

**STUDIES ON THE CONFORMATIONAL LANDSCAPE OF TERT-BUTYL
ACETATE USING MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL
CALCULATIONS**

Y. Zhao¹, H. Mouhib¹, G. Li¹, W. Stahl¹, I. Kleiner²

¹ Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074
Aachen, Germany

²Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583
(CNRS/Univ. Paris Est & Paris Diderot), 61 avenue du Général de Gaulle, F-94010 Créteil
cedex, France

The *tert*-butyl acetate molecule was studied using a combination of quantum chemical calculations and molecular beam Fourier transform microwave spectroscopy in the 9.0 to 14.0 GHz range.

Due to its rather rigid frame, the molecule possesses only two different conformers: one of C_s and one of C_1 symmetry. According to *ab initio* calculations, the C_s conformer is 46 kJ/mol lower in energy and is the one observed in the supersonic jet. We will report on the structure and dynamics of the most abundant conformer of *tert*-butyl acetate, with accurate rotational and centrifugal distortion constants. Additionally, the barrier to internal rotation of the acetyl methyl group was determined. Splittings due to the internal rotation of the methyl group of up to 1.3 GHz were observed in the spectrum. Using the programs XIAM and BELGI-Cs, we determine the barrier height to be about 113 cm^{-1} and compare the molecular parameters obtained from these two codes. Additionally, the experimental rotational constants were used to validate numerous quantum chemical calculations.

This study is part of a larger project partly supported by the PHC PROCOPE 25059YB which aims at determining the lowest energy conformers of organic esters and ketones which are of interest for flavor or perfume synthetic applications.

**THE EFFECTS OF INTERNAL ROTATION AND
¹⁴N QUADRUPOLE COUPLING IN N,N-DIETHYLACETAMIDE**

Raphaela Kannengießer, Ha Vinh Lam Nguyen, Wolfgang Stahl

Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen,
Germany

Acetyl- and nitrogen containing substances play an important role in many chemical, physical, and especially biological systems. These both aspects are present in acetamides. In this work, N,N-diethylacetamide was investigated by a combination of molecular beam Fourier transform microwave (MB-FTMW) spectroscopy and quantum chemical calculations. This molecule undergoes internal rotation of the acetyl methyl group and quadrupole coupling due to the nitrogen atom, which cause fully resolved fine and hyperfine splittings in the spectrum.

The measurements have been carried out using a MB-FTMW spectrometer in Aachen, which has the experimental accuracy of about 2 kHz. In a scan from 9 to 15 GHz, more than 75 lines were observed. Each of these lines appears as a group of transitions in the high resolution measurements.

Quantum chemical calculations were carried out at the MP2/6-311++G(d,p) level of theory in order to assign the spectrum. The conformational analysis yielded five stable conformers with a maximal energy difference of 7 kJ/mol. The two lowest energy conformers (conformer I and II) could be assigned in the microwave spectrum. They both have C₁ symmetry, where the two ethyl groups are tilted out of the molecular plane.

The barriers to internal rotation of the acetyl methyl group were found to be approximately 517.1 cm⁻¹ and 619.5 cm⁻¹ for conformer I and II, respectively. The fine splittings due to the internal rotation are of a few tens to hundredths kHz, in the same order of magnitude as the ¹⁴N quadrupole coupling splittings. For both conformers, global fits using the rotational constants *A*, *B*, and *C*, the centrifugal distortion constants, the internal rotation parameters as well as the quadrupole coupling constants χ_{aa} and χ_c were carried out with excellent standard deviations within the experimental accuracy of our spectrometer.

MICROWAVE SPECTRUM OF METHYL ARSINE

Roman A. Motiyenko¹, Jean Demaison¹, Laurent Margulès¹, Harald Møllendal², Jean-Claude Guillemin³, Vadim V. Ilyushin⁴

¹ Laboratoire PhLAM, UMR8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq, France

² Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, PO Box 1033 Blindern, NO-0315 Oslo, Norway

³ Institut des Sciences Chimiques de Rennes, ENSC Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

⁴ Institute of Radio Astronomy of NASU, 4 Chervonopraporna st., 61002 Kharkov, Ukraine

The rotational spectrum of organoarsenic compound, methyl arsine, CH_3AsH_2 , was recorded in the frequency range 15 – 80 GHz using the Stark-modulated spectrometer in Oslo, and in the frequency range 150 – 660 GHz using the spectrometer in Lille. The experimental work was augmented by high-level *ab initio* calculations. The analysis of the rotational spectrum of CH_3AsH_2 is complicated by several factors: (i) the asymmetry parameter of the molecule is very close to -1, which leads to a tight grouping of rotational transitions; (ii) whereas the barrier to internal rotation of the methyl top is of intermediate height, $V_3 = 520 \text{ cm}^{-1}$, the internal rotation parameter ρ is high, $\rho = 0.41$, that results in relatively large A-E splittings in the spectra; and finally (iii) rather high value of the arsenic nuclear quadrupole moment, $\chi_{aa} = 35.5 \text{ MHz}$, $\chi_{bb} = 117 \text{ MHz}$, is leading additionally to relatively large hyperfine splittings. To fit the observed rotational transitions we use the RAM36 code modified to take nuclear quadrupole hyperfine structure into account. The analysis, which is in progress, includes the ground vibrational state as well as $\nu_t = 1$ and $\nu_t = 2$ excited torsional states. The latest results will be presented.

