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# Structure and Internal Dynamics of *n*-Propyl Acetate Studied by Microwave Spectroscopy and Quantum Chemistry

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## Abstract

The gas phase structure of *n*-propyl acetate was determined using molecular beam Fourier transform microwave spectroscopy from 2 to 40 GHz supplemented by quantum chemical calculations. The experimental spectrum revealed only one conformer with *trans* configuration and  $C_1$  symmetry. Torsional splittings occurred for each rotational transition due to the internal rotation of the acetyl methyl group with a barrier height of approximately  $100\text{ cm}^{-1}$ . The *XIAM* and *BELGI-C<sub>1</sub>* codes were applied to reproduce the spectrum within the measurement accuracy. This investigation on *n*-propyl acetate has accomplished our studies on saturated linear aliphatic acetates  $\text{CH}_3\text{COOC}_n\text{H}_{2n+1}$  ( $n = 1-6$ ).

Key Words: rotational spectroscopy, internal rotation, large amplitude motion, conformational landscape, *ab initio* calculations.

## 1. Introduction

During several years, we have published a number of microwave spectroscopic studies on  $\alpha,\beta$ -saturated acetates (acetic acid esters),  $\text{CH}_3\text{COOC}_n\text{H}_{2n+1}$ , which are methyl acetate ( $n = 1$ ) [1], ethyl acetate ( $n = 2$ ) [2], *n*-butyl acetate ( $n = 4$ ) [3], *n*-pentyl acetate ( $n = 5$ ) [4], and *n*-hexyl acetate ( $n = 6$ ) [5] using the molecular beam Fourier transform technique. Some acetates where the alkyl chain is branched such as isopropyl acetate [6] and isoamyl acetate [7], are also investigated. *n*-Propyl acetate ( $n = 3$ ) is still missing in the family of  $\alpha,\beta$ -saturated acetates with linear alkyl chain.

The title compound is widely used as printing ink solvent as well as in food and perfumery industries. Gas chromatography analysis has identified the existence of this substance in different kind of fruits such as bananas [8], apples [9], and nectarines [10]. *n*-Propyl acetate thus belong to the class of fruit esters. Its gas phase structure obtained by microwave spectroscopy might give important information towards a reasonable explanation for the structure-odor relation.

Not only the structure of *n*-propyl acetate has attracted our attention but also its internal dynamics, which is represent by the internal rotation of the acetyl methyl group. Such large amplitude motion (LAM) has been found in all other acetates mentioned above [1-7]. Currently, we believe that all  $\alpha,\beta$ -saturated acetates have a barrier to internal rotation of the acetyl methyl group of about  $100\text{ cm}^{-1}$  [11]. However, at the time we studied *n*-propyl acetate, this statement was not well-substantiated, since only methyl acetate [1,12], ethyl acetate [2], and isoamyl acetate [7] were investigated before.

## 2. Quantum chemical calculations

By rotating the C<sub>1</sub>-O<sub>3</sub>, O<sub>3</sub>-C<sub>8</sub>, and C<sub>8</sub>-C<sub>11</sub> bonds, different conformations of *n*-propyl acetate can be generated (for atom numbering see Figure 1). The rotation about the C<sub>1</sub>-O<sub>3</sub> bond by varying the dihedral angle  $\theta_1 = \angle(\text{O}_2, \text{C}_1, \text{O}_3, \text{C}_8)$  results in *trans* ( $\theta_1 = 0^\circ$ ) and *cis* ester ( $\theta_1 = 180^\circ$ ) conformations. We only take the *trans* conformations into consideration, since from our previous investigation on ethyl acetate at that time [2] and theoretical studies [13], *cis* esters are much higher in energy and cannot be observed under our molecular beam conditions, where the rotational temperature is very low, approximately 2 K.

At a starting value of  $\theta_1 = 0^\circ$ , we created 9 *trans* ester starting geometries by varying the dihedral angles  $\theta_2 = \angle(\text{C}_1, \text{O}_3, \text{C}_8, \text{C}_{11})$  and  $\theta_3 = \angle(\text{O}_3, \text{C}_8, \text{C}_{11}, \text{C}_{14})$  in a grid of  $120^\circ$ . These conformations were optimized at the MP2/6-311++G(d,p) level of theory using the GAUSSIAN03 package [14] to five conformers, which are illustrated in Figure 2 in the order of their energies. The conformers are named according to the antiperiplanar conformational arrangement of the dihedral angle  $\theta_2$  and  $\theta_3$  using the nomenclature describe in Ref. [3].

