (E-A) splittings of the rotational transitions in the v_α, v_q = (0, 0), (1, 0) and (0, 1) states[a].

		I[d]	II[e]	III[f]	IV[g]	V[h,i]
V_3	GHz	12567 ± 12	12588 ± 14	12563 ± 7	12566 ± 168	12689 ± 42
	cal mol^{-1}[b]	1198 ± 1	1200 ± 1	1198.0 ± 0.6	1207 ± 16	1210 ± 4
V_6	GHz	−138 ± 15	−65 ± 73	−141 ± 14		
	cal mol^{-1}	− 13 ± 1	− 6 ± 7	− 13 ± 1		
V_{3c}'	GHz rad^{-1}	3249 ± 196	2760 ± 133	2780 ± 76		
	cal mol^{-1} rad^{-1}	309 ± 18	263 ± 13	265 ± 7		
V_{3c}''	GHz rad^{-2}	5915 ± 579	4709 ± 499	5399 ± 285		
	cal mol^{-1} rad^{-2}	564 ± 55	449 ± 47	514 ± 27		
k_{2q}	GHz rad^{-2}	169084	169084	169084		
	cal mol^{-1} rad^{-2}	16124	16124	16124		
k_{3q}	GHz rad^{-3}	0[c]	0[c]	0[c]		
k_{4q}	GHz rad^{-4}	0[c]	0[c]	0[c]		
RMS deviation of the fitted splittings (in MHz)		0.387	0.331	0.312	0.192	0.170
Percentage deviation (in MHz)		1.1	0.8	0.7	1.8	1.9

[a] Quoted uncertainties are standard errors.
[b] Conversion factor 1 GHz = 0.09536 cal mol^{-1}.
[c] Assumed (see text).
[d] Only splittings of 14N species fitted.
[e] Only splittings of 15N species fitted.
[f] Splittings of both 14N and 15N species fitted.
[g] Obtained by the analysis of the ground state splittings of 14N species with RF-RT model.
[h] Obtained by the analysis of the ground state splittings of 15N species with RF-RT model.
[i] The s value for columns III, IV and V are 33.44, 33.68 and 33.83 respectively.

Table 10. Correlation coefficients of the fitted potential parameters V_3, V_6, V_{3c}', V_{3c}''.

V_3	1.000			
V_6	− 0.003	1.000		
V_{3c}'	0.130	0.308	1.000	
V_{3c}''	− 0.826	0.185	0.389	1.000

Table 11. Mean partial derivative* of the (E-A) rotational splittings (Tables 7 and 8) with respect to the fitted potential parameters V_3, V_6, V_{3c}', V_{3c}''.

$\overline{(\partial\Delta\nu/\partial V_3)}$	$= 9.4 \cdot 10^{-3}$	MHz/GHz
$\overline{(\partial\Delta\nu/\partial V_6)}$	$= 1.5 \cdot 10^{-3}$	MHz/GHz
$\overline{(\partial\Delta\nu/\partial V_{3c}')}$	$= 6.6 \cdot 10^{-4}$	MHz/(GHz rad^{-1})
$\overline{(\partial\Delta\nu/\partial V_{3c}'')}$	$= 2.7 \cdot 10^{-4}$	MHz/(GHz rad^{-2})

* Defined as $1/N \sum_{i=1}^{N} |\partial\Delta\nu_1/\partial x|$ for the N splittings, with $x = V_3$, V_6, V_{3c}', V_{3c}''.

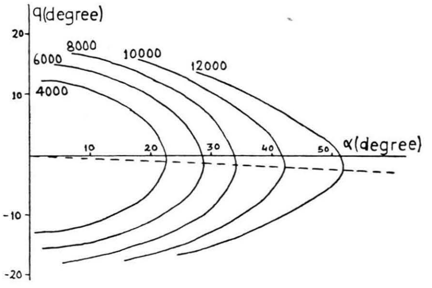

Fig. 2. Potential surface $V(\alpha, q)$ of the torsion vibration for CH_3COCN ----- minimum energy path for the internal rotation. The unit of energy values mentioned on the diagram is GHz.

tional transitions in the ground, first excited torsional and first excited vibrational states simultaneously. The observed and calculated E-A rotational splittings are summarized in Table 7 and 8 for the two isotopic species respectively. The potential constants, which where fitted together with those assumed and precalculated are listed in Table 9 (column III). For comparision this table also includes the results obtained from the ground state E-A rotational splittings by the RF-RT model (columns IV and V). Table 10 presents the correlation coefficients of the four fitted potential constants and Table 11 gives the mean partial derivatives of the E-A rotational splittings with respect to these constants. For illustration Fig. 2 shows the cross section of the equipotential surfaces in the (α, q) plane. A consequence of the V_{3c}' parameter is that the minimum energy path for the internal rotation is curvilinear in the (α, q) plane. By this picture, the RTV model is related to the r_e-relaxation method of Bauder et al. [21] where the minimum energy path is introduced parametrically. Thus the number of degrees of freedom (three rotation and one torsion) is reduced in the r_e-relaxation method.

