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The Microwave Spectrum of Allyl Acetate

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Abstract

The Fourier transform microwave (FTMW) spectrum of allyl acetate ($\text{CH}_3\text{-COO-CH}_2\text{-CH=CH}_2$) has been measured under molecular beam conditions. By comparing the experimental data with quantum chemical calculations we identified one conformer of C_1 symmetry, in which the ethylene group is bent by an angle of approximately 129° against the plane of the C-COO-C backbone. Large A-E splittings (in some cases up to 1 GHz) of all lines due to internal rotation of the acetate methyl group were found. Analyzing the spectrum with the program BELGI- C_1 yielded a torsional barrier of only $98.58(15) \text{ cm}^{-1}$.

Keywords: Microwave spectroscopy, Allyl acetate, Internal rotation

1. Introduction

Molecular beam Fourier transform microwave (MB-FTMW) spectroscopy is an excellent tool to study the structure and dynamics of molecules in the gas phase. By this way a large number of molecules has been investigated, but surprisingly, only very few esters were among them, though they are a very important class of compounds in chemistry. This might be due to the fact that even small esters contain quite a large number of atoms which makes them too big for classical structure determination by isotopic substitution. Moreover, even under molecular beam conditions usually several conformers exist. Low barrier internal rotation of the acetate methyl group additionally increases the complexity of the spectra and makes assignment difficult. We tried to identify conformers of esters by comparing the experimental data with quantum chemical calculations and succeeded for some aliphatic esters such as ethyl acetate [1]. We were interested in allyl acetate because it is one of the smallest unsaturated ester. To our knowledge no microwave studies on allyl acetate have been carried out before.

Another motivation for this work was our interest in large amplitude motions. The acetate methyl group of allyl acetate shows internal rotation. From investigations on methyl acetate [2], where a barrier of the acetate methyl group of $99.559(83) \text{ cm}^{-1}$ was observed and from our own studies on ethyl acetate [1], where we found a barrier of $101.606(23) \text{ cm}^{-1}$, we expected also in this case a rather low hindering barrier on the order of 100 cm^{-1} . On the other hand we could not exclude to observe a different value since an interaction with the ethylene double bond appeared possible.

Finally, our quantum chemical calculations on allyl acetate, carried out before beginning the experimental work, made us curious. A conformer with the ethylene group bent against the plane containing the ester group was predicted, whereas our intuition told us, that all heavy atoms should be located in a mirror plane. For the latter geometry the theoretical calculations predicted a local maximum in the potential. We expected that a microwave study would allow us to decide, which structure is the correct one.

2. Experimental

All spectra were recorded using two MB-FTMW spectrometers in the frequency ranges 4 to 26.5 GHz [3, 4] and 26.5 to 40 GHz [5], respectively. Allyl acetate was obtained from Merck Schuchardt OHG, Hohenbrunn, Germany, and used without further purification. A gas mixture containing 1% allyl acetate in helium at a total pressure of 100 to 200 hPa was used throughout. We have chosen helium as a carrier gas because the cooling is not as effective as with argon or neon and therefore also higher J levels can still be observed.

The spectrometers can be operated in two different modes, the high resolution mode and the scan mode. In the high resolution mode all lines are split into doublets due to the Doppler effect. The molecular transition frequency is the center frequency, the splitting depends on both, the center frequency and the velocity of the molecular beam. The line width was approximately 8 kHz, the line positions can be determined with an accuracy of 1 kHz for strong lines and 5 kHz for weaker lines. A typical spectrum is shown in Fig. 1.