Only conformer **aa** has C<sub>s</sub> symmetry; all other conformers, **aM/aP**, **Pa/Ma**, **PM/MP**, and **PP/MM**, exhibit C<sub>1</sub> symmetry and exist as enantiomeric pairs. The enantiomers possess the same electronic energy and rotational constants, and therefore cannot be distinguished under our measurement conditions. The energetically most favorable conformer **aM/aP** has the propyl methyl group tilt out of the molecular frame spanned by the C<sub>4</sub>, C<sub>1</sub>, O<sub>2</sub>, C<sub>3</sub>, C<sub>8</sub>, C<sub>11</sub> atoms by an angle of  $63.0^\circ$ . The rotational constants *A*, *B*, *C* of all conformers and their energies relative to that of conformer **aM/aP** are summarized in Table 1. The atom positions in the principal axis system can be found in Table S1 in the supplementary materials.

### 3. Microwave spectroscopy

#### 3.1. Experimental setup

The microwave spectrum of *n*-propyl acetate was measured using two molecular beam Fourier transform spectrometers operating in the frequency range 2–26.5 GHz [15] and 26.5–40 GHz [16]. The substance was purchased from Merck Schuchard, Hohenbrunn, Germany, and used without any further purification. *n*-Propyl acetate is a clear, volatile liquid with a boiling point of 101.5°C (at 1013 hPa). Its vapor pressure of approximately 33 hPa at room temperature is relatively high and thus simplified the measurement process. For all measurements, we used a gas mixture containing 1% *n*-propyl acetate in helium at a total pressure of 100 to 200 hPa. Helium was chosen as carrier gas because the rotational cooling might not be as effective as with neon or argon, and it was possible to observe relatively high *J* values with sufficient intensity.

The spectrometers can be operated in two different modes, the high resolution mode and the scan mode. In the high resolution mode, all lines appear as 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 estimated measurement accuracy is better than 2 kHz [17]. 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 broadband scan.

#### 3.2. Spectral analysis

Due to the LAM of the acetyl methyl group, all rotational lines in the spectrum split into two torsional components, called the A and the E species. At the beginning, we neglected this effect and treated *n*-propyl acetate as a rigid rotor, i.e. we only considered the A species. The results of *ab initio* calculations in section 2 indicated five conformers within an energy range

of  $3.5 \text{ kJ}\cdot\text{mol}^{-1}$ . We started the assignment with the lowest energy conformer **aM/aP** and calculated its microwave spectrum using the predicted rotational constants. In the frequency range from 9 to 11 GHz, we expected some *a*-type *R* branch transitions. A broadband scan in this frequency region was recorded; a portion is shown in Figure 3. The  $J = 4 \leftarrow 3$  *a*-type lines were assigned readily and fitted using the program *XIAM* [18], whereby only the *B* and *C* rotational constants were obtained, while the *A* rotational constant was still fixed to its *ab initio* value. Thereafter, we could also identify some *b*- and *c*-type transitions and fix the *A* rotational constant. Finally, the centrifugal distortion constants could be determined, and the *A* species lines in the scan were reproduced with a rigid-rotor fit to measurement accuracy. More *A* species lines out of the scan region could be found easily using the prediction of this fit.

After the *A* species of *n*-propyl acetate was assigned, another characteristic *a*-type *R* branch remained in the scan, which was presumably the *E* species components of the same rotational transitions. To predict the *E* species lines, the rotational constants and centrifugal distortion constants of the *A* species fit were used as an initial guess. The hindering barrier of the acetyl methyl group was set to  $100 \text{ cm}^{-1}$ , which is approximately the barrier found for methyl acetate [12], ethyl acetate [2], and isoamyl acetate [7]. The angles between the internal rotor axis and the principal axes were derived from the geometry of conformer **aM/aP** obtained by *ab initio*. The *E* species frequencies of the  $J = 4 \leftarrow 3$  *a*-type transitions calculated by the program *XIAM* agreed nicely with those observed in the spectrum. The *A*-*E* splittings for *b*- and *c*-type transitions were larger, but could also be assigned straightforward. It should be noted that the *A* and *E* component lines have different intensities, as can be recognized in Figure 3. This might be due to a change of the sensitivity of the spectrometer within the scan range or a change of the sample conditions (pressure) during the scans.

Finally, we carried out a fit including both, the *A* and *E* species, and floated at the beginning only the  $V_3$  barrier and the angles between the internal rotor axis and the principal

axes. The root-mean-square (rms) deviation decreases by involving the higher-order terms  $D_{\text{pi}2J}$ ,  $D_{\text{pi}2-}$ ; however, a reasonable rms deviation close to the measurement accuracy could only be achieved by including the internal rotation constant  $F_0$  in the fit.

### 3.3. Results of the fits

A total of 98 A species and 50 E species lines were fitted with the program *XIAM* using three rotational constants, five quartic centrifugal distortion constants  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ ,  $\delta_K$ , the  $V_3$  barrier to internal rotation, the polar coordinates  $\delta$  and  $\varepsilon$  of the internal rotor axis in the principal axis system, the effective parameters  $D_{\text{pi}2J}$  and  $D_{\text{pi}2-}$ , and the internal rotation constant  $F_0$ . The fitted parameters are given in Table 2. A complete list of all fitted transitions along with their residuals is available in Table S2 in the supplementary materials. The rms deviation of 4.7 kHz obtained with the program *XIAM* is still twice the estimated measurement accuracy (2 kHz).

