



A Characterization of Valinol with High-resolution Rotational Spectroscopy

Sophie Fischer, Humboldt-Universität zu Berlin

September 5, 2017

Abstract

Interstellar molecules can be identified by the analysis of observational spectra recorded by specific telescopes like ALMA. There is an increasing interest in interstellar, astrobiological molecules, including the search for interstellar amino acids. This is one reason why valinol - on which this study will focus - has astrochemical relevance. This work shows a spectroscopic analysis of valinol in the frequency ranges 2 - 8 GHz and 75 - 110 GHz. Due to the large frequency range and different measuring conditions the data can provide two different types of information. On the one hand the individual fingerprint of valinol will be identified - which can be an aid for astrochemical research - and on the other hand the data gives information about structural details like stable conformers, bond lengths and vibrational states.

Contents

1	Introduction	3
2	Theoretical background	3
2.1	Fundamentals of rotational spectroscopy	3
2.2	Hyperfine splitting	6
2.3	Fundamentals of quantum mechanical calculations	6
3	Methods	7
3.1	COMPACT (2 - 8 GHz)	7
3.2	Millimeter-wave spectrometer (75 - 110 GHz)	8
3.3	Structure calculations	8
4	Results	9
4.1	Structure calculation	9
4.2	COMPACT (2-8 GHz)	10
4.3	Millimeter-wave spectrometer (75 - 110 GHz)	13
5	Discussion and conclusions	14
	Acknowledgments	14
	List of Abbreviations	15
	References	16

1 Introduction

Spectroscopy is a way to analyze the interaction between electromagnetic waves and matter. These interactions are molecule specific and leads to an individual fingerprint of each molecule. [1] Rotational spectroscopy, which is used for this project, is a powerful tool for structure determination of small and medium-sized molecules [2]. A detailed knowledge about a molecule's structure is key for a better understanding of the physical and chemical properties as well as the specific functions. Pure rotational spectra can be achieved with measurements in the gas phase at low temperatures because all the molecules are in their ground vibrational level. Whereas, measurements in the millimeter-wave region performed at room temperature can give information about vibrational states. Besides the size-limitation, microwave spectroscopy requires a permanent dipole moment of the molecule [3]. Most of the medium-sized molecules exhibit a dipole moment due to their degree of asymmetry. Valinol - a potential amino acid precursor - has a large dipole moment because of its nitrogen and oxygen atoms.

The characterization of valinol with microwave spectroscopy from 2 - 8 GHz and 75 - 110 GHz will be presented in the following report. This study of valinol's rotational and vibrational states is set in the wide context of analyzing molecules to characterize the chemical complexity of the interstellar medium, and furthermore to find answers to fundamental questions in astrobiology. Organic matter is the cornerstone for living beings on Earth but organic molecules are not exclusive to our planet since many have been detected in the interstellar medium [4, 5]. The investigation of organic molecules in the interstellar medium is realized by the analysis of signals from dense gas clouds. These molecular signals can be detected by powerful radio telescopes such as Atacama Large Millimeter Array (ALMA) [6]. The radio telescope provides spectra that contain information about different molecules. Since the analysis of those multispectral images can be difficult, the analysis of spectra recorded under laboratory conditions can help to detect molecules by comparing laboratory data to the observational dataset. [7, 5]. The combination of quantum mechanical calculations and microwave spectroscopy is a great tool for structural analysis and can be used to support astrochemical research.

2 Theoretical background

2.1 Fundamentals of rotational spectroscopy

The total excitation energy of a molecule is described by the sum of rotation energy, vibration energy and electron excitation. Rotational transitions are between rotational levels of one vibrational state. Hence just the quantum number J changes, where J is called the total angular momentum quantum number and characterizes the rotation level. In the case of vibrational transitions not only J changes but also the vibrational level v . Energy levels are quantized so there are discrete energy quanta needed for the transition from one state to another. Such changes in the state of the molecule can be measured with microwave spectroscopy.

