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D. Jelisavac, D.C. C Cortés Gómez, Ha Vinh Lam Nguyen, L.W. W Sutikdja, Wolfgang Stahl, et al.. The microwave spectrum of the trans conformer of ethyl acetate. *Journal of Molecular Spectroscopy*, 2009, 257 (2), pp.111-115. 10.1016/j.jms.2009.07.002 . hal-03183174

HAL Id: hal-03183174

<https://hal.science/hal-03183174>

Submitted on 27 Mar 2021

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The Microwave Spectrum of the *trans* Conformer of Ethyl Acetate

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Abstract

The Fourier transform microwave spectrum of ethyl acetate has been measured under molecular beam conditions. The *trans* conformer, where all heavy atoms are located within a mirror plane, was identified after analyzing the spectrum by comparison with theoretical calculations. The barrier to internal rotation of the acetate methyl group was found to be only 99.57(11) cm⁻¹ whereas for methyl torsion in the ethyl group a barrier of 1112.3(37) cm⁻¹ was determined. A comparison between two theoretical approaches treating the internal rotation, the so-called RAM (Rho-Axis-Method) and CAM (Combined Axis Method), is also performed.

Keywords: Microwave spectroscopy, Ethyl acetate, Internal rotation

Introduction

Ethyl acetate is a widely used solvent and it is also abundant in many fruits contributing to their odors. From a chemical point of view it is a small aliphatic ester, obtained by condensation of ethanol and acetic acid using some acid as catalyst. Surprisingly, to our knowledge only one electron diffraction study [1] deals with the structure of this important molecule in the gas phase and no microwave studies have been reported.

Sugino et al. [1] suggested that ethyl acetate exists in two conformers, the *trans* conformer which has C_s symmetry with all heavy atoms being located within the mirror plane, and a *gauche* conformer with C_1 symmetry. Both conformers are shown in Fig. 1. Here, we will report on microwave studies on the *trans* conformer only.

<< Fig. 1 approximately here >>

Ethyl acetate has two methyl groups that could show internal rotation. For the acetate methyl group, henceforward called methyl group I, we expected a low barrier to internal rotation on the order of 100 cm^{-1} , for the ethyl methyl group, henceforward called methyl group II, the barrier was expected to be considerably higher, on the order of 1000 cm^{-1} .

The motivation for this work was predominantly the interest in accurate internal rotation parameters of methyl group I. Another motivation was a comparison of two different computer programs, BELGI- C_s and XIAM, both of them treating internal rotation effects in rotational spectra using the rho axis method (RAM) [2] and the combined axis method (CAM) [3], respectively.

Experimental

All spectra were recorded using two molecular beam Fourier transform microwave (MB-FTMW) spectrometers in the frequency ranges 4 to 26.5 GHz [4, 5] and 26.5 to 40 GHz [6], respectively. Ethyl acetate was obtained from Sigma-Aldrich, Steinheim/Germany, and used without further purification. A gas mixture containing 1 to 3 % ethyl acetate in helium at a total pressure of 80 to 120 kPa was used throughout. Helium was chosen as carrier gas because the rotational cooling is not as effective as with neon or argon. This enabled us to observe also relatively high J values with satisfactory intensity.

Spectral Analysis

At the beginning of our measurements broadband scans in the frequency range from 10.0 to 11.9 GHz were carried out. In total 65 lines were found, many of them were quite strong. All of them were remeasured at high resolution and almost all lines were broadened, some lines were clearly split by up to some 100 kHz. A typical spectrum is shown in Fig. 2. The instrumental resolution and the measurement accuracy are given in the caption of Fig. 2.

<< Fig. 2 approximately here >>

In ethyl acetate the rotational lines are split due to two large amplitude motions, the internal rotation of methyl group I and methyl group II. For methyl group I we assumed the barrier to internal rotation to be almost the same as Sheridan et al. [7] found for the acetate methyl group in methyl acetate, which is $99.559(83) \text{ cm}^{-1}$. This is a rather low barrier and we expected very large A-E splittings from a few MHz to a few GHz, depending on the respective transition.