As an alternative, the same data set was fitted with the program *BELGI-C<sub>1</sub>* [19], which is available at the PROSPE website [20]. A comparison of the two programs was described elsewhere [2,3] and will only be repeated briefly here. The program *XIAM* uses a combination of the principal axis method and the rho axis method. The Hamilton matrix of each internal rotor is set up in its own rho axis system. After diagonalization, the eigenvalues and torsional integrals are used to set up the Hamilton matrix in the principal axis system. Matrix elements of each internal rotor are added to the Hamilton matrix, which also contains the matrix elements of the overall rotation. Finally, the matrix is diagonalized to obtain the rotorsional eigenvalues.

The program *BELGI-C<sub>1</sub>* uses a two-step diagonalization procedure, both of which are carried out in the rho axis system. In the first step the torsional Hamiltonian which contains a one-dimensional potential function  $V(\alpha)$  and a rotation–torsion

kinetic term  $F(\mathbf{p}_\alpha - \rho \mathbf{P}_a)^2$  is diagonalized in the basis set  $\exp[i(3k + \sigma)\alpha] |K\rangle$  [21], where  $k$  is an integer with  $-10 \leq k \leq 10$ ,  $|K\rangle$  is the symmetric top eigenfunction,  $\sigma$  is either 0 for the A species or  $\pm 1$  for the E species,  $\mathbf{p}_\alpha$  is the internal rotation angular momentum conjugate to the torsional angle  $\alpha$ ,  $\mathbf{P}_a$  is the a component of the total rotational angular momentum, and  $\rho$  is the coupling constant between the internal rotation and the global rotation. In the second step, we used a basis set consisting of products of the torsional eigenfunctions obtained from the first step diagonalization and the symmetric top wavefunctions  $|JKM\rangle$  to diagonalize the rest of the terms of the Hamiltonian, i.e. the rotational part  $H_R$ , the centrifugal distortion part  $H_{CD}$ , and higher order interaction terms between torsion and rotation  $H_{int}$  allowed for the  $C_1$  symmetry [19].

We derived the initial values of the rotational constants by a transformation of the values obtained from the *XIAM* fit given in Table 2 into the rho axis system. The starting value of  $V_3$  was taken directly from the *XIAM* fit. The off-diagonal element  $D_{ab}$  of the moment of inertia tensor and the  $F$  parameter were estimated from *ab initio* calculations. A rms deviation of 1.8 kHz, which is within the measurement accuracy, was obtained straightforward by floating 15 parameters. Because of the  $C_1$  symmetry of the assigned conformer, the  $D_{ac}$  parameter, which multiplies the off-diagonal  $\mathbf{P}_a \mathbf{P}_c + \mathbf{P}_c \mathbf{P}_a$  term, is needed. The *BELGI-C<sub>1</sub>* parameters in the rho axis system are collected in Table 3. Parameters which can be transformed into the principal axis system are also given in Table 2.

#### 4. Discussion

In Figure 4, the experimentally deduced rotational constants  $A$ ,  $B$ , and  $C$  are plotted as straight horizontal lines. These can be compared with the predicted values of the five conformers mentioned in section 2, which are illustrated as dots. Figure 4 confirms unambiguously that the assigned conformer is conformer **aM/aP**. All three calculated rotational constants match perfectly the experimental values.



The barrier to the internal rotation of the acetyl methyl group in *n*-propyl acetate is found to be 103.341(18) cm<sup>-1</sup> using the program *BELGI-C<sub>1</sub>* and 97.3015(56) cm<sup>-1</sup> using the program *XIAM*, which is as expected approximately the same values found for other  $\alpha,\beta$ -saturated acetates [11]. For this parameter, the *XIAM* and *BELGI-C<sub>1</sub>* programs are not consistent with a deviation of about 6 cm<sup>-1</sup>, because different parameter sets were fitted (see Table 2 and 3) and the correlations amount these parameters are different.

The moment of inertia  $I_\alpha$  of 3.33085(20) uÅ<sup>2</sup> (derived from  $F_0 = \frac{\hbar^2}{2I_\alpha}$ ) obtained by the *XIAM* fit is rather high in comparison to the value of a methyl rotor at equilibrium predicted by *ab initio*. Fixing  $I_\alpha$  at the *ab initio* value of 3.197 uÅ<sup>2</sup> changes the hindering barrier to 101.3169(90) cm<sup>-1</sup> (because of the strong correlation between  $V_3$  and  $I_\alpha$ ) and increases the standard deviation significantly to 374 kHz. Furthermore, the quartic centrifugal distortion constants can no longer be well-determined. Other parameters such as the rotational constants and angles between the internal rotor axis and the principal axes agree well with the values from the *BELGI-C<sub>1</sub>* fit. However, they do not agree within the errors for the same reason as in the case of the  $V_3$  barrier.