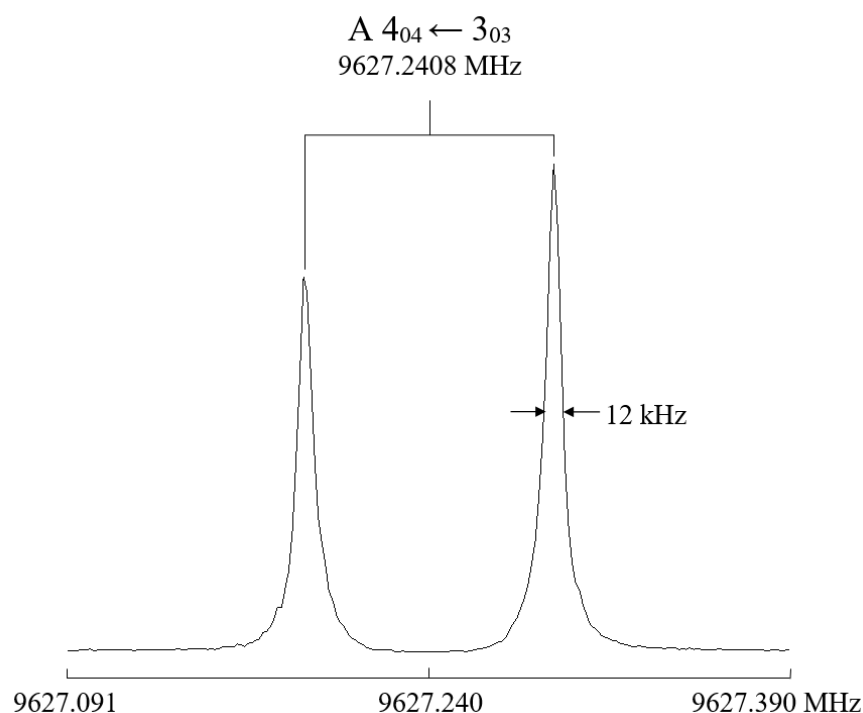


Fig. 1: A typical spectrum of allyl acetate.

The experimental resolution was 0.8 kHz, the typical experimental line width 8 kHz as indicated in the spectrum. The large splitting is due to the Doppler effect. For this spectrum 60 FIDs were co-added.

In the scan mode a series of overlapping spectra taken in the high resolution mode are automatically recorded and only the presence of lines is indicated in a broad band scan. An example is given in Fig. 2.

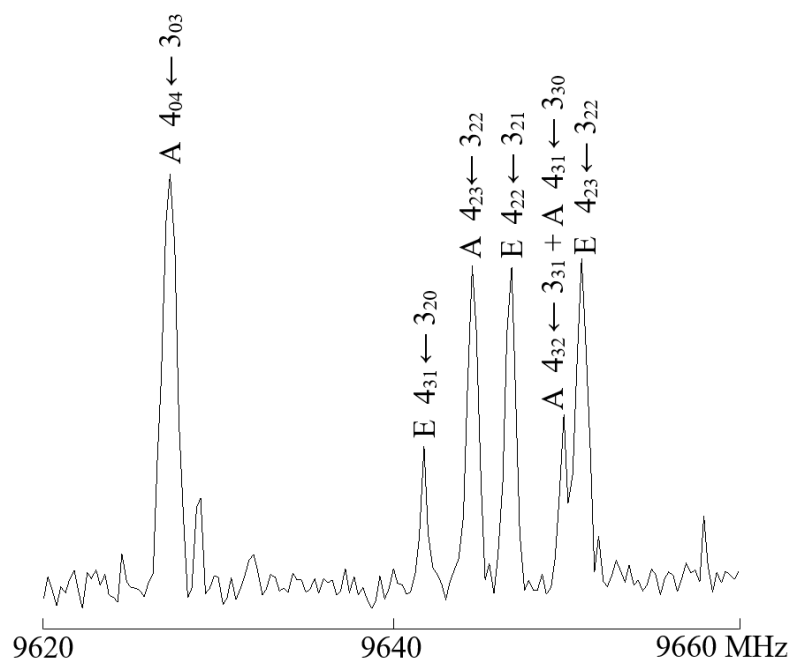


Fig. 2: A typical scan of allyl acetate

The spectral range of 40 MHz was covered by overlapping spectra with a step width of 250 kHz. For each single measure 50 FIDs were co-added.

3. Spectral Analysis

We started our investigations by recording broadband scans in the frequency range from 9.3 to 10.0 GHz. Additionally, during the process of spectral assignment some smaller ranges on the order of 100 to 200 MHz were scanned. In total 274 lines were found, many of them were quite strong. All lines were remeasured in the high resolution mode.

At the beginning of our studies on allyl acetate we assumed, the C_s conformer with a symmetry plane (conformer I, shown in Fig. 3) should exist and it should be the most stable one. Taking this mirror plane as a constraint in quantum chemical calculations carried out with the program *Gaussian 03* [6], we predicted the rotational constants and tried to use them for assigning the spectrum. The rotational constants are given along with the dipole moment components in Tab. 1. However, we found that the experimental and the theoretical spectra did not match at all.

