

SUBMILLIMETER-WAVE SPECTROSCOPY OF NITROGEN CONTAINING
MOLECULES OF ASTROPHYSIC INTERESTL. Margulès¹, R.A. Motiyenko¹, J.C. Guillemin²¹Laboratoire PhLAM, UMR8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq,
France²Institut des Sciences Chimiques de Rennes, ENSC Rennes, CNRS, UMR 6226, 11 Allée de
Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

Almost 30 nitrile molecules, which contain the cyano group ($C\equiv N$), have been detected in the interstellar medium (ISM) so far. The simplest of these nitriles, the cyano radical $C\equiv N$, was found in 1940 [1,2]. The most complex of all nitriles, HC11N, having a total of 13 atoms, was detected [3]. The vast majority of these nitriles have been detected in the dense molecular clouds Sgr A and B, and TMC-1 by means of their rotational spectra. The formation mechanisms of many of these compounds are not well understood.

In particular, many isocyanide compounds with a high kinetic instability, are poorly studied in laboratory. We investigated recently two of these compounds: diisocyanomethane $CH_2(NC)_2$ [4], and allyl isocyanide CH_2CHCH_2NC [5]. Following these studies we will report recent results about two others isocyanides: ethylisocyanide CH_3CH_2NC , and iso-cyanomethane $NCCH_2NC$.

Like many others complex organic molecules of astrophysics interest some of the nitriles exhibit large amplitude motions that make delicate the analysis of their spectra. This is the case of hydroxyacetonitrile, $HOCH_2CN$ and acetyl isocyanate, CH_3CONCO , which are currently studied. The latest results on these two molecules will be also presented.

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**MILLIMETER AND SUB-MILLIMETER WAVE ROTATIONAL SPECTRUM OF
METHYL NITRATE**

JESSICA THOMAS¹, DOUGLAS PETKIE¹, IVAN MEDVEDEV¹ and DAVID DOLSON²

¹Department of Physics, Wright State University, Dayton, OH, USA

²Department of Chemistry, Wright State University, Dayton, OH, USA

We are reporting on our ongoing study of the millimeter and sub-millimeter wave rotational spectrum of methyl nitrate. Methyl nitrate (CH_3NO_3), can be produced via reaction of methanol and nitric acid, both present in the interstellar medium. Thus, it is likely to be present in molecular clouds in detectable quantities. We have previously reported on our study of its ground state spectrum in 210-270 GHz range. We are presently working on extending this range to 500 GHz and will present the results of our investigation in this presentation.

**LINE-SHAPES AND BROADENINGS OF ROTATIONAL LINES OF CH₃³⁵Cl IN
COLLISION WITH He, Ar AND Kr**

V. Gupta^{1,2}, F. Rohart³, L. Margulès³, R.A. Motiyenko³, J.V. Buldyreva¹

¹ Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté,
16 Route de Gray, F-25030 Besançon, France

² Department of Physics, University of Lucknow, 226007 Lucknow, India

³ Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523,
Université Lille 1, F-59655 Villeneuve d'Ascq cedex, France

Methyl chloride is well known as the most abundant halocarbon in the Earth's atmosphere and the main source of stratospheric chlorine atoms involved in the chemical reactions of ozone layer depletion. Its spectroscopic parameters for perturbation by main terrestrial-atmosphere gases have been very intensively studied over last years (updated line positions and intensities [1] as well as N₂-, O₂-, air-, H₂-, CO₂- and self-broadening coefficients [2-6]). In the present work we extend these measurements to the case of some atomic perturbers: He, Ar and Kr.

Experiments were performed with a frequency-modulated spectrometer operating in the 180-950 GHz range. It consists of a 10-18.5 GHz frequency synthesizer followed by a frequency multiplier chain based on solid-state devices, a 1.1 meter long absorption cell and a bolometric detection.

Rotational lines R(6), R(10), R(17), R(22), R(31) and R(33), ranging from 186 up to 901 GHz, have been studied in details. Their line-shapes were analyzed with various models (Voigt, Galatry, Speed-Dependent Voigt) in order to probe velocity-dependence and diffusion effects. The hyperfine structure related to the ³⁵Cl atom was included and the full implementation of the Beer-Lambert law was considered in order to take account of the large absorbance of CH₃Cl lines [4].