A correlation coefficient close to +1 is frequently found between  $V_3$  and  $F_0$  in our previous investigations on molecules exhibiting the internal rotation of a methyl group. Therefore, in some cases  $F_0$  has to be fixed to a reasonable value. In other cases both quantities can be fitted, but  $F_0$  and therefore also  $I_\alpha$  sometimes take values which hardly agree with the moment of inertia of a methyl group. However, the product  $V_3 \cdot I_\alpha$  is almost constant for small changes of  $I_\alpha$  and it is possible to obtain a  $V_3^0$  potential for any reasonable reference value  $I_\alpha^0$  via the equation  $V_3^0 = V_3 \cdot I_\alpha / I_\alpha^0$ . In Table 4, we report the  $V_3^0$  potentials of some acetates referred to  $I_\alpha^0 = 3.197$  uÅ<sup>2</sup>. It can be seen that  $V_3^0$  of  $\alpha,\beta$ -saturated acetates is

amazingly close to  $100\text{ cm}^{-1}$ , whereas  $\alpha,\beta$ -unsaturated acetates show much higher values. We discussed the origin of these higher  $V_3^0$  values in Ref. [11].

According to Table 1 and Figure 2, conformers **PP/MM** and **aa** are less than  $1.5\text{ kJ}\cdot\text{mol}^{-1}$  higher in energy than the assigned conformer **aM/aP**. Both of them might be present in the experimental spectrum under our molecular beam conditions using helium as carrier gas, because the rotational cooling is not as effective as with neon or argon and higher energy conformers might be still populated. On the other hand, as can be seen in Figure 3 all strongest lines were assigned to the most stable conformer **aM/aP**. There are still some weak unassigned lines in the spectrum, which might belong to conformers **PP/MM** and **aa**. However, there are not enough of them to lead to a successful assignment.

Finally, it is notable that a few of the measured lines appear as narrow doublets or triplets. These hyperfine structures might be due to the spin-spin or spin-rotation coupling arise from the protons in the molecule, but also very probably due to the internal rotation of the propyl methyl group. Sample two-top calculations with an estimated barrier height of  $1100\text{ cm}^{-1}$ , similar to that of the ethyl methyl group in ethyl acetate [2], have shown that the expected splittings are up to 15 kHz.

## 5. Conclusion

The enantiomeric pair **aM/aP** of *n*-propyl acetate, which was predicted as the lowest energy conformer by *ab initio*, was assigned in the microwave spectrum and fitted using the *XIAM* code. The fit quality was improved to measurement accuracy using the *BELGI-C<sub>1</sub>* code, and the standard deviation decreased from 4.9 kHz to 1.8 kHz. The hindering barrier of the acetyl methyl group was determined by *XIAM* to be  $97.3015(56)\text{ cm}^{-1}$  and by *BELGI-C<sub>1</sub>* to be  $103.341(18)\text{ cm}^{-1}$ , which is almost the same as that in other  $\alpha,\beta$ -saturated acetates. The slightly lower barrier obtained by *XIAM* is connected to the unusually large moment of inertia

of the methyl rotor fitted by this program, which is a consequence of a strong correlation in the torsion parameters of the model.

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## References

- [1] M. Tudorie, I. Kleiner, J.T. Hougen, S. Melandri, L.W. Sutikdja, W. Stahl, A fitting program for molecules with two inequivalent methyl tops and a plane of symmetry at equilibrium: Application to new microwave and millimeter-wave measurements of methyl acetate, *J. Mol. Spectrosc.* 269 (2011) 211.
- [2] D. Jelisavac, D.C. Cortés Gómez, H.V.L. Nguyen, L.W. Sutikdja, W. Stahl, I. Kleiner, The microwave spectrum of the trans conformer of ethyl acetate, *J. Mol. Spectrosc.* 257 (2009) 111.
- [3] T. Attig, L.W. Sutikdja, R. Kannengießer, I. Kleiner, W. Stahl, The microwave spectrum of n-butyl acetate, *J. Mol. Spectrosc.* 284-285 (2013) 8.
- [4] T. Attig, R. Kannengießer, I. Kleiner, W. Stahl, Conformational analysis of n-pentyl acetate using microwave spectroscopy, *J. Mol. Spectrosc.* 290 (2013) 24.
- [5] T. Attig, R. Kannengießer, I. Kleiner, W. Stahl, The microwave spectrum of n-hexyl acetate and structural aspects of n-alkyl acetates, *J. Mol. Spectrosc.* 298 (2014) 47.
- [6] H. Mouhib, D. Jelisavac, W. Stahl, R. Wang, I. Kalf, U. Englert, The conformation of odorants in different states of aggregation: A joint venture in microwave spectroscopy and X-ray diffraction, *ChemPhysChem* 12 (2011), 761.
- [7] L. W. Sutikdja, D. Jelisavac, W. Stahl, I. Kleiner, Structural studies on banana oil, isoamyl acetate, by means of microwave spectroscopy and quantum chemical calculations, *Mol. Phys.* 110 (2012) 2883.
- [8] C. Macku, G. Jennings, Production of volatiles by ripening bananas, *J. Agric. Food Chem.* 35 (1987) 845.
- [9] A. Plotto, M.R. McDaniel, J.P. Mattheis, Characterization of changes in 'Gala' apple aroma during storage using osme analysis, a gas chromatography-olfactometry technique, *J. Amer. Soc. Hort. Sci.* 125 (2000) 714.