For a two-atom system a description based on classical physics is the rigid rotor model. The classical rotation energy (1) of this body can be expressed with:

$$E_{rot} = \frac{1}{2} \cdot I \cdot \omega^2 \quad (1)$$

and depends on the moment of inertia I , with the distances z_1 and z_2 between atoms with the masses m_1 and m_2 and the center of gravity:

$$I = m_1 z_1^2 + m_2 z_2^2 \quad (2)$$

and the angular velocity ω which will change of the rotation angular ϕ over the time [2]:

$$\omega = \frac{\Delta\phi}{\Delta t} \quad (3)$$

A comparison between values calculated with (1) and experimental data leads to the fact that quantum mechanics have to be taken into account. The rotation energy of a two-atomic system depends on the quantized energy levels and can be calculated with:

$$E_{rot} = hB \cdot J(J+1) \quad (4)$$

The rotational constant B is a molecule-specific value derived from the experimental data, where B depends on the momentum of inertia:

$$B = \frac{h}{2\pi^2 I} \quad (5)$$

The distortion constant D includes the impact of the centrifugal force on the rotational energy:

$$E_{rot} = hB \cdot J(J+1) - hD \cdot [J(J+1)]^2 \quad (6)$$

All molecules experience the centrifugal force but the impact depends on the size of the molecule and the frequency range. The classical model of the non-rigid rotor includes the impact of the centrifugal force on the two-atomic molecule by describing the bond between the nuclei as a spring constant [2].

For the description of the polyatomic system, the moment of inertia is split into three principle moments of inertia. The three moments of inertia correspond to three molecular fixed axes (x , y , z) of a Cartesian coordinate system with the molecule's center of mass located at the point of origin. The classical rotation energy of a polyatomic system depending on the angular momentum L is [8]:

$$E = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z} \quad (7)$$

Due to the molecule's symmetry a moment of inertia can be zero or two moments of inertia can be equal. That causes the following classification of molecules in rotational spectroscopy:

- linear molecules: for this type $I_x = 0$ while $I_y = I_z$
- spherical-top molecules: for molecules of this type $I_x = I_y = I_z$
- symmetric-top molecules: for a oblate symmetric molecules $I_x = I_y < I_z$ and for a prolate symmetric molecules $I_x < I_y = I_z$
- asymmetric-top molecules: for this type of molecules all moments of inertia are different from each other symmetric molecules $I_x \neq I_y \neq I_z$

A quantum mechanical description of a polyatomic system requires the Schrödinger equation:

$$E\psi = \hat{H}\psi \quad (8)$$

Where the properties of a particle are described as a the wave function ψ . The energy E includes the energy of the quantum system and \hat{H} is the Hamiltonian operator. [1] \hat{H} is the quantized Hamilton function [2] and is described as the sum of a kinetic energy term \hat{T} a potential energy term \hat{V} :

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2m_0} \left(\frac{\hbar}{i} \nabla \right)^2 + V(r) \quad (9)$$

Here, the kinetic energy term is expressed with the mass of the electron m_0 , the impulse operator $\left(\frac{\hbar}{i} \nabla \right)^2$ and the location-dependent potential energy term $V(r)$ [2].

The total Hamiltonian is a sum of Hamiltonians for the kinetic and potential energy of the system's electrons and protons. Hence, a quantum mechanical description of the rotational transition is a rotational Hamiltonian.

Vibrational transitions - these transitions are faster than rotational ones and can be understood as displacements of the molecule's atoms. There are different types of vibrational motions like stretching, rocking or scissoring. The classical description of the vibration energy W_{vib} is based on the model of the harmonic oscillator:

$$W_{vib} = \frac{\frac{1}{2} p^2}{\mu + \frac{1}{2} k q^2} \quad (10)$$

with p the vibrational moment, μ the reduced mass, k the force constant and q the vibrational coordinate. The model of a harmonic oscillator is a simplification to a one-body problem. A quantum mechanical description is a vibrational Hamiltonian. [1]

2.2 Hyperfine splitting

Hyperfine structures in a spectrum can be caused by the quadrupole coupling. The underlying process for the quadrupole coupling is the interaction of a nuclei’s quadrupole and the electric field gradient around the nucleus. This nuclear quadrupole moment is caused by an asymmetric charge distribution in the atom which just occurs when the nuclei spin $I > \frac{1}{2}$ like nitrogen [7].

