A touch of lavender: gas-phase structure and dynamics of the monoterpene linalool validated by microwave spectroscopy

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A Touch of Lavender: Gas-phase Structure and Dynamics of the Monoterpene Linalool validated by Microwave Spectroscopy

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The microwave spectrum of linalool, an acyclic monoterpene, was recorded for the first time in the range from 9 to 16 GHz. The only conformer observed under molecular beam conditions was assigned. Fitting the rotational spectrum with two different programs treating internal rotation yielded the rotational constants $A = 1.64674020(46)$ GHz, $B = 0.68219862(16)$ GHz, $C = 0.61875100(20)$ GHz, and the
10 centrifugal distortion constants. The standard deviation of the fit was close to experimental accuracy. A−E splittings due to the internal rotation of one methyl group could be resolved and the internal rotation barrier was determined to be 400.20(64) cm^{-1}. The results from microwave spectroscopy were used to validate the molecular geometry obtained from quantum chemical calculations.

1 Introduction

15 Terpenes in general comprise a large class of compounds containing the building block isoprene, CH_3-C(=CH_2)-CH=CH_2. They provide a broad variety of scents in nature. They are present in more than 200 species of plants, spices, and in fruits (like in grapes and wine). Numerous terpenes such as linalool, citronallol,
20 citral, and eugenol were an important source of inspiration for perfumers in the 19th century.[1] Nowadays, they find various applications in the perfumery and scent industry. Linalool and linalyl acetate are known to possess several biological activities such as anti-inflammatory properties.[2]

25 Furthermore, terpenes are considered as atmospheric pollutants and therefore play an important role in atmospheric chemistry.[3] The large production and emission of the biogenic volatile organic compounds (BVOCs) by plants are known to contribute to the oxidation capacity of the atmosphere, to the particle
30 production, and to the carbon cycle. Terpenes react rapidly with OH and NO_3 radicals and O_3. They contribute to the chemistry of the troposphere.[4]

Information about the structures of such metabolic compounds is thus very important and it is necessary to study all those
35 phenomena in details. However, compounds found in natural substances are still not studied too much by high resolution spectroscopy. Only recently, the rotational spectrum of *o*-vanilin and its derivatives were studied using a supersonic jet expansion and microwave Fourier transform technique.[5,6]

40 The only currently available gas-phase structure of a terpene is that on perillaldehyde, a cyclic monoterpene.[7] Almost no reports on gas-phase structures of acyclic monoterpenes have been published except for the millimeter-wave measurements of linalool,[8] geraniol, and verbenone[9] which were very recently
45 recorded, but for which no assignments are available in the literature. This might be due to the fact that even smallest acyclic terpenes contain a large number of atoms and possess many possible conformers with energy differences below 10 kJ/mol. Furthermore, the vapor pressures are often too low (below 1 hPa)
50 for gas-phase studies at room temperature.

Linalool, $(CH_3)_2$C=CH-C_2H_4-CCH_3OH-CH=CH_2, is an acyclic monoterpene which is present in a lot of essential oils of plants such as ho-leaf (80%), coriander (70%), and lavender (40%). It is also widely accepted as one of the few compounds directly
55 contributing to the hop aroma in beer. Linalool possesses an agreeable, floral, and refreshing scent, which is also reminiscent of citrus fruits. From a spectroscopic point of view, linalool is a very interesting molecule. There are three methyl groups which can undergo internal rotation. The -C**CH₃**OH- methyl group
60 should have a high barrier over 1000 cm^{-1}, since no splittings from such a methyl group were reported in similar cases like isopropanol[10] and 2-butanol.[11] From a study on 1-chloro-2-methylpropene,[12] we know that the barriers of the *trans* and *cis* methyl groups fixed to the double bond are 304.34(2) cm^{-1} and
65 928.0(17) cm^{-1}, respectively. Therefore, we expected to be able to resolve the splittings due to internal rotation of these two methyl groups also in the microwave spectrum of linalool.