MICROWAVE AND FAR-INFRARED SPECTRUM OF DIMETHYL SULFIDE

A. Jabri¹, V. Van², H. V. L. Nguyen¹, F. Kwabia Tchana¹, L. Manceron³, I. Kleiner¹, W. Stahl²,
B. Tercero⁴, J. Cernicharo⁴

¹Laboratoire Interuniversitaire des Systèmes atmosphériques (LISA), CNRS et Universités
Paris Est et Paris Diderot, 61 av Général de Gaulle 94010 Créteil, France

²Institut für Physikalische Chemie, RWTH Aachen University, Landoltweg 2, 52056
Aachen, Germany

³Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette,
France, et MONARIS, CNRS UMR 8233, 4 Place Jussieu, F-75252 Paris Cedex, France

⁴Department of Astrophysics, CAB. INTA-CSIC. Crta Torrejon-Ajalvir, km. 4. 28850
Torrejon de Ardoz. Madrid. Spain

Dimethyl sulfide CH₃SCH₃ (DMS) is a non-rigid molecule containing sulfur atom whose astronomical detection is considered as possible. DMS has two equivalent internal rotors with internal rotation barriers of about 720 cm⁻¹. The microwave spectrum of the DMS molecule has been re-measured in the 4-40 GHz frequency range, using the two MB-FTMW spectrometers in Aachen [1], with an instrumental uncertainty of a few kHz for unblended lines.

A part of the millimeter spectra has been also measured for the first time in the 50-100 GHz range using the millimeter spectrometer in Aachen with an uncertainty of 40 kHz.

A fit including the new measurements and previous transitions from the literature [2] for the ground torsional state $v_t = 0$ has been performed using the XIAM and the BELGI codes. The results will be discussed. The far-infrared spectrum has also been recorded for the first time at high resolution using the Fourier-transform spectrometer and the newly built cryogenic cell at the French SOLEIL synchrotron [3] and the assignments for the $v_t=1 \leftarrow 0$ torsional band under course will be presented.

This investigation supported by the Funds of Chemical Industry, the Land Nordrhein-Westfalen (Germany) and by the "Groupe De Recherche International" GdRI HiResMIR (France), has served as basis to an astrophysical search for the DMS molecule in the interstellar cloud Orion without success, concluding to the fact that DMS could be detected without ambiguity.

[1] U. Andresen, H. Dreizler, J.-U. Grabow, W. Stahl, Rev. Sci. Instrum. **61**, 3694 (1990).

[2] J. M. Vacherand, G. Wlodarczak, A. Dubrulle and J. Demaison, Can. J. Phys. **65**, 1159 (1987).

[3] F. K. Tchana, F. Willaert, X. Landsheere, J.M Flaud, L. Lago, M. Chapuis, P. Roy and L. Manceron, Rev. Sci. Instrum. **84**, 093101 (2013).

INTRA- AND INTERMOLECULAR HYDROGEN BONDING INTERACTIONS IN
THE TRIFLUOROETHANOL-AMMONIA DIMERJavix Thomas, Yisi Yang, Wolfgang Jäger, Yunjie Xu

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

We investigated the hydrogen-bonding topology and internal rotation dynamics of the binary adduct 2,2,2-trifluoroethanol (TFE)-ammonia, using chirped pulse and cavity based Fourier transform microwave spectroscopy, together with high level ab initio calculations. One *insertion* and two *addition* conformers were found at the MP2/6-311++g(2d,p) level. We noted that *trans* TFE changes into the *gauche* configuration upon complex formation with ammonia. Rotational spectra of the most stable binary TFE-¹⁴NH₃ conformer and the corresponding ¹⁵NH₃ isotopologue were assigned unambiguously. A strong preference for the *insertion* binding topology, where ammonia is inserted into the existing intramolecular hydrogen-bonded ring of TFE, was observed. This is similar to the case of the TFE-water complex. Both ¹⁴N nuclear quadrupole hyperfine structures and internal rotational tunnelling splittings of NH₃ were observed.

**GAS PHASE STRUCTURES OF 2-METHYLTETRAHYDROTHIOPHENE
INVESTIGATED BY ROTATIONAL SPECTROSCOPY**

Vinh Van, Ha Vinh Lam Nguyen, and Wolfgang Stahl

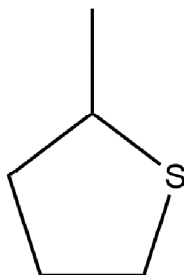
Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074
Aachen, Germany

2-Methyltetrahydrothiophene (MTTP) is a five-membered heterocyclic molecule and a sulfur analog of 2-methyltetrahydrofuran. It is a natural sulfur-containing aroma in wine.