2.3 Fundamentals of quantum mechanical calculations

Quantum mechanical calculations can be a powerful tool in determining molecular parameter. Their impact increases due to the continuous technical progress. The calculated parameters can be helpful for the analysis of spectroscopic data. The underlying principle of many quantum mechanical calculations is the Schrödinger equation, where the molecules are treated as a composition of electrons and nuclei. Since the Schrödinger equation can only be solved analytically for the one electron-system, approximations are needed to solve the problem for polyatomic systems. The differences between quantum mechanical models are in the chosen approximations and this leads to different capabilities and reliabilities.

The Born-Oppenheimer approximation assumes that there is no movement of the molecule’s nuclei. This is an approximation because the nuclei does move but much slower than the electrons, which move with the speed of light. The Born-Oppenheimer approximation leads to the electronic Schrödinger equation (11).

$$E^{el}\psi^{el} = \hat{H}^{el}\psi^{el} \quad (11)$$

To solve the Schrödinger equation for a polyatomic system, more than the Born-Oppenheimer approximation is needed. To simplify further, the Hartree-Fock approximation describes a system where the electrons move independent from each other. Therefore each electron is moving in an average field of the other electrons in molecular orbitals.

While the Hartree-Fock wave function is an approximate solution for the Schrödinger equation, the Møller-Plesset models try to find solutions by solving an analogous problem. Those models assume that the solutions from the Hartree-Fock calculations are close to the exact wave function and can be used to calculate an exact Hamiltonian \hat{H} (12) where \hat{V} is a perturbation and λ a dimensionless parameter. [9]

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \quad (12)$$

3 Methods

3.1 COMPACT (2 - 8 GHz)

The chirped-pulse broadband rotational spectrometer (COMPACT) is useful to perform experiments to gain structural information of samples in the gas phase at low temperatures. The low frequency range allows to measure bigger sized molecules [3]. COMPACT uses a chirped-pulse Fourier transformation microwave (CP-FTMW) method which will be explained in more detail in the following. Chirped pulse provides the advantage that a whole spectrum from 2 - 8 GHz can be measured in a single run and makes the data acquisition faster, than traditional methods. The molecules are supersonically expanded in the vacuum chamber. Thus cooling the molecules to rotational temperature of approximately 5 Kelvin [10, 11]. During this process the molecules undergo a high number of collisions with the carrier gas which leads to an energy loss [12].

The experiment is performed as the following :

1. the sample in the molecule reservoir (directly above the pulsed nozzle) is heated to evaporate into the vapor phase
2. the sample is frequently released into the chamber *via* the pulsed valve
3. a chirped pulse of microwaves is generated and amplified
4. the pulse is broadcasted into the chamber *via* a Horn antenna
5. the wave interacts with the sample inside the chamber
6. the Free induction decay of the rotationally excited state will be received by a second Horn antenna
7. the molecular emission will be detected by the oscilloscope after it passes the low-noise amplifier
8. the FID undergoes a Fourier transformation, giving frequency domain spectrum in the range of 2 - 8 GHz

The excitation by the microwaves causes macroscopic polarizations which can be detected as a free induction decay (FID) by the oscilloscope. The FID will be Fourier transformed from the time domain into the frequency domain [10].