Without this constraint using the MP2 method and the 6-311++G** basis set a fully optimized structure was obtained, where the plane of the ethylene group was bent by an angle of 121.57°

against the ester group (conformer II, shown in Fig. 4). The rotational constants of this C_1 conformer are also given in Tab. 1. We tried again to assign the spectrum with the new rotational constants and succeeded. However, the calculated and the experimental rotational constants differed by up to 2.5 %. The origin of this will be discussed later in this paper.

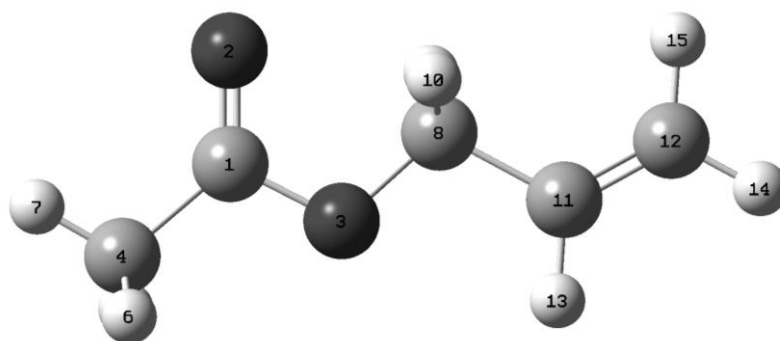


Fig. 3: The planar conformer (conformer I) of allyl acetate.

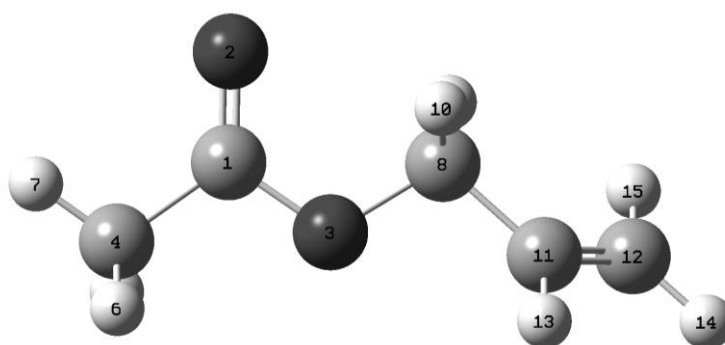


Fig. 4: The bent conformer (conformer II) of allyl acetate from *Gaussians* optimization. The dihedral angle $O_3 - C_8 - C_{11} - C_{12}$ is 121.57° .

We started the assignment with the lines of the A species, which could be treated as an effective rigid rotor spectrum. On the basis of the rotational constants obtained by *ab initio* methods we predicted the spectrum with the program XIAM [7]. By trial and error the typical pattern of the *a*-type $4 \leftarrow 3$ R-branch could be identified. Fitting these lines with XIAM yielded already quite accurate B and C rotational constant, which were still improved by including other *a*-type R-branches. Finally, also *b*-type Q-branch transitions were identified, which enabled us to fit the A constant as well.

It should be noted that by our quantum chemical calculations the *c* dipole moment component is predicted to be small but not zero. Therefore we were surprised that no *c*-type transitions could be found at all in the scans. After the spectrum had been assigned we were able to measure some *c*-type transitions using polarizing pulses with a power of 1 or 2 W, whereas for *a*- and *b*-type transitions a few mW turned out to be sufficient. The existence of *c*-type

transitions proofs that no mirror plane is present within the conformer studied. It should also be noted that the *c*-type transitions were not split, which indicates that no tunneling of the ethylene group through the plane of the ester group occurs on the time scale of our experiment. A list of some *c*-type transitions is given as supplementary data (Tab. S3). Those *c*-type transitions were however very weak and we did not include them in our fits.