From many current studies, it is known that a combination of microwave spectroscopy and quantum chemistry is a good tool
70 for analyzing the rotational spectra of large molecules like esters, ketones, and amines.[13,14,15] This method has also been successfully used to investigate the structures of cassyrane, an artificial blackcurrant odorant,[16] and green apple flavor, the small fruit ester ethyl valerate.[17] Quantum chemical calculations are
75 suitable for predicting the geometries of various conformers. However, their energies are often within a very narrow range and an unambiguous identification of the lowest energy conformer is not always possible. Under molecular beam conditions, where the temperature is extremely low, only the lowest energy conformers
80 are sufficiently populated and by comparison of the theoretical and experimental rotational constants their identification becomes

possible. Here, we report on the first gas-phase structure of an acyclic monoterpene calculated by quantum chemical methods and validated using molecular beam Fourier transform microwave (MB-FTMW) spectroscopy.

2 Experimental

Linalool, (±)-3,7-dimethyl-1,6-octadien-3-ol, was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. The purity was stated to be 97%, the vapor pressure 0.17 mmHg (0.23 hPa) at 25 °C. The microwave spectrum was observed with a MB-FTMW spectrometer operating in the frequency range of 4 – 26.5 GHz.[18] Since the vapor pressure of linalool is rather low, the sample was heated. For this purpose a few drops of linalool were placed on a 5 cm piece of a pipe cleaner and then inserted into a stainless steel tube with an inner diameter of 4 mm. The tube, mounted upstream the nozzle, was heated to a temperature of approximately 350 K and helium at a pressure of 150 – 200 kPa was allowed to flow over the sample. For assignment purposes, a broadband scan was recorded in the range of 9.00 – 15.25 GHz. Afterwards, all lines were remeasured in the high resolution mode of the spectrometer. The measurement accuracy is 2 kHz for isolated lines but it becomes worse when the lines are broadened by overlapping transitions.

A spectrum of linalool in the scan mode is shown in the lower trace of Fig. 1. We also found it interesting to record the spectrum of the natural product (essence de lavendin, purchased in the Provence, France) in the same spectral range (see Fig. 1, upper trace). Most of the lines in the linalool spectrum could be observed in the spectrum of lavender oil with very similar intensity. This opens a direction where high resolution spectroscopy can be used as an analytic tool to study the compounds of olfaction as well as to determine which compounds play an important role for the scent of a perfume.

3 Quantum chemical calculations

Quantum chemical calculations were carried out only for the (S)-enantiomer of linalool, since enantiomers possess equal sets of rotational constants and cannot be distinguished in the microwave spectrum. To obtain theoretical rotational constants as an initial guess to predict the microwave spectrum of (S)-linalool, 167 different starting geometries were preselected by force field methods and optimized at the MP2/6-311++G(d,p) level of theory using the Gaussian09 program package.[19] This level of theoretical calculations was chosen since it is widely used in the microwave spectroscopic community and since it is known to yield rotational constants which are usually in good agreement with the experimental results. Harmonic frequency calculations were performed to verify the nature of the stationary points. Totally, 54 energy minima were found.

Among these 54 conformers, the fifteen lowest energy conformers were re-optimized using the DFT method with two different hybrid functionals, B3LYP and B3PW91, and the MP2 method. Different basis sets were used in all cases. We decided to carry out DFT calculations using the hybrid functional B3PW91, since electric field gradient calculations at the B3PW91/6-311+G(d,p) level of theory yielded excellent results on the quadrupole coupling constants for triethyl amine.[15] Since two
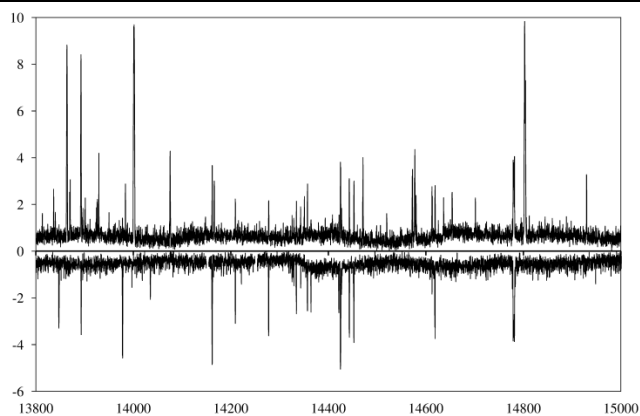

Fig. 1 The spectrum of lavender oil (essence de lavendin, upper trace) and linalool (lower trace). Frequencies are given in MHz, intensities in arbitrary units.

double bonds are present in linalool and the electric effect from the π electrons might affect the molecular structure, the B3PW91 functional could also be useful for this molecule. In all combinations of methods and basis sets, the conformer indicated in Fig. 2 (called conformer I) is present as the most energetically favorable conformer of linalool. The results calculated at the MP2/6-311++G(d,p) level of theory are given in Table 1, where the calculated rotational constants and energy values of the fifteen lowest energy conformers are given. Two main structures occur with a globular or a prolate form (marked with (g) or (p) in Table 1, respectively).The complete data sets are given in Table S1, the corresponding Cartesian coordinates of the five lowest energy conformers in the principal axes of inertia in Table S2 (ESI). The calculated rotational constants of conformer I were used as a starting point for the spectral assignment.