To determine the structure of a molecule, the natural abundance of carbon isotopes can be exploited. Since B depends on the moment of inertia, which in turn depends on the mass of the atoms, the isotopes will influence the rotational constants. This fact can be used to calculate bond lengths between carbon atoms. [3] To achieve this, Kraitchman's equations (implemented in the KRA program package) can be used to obtain the coordinates of the ^{13}C atoms. These coordinates can be used to calculate the distances based on linear algebra. [13]

3.2 Millimeter-wave spectrometer (75 - 110 GHz)

A commercial instrument from BrightSpec was used for chirped-pulse Fourier transform millimeter-wave spectroscopy experiment in the region 75 - 110 GHz. On this instrument the measurements were performed at room temperature. So, one obtain pure rotational spectra of individual vibrationally excited states. There are two different types of measuring modes: (I) the fast mode where the frequency range is divided in even 45 chirps, (II) the high dynamic range (HDR) mode where the frequency range is divided into smaller segments which increases the signal quality. The whole bandwidth is obtained by effectively stitching the segments together.

The experiment in the HDR mode is performed as the following [14]:

1. the sample in the external (to the vacuum chamber) reservoir is heated to evaporate into the vapor phase
2. the gaseous sample flows into the single-pass vacuum chamber (the chamber acts as a slow gas flow cell)
3. a pulse of microwaves is generated and broadcasted in the chamber *via* a Horn antenna
4. the wave interacts with the sample inside the chamber
5. the Free Induction Decay will be received by a second Horn antenna
6. the molecular emission will be detected with real-time digitizer

This measurement is particularly relevant for an astrochemical approach, since the frequency range overlaps with the ALMA Band 3 (84 - 116 GHz).

3.3 Structure calculations

There are a variety of methods to perform quantum mechanical calculations. On the one hand there are semi-empirical calculations, where known parameters of the molecule are included in the calculation, and on the other hand there are *ab-initio* calculations, which solves the quantum mechanical problem independent from experimental data. MP2 belongs to the group of *ab-initio* calculations. This type is based on a Hartree-Fock calculation followed by a Møller-Plesset model. [15] From these calculations one can obtain detailed information such as rotational constants, energy values or coordinates for the atoms in the molecule.

4 Results

4.1 Structure calculation

The MP2 calculation generated a whole bunch of information about the molecules. The method were applied on the six valinol conformers which are shown in Figure 1 .

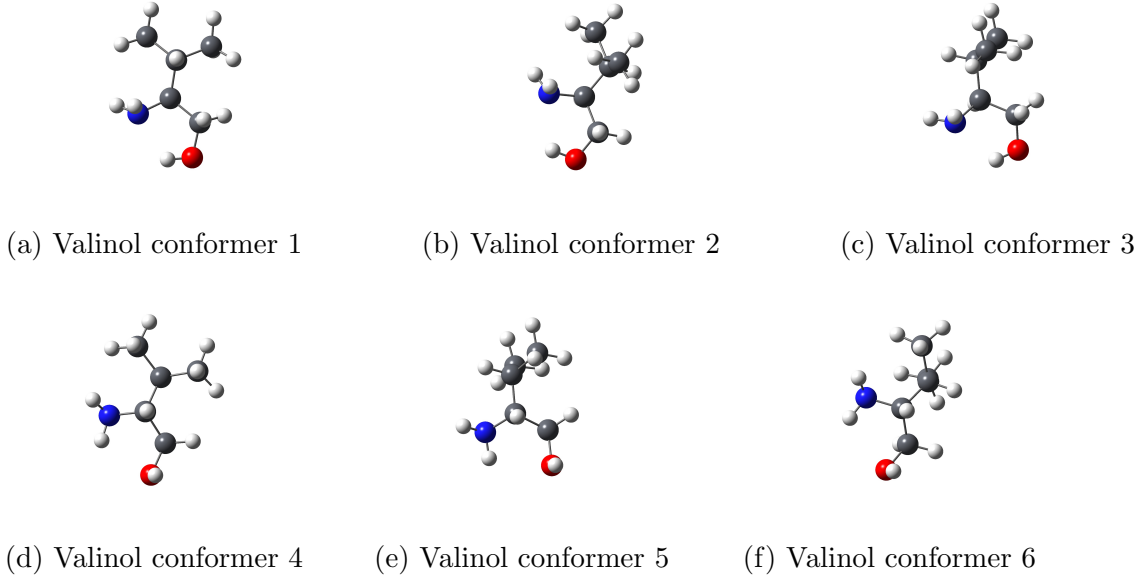


Figure 1: The six valinol structures which were used for the MP2 calculations.