The internal rotation of methyl group II should be comparable to that in ethyl chloride, where a barrier of $3602(10) \text{ cal mol}^{-1}$, which is $1260(4) \text{ cm}^{-1}$, was found [8]. This would cause only broadened lines or narrow splittings for those transitions observable in the molecular beam and it explains the broadened and split lines we observed.

At first we tried to assign the A species (referred to methyl group I) spectrum treating it as an effective rigid rotor spectrum. Therefore we used rotational constants obtained from quantum chemical calculations on various levels of theory for the *trans* and the *gauche* conformer (Tab. 1). By trial and error some *a*-type R-branch transitions of the *trans* conformer could be identified yielding the B and C rotational constants. Later, also some *b*-type Q-branch transitions were assigned and also the A constant was fixed. This enabled us to predict the whole rigid rotor spectrum with sufficient accuracy to find all remaining A species lines and, subsequently, to fit the (effective) quartic centrifugal distortion constants. The standard deviation after fitting 60 A species transitions was 3 kHz, which is almost experimental accuracy. It should be noted that despite an intense search no *c*-type transitions were found, which means that the *c* dipole moment component is near zero and which confirms that we indeed observed the *trans* conformer with a mirror plane perpendicular to the *c* axis.

In a next step we predicted both, the A and E species (referred to methyl group I) transitions using program XIAM [3]. The barrier was taken from methyl acetate, approximately 100 cm⁻¹, the angle between the internal rotor axis and the inertial *a* axis we calculated from our *ab initio* result on MP2/6-311++G** level to be approximately 45°. The inertia of the methyl group was fixed to 3.2 uÅ², which we considered to be a reasonable value found in many molecules where methyl internal rotation has been analyzed. The predicted spectrum was in close agreement with lines we observed in our scan and the assignment was straight forward for the *a*-type R branch transitions, where the A-E splittings were only on the order of 10 to 100 MHz. The assignment of *b*-type Q branch lines, split by a few 100 MHz up to a few GHz, was more difficult. Here the search for lines which form closed cycles in the energy level diagram turned out to be very helpful. Finally, 60 A species lines and 66 E species lines could be assigned. Levels up to J = 19 and K_a = 4 were included in the fit (see also Tab. S1). The results are given in Tab. 2, a complete list of all fitted transitions is available as supplementary material (Tab. S1 and S2). It should be noted that the experimental data are obtained from the vibrational ground state. In contrast, the values from Gau03 are equilibrium data.

The internal rotation of methyl group II causes the A species lines of methyl group I to split into doublets ($|\sigma_1, \sigma_2\rangle = |0, 0\rangle, |0, \pm 1\rangle$), the E species lines into triplets ($|\pm 1, 0\rangle, |\pm 1, \pm 1\rangle, |\pm 1, \mp 1\rangle$). Here the torsional states are labeled by the torsional symmetries σ_1 and σ_2 of group I

and II [9]. Sample calculations with XIAM have shown that the splittings of the A species lines are usually too narrow to be resolved. However the E species lines of some selected transitions were split by up to 80 kHz. With the splittings observed for three E species transitions (Table S3) and keeping all other parameters fixed we found the barrier of methyl group II to be $V_3 = 1112.3(37) \text{ cm}^{-1}$. A typical splitting is shown in Fig. 3.

<< Fig. 3 approximately here >>

Here the angle between the internal rotor axis and the principal a axis $\angle(i,a) = 147.7^\circ$ was taken from *ab initio* calculations.

Theoretical calculations

In order to get rotational constants and also the angle between the internal rotor axis and the a axis as starting values for assigning the spectra, theoretical calculations were carried out at the workstation cluster of the Center for Computing and Communication at the RWTH Aachen University using the program package Gaussian 03 [10]. In all cases a fully optimized structure was obtained. Also the dipole moment components were calculated to get an impression of the relative strength of a -, b -, and c -type transitions. At first we focussed our calculations on the *trans* conformer to compare the results of DFT and MP2 calculations with various basis sets. From former DFT studies given by Nagy et al. [11] two stable conformers of ethyl acetate were known. Our calculations with different start geometries and full relaxation of all structural parameters yielded three conformers. The results are summarized in Tab. 1. We found that the 6-311++G** basis set used for the MP2 or B3LYP method gave reasonable agreement with the experimental results, therefore we used only this basis set for our calculations on the *gauche* and *cis* conformer. The *cis* conformer, has an energy of about 3 kJ/mol above the *trans* conformer and appeared unlikely to be visible under molecular beam conditions. However, the optimized structural parameters of all conformers are given in Table S4.