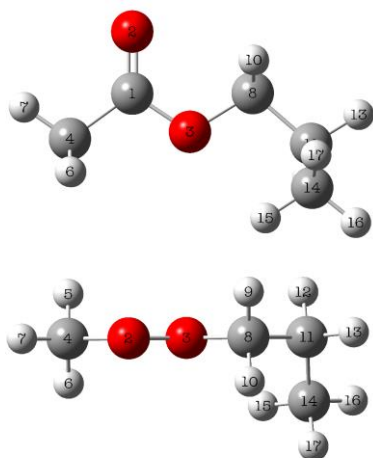
- [10] T. Lavilla, I. Recasens, M.L. Lopez, J. Puy, Multivariate analysis of maturity stages, including quality and aroma, in ‘Royal Glory’ peaches and ‘Big Top’ nectarines, *J. Agric. Food Chem.* 82 (2002) 1842.
- [11] A. Jabri, V. Van, H.V.L. Nguyen, W. Stahl, I. Kleiner, Probing the methyl torsional barriers of the *E* and *Z* isomers of butadienyl acetate by microwave spectroscopy, *ChemPhysChem* 17 (2016), 2660.
- [12] J. Sheridan, W. Bossert, A. Bauder, Internal rotation of molecules with two inequivalent methyl groups: The microwave spectrum of methyl acetate, *J. Mol. Spectrosc.* 80 (1980) 1.
- [13] M. Oki, H. Nakanishi, Conformations of the ester group, *Bull. Chem. Soc. Jpn.* 43 (1970) 2558.
- [14] M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT (2004).
- [15] J.-U. Grabow, W. Stahl, H. Dreizler, A multioctave coaxially oriented beam resonator arrangement. Fourier-transform microwave (COBRA-FTMW) spectrometer, *Rev. Sci. Instrum.* 67 (1996) 4072.

- [16] I. Merke, W. Stahl, H. Dreizler, A molecular beam Fourier transform microwave spectrometer in the range 26.5 to 40 GHz. Tests of performance and analysis of the D- and  $^{14}\text{N}$ -hyperfine structure of methylcyanide- $\text{d}_1$ , *Z. Naturforsch.* 49a (1994) 490.
- [17] J.-U. Grabow, W. Stahl, A pulsed molecular beam microwave Fourier transform spectrometer with parallel molecular beam and resonator axes, *Z. Naturforsch.* 45a (1990) 1043.
- [18] H. Hartwig, H. Dreizler, The microwave spectrum of trans-2,3-dimethyloxirane in torsional excited states, *Z. Naturforsch.* 51a (1996) 923.
- [19] I. Kleiner, J.T. Hougen, Rho-axis-method Hamiltonian for molecules having one methyl rotor and  $\text{C}_1$  point-group symmetry at equilibrium, *J. Chem. Phys.* 119 (2003) 5505.
- [20] <http://www.ifpan.edu.pl/~kisiel/prospe.htm>.
- [21] E. Herbst, J.K. Messer, F.C. DeLucia, P. Helminger, A new analysis and additional measurements of the millimeter and submillimeter spectrum of methanol, *J. Mol. Spectrosc.* 108 (1984) 42.
- [22] H.V.L. Nguyen, H. Mouhib, W. Stahl, I. Kleiner, The microwave spectrum of allyl acetate, *Mol. Phys.* 108 (2010) 763.
- [23] Y. Zhao, H. Mouhib, G. Li, I. Kleiner, W. Stahl, Conformational analysis of tert-butyl acetate using a combination of microwave spectroscopy and quantum chemical calculations, *J. Mol. Spectrosc.* 322 (2016) 38.
- [24] H.V.L. Nguyen, W. Stahl, The microwave spectrum of isopropenyl acetate : An asymmetric molecule with two internal rotors, *J. Mol. Spectrosc.* 264 (2010) 120.
- [25] H.V.L. Nguyen, A. Jabri, V. Van, W. Stahl, Methyl internal rotation in the microwave spectrum of vinyl acetate, *J. Phys. Chem. A* 118 (2014) 12130.