In the structures 1- 3 the hydrogen from the hydroxyl group forms a hydrogen bond together with the nitrogen. This situation is reversed in the structures 4 - 6. The differences between the structures 1- 3 and 4 - 6 comes from the orientation of the isopropyl group of valinol. Table 1 lists the calculated molecular parameters for the six structures.

Table 1: The rotational constants, dipole moments and relative energies of valinol obtained from the MP2 calculations. The numbers 1 - 6 are corresponding to the structures in 1.

conformer	1	2	3	4	5	6
A [MHz]	4035.77	4247.54	3644.76	4052.12	3610.42	4280.02
B [MHz]	1709.83	1574.55	1690.84	1690.97	1691.63	1582.28
C [MHz]	1290.91	1408.38	1480.76	1283.89	1491.74	1409.44
μ_A [Debye]	3.21	3.26	-2.93	-1.57	-1.03	0.80
μ_B [Debye]	-1.18	0.31	-1.74	-0.81	-1.01	0.74
μ_C [Debye]	-0.75	0.72	-0.36	-1.97	-1.99	2.12
ΔE [kJ/mol]	0	0.38	2.86	94.22	110.82	106.79

4.2 COMPACT (2-8 GHz)

Values for the energy, rotational constants and dipole moments of six different valinol conformers are known from the MP2 calculations (table 1). The conformer with a relative energy of zero (conformer 1 from Table 1) is most likely the conformer with the highest incidence of these six. That is why this conformer was chosen among the different conformers to start the analysis of this COMPACT spectrum with.

The experimental spectrum was assigned with the aid of a simulated one (simulation with PGOPHER) to determine the rotational constants of a conformer of valinol from the measured data. The rotational constants, dipole moments and quadrupole coupling constants obtained from the structural optimization calculation were used for the simulation. The assignment of the spectra for the conformer 1 is shown in Figure 2.

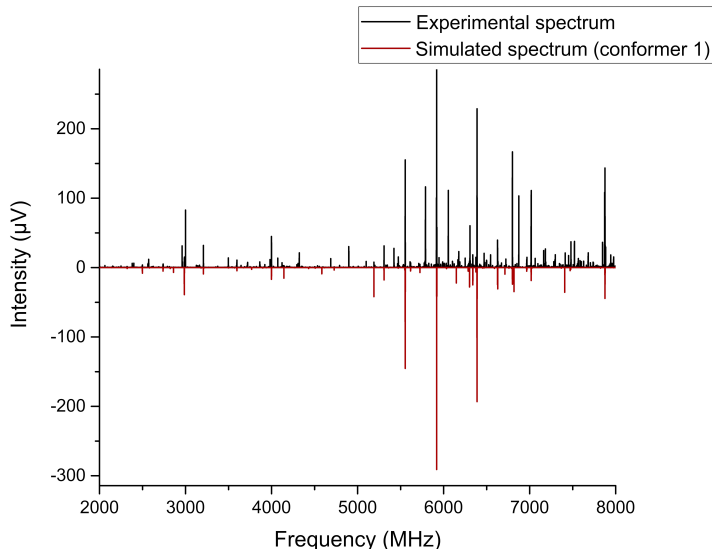


Figure 2: The spectrum shows the assignment of the experimental spectrum (COMPACT 2 - 8 GHz) with the simulated spectrum of the experimentally fitted constants for the conformer 1.

A zoom-in (Figure 3) allows the hyperfine structure caused by the nitrogen atom to be seen.