Because of complications resulting from the hyperfine structure related to the ³⁵Cl atom, higher frequency lines were analyzed first. For the He-induced relaxation case, the observed line shapes have been rather well explained by using Voigt profile model. By contrast, in the case of heavier buffer atoms, Ar and most of all Kr, strong departures from the Voigt profile have been stated and attributed partly to the molecular diffusion but mainly to the speed-dependence of relaxation rates.

With the support of this preliminary study, all recorded lines have been analyzed using the meaningful Speed-Dependent Voigt profile. For completeness, the Voigt profile has been also employed since it still continues to be used in applications. The presented results concern the dependence of relaxation rates on the quantum numbers *J* and *K* as well as on the R(6)-line hyperfine components.

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**MILLIMETRE-WAVE SPECTRUM OF THE MONO-DEUTERATED
ISOTOPOLOGUES OF ETHANOL FOR RADIO-ASTRONOMY**

Adam Walters^{1,2}, Mirko Schäfer³, Holger S.P. Müller³, Matthias H. Ordu³, Frank Lewen³,
Stephan Schlemmer³

¹ Université de Toulouse; UPS-OMP; IRAP; Toulouse, France.

² CNRS; IRAP; 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France.

³I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany.

The rotational spectra of the anti-conformer of $\text{CH}_3\text{CH}_2\text{OD}$, CH_3CHDOH , *a*- $\text{CH}_2\text{DCH}_2\text{OH}$, and *s*- $\text{CH}_2\text{DCH}_2\text{OH}$ have been measured between 35-500 GHz using several spectrometers at the Cologne Laboratory Astrophysics group based on amplified harmonic generation. Approximately 1500 new lines have been measured. Previously these species had been measured to no higher than 60 GHz, with a much more restricted data set, but facilitating the initial analysis [1]. The purpose of this present work is to create a reliable catalogue for radio-astronomy, in particular for spectra taken with ALMA. Parent ethanol has been detected in the interstellar medium but there is as yet no identification of its isotopologues. This work is a follow-up of our measurements of ^{13}C -substituted ethanol[2].

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**COMPREHENSIVE ANALYSIS OF THE MOLECULAR OXYGEN 60 GHZ BAND:
EXPERIMENT AND MODELLING**

Maksim Koshelev, Ilya Vilkov, Dmitrii Makarov, Evgeny Serov, Vladimir Parshin and
Mikhail Tretyakov

Institute of Applied Physics, Russian Academy of Sciences
603950, Russia, Nizhny Novgorod, Ulyanov str. 46

Large set of accurate experimental data was obtained for the molecular oxygen band centered near 60 GHz. The band is formed by fine-structure transitions. Modelling of the band profile at various conditions is of significant importance for spectroscopic applications including atmosphere remote sensing and wireless communication.

Running the experiments, two broadband spectrometers were used to cover wide pressure range [1]. Radioacoustic spectrometer was used to study individual collisionally-broadened fine-structure line profiles at pressures up to 10 Torr and temperatures from 238 up to 348 K. Dependencies of the self-broadening and nitrogen broadening coefficients on temperature were studied.

Complementary to the previous one, the resonator spectrometer equipped with a gas chamber with accurately controlled pressure and temperature was used to carry out measurements at higher pressure values ranging from 75 to 1000 Torr. By means of the resonator spectrometer, whole absorption band profile in the range 46 – 81 GHz was recorded in pure oxygen and in air. Influence of the collisional coupling effect on the band shape was studied.

Obtained data allow thorough analysis of the 60 GHz band similar to works [2,3]. Models of the molecular oxygen absorption in the mm- and submm-range will be updated using the acquired data.

The study is partially supported by RFBR.