In allyl acetate the rotational lines are split due to internal rotation of the acetate methyl group, which has a low barrier to internal rotation. Thus we expected very large A-E splittings from a few MHz up to 1 GHz or more, depending on the respective transition. In the next step we predicted the E species transitions using XIAM. The barrier to internal rotation was assumed to be approximately 100 cm^{-1} as is was also reported for methyl acetate [2] and ethyl acetate [1]. The inertia of the methyl group was fixed to $3.2\text{ u}\text{\AA}^2$, which we considered to be a reasonable value found in many molecules with methyl internal rotation. The angles between the internal rotor axis and the principal inertial axes of the molecule were calculated from the *ab initio* geometry given in Tab. S4. The angles are given in Tab. 2.

We started the assignment of the E species lines with those which were close to the respective A species transitions. This holds for the *a*-type R-branch transitions, where the A-E splittings were only on order of 10 to 100 MHz. After fitting the internal rotation parameters and thereby improving our predictions, also *b*-type Q-branch transitions could be assigned, which were split by several 100 MHz up to 1 GHz. In some cases scanning a small range of 5 MHz was necessary to find the lines.

Using XIAM the barrier to internal rotation was determined to be $98.093(12)\text{ cm}^{-1}$. This can be compared to the barrier of the acetate methyl group of methyl acetate which is $99.559(83)\text{ cm}^{-1}$ and to the barrier of $101.606(23)\text{ cm}^{-1}$, which was found for ethyl acetate. All barriers are very close together, and obviously the double bond of allyl acetate does not affect the internal rotation.

Finally 109 A species and 62 E species lines were assigned and fitted again with the program BELGI-C₁ using the Rho Axis Method (RAM) [8]. This code allows us to calculate and fit transitions for asymmetric top molecules containing one C_{3v} internal rotor (like the CH₃ group) and having a C₁ point-group symmetry at equilibrium. The global BELGI-C₁ code was used only twice up to now and compared to a perturbation treatment in the PAM axis system used in the JB95 code [9, 10]. The results are shown in Tab. 2 and Tab. 3. A complete list of all fitted transitions is given as supplementary data (Tab. S1 and S2).

As we have discussed in [1], XIAM is very user-friendly, and easier to use for assignment purposes, whereas BELGI-C₁ is usually a better model to treat the internal rotation problem for low barrier molecules very accurately (see next section).

4. Results and Discussion

The microwave spectrum of allyl acetate has been assigned with the programs XIAM and BELGI-C₁. A comparison of XIAM and BELGI has been given in [1] and will not be repeated here again in detail. With XIAM a global fit of the A and E species was carried out (Fit II in Tab. 3). A standard deviation of 54.0 kHz was obtained for 171 lines with $J_{max} = 15$ and $K_{a max} = 6$ (5) for the A (E) species respectively. In a second fit with XIAM (Fit III in Tab. 3) the internal rotation parameters were fixed to the values obtained from Fit II and only the A species lines were fitted. Here a standard deviation of 2.7 kHz was found, which is close to the experimental accuracy. A global fit with BELGI-C₁ allowed to fit together the A species with a standard deviation of 2.7 kHz and the E species with 1.2 kHz. The overall standard deviation is 2.3 kHz which indicated that the model used in BELGI-C₁ almost perfectly describes the observed spectrum. The reason for the better standard deviations obtained by the BELGI-C₁ code is that it uses a global approach dealing with the total set of torsional v_t states (to a certain truncation level) associated with the internal rotation, and using one Hamiltonian and one set of parameters to fit the data. The model used in BELGI does therefore include all torsion-rotation interaction between different torsional states. On the other hand, in the local method used in XIAM, each torsional state is treated separately using its own Hamiltonian. In XIAM, certain off-diagonal matrix elements in v_t are thus neglected (after removal by van Vleck transformations) which is a good assumption only in the high barrier limit. In the present case, the so called reduced barrier height $s = 4V_3/9F$ is small (8.17) and thus the effect of those matrix elements are important and cannot be neglected. We note that in Tab. 2, we needed two terms which are symmetry allowed only for a C₁ internal rotor molecule. The D_{ac} parameter (multiplying the $P_a P_c + P_c P_a$ operator) which essentially allows for the fact that the methyl top axis is not required by symmetry to lie in the principal inertial axis ab plane is actually rather large. We also needed d_{ac} , which is its torsional dependence.