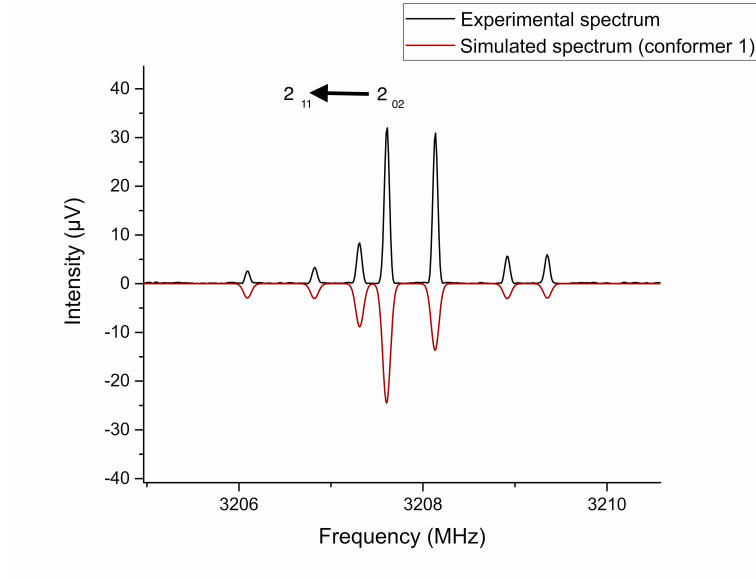


Figure 3: This zoom-in out of Figure 2 shows the hyperfine structure caused by multi-resonance effects. The transition is from rotational state 2_{02} to the state 2_{11} .

From the assignment of the spectra as shown in Figure 2, the rotational constants can be determined. Table 2 summarizes all received rotational constants for conformer 1 and its isotopic species, which are observed in natural abundance.

Table 2: The experimental rotational constants for conformer 1, conformer 2, conformer 3 and isotopic forms of conformer 1. The C atoms are marked in Figure 4.

species	A [MHz]	B [MHz]	C [MHz]	Nr of lines	error of the fit
conformer 1	4023.530 (15)	1701.3153 (52)	1284.2118 (49)	136	0.08
1. isomer	4020.204 (87)	1692.8354 (22)	1279.6422 (25)	24	0.03
2. isomer	4018.481 (19)	1700.1284 (74)	1283.2871 (57)	21	0.07
3. isomer	4004.577 (58)	1691.5860 (20)	1277.0830 (21)	24	0.03
4. isomer	3948.627 (30)	1686.7596 (15)	1268.25251 (15)	48	0.03
5. isomer	4000.922 (21)	1672.7163 (13)	1265.7081 (13)	44	0.02
conformer 2	4246.456(10)	1546.6043 (34)	1414.1087 (35)	42	0.05
conformer 3	3631.890 (14)	1691.7484 (46)	1470.4196 (46)	39	0.05

From the assignment of the parent species the distortion constants D can be determined. The D values for the this conformer are shown in Table 3.

Table 3: The distortion constants of assigned spectra for the conformer 1.

species	D_K [KHz]	D_J [KHz]
conformer 1	0.28 (18)	0.307 (44)
conformer 2		0.232 (13)
conformer 3	2.63 (47)	

As explained in the Method section the bond lengths can be calculated from the coordinates of the ^{13}C atoms. Moreover these coordinates can be used to compare the theoretical calculated structure with the results from the experimental analysis (Figure 4).

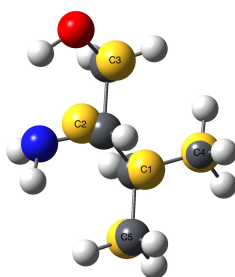


Figure 4: Comparison between the theoretical conformer 1 and the experimental determined carbon atom positions, which are marked in yellow.

Table 4: Calculated bond length from the isotopic forms of the first conformer compared to the one from the theoretical calculations.

	experimental	theoretical
C1-C5	149.62 pm	153.11 pm
C1-C4	154.52 pm	153.28 pm
C1-C2	173.19 pm	153.71 pm
C2-C3	146.26 pm	153.14 pm

4.3 Millimeter-wave spectrometer (75 - 110 GHz)

The spectrum in Figure 5 shows rotational transitions of the ground state of the molecule and its vibrational excited states. The measurement took place at room temperature so the spectrum is much more congested because of the vibrational states.