## Figures

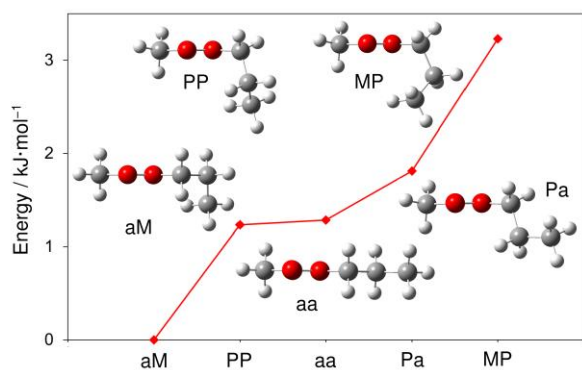
**Fig. 1.**

Optimized geometry of conformer **aM/aP** of *n*-propyl acetate calculated at the MP2/6-311++G(d,p) level of theory. Upper diagram: front view, lower diagram: view along the C<sub>1</sub>-O<sub>2</sub> bond.



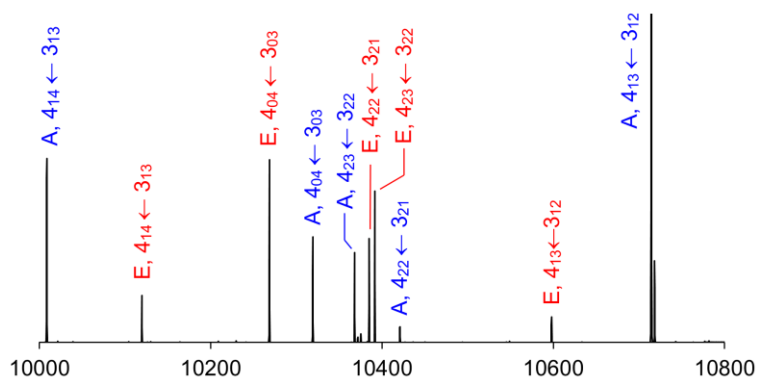
**Fig. 2.**

The *trans* conformers of *n*-propyl acetate in order of their energies (including vibrational zero-point correction) relative to that of the most stable conformer **aM/aP** (for values see Table 1).



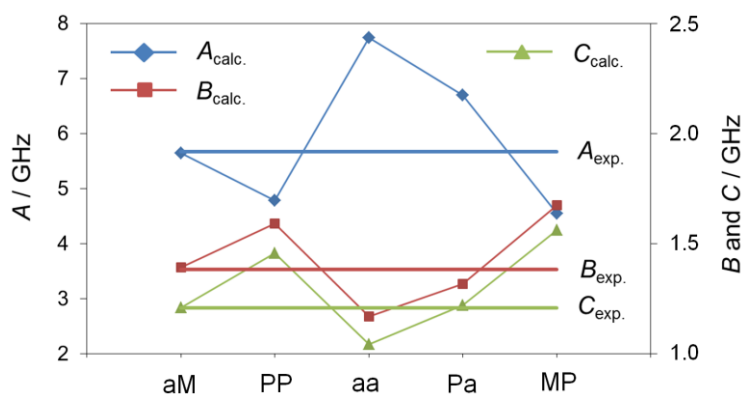
**Fig. 3.**

A portion of the broadband scan of *n*-propyl acetate in the frequency range from 10000 to 10800 MHz. The  $J = 4 \leftarrow 3$  *a*-type transitions with  $K_a = 0, 1, 2$  are marked with their respective quantum numbers and torsional species.



**Fig. 4.**

Rotational constants of the *trans* conformers of *n*-propyl acetate calculated at the MP2/6-311++G(d,p) level of theory in comparison with experimental results to identify the assigned conformer. The experimentally deduced rotational constants ( $A_{\text{exp.}}$ ,  $B_{\text{exp.}}$ , and  $C_{\text{exp.}}$ ) are visualized as horizontal lines, the calculated values as separated points connected by lines, which are only present for a better tracing.





**Table 1.** The rotational constants  $A$ ,  $B$ ,  $C$  (in GHz), dipole moment components  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  (in Debye), and relative energies  $E_{\text{rel}}$ . (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) of the *trans* conformers of *n*-propyl acetate calculated at the MP2/6-311++G(d,p) level of theory. The dipole moment components are with respect to the principal axes of inertia; signs refer to coordinates given in the supplementary materials. All energies are electronic energies including vibrational zero-point correction and are relative to the lowest energetic conformer I with its absolute energy of  $E + \text{ZPE} = -345.99321$  Hartree.

| <b>Conf.</b>             | <b><math>A</math></b> | <b><math>B</math></b> | <b><math>C</math></b> | <b><math>\mu_a</math></b> | <b><math>\mu_b</math></b> | <b><math>\mu_c</math></b> | <b><math>E_{\text{rel}}</math></b> |
|--------------------------|-----------------------|-----------------------|-----------------------|---------------------------|---------------------------|---------------------------|------------------------------------|
| <b>aM</b>                | 5.644                 | 1.392                 | 1.210                 | 1.276                     | 1.723                     | 0.647                     | 0.00                               |
| <b>PP</b>                | 4.780                 | 1.592                 | 1.457                 | 0.665                     | 1.632                     | 0.842                     | 1.23                               |
| <b>aa</b>                | 7.734                 | 1.169                 | 1.042                 | -0.883                    | -2.072                    | 0.000                     | 1.29                               |
| <b>Pa</b>                | 6.696                 | 1.317                 | 1.220                 | 0.199                     | -1.879                    | 0.450                     | 1.81                               |
| <b>PM</b>                | 4.544                 | 1.674                 | 1.562                 | -0.482                    | -1.393                    | -1.402                    | 3.23                               |
| <b>Expt.<sup>a</sup></b> | <b>5.667</b>          | <b>1.382</b>          | <b>1.208</b>          |                           |                           |                           |                                    |