Additionally, the barriers to internal rotation of all three methyl groups of linalool were calculated at the MP2/6-311++G(d,p) level of theory. The barriers were determined to be 1327 cm^{-1}, 324 cm^{-1}, 776 cm^{-1} for methyl group 1, 2, and 3, respectively. For methyl group numbering see Fig. 2. According to these barriers, splittings due to internal rotation were expected for methyl group 2 and 3, whereas those of methyl group 1 are too narrow to be resolved. The calculated angles between the internal rotor axis of methyl group 2 and the principal axes of inertia are also given in Table 1.
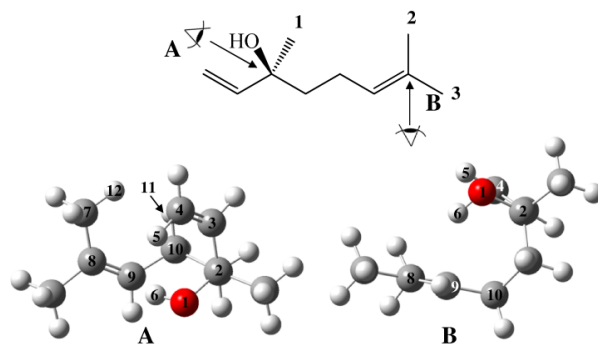

Fig. 2 Geometry of the lowest energy conformer optimized at the MP2/6-311++G(d,p) level of theory. Different views are presented. The structures A and B correspond to the respective Newman projections shown in the upper part of the picture. Methyl groups, which can undergo internal rotation, are labelled with numbers.

Table 1 The rotational constants, energy values, and angles between the internal rotor axis of methyl group 2 (see Fig. 2) and the principal axes of 15 most energetically favorable conformers of linalool calculated at the MP2/6-311++G(d,p) level of theory. Conformers with globular structure are marked with (g), with prolate structure with (p).

Conformer	A / GHz	B / GHz	C / GHz	$\|\mu_a\|$ / D	$\|\mu_b\|$ / D	$\|\mu_c\|$ / D	E_{MP2} Hartree	rel. E kJ/mol	$\angle(i,a)$ / °	$\angle(i,b)$ / °	$\angle(i,c)$ / °
I (g)	**1.6378**	**0.7003**	**0.6355**	**1.118**	**0.040**	**1.866**	**−465.796119**	**0.00**	**86.31**	**29.10**	**61.18**
II (g)	1.6701	0.6670	0.6115	1.252	0.598	1.608	−465.794307	4.76	72.19	19.38	82.59
III (g)	1.6364	0.6905	0.6366	0.907	1.279	1.322	−465.793107	7.91	85.96	18.20	72.28
IV (g)	1.6208	0.7540	0.6629	1.383	0.221	1.096	−465.792614	9.20	87.50	75.18	15.04
V (p)	2.0836	0.4762	0.4567	1.253	0.305	0.843	−465.792520	9.45	85.78	47.50	42.82
VI (g)	1.6930	0.7156	0.6398	0.832	0.801	1.009	−465.792487	9.54	87.33	63.79	26.37
VII (p)	1.9671	0.4913	0.4586	0.843	0.568	1.470	−465.792437	9.67	82.75	29.28	61.80
VIII (p)	2.1629	0.4585	0.4395	1.129	1.052	0.588	−465.791727	11.53	88.62	38.49	51.55
IX (g)	1.6150	0.7276	0.6490	1.231	1.204	0.860	−465.791489	12.16	89.92	73.73	16.27
X (p)	2.0115	0.4878	0.4562	1.230	0.572	0.420	−465.791368	12.47	76.31	44.59	48.63
XI (g)	1.6159	0.6593	0.5870	1.376	0.275	1.271	−465.791306	12.64	74.55	48.64	45.43
XII (g)	1.7368	0.6752	0.6357	1.253	1.064	0.560	−465.791234	12.83	75.64	43.74	49.81
XIII (g)	1.6502	0.6589	0.6033	1.249	1.363	0.585	−465.791102	13.17	85.00	26.41	64.14
XIV (g)	1.6809	0.6262	0.5790	1.364	0.541	1.195	−465.791065	13.27	87.57	6.14	84.36
XV (p)	1.9160	0.5037	0.4667	0.441	1.168	1.139	−465.791042	13.33	77.74	24.03	69.66
Experiment	**1.6467**	**0.6822**	**0.6188**						**85.04**	**30.01**	**60.49**