VIII. Discussion

The satisfactory agreement between the observed and calculated (E-A) rotational splittings (RMS

Table 12. Difference between experimental and calculated effective rotational constants (MHz) of the ground (v_α, v_q = 0, 0) and excited (v_α, v_q = 1, 0 and 0, 1) states.

		Experimental	Calculated
CH_3COCN	$A_{00}-A_{10}$	10.76	15.52
	$B_{00}-B_{10}$	15.82	9.05
	$C_{00}-C_{10}$	2.02	− 0.33
	$A_{00}-A_{01}$	27.67	11.10
	$B_{00}-B_{01}$	− 18.62	− 28.60
	$C_{00}-C_{01}$	− 2.79	− 10.47
$CH_3COC^{15}N$	$A_{00}-A_{10}$	11.41	15.46
	$B_{00}-B_{10}$	14.96	8.43
	$C_{00}-C_{10}$	1.99	− 10.29
	$A_{00}-A_{01}$	26.67	10.57
	$B_{00}-B_{01}$	− 17.85	− 27.58
	$C_{00}-C_{01}$	− 2.80	− 10.35

deviation = 312 kHz or 0.7%) indicates that the RTV model is a far better approximation than the RF-RT model. It would be desirable to have the data of two or more isotopic species of the molecule. This is evident from a comparision of columns I, II and III of Table 9. The simultaneous fitting of the splittings for both the isotopic species reduces the standard deviation of the adjustable parameters as well as the RMS deviation of the fitted splittings. We feel that the measurements of b type Q-branch lines in the excited states are necessary for an analysis of this kind, as their splittings are about two orders of magnitude more sensitive to the adjustable parameters. It must be mentioned that while the E-A rotational splittings are correctly reproduced, the frequencies of the corresponding transitions are not. An illustration of this problem is presented in Table 12, where experimental and calculated differences in rotational constants are compared. This seems to be a general problem, since all the analysis done with the RTV model led to similar discrepancies. For a fit of both the rotational constants and rotational splittings, the present form of the RTV model, in which only one more vibration which lies nearest to torsion in energy is considered is not sufficient.

As the determination of the structure of this molecule encountered some difficulties [19], we investigated the influence of the structure on the potential parameters. A systematic study of this point has only been attempted by Heise et al. [4] in a preliminary way. We feel that the structural parameters, which are connected to the considered torsion and vibration should mostly influence the results. With this belief, we calculated the E-A splittings with the potential parameters fixed as given in column III of Table 9, the mode of vibration fixed as described before but slightly changed values (approximately within the experimental uncertainty) for the following structural parameters: C—H bond length, ∢ C—C—H, C—N and C_{carb}-$C_{cyanide}$ bond lengths and ∢ C—C—N. Surprisingly, the splittings of some of the lines changed remarkably. Table 13 summarizes the three strongest changes for the splittings in each of the v_α, v_q = (0,0), (1,0) and (0,1) state spectra for the ^{14}N species of the molecule. We thus conclude, that a precise structure is necessary for an analysis of this kind and that the uncertainties in the structural parameters should show its effect on the uncertainty of the determined potential parameters. Our attempt of fitting these structural parameters to the line frequencies (in fact the rotational constants in all the three states for both the isotopic species of the molecule) ended in only a partial success. (The RMS deviation decreased from 30.6 MHz to 4.4 MHz, with the fitted structural parameters approximately within the experimental uncertainty. This is what one should expect.

Table 13. Dependence of the calculated splittings (in MHz) of selected rotational transitions on the considered structural parameters (^{14}N species).

Transition $(J_{K_-K_+} - J'_{K_-'K_+'})\, v_\alpha\, v_q$	Calculated splittings with Normal set of parameters	Δ(C—H)* = 0.005 Å	Δ(C—C—H)* = 1 degree	Δ(C—N) = 0.005 Å	$\Delta(C_{carb}-C_{cy})$ = 0.005 Å	Δ(C—C—N) = 1 degree
$(3_{30} - 3_{21})_{00}$	26.97	27.34	27.42	27.01	27.02	27.48
$(3_{31} - 3_{22})_{00}$	- 31.59	− 32.06	− 32.16	− 31.64	− 31.65	− 32.34
$(4_{31} - 4_{22})_{00}$	10.75	10.99	11.11	10.88	10.93	11.11
$(2_{02} - 1_{11})_{10}$	106.67	108.64	109.05	106.95	107.05	110.06
$(2_{11} - 2_{02})_{10}$	129.55	132.22	132.64	129.38	129.28	131.44
$(3_{12} - 3_{03})_{10}$	141.63	144.52	145.24	141.39	141.26	142.49
$(2_{11} - 2_{02})_{01}$	− 1.37	− 1.45	− 1.48	− 1.37	− 1.37	− 1.40
$(3_{12} - 3_{03})_{01}$	− 2.64	− 2.79	− 2.84	− 2.62	− 2.62	− 2.64

* For these calculations V_3 was modified to take into account the change in I_α.

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