Results and Discussion

The microwave spectrum of ethyl acetate has been analyzed by means of two different programs, XIAM [3, 12], and BELGI-C_s [2, 12]. XIAM sets up the Hamiltonian in the principal axis system of the entire molecule. The internal rotation operator of each top is set up in its own rho axes system and after diagonalization, the resulting eigenvalues are transformed (rotated) into the principal axis system. Only centrifugal distortion constants, but no higher order coupling terms between internal rotation and overall rotation are implemented. A global fit of A and E species transitions is possible, however in cases with rather low barriers E species transitions are not satisfactorily predicted. The situation can be improved by fitting the A and E state separately, using two sets of rotational constants, but taking the same set of centrifugal distortion and internal rotation constants. This method significantly reduces the uncertainties in the fit, however

the physical meaning becomes somewhat unclear. In our case the A species could be fitted with a standard deviation of 2.9 kHz, but for the E species 85.3 kHz was obtained.

As an alternative, a global fit with BELGI-C_s was carried out. In this program the calculations are carried out in the rho axes system (also referred in the literature often as RAM for “rho axis method”), and all parameters obtained in the fit are referred to the rho axes system. The method based on the work of Kirtman [13], Lees and Baker [14] and Herbst et al. [15] takes its name from the choice of the axis system, the rho axis system, which is related to the principal axis system by a rotation chosen to eliminate the $-2FP_\gamma\rho_xJ_x$ and $-2FP_\gamma\rho_yJ_y$ coupling terms in the kinetic energy operator where F is the internal rotation constant, P_γ is the internal angular momentum, J_x and J_y are the usual x and y components of the global rotation angular momentum and ρ is a vector that expresses the coupling between the angular momentum of the internal rotation P_γ and the global rotation J . Unlike XIAM, BELGI-C_s which was used successfully to describe the spectra for internal rotors with very low internal rotation barriers ($V_3 \cong 25 \text{ cm}^{-1}$) such as acetamide [16], and also for peptide mimetics such as the ethylacetamidoacetate molecule [17] and the N-acetyl alanine methyl ester [18] allows for fitting many higher order terms not only in the total angular momentum J , but also in the angular momentum of the internal rotor P_γ and in cross-terms between them. BELGI-C_s uses a two-step diagonalisation procedure in which the first step is the diagonalisation of the torsional Hamiltonian consisting of the one dimensional potential function $V(\gamma)$ together with a torsion-rotation kinetic operator diagonal in K, the rotational quantum number. A first set of torsional calculations, one for each K values, is carried out using a 21 x 21 torsional basis set : $|K \nu_t \sigma\rangle = \exp [i(3k+\sigma)\gamma]$ where ν_t is the principal torsional quantum number and k is an integer running from -10 to +10 for BELGI-C_s. For XIAM this indices k runs from -15 to 15. This basis is then reduced by discarding all but the nine lowest torsional eigenfunctions for each K. Finally the torsional eigenfunctions are multiplied by the symmetric top rotational function $|J,K,M\rangle$ to form a basis set which is then used to diagonalize, in the second step, the zeroth-order asymmetric rotor terms and higher order terms in the Hamiltonian.

Using BELGI-C_s, the same data set of 60 A species and 66 E species transitions was fitted with 15 parameters to experimental accuracy with a standard deviation of 2.9 kHz for the A state and 3.0 kHz for the E state. The results are presented in Tab. 2 and Tab. 3.

The standard deviation is in the same order for the A species for both programs, XIAM and BELGI-C_s, but it is much smaller for the E species in the fit of BELGI-C_s. Therefore the predictive power of BELGI-C_s is much better than XIAM, however, for assignment purposes XIAM is in some aspects more convenient to use since it is somewhat faster than BELGI-C_s.