It should be noted that the internal rotation problem in BELGI-C₁ is treated in the rho axis system (RAM system) and consequently all parameters obtained also refer to this coordinate system. The original parameters from the BELGI-C₁ fit are given in Tab. 2. To compare these values with those obtained from XIAM, which refer to a principal inertial axis system (PAM

system); all BELGI-C₁ parameters given in Tab. 2 were transformed from the rho axis system to the principal inertial axis system (Tab. 3).

To facilitate this transformation in a first step the tensor formed by the diagonal A, B, and C rotational constants and the off-diagonal elements D_{ab}, D_{bc}, and D_{ac} is diagonalized yielding A, B, and C in the PAM system as well as the transformation matrix v. The transformation matrix is used to calculate the elements of the rho vector $\rho_a = \rho \cdot v_{11}$, $\rho_b = \rho \cdot v_{12}$, and $\rho_c = \rho \cdot v_{13}$ in the PAM system. In a next step the moment of inertia of the methyl group F₀ and the direction cosines λ_{ia} , λ_{ib} , λ_{ic} between the internal rotor axis and the principal inertial axes a, b, and c are calculated

$$F_0 = \sqrt{\frac{1}{\frac{\rho_a^2}{A^2} + \frac{\rho_b^2}{B^2} + \frac{\rho_c^2}{C^2}}},$$

$$\lambda_{ia} = \rho_a \cdot \frac{F_0}{A}, \quad \lambda_{ib} = \rho_b \cdot \frac{F_0}{B}, \quad \lambda_{ic} = \rho_c \cdot \frac{F_0}{C}.$$

The barrier to internal rotation of the acetate methyl group is 98.55(13) cm⁻¹ using BELGI-C₁ and 98.093(12) cm⁻¹ using XIAM. The moments of inertia of the methyl group were fitted to yield 3.1861(17) uÅ² and 3.29046 (33) uÅ², using BELGI-C₁ and XIAM, respectively. Here the BELGI-C₁ value appears somewhat smaller, whereas the XIAM value is slightly too high if compared with the methyl rotors in methyl acetate (3.2085(26) uÅ²) [2] and ethyl acetate (3.16067(76) uÅ²) [1]. However this discrepancy may also indicate that non-rigidity effects are important for I_r and these effects are treated very differently by the two methods. In the BELGI code, deviations of the C_{3v} symmetry for the methyl group is taken into account by higher-order interaction terms, whereas in XIAM only some higher (4th order) coupling terms between internal rotation and overall rotation are implemented.

For an unambiguous identification of the assigned conformer *ab initio* calculations on MP2/6-311++G** level were carried out. From calculations on ethyl acetate and other esters we knew that this method gives reliable rotational constants, however it should be considered that the torsional force constant of the C—COO bond is quite low and sometimes a rotation of both molecule fragments around this bond still improves the result. This rotation can be facilitated by freezing the dihedral angle φ (O₃ – C₈ – C₁₁ – C₁₂) at certain fixed values while all other parameters were optimized. In this case we calculated a full rotation of 360° with a 10° step width. The corresponding potential function is shown in Fig. 5.