4 Spectral assignment and fits

Among the geometries of linalool predicted by quantum chemical methods, both, prolate and globular shapes are found. At the beginning, we expected the most stable conformer of linalool to be one of the prolate conformers S-I or S-II (for the structures see Fig. S1 and S2 in ESI) and tried to assign the spectrum using the calculated rotational constants. However, no agreement between the experimental and the theoretical spectrum was found. On the other hand, we identified three small ranges in the spectrum where many lines were concentrated. The distance between these ranges was about 1.3 GHz, which could correspond to the distance between two *a*-type *R* branches with a separation of approximately *B*+*C* or to a *b*-type *Q* branch structure with a band head separation of approximately *A*–(*B*+*C*)/2. The idea of *a*-type *R* branches could be excluded immediately, since the typical detail structure with two limiting *K* = 1 lines was not found. On the other hand, *A*–(*B*+*C*)/2 was too small for those conformers with a prolate shape. However, a globular structure of linalool, where an interaction between the two double bonds could have a stabilizing effect, appeared reasonable. Since all globular conformers were missing in our quantum chemical data at that moment, some additional calculations were done, which confirmed that the globular conformers have lower energies than the conformers with a prolate shape. The most stable conformer (conformer I) has two layers, O_1–C_2–C_3–C_4–H_5–H_6 and C_7–C_8–C_9–C_{10}–H_{11}–H_{12}, with almost a six-member ring structure in each layer, as shown in Fig. 2. We used the calculated rotational constants of conformer I and succeeded to assign the rigid-rotor spectrum, where we neglected internal rotation of the methyl groups. It should be noted that the dipole moment in *b*-direction is too small and only *a*- and *c*-type transitions could be observed.

In a second step, we assumed the barrier to internal rotation of methyl group 2 to be 300 cm⁻¹, similar to the value found for the *trans*-methyl group in 1-chloro-2-methylpropene.[12] The angles between the internal rotor axis and the principal axes of inertia were taken from the optimized geometry. Due to internal rotation of methyl group 2, all lines in the spectrum should split into doublets, which are called the A and the E species.[20]

To fit the data in this work, we combine the quantum chemical calculations and an effective Hamiltonian using two different methods and codes: the XIAM code and the BELGI-C_1 code which allow us to treat internal rotation effects in rotational spectra, either using the combined axis method (CAM)[21] or the rho axis method (RAM),[22] respectively. Both methods have been discussed in details several times[13,23,24] and will not be repeated here.

Totally, 46 A species and 37 E species lines could be fitted with the program XIAM with a standard deviation of 4.6 kHz. The standard deviation obtained from the BELGI-C_1 program is 6.3 kHz for 46 A species lines and 31 E species lines. The fitted parameters for both methods are given in Table 2. Some additional parameters fitted with the program BELGI-C_1 as well as a list of all fitted transitions are available as ESI in Table S3 and S4, respectively.

Due to internal rotation of methyl group 3, all A species lines were expected to split into doublets and E species lines into triplets.[20] However, we found only some transitions where additional splittings in the order of 10 kHz arise. For all other transitions, only broadened lines were found. Therefore, we conclude that the splittings due to internal rotation of methyl group 3 cannot be resolved even in the high resolution mode of the spectrometer. Since methyl group 1 should have an even higher barrier to internal rotation than methyl group 3, no additional splittings are expected.