In order to compare the results from BELGI-C_s referring to a rho axes system with the more usual constants given in a principal axis system, some transformations can be made. A_{RAM} , B_{RAM} , C_{RAM} , and D_{AB} are proportional to the elements of the inverse inertia tensor. Diagonalizing it by rotation around the c axis by an angle θ_{RAM} yields the PAM constants A and B:

$$A = \frac{1}{2}(A_{RAM} + B_{RAM} + \sqrt{(A_{RAM} - B_{RAM})^2 + 4D_{ab}^2}) \quad (1)$$

$$B = \frac{1}{2}(A_{RAM} + B_{RAM} - \sqrt{(A_{RAM} - B_{RAM})^2 + 4D_{ab}^2}) \quad (2)$$

with

$$\tan(2\theta_{RAM}) = \frac{2D_{ab}}{(A_{RAM} - B_{RAM})}. \quad (3)$$

For the *trans*-ethyl acetate molecule this is 13°.

The centrifugal distortion constant D_J has the same meaning in both coordinate systems, because the J^4 operator is invariant under rotation.

To determine the rotational constant F_0 of the internal rotor, we start with the definition of the $\vec{\rho}$ vector $\vec{\rho} = (\rho_a, \rho_b, \rho_c)$. Its elements are defined by

$$\rho_a = \frac{\lambda_a I_\gamma}{I_a}, \quad \rho_b = \frac{\lambda_b I_\gamma}{I_b}, \quad \rho_c = \frac{\lambda_c I_\gamma}{I_c}, \quad (4)$$

where I_a , I_b , I_c are the principal moments of inertia of the entire molecule and I_γ is the moment of inertia of the internal rotor. λ_a , λ_b , λ_c are the direction cosines between the internal rotor axis and the principal axes a , b , c , with

$$\lambda_a^2 + \lambda_b^2 + \lambda_c^2 = 1. \quad (5)$$

The relations (4) may also be expressed with the respective rotational constants A, B, C, and F_0 of the molecule and the internal rotor

$$\rho_a = \frac{\lambda_a A}{F_0}, \quad \rho_b = \frac{\lambda_b B}{F_0}, \quad \rho_c = \frac{\lambda_c C}{F_0}. \quad (6)$$

Note that in relation (6) above, the definition of F_0 is different from that of the “reduced” F given in Eq (9) of [2] :

$$F = \frac{\hbar^2}{2rI_\gamma} \text{ with } r = 1 - I_\alpha \left(\frac{\lambda_a^2}{I_a} + \frac{\lambda_b^2}{I_b} + \frac{\lambda_c^2}{I_c} \right).$$

The length of the vector $\vec{\rho}$ is given by

$$\rho = \sqrt{\rho_a^2 + \rho_b^2 + \rho_c^2}. \quad (7)$$

In our case $\lambda_c = 0$, and with (5), (6), and (7) we obtain

$$\rho^2 F_0^2 = \lambda_a^2 (A^2 - B^2) + B^2. \quad (8)$$

The a component of $\vec{\rho}$ is available from

$$\rho_a = \rho \cos \theta_{RAM}, \quad (9)$$

and with (6) we find

$$\lambda_a = \frac{F_0 \rho_a}{A}. \quad (10)$$

The system of equations (8) and (10) may be solved to yield

$$F_0 = \frac{B}{\rho \sqrt{1 - \frac{A^2 - B^2}{A^2} \cos^2 \theta_{RAM}}} \quad (11)$$

and

$$\lambda_a = \sqrt{\frac{\rho^2 F_0^2 - B^2}{A^2 - B^2}}. \quad (12)$$

From (11) and (12) the angle between the internal rotor axis and the inertial a axis is obtained by

$$\angle(i, a) = \arccos \lambda_a. \quad (14)$$

All results, obtained with XIAM, BELGI-C_s, and by theoretical calculations, referred to the principal axis system, are summarized in Tab. 2.