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THE EFFECTS OF TWO INTERNAL ROTATIONS IN THE MICROWAVE SPECTRUM OF ETHYL METHYL KETONE

Ha Vinh Lam Nguyen^{1,2}, Vinh Van¹, Wolfgang Stahl¹, Isabelle Kleiner²

¹Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 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

Using two molecular beam Fourier transform microwave spectrometers both, the torsional fine structure with all five rotational-torsional species arising from two inequivalent methyl groups, the acetyl methyl group $-\text{COCH}_3$ and the ethyl methyl group $\text{CH}_3\text{CH}_2\text{CO}-$, could be fully resolved and analyzed in a global fit using two codes, BELGI-Cs-2Tops and XIAM. Molecular parameters like the rotational constants and the centrifugal distortion constants were determined with very high accuracy. The acetyl methyl group has a relatively low barrier to internal rotation ($181.502(98) \text{ cm}^{-1}$, as determined by the BELGI-Cs-2Tops code) causes splittings up to 1.2 GHz in the spectrum. Splittings due to the internal rotation of the ethyl methyl group with a barrier height of $763.87(65) \text{ cm}^{-1}$ are much smaller, in the order of a few hundred MHz up to 4 MHz. We found that for this molecule, the program BELGI-Cs-2Tops is much more suitable to analyze the spectrum compared to the XIAM code, since some additional parameters can be added. Using BELGI-Cs-2Tops, the spectrum could be reproduced within our experimental accuracy using 19 fitted parameters for 295 lines with a ratio of 15.5 lines/parameter. For the first time, the spectroscopic work was supplemented by quantum chemical calculations for this molecule. On the other hand, quantum chemical calculations were validated by rotational spectroscopy. We found reasonable agreements between the calculated and experimental results obtained from both XIAM and BELGI-Cs-2Tops fits. With advanced quantum chemical methods, it could be shown that the equilibrium geometry of the lowest energy conformer has no mirror plane. However, in the torsional ground state an effective C_s symmetry was found and BELGI-Cs-2Tops could be used with some success. A full two-dimensional potential energy surface depending on both, the torsional angle of the entire ethyl group and the acetyl methyl group was calculated using MP2 and DFT methods. This gives a clear picture of the rather complex tunneling path of the acetyl methyl internal rotation. It also explains the rather large V_6 contribution of the one-dimensional acetyl methyl potential curve.

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**TERAHERTZ LABORATORY EMISSION SPECTROMETER (TELM):
ROTATIONAL SPECTRUM AND PRESSURE BROADENING
OF METHANOL NEAR 800 GHz**

Alexey Potapov, Silvia Spezzano, Frank Lewen, Matthias H. Ordu, Ronan Higgins, Karl Jacobs, Stephan Schlemmer, Urs U. Graf

I. Physikalisches Institut, University of Cologne, Zùlpicher Str. 77, 50931, Cologne, Germany
potapov@ph1.uni-koeln.de

Reliable laboratory data play an important role in the analysis of astronomical spectral line surveys. That is why the success of space, stratospheric and ground-based submillimeter-wave observatories, such as HERSCHEL, SOFIA, ALMA, and NANTEN, drives the high resolution spectroscopic laboratory studies to the Terahertz spectral region. Absorption spectroscopy is the main tool for measurements of rotational spectra of astrophysically important species in the THz. But in the modern time, the development of highly sensitive heterodyne detectors and digital Fast Fourier transform spectrometers (FFTSs) makes emission spectroscopy very attractive, in the light of its advantages, such as the possibility of fast measurements of broadband spectra with high sensitivity and precise line intensities.

Our institute has a long tradition of designing and building near quantum-limited SIS and HEB mixer-based heterodyne receivers for astronomical observatories, such as Herschel [1], SOFIA [2], and NANTEN [3]. This served as one of the reasons for the realization of the present project.

The Terahertz Laboratory eMISSION spectrometer (TELM) has been developed to measure high resolution emission spectra of complex molecules of astrophysical interest. The instrument consists of a decommissioned astronomical SIS-receiver using a Gunn oscillator based LO and a new FFTS backend. It is looking through a 2.5 meter long glass cell with liquid nitrogen as a background. The receiver enables us to detect directly the weak thermal emission (some 10^{-15} W within a typical 1 MHz spectroscopic line width [4]) of gaseous molecular samples.

As a proof of principle, the emission spectrum of methanol has been measured in the frequency range of 800.5 – 808.5 GHz and assigned with the help of the CDMS database. The self-pressure broadening of the observed transitions as well as the hydrogen and helium pressure broadening of the strongest line at 807866 MHz have been obtained at room temperature. The emission spectrum of methanol has been compared with the absorption spectrum also measured by us, showing the promising perspective for the emission spectroscopy technique.