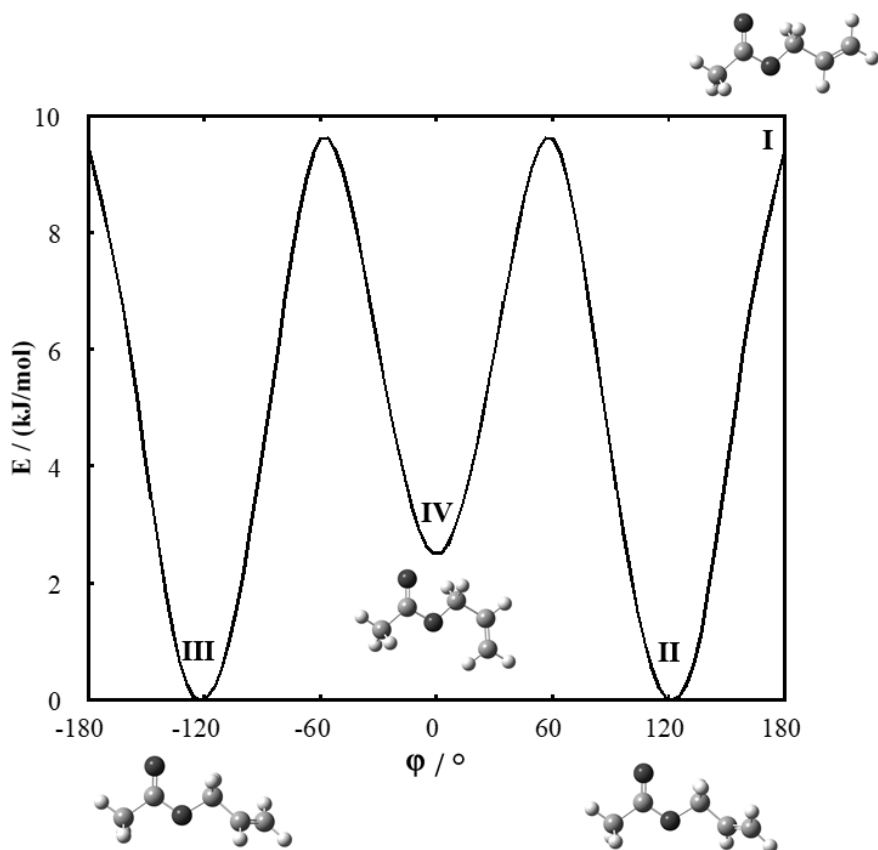


Fig. 5: The minimum energy path of allyl acetate obtained by rotating the ethylene group.

For all dihedral angles φ all other structural parameters were allowed to relax. The relative energy with respect to the lowest energy conformers II/III is given. Conformer III is the enantiomer of conformer II with the same rotational constants.

Obviously three stable conformers are generated by this rotation. Conformer II and III are a pair of enantiomers with the same rotational constants. A further conformer (conformer IV) is less stable and should have a symmetry plane. We also indicated a non-stable transition state (“conformer I”) which is also of C_s symmetry. All conformers described here are *trans* conformers. By rotation around the $O_3 - C_8$ axis also three stable *cis* esters can be found, however these are much higher in energy and are unlikely to be observed under molecular beam conditions. Therefore we will not discuss them here. All geometry parameters are given in Tab. S4 to S7.

As can be recognized from Fig. 5 the dihedral angle φ ($O_3 - C_8 - C_{11} - C_{12}$) for the energy minimum is $\pm 121.57^\circ$ for the conformers II/III. In Fig. 6 the rotational constants vs. φ are drawn.