The torsional barrier determined for the acetate methyl rotor is 99.57(11) cm⁻¹ using BELGI-C_s and 101.606(23) cm⁻¹ using XIAM. These differences are within a few percent. The discrepancies are, however, larger than the standard deviation of the parameters by one order of magnitude and are likely a result of systematic errors in the models. The differences between the methyl rotor angles are only about 0.025° when comparing the two methods.

Also the agreement with the theoretical results allows to conclude, that we indeed observed the *trans* conformer of ethyl acetate. This is also supported by the absence of *c*-type transitions, which indicates that a mirror plane perpendicular to the *c* axis is present. Finally we can also note that the fit achieved with BELGI-C_s, which reproduced the experimental data within experimental accuracy, did not required any out-of-plan type terms of symmetry A₂.

It should be noted, that with both, XIAM and BELGI-C_s, a strong correlation between V₃ and I_γ is present which is due to the fact that only v_t = 0 ground torsional state transitions are included in the analysis. However, both programs converged at almost the same I_γ.

We can compare the internal rotation parameters with those of the acetate methyl group of methyl acetate [7]. Here, V₃ and I_γ are 99.559(83) cm⁻¹ and 3.2085(26) uÅ², respectively. For ethyl acetate we found 99.57(11) cm⁻¹ and 3.16067(76) uÅ². This is almost the same and there seems to be no influence of the alkyl group in alkyl esters. If this also holds for bigger alkyl groups we will study in future work.

The barrier of methyl group II is 1112.3(37) cm⁻¹, which is quite close to the barrier of 1260(4) cm⁻¹ found in ethyl chloride.

Finally it should be mentioned that only about 30% of all measured lines could be assigned. The still unassigned lines might be due to the *gauche* or other conformers, to excited torsional states, and also due to other vibrational states. Also some lines probably arise from isotopomers of

strong lines of *trans* ethyl acetate. However, due to the complexity of the spectrum, none of these species could be presently assigned.

Acknowledgement

We thank the Center for Computing and Communication of the RWTH Aachen University for free computer time and the Land Nordrhein-Westfalen for funds.

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Tables

Table 1: Rotational constants (in GHz) and dipole moments (in Debye) of ethyl acetate (*trans* and *gauche* conformer) obtained by DFT and *ab initio* methods using the Gaussian 03 package.

Method / Basis set	A	B	C	μ_a	μ_b	μ_c	μ_{total}
trans conformer							
B3LYP/6-31++G**	8.3797	2.0686	1.7122	1.19	1.79	0.00	2.15
B3LYP/6-311++G**	8.4184	2.0738	1.7172	1.17	1.74	0.00	2.09
B3LYP/cc-PVTZ	8.4576	2.0827	1.7246	1.08	1.70	0.00	2.01
MP2/6-311G**	8.3958	2.1069	1.7390	0.90	1.85	0.00	2.05
MP2/6-311++G**	8.3907	2.0994	1.7339	0.99	1.93	0.00	2.17
MP2/cc-PVTZ	8.4491	2.1134	1.7452	0.93	1.92	0.00	2.13
gauche conformer							
B3LYP/6-311++G**	7.3909	2.2752	2.0174	0.61	1.79	0.13	1.90
MP2/6-311++G**	7.2396	2.3602	2.0830	0.34	1.92	0.31	1.98
cis conformer							
B3LYP/6-311++G**	7.9554	2.0946	1.7113	2.69	3.94	0.00	4.77
MP2/6-311++G**	7.9442	2.1184	1.7269	2.83	4.41	0.00	5.24
Experimental ^a	8.4117	2.0948	1.7341			0.00 ^b	

^a This work, rounded, for exact rotational constants see Tab. 2.

^b Concluded from the absence of *c*-type lines.

Table 2: Molecular constants of ethyl acetate (*trans* conformer) obtained with program XIAM and comparison with results of BELGI-C_s and *ab initio* results.