The work was supported by Deutsche Forschungsgemeinschaft through grant SFB 956.

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ACCURATE REST FREQUENCIES OF HC₃N AND ITS ISOTOPOLOGUES

Alexander V. Lapinov^{1,2}, German Yu. Golubiatnikov¹, Alexander P. Velmuzhov^{2,3},
Jens-Uwe Grabow⁴, Antonio Guarnieri⁵

¹Institute of Applied Physics of RAS, 46 Ulyanov str., 603950 Nizhny Novgorod, Russia

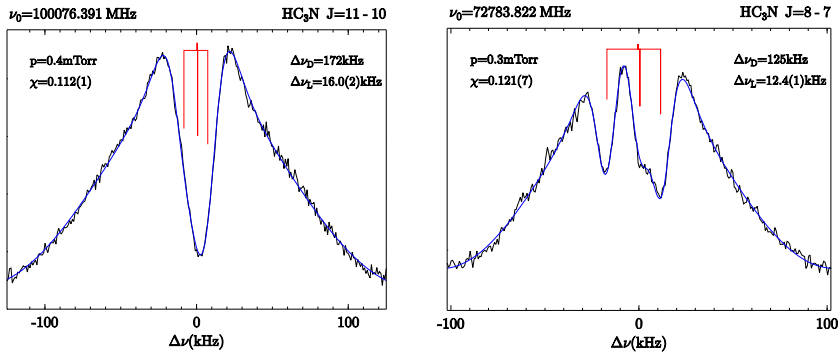
²Lobachevsky State University of Nizhny Novgorod, 23 Gagarin ave., 603950 Nizhni Novgorod, Russia

³G.G. Devyatikh Institute of Chemistry of High Purity Substances of RAS, 49 Tropinin str., 603950 Nizhny Novgorod, Russia

⁴Institute of Physical Chemistry and Electrochemistry, Leibniz University of Hannover, Callinstrasse 3A, 30167 Hannover, Germany

⁵Technical Faculty of Christian Albrecht University of Kiel, Kaiserstrasse 2, 24143 Kiel, Germany

We report results of significant improvement of laboratory frequencies for HC₃N, H¹³CCCN, HC¹³CCN, HCC¹³CN and HCCC¹⁵N measured with Lamb-dip spectrometer of the IAP RAS at 36 – 527 GHz. Hyperfine structure of rotational transitions of above species below 27 GHz were measured using FTMW spectrometer of the University of Hannover. Final relative accuracy for all ground state rotational transitions below 527 GHz is $\leq 10^{-9}$. Typical examples of Lamb-dip measurements of HC₃N rotational transitions with sub-Doppler spectrometer of the IAP RAS and their fits are reported in the figure below.



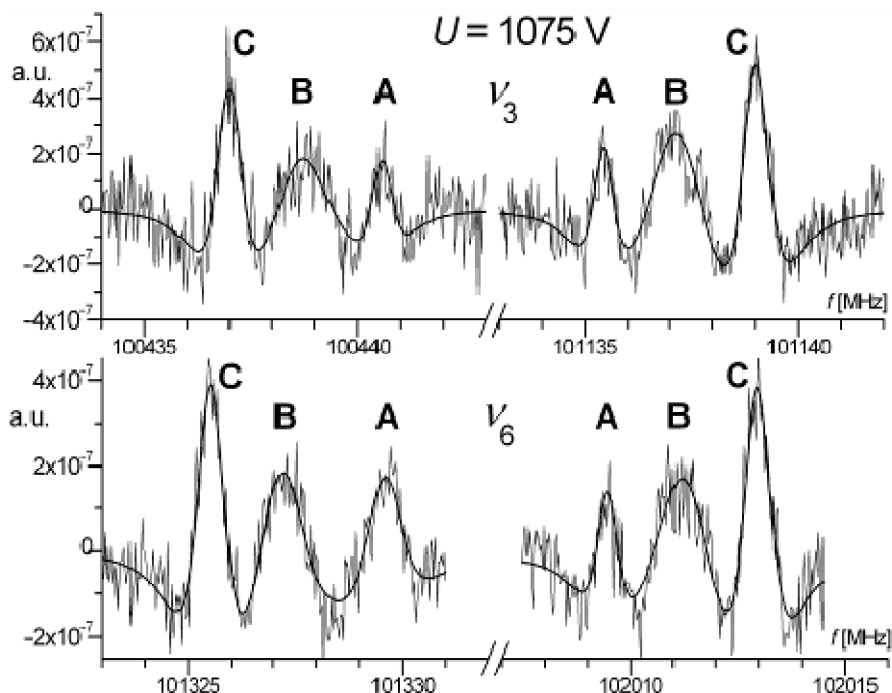
New laboratory frequencies are of great importance for precise studies of systematic velocity motions in star-forming regions as well as for a search of possible m_e/m_p variations from comparison of radio astronomical and laboratory frequencies.