5 Results and discussion

The most stable conformer of linalool observed under molecular beam conditions was assigned. Only splittings due to internal rotation of methyl group 2 could be resolved. In some cases, those splittings are responsible for large line broadening, which forced us to weight them to 20 kHz, larger than the experimental accuracy of isolated lines. The rotational constants, centrifugal

Table 2 Molecular parameters of linalool obtained from the programs XIAM, BELGI-C_1, and quantum chemical calculations.

| Constant | Fit I | Fit II | Calc.[e] | Exp.[f] – |
	XIAM	BELGI-C_1		Calc.
A/GHz	1.64674020(46)	1.641421(55)	1.6376	0.009
B/GHz	0.68219862(16)	0.683387(23)	0.7004	–0.018
C/GHz	0.61875100(20)	0.616598(21)	0.6355	–0.017
Δ_J/kHz	0.11550(54)			
Δ_{JK}/kHz	0.3843(36)			
δ_J/kHz	0.00735(32)			
δ_K/kHz	0.234(20)			
V_3/cm^{-1}	400.20(64)[a]	399.4 (17)	324	76
I_α/uÅ^2	3.1586 [b]			
$\angle(i,a)$/°	85.04(10)	78(4)	86.40	–1.36
$\angle(i,b)$/°	30.01(39)	30(4)	29.08	0.93
$\angle(i,c)$/°	60.49(38)	62(4)	61.19	–0.70
σ[c]/kHz	4.6	6.6		
N_A/N_E[d]	46/37	46/31		

All constants refer to the principal inertial axis system. For the centrifugal distortion constants, Watson's A reduction and I^r representation was used.[25] Parameters are given with one standard uncertainty in parentheses.
[a] Hindering potential, calculated from the value in frequency units.
[b] Moment of inertia I_α of the internal rotor, fixed to the value corresponding to a rotational constant of $F_0 = 160$ GHz.
[c] Standard deviation of the fit.
[d] Number of the fitted A/E transitions.
[e] Calculated at the MP2/6-311++G(d,p) level of theory using the program *Gaussian09*.
[f] Experimental values

distortion constants, the barrier to internal rotation, and the angles between the internal rotor axis and the principal axes of inertia were determined with the programs XIAM and BELGI-C_1. In the XIAM fit, the centrifugal distortion constant Δ_K and the moment of inertia of the methyl group I_α could not be fitted since they are highly correlated with $A-(B+C)/2$ and the barrier V_3, respectively. I_α was set to 3.1586 uÅ^2, corresponding to $F_0 = 160$ GHz, a typical value found for a methyl group.

Using the program XIAM, 83 rotational transitions were fitted to a standard deviation of 4.6 kHz. This is on the order of magnitude of our experimental accuracy of about 2 kHz. In the case of methyl propionate,[26] where the barrier to internal rotation of the methoxy methyl group is slightly higher than that of methyl group 2 of linalool, XIAM could fit the data set to a standard deviation of 3.4 kHz. As discussed in many previous studies, XIAM gives a satisfactory standard deviation in high barrier cases. The standard deviation of the diethyl ketone fit is 3.5 kHz, where a barrier of approximately 800 cm^{-1} was found.[27] In the case of diethyl amine with a barrier around 1050 cm^{-1},[28] we found a standard deviation of 0.7 kHz, as good as in a typical rigid-rotor fit like ethyl pivalate[29] and ethyl valerate.[17] In lower barrier cases like methyl isobutyl ketone[14] and allyl acetate,[23] the standard deviation obtained by a XIAM fit is much higher than the experimental accuracy. An overview of the standard deviation in dependence on the barrier to internal rotation is given in Table 3. All fits were carried out under very similar conditions, e.g. the same number of fitted parameters.

In contrast, the programs BELGI-C_1 and BELGI-C_s (a similar code to BELGI-C_1, but specified for molecules with a symmetry plane) yielded excellent standard deviations, which are within the experimental accuracy, in low barrier cases like ethyl acetate[24] and allyl acetate.[23] However, in the intermediate barrier cases like