Unit		XIAM		BELGI-C _s	Gau03 ^g
A	GHz	A species	8.452754 (16)	8.41174 (28) ^a	8.391
		E species	8.4486787 (97)		
B	GHz	A species	2.09388122 (83)	2.094799 (70) ^a	2.099
		E species	2.09403132 (48)		
C	GHz	A species	1.73342466 (24)	1.734069 (58) ^a	1.734
		E species	1.73352516 (28)		
Δ_J	kHz		0.1727 (16)	0.1812 (6)	
Δ_{JK}	kHz		1.376 (12)		
Δ_K	kHz		12.86 (19)		
δ_J	kHz		0.03451 (71)		
δ_K	kHz		0.625 (39)		
F ₀	GHz		159.896 (38)	159.98 (13)	
I _γ	uÅ ²		3.16067 (76) ^b	3.1590 (25) ^b	
V ₃	GHz		3046.07 (69)	2984.9 (30)	
	cm ⁻¹		101.606 (23) ^c	99.57 (10) ^c	
	kJ/mol		1.21548 (28) ^c	1.1911 (13) ^c	
<(i,a)	°		43.0747 (4)	43.0537 (5)	44.75
<(i,b)	°		46.9253 (4) ^d	46.9463 (5) ^d	45.24
<(i,c)	°		90.0000 ^e	90.00 ^e	90.00
s			8.176274 ^f	8.109929	

Unit		XIAM		BELGI-C _s	
		A species	E species	A species	E species
Number of lines		60	66	60	66
Std. deviation	kHz	2.9	85.3	2.9	3.0
Fitted params.		14		15	

Note: All constants refer to the principal axis system, for the centrifugal distortion constants Watson's A reduction and a I' representations was used.

^a Obtained by transformation from rho axis system to principal axis system, see text.

^b Moment of inertia I_γ of the internal rotor, calculated from its rotational constant F.

^c Hindering potential, calculated from value in frequency units.

^d Calculated from <(i,b) = 90° - <(i,a).

^e Fixed due to symmetry.

^f Reduced barrier $s = \frac{4V_3}{9F}$.

^g Calculation on MP2/6-311++G** level using Gaussian 03.

Table 3: Molecular constants of ethyl acetate (*trans* conformer) obtained by a global fit using program BELGI-C_s.

Operator ^a	Constant ^b	Unit ^c	Value
P_a^2	A	GHz	8.08735 (41)
P_b^2	B	GHz	2.419190 (32)
P_c^2	C	GHz	1.73406873 (89)
$\{P_a, P_b\}$	D_{AB}	GHz	-1.394249 (60)
$-P^4$	D_J	kHz	0.1812 (5)
$-P^2 P_a^2$	D_{JK}	kHz	-0.349 (17)
$-2P^2 (P_b^2 - P_c^2)$	δ_J	kHz	0.0372 (1)
P_γ^2	F	GHz	163.58 (13)
$(1/2) (1 - \cos 3\gamma)$	V_3	GHz	2984.9 (30)
$P_a P_\gamma$	ρ	unitless	0.039446 (19)
$P_a^3 P_\gamma$	k_1	MHz	-0.2110 (31)
$(1 - \cos 3\gamma) P_a^2$	K_5	MHz	114.6 (12)
$(1 - \cos 3\gamma) P^2$	F_V	MHz	-3.531 (45)
$(1 - \cos 3\gamma) (P_b^2 - P_c^2)$	C_2	MHz	-1.781 (45)
$(1 - \cos 3\gamma) \{P_a, P_b\}$	d_{AB}	MHz	-6.69 (17)

	Unit	A species	E Species
Number of lines		60	66
Standard deviation	kHz	2.9	3.0

Note:

^a All constants refer to a rho-axis system, therefore the inertia tensor is not diagonal and the constants cannot be directly compared to those of a principal axis system. P_a , P_b , P_c are the components of the overall rotation angular momentum, P_γ is the angular momentum of the internal rotor rotating around the internal rotor axis by an angle γ . $\{u, v\}$ is the anti commutator $uv + vu$.

^b The product of the parameter and operator from a given row yields the term actually used in the vibration-rotation-torsion Hamiltonian, except for F, ρ , and A, which occur in the Hamiltonian in the form $F(P_\gamma - \rho P_a)^2 + A P_a^2$.

^c Values of the parameters from the present fit. Statistical uncertainties are shown as one standard uncertainty in the last digit.