DIPOLE MOMENTS OF CH₃F IN THE ν_3 AND ν_6 VIBRATIONAL EXCITED STATES FROM THE STARK EFFECT

Jindřich Koubek, Patrik Kania, Štěpán Urban

Institute of Chemical Technology Prague, Department of Analytical Chemistry, Technická 5,
16628 Prague, Czech Republic

Both the parallel and perpendicular rotational Stark components of the methyl fluoride J, k, l : $2, \pm 1, 0 \leftarrow 1, \pm 1, 0$ and $2, \pm 1, 71 \leftarrow 1, \pm 1, 71$ lines in the ν_3 and ν_6 excited vibrational states were measured in the microwave region of ca 100 GHz at the Stark fields in the range of ca 150 – 1100 V/cm (distance of 0.978234(47) cm (combined uncertainty, $k = 2$) between Stark electrodes are based on calibration using Ref. [1]). The analysis of the Stark components was complicated by hyperfine structure patterns (denoted as A, B and C in the figure) spanning a few MHz which were observed for M_J components with large Stark shifts (> 300 MHz), most probably due to an enhancement through the Stark effect. The permanent electric dipole moments for these two vibrational states were derived from selected separated hyperfine components of the Stark components: $\mu_3 = 1.90345(46)$ D, $\mu_6 = 1.86394(32)$ D (the expanded uncertainties are given with the coverage factor $k = 2$). The significant perturbational second-order Stark contributions were simply eliminated using a Stark component difference approach. Third-order Stark contributions were included in the analysis, higher-order Stark contributions and polarizability contributions were neglected since they are inconsequential in this study.



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**HIGH-RESOLUTION ROTATIONAL MOLECULAR SPECTROSCOPY:
A POWERFUL TOOL TO UNVEIL THE UNIVERSE**

Valerio Lattanzi^{1,2}, Cristina Puzzarini¹

¹Dipartimento di Chimica “G. Ciamician”, Università di Bologna

²Max Planck Institute for Extraterrestrial Physics

Millimeter and sub-millimeter molecular astronomy is an invaluable probe to explore and understand the different environments of our Universe. These wavelengths are becoming more and more attractive for the astrophysical studies thanks to a combination of new astronomical facilities and upgraded instrumentation.

To face the challenge coming from the observational community, laboratory data of molecular spectra must be extended to higher frequency (THz region), acquired with higher spectral resolution and including isotopic species, likely to be revealed in the future astrophysical spectra.

Our research is particularly interested to the laboratory techniques to create, acquire and analyze rotational spectra of reactive species, such as positive and negative ions, and radicals. In this talk we will review some of our recent discoveries in this field, showing the laboratory techniques developed to observe them and the possible astronomical implications.

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SUB-DOPPLER RESOLUTION IN THE THz FREQUENCY DOMAIN

Gabriele Cazzoli, Cristina PuzzariniDipartimento di Chimica “Giacomo Ciamician”, Università di Bologna, Via F. Semi 2,
I-40133, Bologna (Italy)

We report the first thorough investigation of the Lamb-dip effect in the THz region, which in turn allows sub-Doppler resolution to be exploited in this frequency region. It is demonstrated that an accuracy of 1 kHz, or even better (i.e., an accuracy better than 1 part in 10^9), and a frequency resolution of 50 kHz (i.e., a resolution better than 5 parts in 10^8) can be routinely obtained in our laboratory [1]. It has also been shown that Lamb-dip spectra can be recorded using either a Fabry-Perot interferometric cell or a free-space cell. Hydrogen sulfide (H_2S), sulfur dioxide (SO_2), deuterated water (D_2O), and methyl fluoride (CH_3F) have been selected as examples for demonstrating the accuracy and resolution reachable, thus providing the most accurate frequency values in the 1.0-1.2 THz frequency range for these molecules [1].