<sup>a</sup> Experimental values

**Table 2.** Molecular parameters of conformer **aM/aP** of *n*-propyl acetate obtained by the programs *XIAM* and *BELGI-C<sub>1</sub>*.

| Par. <sup>a</sup>       | Unit             | <i>XIAM</i>    | <i>BELGI-C<sub>1</sub></i> <sup>b</sup> |
|-------------------------|------------------|----------------|---|
| <i>A</i>                | GHz              | 5.6670873(20)  | 5.660284(91)                            |
| <i>B</i>                | GHz              | 1.38181941(92) | 1.3841564(96)                           |
| <i>C</i>                | GHz              | 1.20791173(70) | 1.20880589(69)                          |
| $\Delta_J$              | kHz              | 0.30668(61)    |   |
| $\Delta_{JK}$           | kHz              | -1.1117(95)    |   |
| $\Delta_K$              | kHz              | 11.47(43)      |   |
| $\delta_J$              | kHz              | 0.01935(28)    |   |
| $\delta_K$              | kHz              | 2.248(40)      |   |
| $D_{pi2J}$              | kHz              | 140.64(11)     |   |
| $D_{pi2-}$              | kHz              | 74.74(14)      |   |
| $F_0$                   | GHz              | 151.7269(87)   | 157.049(47) <sup>c</sup>                |
| $I_\alpha$ <sup>d</sup> | uÅ <sup>2</sup>  | 3.33085(20)    | 3.21795(96)                             |
| $V_3$                   | cm <sup>-1</sup> | 97.3015(56)    | 103.341(18)                             |
| $s$ <sup>e</sup>        |                  | 8.37889        | 8.44611 <sup>f</sup>                    |
| $\angle(i,a)$           | °                | 52.8392(3)     | 52.83309(40)                            |
| $\angle(i,b)$           | °                | 37.7604(3)     | 37.76055(34)                            |
| $\angle(i,c)$           | °                | 84.2316(4)     | 84.25958(32)                            |
| $\sigma$ <sup>f</sup>   | kHz              | 4.7            | 1.8                                     |
| $N_A/N_E$ <sup>g</sup>  |                  | 98/50          | 98/50                                   |

<sup>a</sup> All parameters refer to the principal axis system. Watson's A reduction in I' representation was used. <sup>b</sup> Obtained by a transformation from the rho axis system (RAM) to the principal axis system (PAM) (for details see Ref. [2]). <sup>c</sup> Fixed in the *BELGI-C<sub>1</sub>* fit. The error in parentheses results from the RAM to PAM transformation. <sup>d</sup> Moment of inertia of the internal rotor, derived from its rotational constant  $F_0$ . <sup>e</sup> Reduced barrier  $s = 4V_3/9F$ . <sup>f</sup> Root-mean-square deviation of the fit. <sup>g</sup> Number of the A ( $N_A$ ) and E species lines ( $N_E$ ).

**Table 3.** Molecular parameters of conformer **aM/aP** of *n*-propyl acetate in the rho axis system obtained by the programs *BELGI-C1*.

| Operator <sup>a</sup>                                    | Par. <sup>b</sup>      | Unit             | Value <sup>c</sup>      |
|--|------------------------|------------------|-------------------------|
| $\mathbf{P}_a^2$   | <i>A</i>               | GHz              | 5.25848(13)             |
| $\mathbf{P}_b^2$   | <i>B</i>               | GHz              | 1.7844216(20)           |
| $\mathbf{P}_c^2$   | <i>C</i>               | GHz              | 1.21034192(63)          |
| $\{\mathbf{P}_a, \mathbf{P}_b\}$                         | <i>D</i> <sub>ab</sub> | GHz              | -1.2472065(26)          |
| $\{\mathbf{P}_a, \mathbf{P}_c\}$                         | <i>D</i> <sub>ac</sub> | GHz              | 0.04549180(73)          |
| $-\mathbf{P}^4$  | $\Delta_J$             | kHz              | 0.6283(46)              |
| $-\mathbf{P}^2\mathbf{P}_a^2$                            | $\Delta_{JK}$          | kHz              | -7.662(96)              |
| $-\mathbf{P}_a^4$  | $\Delta_K$             | kHz              | 20.53(30)               |
| $-2\mathbf{P}^2(\mathbf{P}_b^2 - \mathbf{P}_c^2)$        | $\delta_J$             | kHz              | 0.1787(23)              |
| $-\{\mathbf{P}_a^2, (\mathbf{P}_b^2 - \mathbf{P}_c^2)\}$ | $\delta_K$             | kHz              | -0.501(15)              |
| $\mathbf{P}_a\mathbf{P}_\alpha$                          | $\rho$                 | uniteless        | 0.0228747(82)           |
| $(1/2)(1 - \cos 3\alpha)$                                | <i>V</i> <sub>3</sub>  | cm <sup>-1</sup> | 103.341(18)             |
| $(1 - \cos 3\alpha)\mathbf{P}^2$                         | <i>F</i> <sub>v</sub>  | MHz              | -0.0040305(14)          |
| $(1 - \cos 3\alpha)(\mathbf{P}_b^2 - \mathbf{P}_c^2)$    | <i>c</i> <sub>2</sub>  | MHz              | -0.0024220(16)          |
| $(1 - \cos 3\alpha)\mathbf{P}_a^2$                       | <i>k</i> <sub>5</sub>  | MHz              | 0.02855(35)             |
| $\mathbf{P}_a^2$   | <i>F</i>               | GHz              | 163.025166 <sup>d</sup> |