methyl propionate[26] or linalool, the data sets (when they contain only the ground torsional state $v_t = 0$ transitions and J values up to 14) were fitted with almost the same quality using BELGI and XIAM. In the present case, the BELGI code seems to give slightly worse results than usual for a number of E species lines, which are marked in Table S4 (ESI). The fitting difficulties using the BELGI-C_1 code are related to the fact that the coupling constant between internal rotation and global rotation (ρ parameter) is particularily small (0.010236) and the value of the torsional barrier height V_3 is intermediate (399.4 cm^{-1}). In the ground torsional state of linalool, the internal rotation splittings are thus small and it induces a high correlation between the various parameters ρ, V_3, F, D_{ab}, D_{aci}, and D_{bci} which control at the zero order the internal rotation splittings. In the XIAM code, contrarily to BELGI, the F and ρ parameters are derived (and not fitted) from the fitted angles of the methyl group relative to the principal axis system. XIAM also fits the angles of the methyl group in the molecule (rather the D_{ab}, D_{aci}, and D_{bci} parameters as fitted in BELGI). Therefore, for cases such as linalool, XIAM combines a restricted data set from the ground torsional state and small splitting, and it is a more efficient tool. In the BELGI code, we decided to fix the ρ and the F values whereas the potential barrier height V_3 and the D_{ab} parameter which multiplies the operator $(P_aP_b+P_bP_a)$ are fitted. D_{ab} is also a measure of the angle between the ρ vector and the principal axis system and in fact this angle is rather small (12.44°). In such cases, the internal rotation splittings in the torsional ground state $v_t = 0$ do not carry much information, and only a limited number of low order parameters are necessary to fit our $v_t = 0$ data set. Moreover, as pointed out in the theoretical description of the C_1 program Hamiltonian,[30] the D_{ab}, D_{aci} (multiplying the operator $(P_aP_c+P_cP_a)$), and D_{bci} parameter (multiplying the operator $(P_bP_c+P_cP_b)$) cannot all be determined simultaneously from a fit to experimental data, since one of them can be removed by a suitable rotation around the ρ axis. If we fix one of the D_{aci} or D_{bci} value at zero in the present case, a numerically equivalent fit to the fit shown in Table S4 (ESI) can be obtained. As also verified numerically, this indeterminacy in the quadratic rotational constants is responsible for a rather large deviation of the methyl top axis direction of 4° as shown in Table 2. After numerous trials, we found out that the best fit was obtained by floating D_{ab} and D_{aci} and keeping D_{bci} fixed to its *ab initio* derived value.

The structural information of both codes led to similar results, confirming the quantum chemical calculations, as shown below, but the accuracies of the methyl rotor angles and the potential barrier height determined by the BELGI-C_1 code suffer from the high correlation between the internal rotation parameters mentioned above.

Table 3 Standard deviations obtained from the XIAM fits in dependence on the barrier to internal rotation

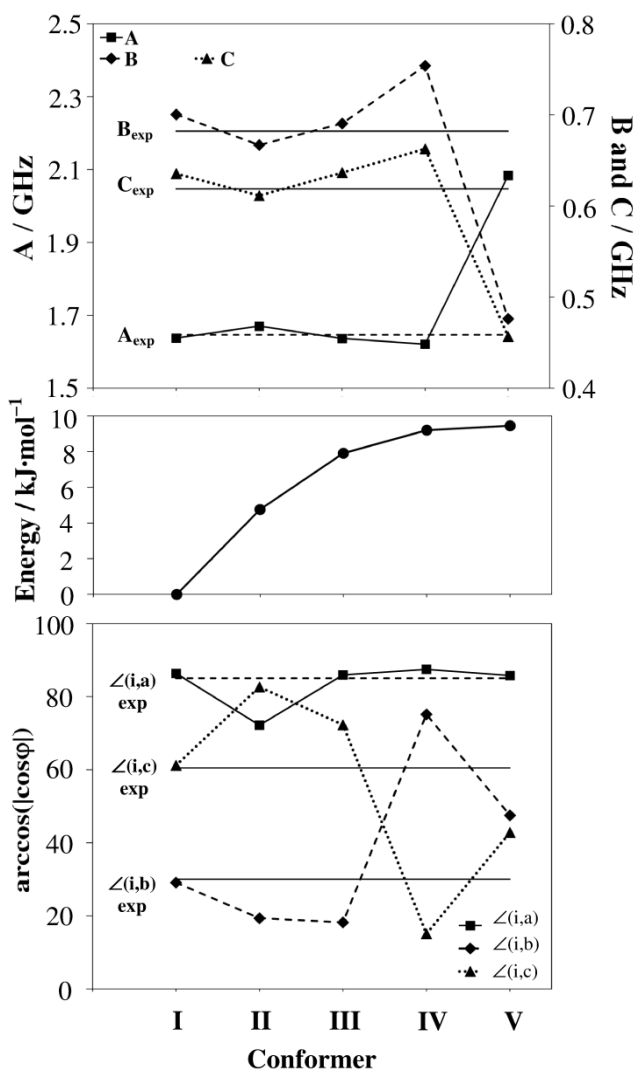|	V_3/cm^{-1}	σ/kHz
Allyl acetate	98.093(12)	54.0
Methyl isobutyl ketone	250.3(19)	17.6
Linalool	400.20(64)	4.6
Methyl propionate	429.324(23)	3.4
Diethyl ketone	771.93(27)	3.5
Diethyl amine	1054.74(57)	0.7
Ethyl pivalate	semi-rigid	0.8

Fig. 3 Comparison of quantum chemical calculations calculated at the MP2/6-311++G(d,p) level of theory and experimental results for identifying the assigned conformer of linalool. The rotational constants are shown in the upper trace, the energy values in the middle trace, and the angles between the internal rotor axis and the principal axes in the lowest trace.