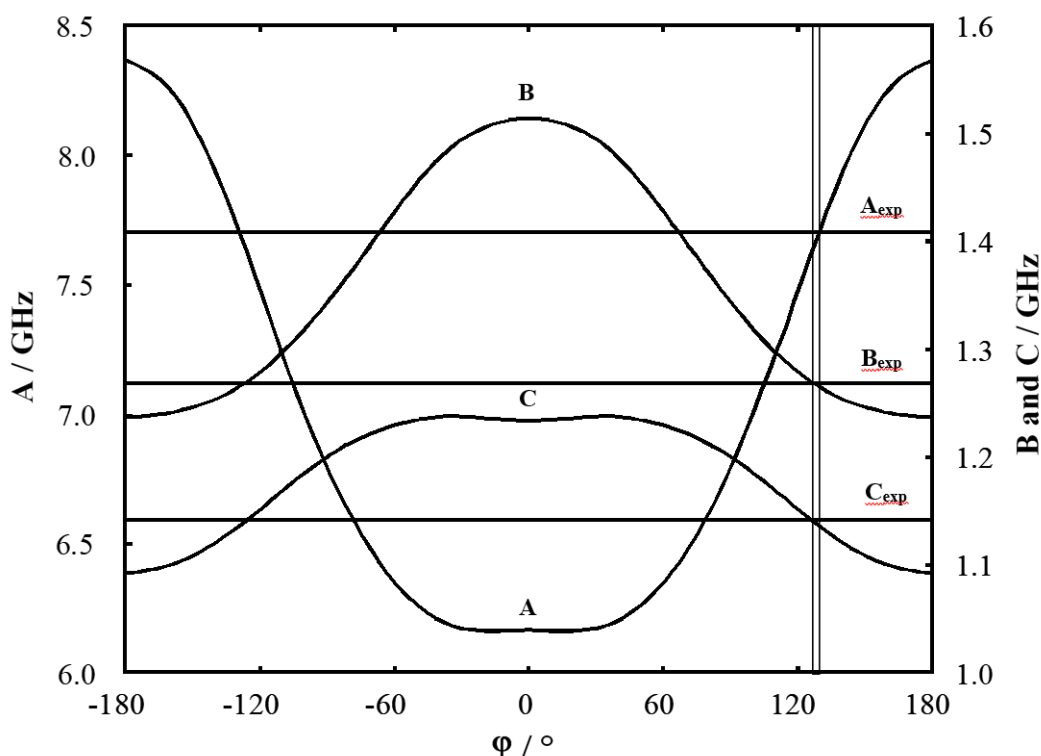


Fig. 6: Comparison of the calculated rotational constants (A, B, C) for different dihedral angle φ with the experimental rotational constants (A_{exp} , B_{exp} , C_{exp}).

The A rotational constant is described at the left scale and the B and C rotational constants at the right scale. The horizontal lines are the experimental rotational constants. The vertical lines show the position where the calculated and the experimental data have the best agreement.

The rotational constants B and C of conformer II have a relative deviation of 0.8%, but for the A constant it is 2.49% which corresponds to an absolute deviation of approximately 200 MHz (see Tab. 1, Calc D). The ground state constants derived experimentally cannot however be directly compared to the computed *ab initio* constants at equilibrium. In the case of *cis* methyl formate molecule HCOOCH_3 , another molecule containing an internal rotor, the theoretical vibration-rotation interaction α constants deduced from the *ab initio* cubic force field were combined with the known experimental ground state rotational constants to yield the semi-experimental equilibrium rotational constants to be compared with the equilibrium constants. The correction did not exceed 1.5% for methyl formate [11], thus less than the 2.49% observed in the case of allyl acetate. In order to obtain a better agreement between the observed and the *ab initio* rotational constants, we rotated the molecular fragment around φ with a step width of 1° and tried to find the angle where the deviation of the rotational constants becomes a minimum. We found that at $\varphi = 129^\circ$ the deviations of A, B, and C are

below 0.5% (see Tab. 2, Calc II). The difference of approximately 7.5° is probably due to the small torsional force constant causing a rather flat minimum. Here very small interactions between both molecular fragments might cause rather large changes in φ . Maybe here a much better quantum chemical method and a larger basis set might increase accuracy by treating these small interactions more correctly. Also the angles between the internal rotor axis and the principal axes of inertia are improved by this empirical correction.

Finally it should be mentioned that only about 50% of all measured lines could be assigned. The still unassigned lines might be due to the planar conformer IV. Also some lines probably arise from isotopologues of strong lines of the assigned conformer. However, due to the complexity of the spectrum, none of these species could be presently assigned.

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Tables

Table 1: Rotational constants, stabilization energies, and dipole moments obtained from *ab initio* calculations.

Conformation		I unstable	II/III ^a stable	II/III corrected ^b stable	IV stable
φ ^c	°	180.0	± 121.57	129.0	0.0
A	GHz	8.370	7.698	7.511	6.164
B	GHz	1.237	1.266	1.277	1.514
C	GHz	1.092	1.137	1.150	1.234
Energy ^d	kJ/mol	9.879	0.000	0.280	2.595
$ \mu_a $ ^e	Debye	0.499		0.713	0.958
$ \mu_b $	Debye	1.902		1.908	1.636
$ \mu_c $	Debye	0.000		0.058	0.001

^a II and III are chiral enantiomers which cannot be distinguished by FTMW spectroscopy

^b Empirical correction by adjusting the dihedral angle φ for best agreement with experimental rotational constants, see text.

^c Dihedral angle $\varphi = \angle(\text{O}_3\text{-C}_8\text{-C}_{11}\text{-C}_{12})$

^d Stabilization energies calculated at MP2/6-311++G** level with respect to the lowest energy conformers II/III at -344.917772 Hartree.

^e dipole moments in principal inertial axes

Table 2: Molecular constants in the RAM system of allyl acetate obtained by a global fit using program BELGI-C₁.