<sup>a</sup> 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.  $\mathbf{P}_a$ ,  $\mathbf{P}_b$ , and  $\mathbf{P}_c$  are the components of the overall rotational angular momentum,  $\mathbf{P}_\alpha$  is the angular momentum of the internal rotor rotating around the internal rotor axis by an angle  $\alpha$ .  $\{u, v\}$  is the anti commutator  $uv + vu$ . <sup>b</sup> 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*,  $\rho$ , and *A*, which occur in the Hamiltonian in the form  $F(\mathbf{P}_\alpha - \rho\mathbf{P}_a)^2 + A\mathbf{P}_a^2$ . <sup>c</sup> Values of the parameters from the present fit. Statistical uncertainties are shown as one standard uncertainty in unit of the last two digits. <sup>d</sup> Fixed.

**Table 4.** The  $V_3^0$  potentials of various acetates referred to the same moment of inertia of the methyl group of  $I_\alpha^0 = 3.197 \text{ u}\text{\AA}^2$  using the equation  $V_3^0 = V_3 \cdot I_\alpha / I_\alpha^0$ .

| Molecule, conformer             | $I_\alpha / \text{u}\text{\AA}^2$ | $V_3 / \text{cm}^{-1}$ | $V_3^0 / \text{cm}^{-1}$ | ref.         |
|---------------------------------|-----------------------------------|------------------------|--------------------------|--------------|
| Methyl acetate                  | 3.21786(53)                       | 101.740(30)            | 102.40                   | [1]          |
| Ethyl acetate                   | 3.16067(76)                       | 101.606(23)            | 100.45                   | [2]          |
| <i>n</i> -Propyl acetate, aM/aP | 3.33085(20)                       | 97.3015(56)            | 101.38                   | <sup>a</sup> |
| <i>n</i> -Butyl acetate, aPa    | 3.38242(28)                       | 94.8219(80)            | 100.32                   | [3]          |
| <i>n</i> -Butyl acetate, aaa    | 3.2972(45)                        | 96.00(12)              | 99.01                    | [3]          |
| <i>n</i> -Butyl acetate, PPa    | 3.3325(10)                        | 95.837(29)             | 99.90                    | [3]          |
| <i>n</i> -Pentyl acetate, aPaa  | 3.4964(15)                        | 91.459(40)             | 100.02                   | [4]          |
| <i>n</i> -Pentyl acetate, aaaa  | 3.197 fixed                       | 98.6768(25)            | 98.68                    | [4]          |
| <i>n</i> -Hexyl acetate, aPaaa  | 3.58101(88)                       | 89.075(21)             | 99.77                    | [5]          |
| Isopropyl acetate               | 3.2801(17)                        | 97.911(68)             | 100.46                   | [6]          |
| Isoamyl acetate, aM(M,a)        | 3.38737(47)                       | 93.953(14)             | 99.55                    | [7]          |
| Allyl acetate                   | 3.29046(33)                       | 98.093(12)             | 100.96                   | [22]         |
| <i>tert</i> -Butyl acetate      | 3.23512(39)                       | 111.380(20)            | 112.71                   | [23]         |
| Isopropenyl acetate             | 3.1586 fixed                      | 135.3498(38)           | 133.72                   | [24]         |
| Vinyl acetate                   | 3.28858(59)                       | 151.492(34)            | 155.83                   | [25]         |
| Butadienyl acetate, E           | 3.1986 fixed                      | 149.1822(20)           | 149.26                   | [11]         |
| Butadienyl acetate, Z           | 3.1986 fixed                      | 150.2128(48)           | 150.29                   | [11]         |

Note: When fits with different fitting programs were carried out, we always give the values obtained with the program *XIAM*. <sup>a</sup> This work.