The structure of linalool cannot be determined only by microwave spectroscopy using traditional methods like isotopic substitutions due to the large number of atoms present in this molecule. For a structure determination, a comparison of the experimental and the calculated rotational constants of the fifteen lowest energy conformers was carried out. This comparison is often sufficient for validating the molecular structure. However, in the case of linalool, the calculated rotational constants of conformer I, II and III are very similar and they are all in good agreement with the experimentally determined rotational constants. This is shown in the first trace of Fig. 3, where the rotational constants of the five lowest energy conformers calculated at the MP2/6-311++G(d,p) level of theory are plotted. To identify the conformer we observed in the microwave spectrum, we additionally needed the structural information provided by the angles $\angle(i,k)$, $k \in \{a,b,c\}$ between the internal rotor axis and the principal axes, which are given in the lowest trace of Fig. 3. It should be noted that from the experimental data

only the absolute value but not the sign of the direction cosine is obtained. In order to make the results comparable we used the expression arccos($|\cos\angle(i,k)|$), which always returns the lowest possible angle. By comparing the calculated with the experimental angles, we see that it is most probable that conformer I is the assigned conformer. The angles of all other conformers have much larger deviations from the experimental ones. Furthermore, the energy values calculated by all combinations of methods and basis sets also indicate that conformer I should be most stable and probably be the observed one under molecular beam conditions. In the middle trace of Fig. 3, the energies relative to the lowest energy conformer I are given. Conformer II, III, and IV are about 5 kJ mol^{-1}, 8 kJ mol^{-1}, and 10 kJ mol^{-1} higher in energy than conformer I. From our experience, this is usually too high to be seen in the microwave spectrum under our experimental conditions.

With the assumption that conformer I is the observed conformer from all reasons mentioned above, we now compared the experimentally determined rotational constants and angles $\angle(i,k)$ of conformer I with the calculated parameters using the DFT and MP2 methods with various basis sets. It turned out that calculated parameters using the MP2 method in combination with the polarisation function (df,pd) and the diffuse function + or ++ and the MP2/cc-pVTZ level of theory are in best agreement with the experimental ones (see Table 4). The rotational constants calculated using B3LYP and basis sets with polarisation functions are in good agreement with the experimental results. However, the angles $\angle(i,k)$ have quite large deviations. Calculations using B3PW91 yielded unsatisfactory results for both, the rotational constants and the angles $\angle(i,k)$. Therefore, this method might be only suitable for calculating electric effects based on an already well optimized structure[15] and not for a structure optimization. The rotational constants, energy values, and the angles between the internal rotor axis and the principal axes of conformer I calculated using the B3LYP and B3PW91 hybrid functional with various basis sets are given in Table S5 (ESI).

Systematic quantum chemical calculations on internal rotation

Table 4 The rotational constants and angle between the internal rotor axis and the principal axes of conformer I calculated using the MP2 method and various basis sets.

Basis set	A / GHz	B / GHz	C / GHz	(i,a) / °	(i,b) / °	(i,c) / °
6-31G(d,p)	1.6481	0.6993	0.6346	86.0	30.5	59.9
6-31+G(d,p)	1.6372	0.6961	0.6305	86.9	28.2	62.0
6-31++G(d,p)	1.6368	0.6962	0.6303	87.2	27.6	62.6
6-311G(d,p)	1.6380	0.7064	0.6401	86.9	28.9	61.3
6-311+G(d,p)	1.6374	0.7013	0.6369	86.0	29.8	60.5
6-311++G(d,p)	1.6378	0.7003	0.6355	86.3	29.1	61.2
6-31G(df,pd)	1.6572	0.7102	0.6448	85.8	31.0	59.3
6-31+G(df,pd)	1.6468	0.7043	0.6376	87.3	27.5	62.7
6-31++G(df,pd)	1.6468	0.7043	0.6370	87.9	26.4	63.7
6-311G(df,pd)	1.6489	0.7126	0.6458	87.0	28.6	61.6
6-311+G(df,pd)	1.6484	0.7070	0.6420	86.1	29.4	60.9
6-311++G(df,pd)	1.6489	0.7061	0.6408	86.4	28.8	61.5
6-31G(3df,3pd)	1.6484	0.7242	0.6560	86.9	30.1	60.1
cc-pVDZ	1.6260	0.7011	0.6350	86.7	30.2	60.1
cc-pVTZ	1.6512	0.7082	0.6422	86.9	28.4	61.8
Experiment	1.6467	0.6822	0.6188	85.0	30.0	60.5