Finally, the high sensitivity of our spectrometer is demonstrated by the recording of the rotational spectrum of H_2^{36}S in the 167 GHz - 1.6 THz frequency range: despite the detection in natural abundance (0.02%), the transitions were recorded with a very good signal-to-noise ratio, thus allowing us to retrieve the corresponding transition frequencies with an accuracy ranging from 30 to 100 kHz [2].

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10.1051/0004-6361/201323298

**FREE JET MILLIMETER WAVE SPECTROSCOPY
OF OXAZOLIDONE COMPOUNDS**

Assimo Maris,¹ Sonia Melandri,¹ Camilla Calabrese,¹
Annalisa Vigorito,¹ and Laura B. Favero²

¹ "Giacomo Ciamician" Department of Chemistry, University of Bologna, Via Selmi 2,
I-40126 Bologna, Italy

² Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati
(CNR-ISMN), via Gobetti 101, I-40129 Bologna, Italy

2-Oxazolidinone (systematic name 1,3-oxazolidin-2-one) is a five-member heterocyclic ring exhibiting potential medicinal properties. It is the pharmacophore of a class of antimicrobial agents which have a unique structure and good activity against Gram-positive pathogenic bacteria (e.g. linezolid, the first in clinical use 2-oxazolidinone antibiotic). Often the functionality of drugs is related to their conformational flexibility and ability to form non covalent interactions with its surroundings. In order to understand how substitution affect these properties, a series of oxazolidone compounds has been studied by means of millimeter wave free jet Stark modulated absorption spectroscopy [1] and quantum mechanical calculations. The achieved data will be presented.

[1] C. Calabrese, A. Maris, L. Evangelisti, L.B. Favero, S. Melandri and W. Caminati, *J. Phys. Chem. A*, **117**, 13712 (2013).

DEUTERATED WATER HEXAMER FROM BROADBAND ROTATIONAL SPECTROSCOPY

Luca Evangelisti^{1,2}, Cristobal Perez², Simon Lobsiger², Nathan A. Seifert², Daniel P. Zaleski², Brooks H. Pate², Zbigniew Kisiel³, Berhame Temelso⁴, George C. Shields⁴

¹Dipartimento di Chimica G. Ciamician, University of Bologna, Bologna, Italy

²Department of Chemistry, The University of Virginia, Charlottesville, VA, USA

³ON2, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland

⁴Department of Chemistry, Bucknell University, Lewisburg, USA

The water hexamer is the first cluster size where three dimensional structures become the most stable. For cluster sizes up to the water decamer, the hexamer is unique because there are three low-lying isomers with distinct oxygen framework geometries that can be observed in pulsed molecular beams: the prism, cage, and book. Each structure has a different number of hydrogen bonds (prism: 9, cage: 8, book: 7). The prediction of the lowest energy form by different water potentials has become a benchmark in computational studies of water clusters. The experimental determination that the cage is the lowest energy form was presented by our group in 2012 using the population changes that occur when different carrier gases are used in the molecular beam expansion. Recently, it has been proposed by Babin and Paesani that the relative energy ordering of these isomers might be useful for testing the ability of theory to include zero-point energy effects [1]. Their calculations suggested that the prism might become the lowest energy isomer in the fully deuterated water hexamer. At the simplest level, this can be explained by the fact that the prism has the most hydrogen bonds and would, therefore, experience the most energy lowering upon isotopic substitution. Broadband rotational spectroscopy in a pulsed supersonic expansion has been used to study the cage, prism and book isomers of deuterated water hexamer. These data, in conjunction with new computational advances, quantify the changes in the oxygen framework structure respect to the normal water hexamers. Moreover, by using different gases in the expansion we have established that the prism isomer becomes the minimum energy structure as suggested by Babin and Paesani.

[1] V. Babin and F. Paesani, "The curious case of the water hexamer: Cage vs. Prism", *Chem. Phys. Lett.* **580**, 1 (2013).