Operator ^a	Constant ^b	Unit ^c	Value
P_a^2	A	GHz	7.51535(31)
P_b^2	B	GHz	1.14266690(55)
P_c^2	C	GHz	1.4324355(43)
$\{P_a, P_c\}$	D_{ac}	GHz	1.011141(13)
$-P^4$	Δ_J	kHz	0.19522(16)
$-P^2 P_a^2$	Δ_{JK}	kHz	-4.1206(37)
$-P_a^4$	Δ_K	kHz	33.975(51)
$-2P^2(P_b^2 - P_c^2)$	δ_J	kHz	-0.03006(13)
$-[P_a^2, (P_b^2 - P_c^2)]$	δ_K	kHz	0.6391(48)
P_γ^2	F	GHz	160.61(19)
		cm ⁻¹	5.3575(62)
$(1/2)(1 - \cos 3\gamma)$	V_3	GHz	2955.3(44)
		cm ⁻¹	98.58(15)
$P_a P_\gamma$	ρ	unitless	0.035007(18)
$(1 - \cos 3\gamma) P_a^2$	k_5	MHz	71.55(87)
$(1 - \cos 3\gamma) P^2$	F_V	MHz	-1.6286(59)
$(1 - \cos 3\gamma)(P_b^2 - P_c^2)$	c_2	MHz	0.7132(61)
$(1 - \cos 3\gamma)\{P_a, P_b\}$	d_{ab}	MHz	5.5(56)
$(1 - \cos 3\gamma)\{P_a, P_c\}$	d_{ac}	MHz	3.857(36)
	$N_A/N_E/N_{tot}$		109 / 62 / 171
	$\sigma_A/\sigma_E/\sigma_{tot}$	kHz	2.7 / 1.2 / 2.3

^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 inertial 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 $F(P_\gamma - \rho P_a)^2 + AP_a^2$.

$N_A/N_E/N_{tot}$ are the numbers of A transitions, E transitions, and the total number of transitions. $\sigma_A/\sigma_E/\sigma_{tot}$ are the respective standard deviations.

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

Table 3: Molecular constants in the PAM system of allyl acetate from different fits and *ab initio* calculations.

constant	unit	Fit I BELGI-C ₁	Fit II XIAM	Fit III XIAM	Calc I ^d	Exp.- Calc. ^e	Dev. [%]	Calc II ^f	Exp.- Calc. ^e	Dev. [%]
A	GHz	7.67929(30) ^a	7.7034352(67)	7.70343360(35)	7.511	0.192	2.49	7.698	0.005	0.06
B	GHz	1.2691224(98) ^a	1.2678319(59)	1.267831492(71)	1.277	-0.009	0.71	1.266	0.002	0.15
C	GHz	1.14203856(61) ^a	1.1415254(63)	1.141526125(76)	1.150	-0.008	0.79	1.137	0.005	0.43
Δ_J	kHz		0.1399(34)	0.13953(17)						
Δ_{JK}	kHz		-1.195(33)	-1.1808(18)						
Δ_K	kHz		32.56(62)	32.337(32)						
δ_J	kHz		0.0045(24)	0.00246(13)						
δ_K	kHz		-0.41 (35)	-0.392(18)						
D_{pi2J}	kHz		87.34(85)	87.34 (fixed)						
D_{pi2-}	kHz		47.89(93)	47.89 (fixed)						
V_3	GHz	2955.3(44)	2940.74(35)	2940.74 (fixed)						
	kJ/mol	1.1793(18) ^c	1.17345 (14)							
	cm ⁻¹	98.58(15) ^c	98.093(12)							
F_0	GHz	158.621(82)	153.589(15)	153.589 (fixed)						
I_γ	uÅ ²	3.1861(17) ^b	3.29046 (33)	3.29046 (fixed)						
$\angle(i,a)$	°	44.45601(64)	44.4871(33)	44.4871 (fixed)	46.73	-2.24		45.73	-1.24	
$\angle(i,b)$	°	134.15842(61)	134.8143(57)	134.8143 (fixed)	136.46	-1.65		135.43	-0.62	
$\angle(i,c)$	°	85.68777(84)	85.832(17)	85.832 (fixed)	86.04	-0.21		85.82	0.01	
σ	kHz	2.3	54.0	2.7						
N_A/N_E		109/62	109/62	109/0						
N_{tot}		171	171	109						

Note: All constants refer to the principal inertial 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 inertial axis system, see text.

^b Moment of inertia I_γ of the internal rotor, calculated from its rotational constant F_0 .

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

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

^e With respect to Fit II

^f Same as Calc I with empirical correction, see text.