Figure Caption

Fig. 1: *Trans* and *gauche* conformer of ethyl acetate.

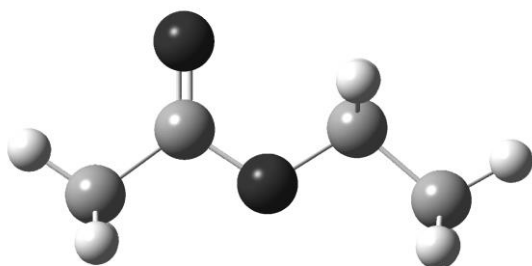
Fig. 2: A typical spectrum of *trans* ethyl acetate.

The experimental resolution was 0.8 kHz, the typical experimental line width 12 kHz as indicated in the spectrum. The large splitting is due to the Doppler effect. For this spectrum 22 FIDs were co-added.

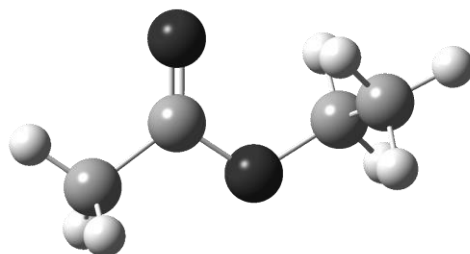
Fig. 3: The $3_{03}-2_{11}$ E-state transition of *trans* ethyl acetate.

The splitting is due to the internal rotation of the methyl group II. Doppler splittings are indicated.

Figure 1



trans conformer



gauche conformer

Figure 2

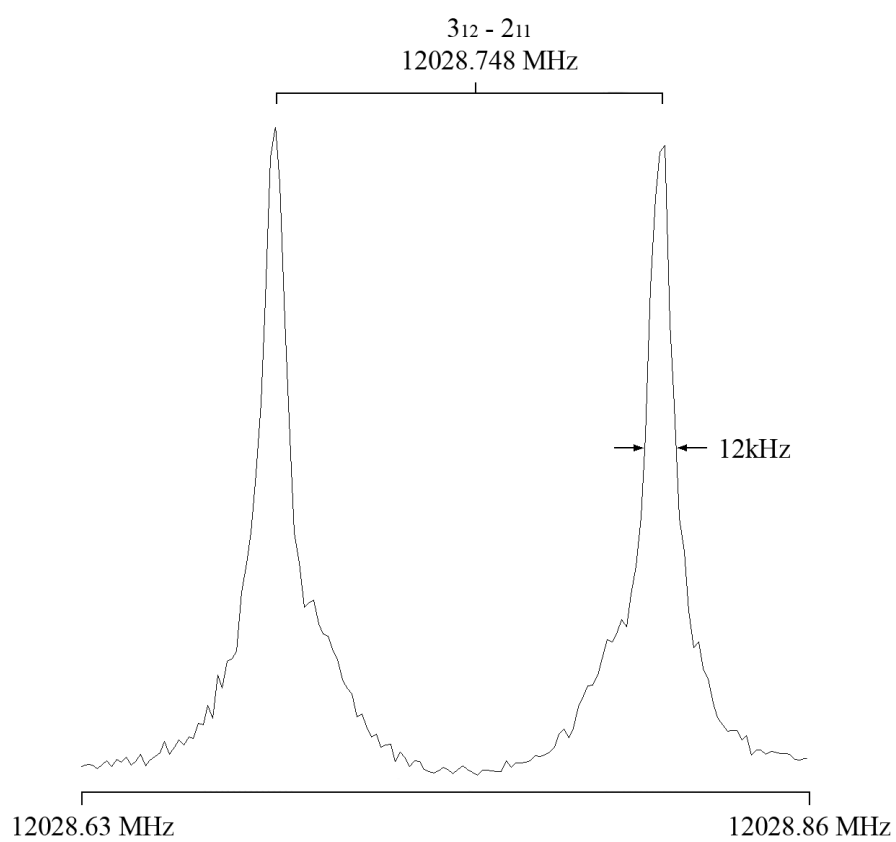


Figure 3