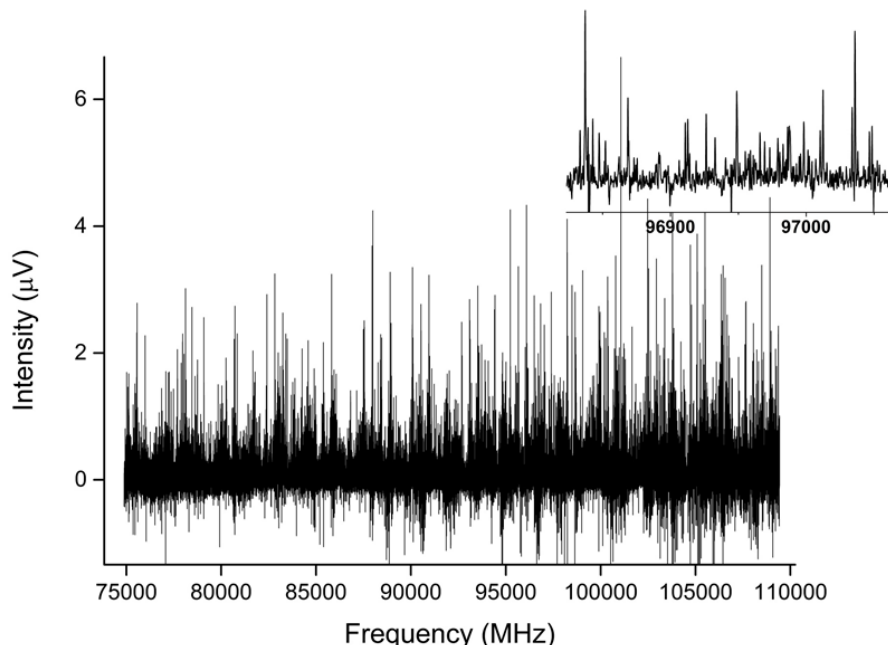


Figure 5: Valinol rotational spectrum measured with the, millimeter-wave spectrometer from 75 to 110 GHz.

The program GaussView 5.0 can visualize motion of the vibrational states - some examples are listed in Table 5. The rotational constants, which were determined with frequency calculations, shown in Table 5 are corrected by using the difference between the theoretical ground state constants and the experimental ground state constants from the 2 - 8 GHz spectrum.

Table 5: Examples of theoretical rotational constants for the fundamental vibrational state of conformer 1 and a description of the main molecular movement.

sates	A [MHz]	B [MHz]	C [MHz]	vibration type
<i>v</i> 54	3963.51	1656.28	1247.57	wagging around the C2
<i>v</i> 53	3952.45	1660.89	1247.78	wagging around the C2, amine and hydroxyl group
<i>v</i> 52	3975.89	1659.67	1246.07	asymmetric stretch of the methy groups C4 and C5

5 Discussion and conclusions

By and large, assigning the spectra indicated clearly that the conformer shown in Figure 4 is the first conformer - the one with the highest abundance. The peaks with the highest intensity which can be observed in the measured spectrum corresponds to the simulated spectrum of the conformer with the lowest energy - from six conformers which were calculated with MP2.

The distortion constants (Table 3) contain error values that need further optimization. This optimization could be achieved with an improvement of the assignment.

For the first conformer of valinol five isotopic forms, one ^{13}C per isotopic form, are assigned. Coordinates were determined with the Kraitchman calculation from the assessed rotational constants for these isotopes. The coordinates of the ^{13}C 's were used for the calculation of bond lengths (Table 4). The bond lengths are not satisfactory yet as the Figure 4 and the comparison with the theoretical values indicate. Since the carbon single bond has an average length of 154 pm [16] most of the determined values are out of range. Optimizing the assignment could lead to better results. At this point one should kept in mind that the structure from the calculation is maybe not the exactly the one with the highest occurrence, and the exact structure is somewhere between the two shown in Figure 4.