barriers of methyl groups have not been carried out much in the past for the size of molecules we study. As written in the quantum chemical calculations section, we only used the calculated rotational barriers as guide values to classify them into low, intermediate, and high barrier cases, since no methods and basis sets, which can calculate this molecular parameter to a good agreement with the experimental value, are currently known. Experimental determination of rotational barriers is often successful only after many trial and errors by starting from the calculated values.

After the internal rotation barrier of methyl group 2 of linalool was experimentally determined, we calculated this parameter again using all combinations of methods and basis sets already mentioned in section 3. The best results were obtained using the DFT method and basis sets which include the diffuse function + or ++ and the polarization function (3df,3pd) as well as the cc-pVTZ basis set. The best calculated value is 378.6 cm^{-1} using the B3LYP/6-311++G(3df,3pd) level of theory, which is close to the experimental value. It should be mentioned that only the rotation-torsional ground state was studied and all the vibrational modes were neglected. The models used to reproduce the spectrum in this case do not take into account the vibration-rotation-torsional interactions.

The barrier height to internal rotation of methyl group 2 was determined to be 400.20(64) cm^{-1}, higher than the value of 304.34(2) cm^{-1} found for the *trans* methyl group in 1-chloro-2-methylpropene (1C2MP).[12] Furthermore, only in a few transitions small splittings due to internal rotation of methyl group 3 could be resolved, i.e. the barrier of this methyl group is also higher than that of the *cis* methyl group in 1C2MP (928.0(17) cm^{-1}). These higher barriers can be explained by the different inductive effects of the substituent on the double bond. In the case of linalool, the substituent is a carbon chain (see Fig. 2) which has a positive inductive effect. For 1C2MP, the negative inductive effect of the chlorine atom might influence the barriers of the methyl groups. For a more precise explanation, further studies on similar molecules are needed.

Finally, it should be noted that all lines in the spectrum were assigned to conformer I, i.e. it is the only conformer of linalool found in the supersonic jet. The globular structure of linalool would be useful for future studies on structure – odor relation. The spectral data of linalool might also be of interest for atmospheric studies since terpenes are important VOCs which might be considered as natural pollutants.

Conclusions

The geometry of the lowest energy conformer of linalool, an important acyclic monoterpene, has been determined by a combination of microwave spectroscopy and quantum chemical calculations. Surprisingly, a globular rather than a prolate shape was found. For identifying the observed conformer, not only the rotational constants but also the internal rotation parameters of one of the methyl groups were needed. Therefore, it was crucial to identify the methyl group, which was responsible for the A−E splittings observed in the spectrum and to carry out an internal rotation analysis. For this purpose, two different programs, XIAM and BELGI-C$_1$, were used and checked against each other. Quantum chemical calculations using the DFT and MP2 methods

with various basis sets were carried out and used in combination with microwave spectroscopy to validate the structure of linalool.

Notes and references

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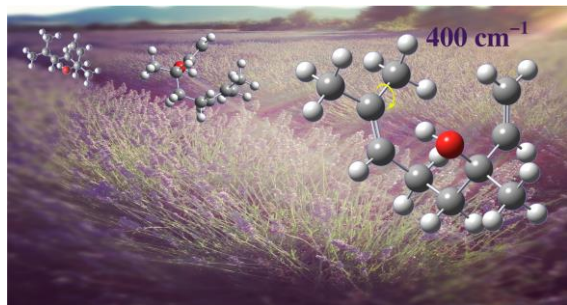
ARTICLE TYPE

Table of contents entry

Color graphic:

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10 **Text:**

The lowest energy conformer of linalool, an acyclic monoterpene and the main component of lavender oil, has been observed in the gas-phase.