**LONE PAIR $\cdots\pi$ INTERACTION: A ROTATIONAL STUDY OF THE
CHLOROTRIFLUOROETHYLENE-AMMONIA ADDUCT**

Qian Gou¹, Lorenzo Spada¹, Yannick Geboes²,
Sonia Melandri¹, Wouter A. Herrebout², Walther Caminati¹

¹Dipartimento di Chimica “G. Ciamician” dell’Università, Via Selmi 2, I-40126 Bologna,
Italy

²Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp,
Belgium

The Fourier transform microwave spectroscopy investigation of the 1:1 complex between chlorotrifluoroethylene (C₂F₃Cl) with H₂O pointed out irrefutably that its more stable configuration is established by oxygen *lp* $\cdots\pi$ interaction and that water undergoes a nearly free rotation [1]. This was one of the first characterizations of this kind of interaction by rotational spectroscopy.

Ammonia, similarly to water, acts as a halogen acceptor when forming complexes with perhalogenated saturated freons [2]. What about complexes of ammonia with perhalogenated un-saturated freons? The rotational spectrum of the adduct C₂F₃Cl-NH₃, showing nuclear hyperfine structure due to the quadrupole coupling effect of ³⁵Cl/³⁷Cl and ¹⁴N nuclei, proved that the nitrogen lone pair of NH₃, similarly to the oxygen lone pair in water, still binds the partner molecule through a *lp* $\cdots\pi$ interaction (see Figure 1). The nuclear quadrupole hyperfine structure considerably complicates the rotational spectrum but its analysis provided useful information on the structure and internal dynamics of the complex [3]. In addition, the values of the ¹⁴N quadrupole coupling constants were useful in estimating the effective orientation of NH₃ in the complex.

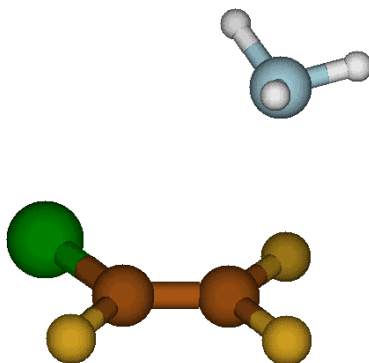


Figure 1. The observed conformer of C₂F₃Cl-NH₃.

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HALOGEN BOND FEATURES REVEALED IN THE GAS PHASE BY ROTATIONAL SPECTROSCOPY

Lorenzo Spada¹, Qian Gou¹, Montserrat Vallejo-Lopez^{1,2}, Andrea Staffolani¹, Alberto Lesarri², Emilio José Cocinero^{1,3}, Walther Caminati¹

¹Dipartimento di Chimica “G. Ciamician” dell’Università di Bologna,
Via Selmi 2, I-40126, Bologna, Italy.

²Departamento de Química Física y Química Inorgánica,
Universidad de Valladolid, E-47011 Valladolid, Spain.

³Departamento de Química Física, Facultad de Ciencia y Tecnología Universidad del País Vasco, (UPV-EHU), Apartado 644, E-48940 Bilbao, Spain.

A typical halogen bond is denoted by the three dots in R–X···Y. R–X is the halogen bond donor where X is any halogen atom with an electron-poor region, R is a group covalently bound to X and Y is halogen bond acceptor with, at least, one electron-rich region [1].

In this context the high resolution microwave spectroscopy in supersonic expansion is a really suitable technique to reveal the features of the halogen bond in molecular systems free from solvent effects.

We have recently characterized with this technique the O···Cl, N···Cl and F···Cl halogen bonds through the studies of the molecular adducts of CF₃Cl with water [2], ammonia [3] and CH₃F [4].

We present here the results of microwave spectroscopy studies of additional molecular complexes, such as Pyridine···ClCF₃.

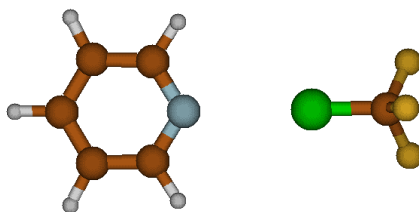


Figure 1. The observed adduct of Pyridine···ClCF₃

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