The microwave spectra of MTTP were recorded in a molecular beam Fourier transform microwave (MB-FTMW) spectrometer of a frequency range from 2 to 26 GHz. Two conformers were assigned. Highly accurate molecular parameters were determined using the XIAM code [1]. In addition, the ^{34}S -isotopologue of the most stable conformer was assigned in the natural abundance of about 4%.

The barrier to internal rotation of the methyl group was predicted by quantum chemical calculations to be higher than 1000 cm^{-1} for both conformers using different methods and basis sets. No splittings due to internal rotation could be observed with the experimental resolution of 2 kHz of our spectrometer, which is in agreement with the calculated barrier heights. Different transition states were optimized at the MP2/6-311++G(d,p) level of theory using the Berny algorithm to illustrate the intramolecular conversion between both conformers.

Geometry optimizations were performed at different level of theories and the calculated rotational constants were compared with the experimental values. The molecular geometries were also compared with other similar five-membered molecules like dihydro-2-methyl-3-thiophenone [2] and 2-methyl-cyclopentanone [3].



[1] H. Hartwig and H. Dreizler, *Z. Naturforsch.* **51a**, 923 (1996).

[2] H. Mouhib, V. Van, and W. Stahl, *J. Phys. Chem. A* **117**, , 6652 (2013).

[3] J.L. Alonso, J. C. López, and R. M. Villamañán, *J. Mol. Spectrosc.* **126**, 348 (1987).

TWO ASPECTS OF PARTIALLY DEUTERATED METHYL GROUP INTERNAL ROTATION: CD₂HOH and CH₂DCOH

L. H. Coudert¹, M. Ndao¹, F. Kwabia Tchana¹, L. Margulès², R. Motiyenko², J.-C. Guillemin³, J. Barros⁴, L. Manceron⁴, P. Roy⁴

¹LISA, UMR 7583 CNRS - Universités Paris Est Créteil et Paris Diderot, 94010 Créteil, France

²Laboratoire PhLAM, UMR 8523 CNRS - Université de Lille 1, Villeneuve d'Ascq, France
³ISCR, UMR 6226, Rennes, France

⁴AILES beam line, Synchrotron Soleil, Gif-sur-Yvette, France

The spectroscopy of non-rigid molecules displaying internal rotation of a partially deuterated CH₂D of CD₂H methyl group was initiated by Quade and *coworkers* [1]. Since that time progress have been made and led to the first analysis of microwave data involving the three lowest lying torsional states of monodeuterated methanol CH₂DOH [2]. In this paper we will report on the analysis of two molecules displaying internal rotation of a partially deuterated methyl group: doubly deuterated methanol CD₂HOH and monodeuterated acetaldehyde CH₂DCOH.

Doubly deuterated methanol shares many features with CH₂DOH, its torsional energy level diagram is, however, qualitatively different from that of this species from the symmetry stand point. Microwave and farinfrared spectra have been recorded. About 600 transitions have been assigned in the former spectrum, from 80 to 650 GHz, and include parallel transitions within the three lowest lying torsional states and perpendicular transitions between these states. The assignments have been carried out up to J = 15 and K = 5 and revealed that the rotational energy levels of torsional states with K < 3 are perturbed. In the farinfrared spectrum, spanning the 20 to 670 cm⁻¹ region, about 40 torsional subbands could be observed. Their assignment is not straightforward and we are hoping that line position analyzes of their rotational structure will allow us to confirm the tentative assignment.

Monodeuterated acetaldehyde is qualitatively similar to monodeuterated methanol CH₂DOH but differs quantitatively as it displays a higher barrier to internal rotation. This allows us to understand its energy level diagram from a tunneling perspective. The submillimeter wave spectrum has been recorded and its assignment is still in progress. Rotational transitions within the lowest lying torsional state could be identified easily as they behave like asymmetric-top transitions. The assignment of transitions involving the two close lying upper torsional states is more problematic as a torsion-rotation Coriolis coupling has to be accounted for. There also exists a Coriolis coupling between the lowest lying torsional state and the two upper ones. Its effects have been evidenced and we hope to be able to assign the transitions linking these three states by the time of the conference.

[1] C. R. Quade, C. C. Lin, J. Chem. Phys. **38**, 540 (1963); C. R. Quade, R. D. Suenram, J. Chem. Phys. **73**, 1127 (1980).

[2] J. C. Pearson, S. Yu, B. J. Drouin, J. Mol. Spec. **280**, 119 (2012); L. H. Coudert, M. Zemouli, R. A. Motiyenko, L. Margulès, S. Klee J. Chem. Phys. **140**, 064307 (2014).