The measurement with the mm-wave spectrometer at room temperature enables rotational transitions of vibrational states to be observed. Hence, the complexity of spectrum in Figure 5 increases compared to the COMPACT spectrum shown in Figure 2. Due to the higher frequencies the impact of the distortion constants is higher. What is more, the low signal level makes the analysis harder. The assignment for the conformer 1 in this spectrum is ongoing.

All-in-all in this work three conformers of valinol could be assigned to determine the experimental rotational constants and distortion constants in the frequency range of 2 - 8 GHz. Moreover five isotopic forms of conformer 1 could be assigned and used for determining carbon atom positions and hence carbon-carbon bond lengths.

Acknowledgments

I would like to express my gratitude to Prof. Melanie Schnell for offering me this project. I am grateful to Anna Krin for her help, support and patience during the first weeks of my summer project. Moreover I like to thank Mariyam Fatima and Benjamin Arenas for their support. Finally I want to thank the organizers of the Summer Student Program for the great opportunities to learn and work at DESY.

List of Abbreviations

J	total angular momentum quantum number
v	quantum number for the vibrational state
I	moment of inertia
m	mass
E	Energy
ω	angular velocity
ϕ	rotation angular
B	rotational constant
h	Planck's constant
L	angular momentum
\hat{H}	Hamiltonian operator
ψ	wave function

References

- [1] JM Brown. Molecular spectroscopy. *Oxford Chemistry Primers*, 55(1):ALL–ALL, 1998.
- [2] H Haken and HCh Wolf. Molekülphysik und quantenmechanik. *Aufl., Kap*, 13, 1991.
- [3] M Schnell. Broadband rotational spectroscopy for molecular structure and dynamics studies. *Zeitschrift für Physikalische Chemie*, 227(1):1–22, 2013.
- [4] S Kwok. Complex organics in space from solar system to distant galaxies. *The Astronomy and Astrophysics Review*, 24(1):8, 2016.
- [5] BE Arenas, S Gruet, AL Steber, and M Schnell. A global study of the conformers of 1, 2-propanediol and new vibrationally excited states. *Journal of Molecular Spectroscopy*, 2017.
- [6] information@eso.org. Alma - das atacama large millimeter/submillimeter array. <http://www.eso.org/public/germany/teles-instr/alma/> (accessed on 01.09.2017).
- [7] S Yamamoto. Introduction. In *Introduction to Astrochemistry*, pages 1–10. Springer, 2017.
- [8] PF Bernath. *Spectra of atoms and molecules*. Oxford university press, 2015.
- [9] WJ Hehre. *A guide to molecular mechanics and quantum chemical calculations*, volume 2. Wavefunction Irvine, CA, 2003.

- [10] D Schmitz, VA Shubert, T Betz, and M Schnell. Multi-resonance effects within a single chirp in broadband rotational spectroscopy: The rapid adiabatic passage regime for benzonitrile. *Journal of Molecular Spectroscopy*, 280:77–84, 2012.
- [11] GG Brown, BC Dian, KO Douglass, SM Geyer, ST Shipman, and BH Pate. A broadband fourier transform microwave spectrometer based on chirped pulse excitation. *Review of Scientific Instruments*, 79(5):053103, 2008.
- [12] TJ Balle and WH Flygare. Fabry–perot cavity pulsed fourier transform microwave spectrometer with a pulsed nozzle particle source. *Review of Scientific Instruments*, 52(1):33–45, 1981.
- [13] J Kraitchman. Determination of molecular structure from microwave spectroscopic data. *American Journal of Physics*, 21(1):17–24, 1953.
- [14] BE Arenas, S Gruet, AL Steber, BM Giuliano, and M Schnell. Chirped-pulse fourier transform millimeter-wave spectroscopy of ten vibrationally excited states of i-propyl cyanide: exploring the far-infrared region. *Physical Chemistry Chemical Physics*, 19(3):1751–1756, 2017.
- [15] Gaussian. Mp methods. <http://gaussian.com/mp/> (accessed on 30.08.2017).
- [16] P Karlson and D Doenecke. *Karlsons Biochemie und Pathobiochemie*. Georg Thieme Verlag, 2005.