

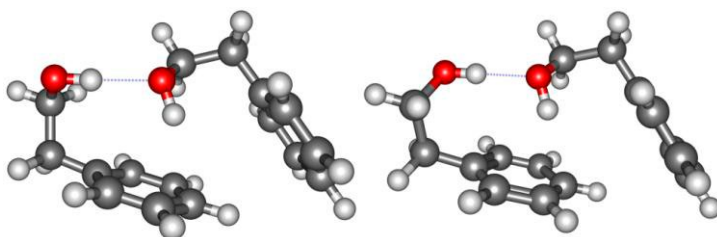
# Observation of two dimers of phenyl ethyl alcohol using rotational spectroscopy

Rizalina Tama Saragi<sup>1</sup>, Marcos Juanes<sup>1</sup>, Alberto Lesarri<sup>1</sup>,  
Lourdes Enríquez<sup>2</sup>, Martín Jaraíz<sup>2</sup>

1) Departamento de Química Física y Química Inorgánica Universidad de Valladolid

2) Departamento de Electrónica, ETSIT, Universidad de Valladolid

Non-covalent interactions can be probed through the analysis of isolated neutral clusters in the gas phase. We examined the dimer and the monohydrate of phenyl ethyl alcohol as part of an on-going investigation on alcohol dimers using rotational spectroscopy. The adducts of phenyl ethanol were generated in a jet-cooled expansion and investigated by chirped-pulse Fourier transform microwave spectroscopy. Two conformers ( $C_1$  and  $C_s$  symmetry) were observed for the monomer, extending previous measurements to all monosubstituted  $^{13}\text{C}$  isotopologues in natural abundance for the most stable species. Two isomers were observed for the dimer ( $g-g+$  and  $g+g+$ ), stabilized by a combination of  $\text{OH}\cdots\text{O}$ ,  $\text{OH}\cdots\pi$  and  $\text{C}-\text{H}\cdots\pi$  interactions. Structural comparisons with the monohydrate illustrate the structural role of the aromatic ring in the dimer. Ab initio and DFT calculations will also be presented.



# Self-aggregation process in CH<sub>2</sub>F<sub>2</sub>: large homoclusters studied by rotational spectroscopy

Camilla Calabrese<sup>1</sup>, Luca Evangelisti<sup>2</sup>, Iciar Uriarte<sup>1</sup>, Brooks Pate<sup>3</sup>, Emilio J. Cocinero<sup>1</sup>

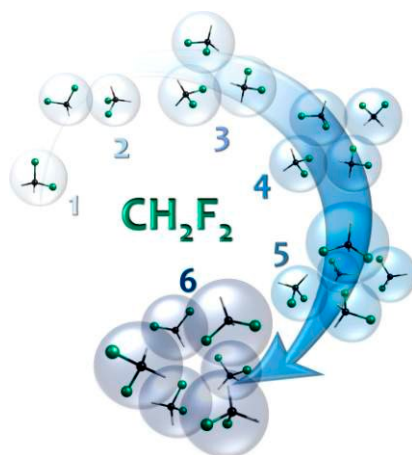
- 1) Physical Chemistry Department, Universidad del País Vasco (UPV/EHU), Bilbao, Spain. Biofisika Institute (CSIC, UPV/EHU), Universidad del País Vasco (UPV/EHU), Bilbao, Spain.
- 2) Chemistry Department "G. Ciamician", Università di Bologna, Bologna, Italy.
- 3) Department of Chemistry, The University of Virginia, Charlottesville, VA, USA.

The interest in halocarbons is still open. From an environmental point of view, the search for compounds alternative to freon is addressed to resolve the problem of the global warming; while from a strictly chemical point of view, non-covalent interactions that keep these molecules together are part of weak interactions, which behavior differ from the typical of strong ones (like H-bonds), enhancing their interest. Actually, the weak interactions characterizing the aggregation of these systems allow testing both the computational and the experimental fields, since predicting and measuring clusters held together by small binding energies is even today a challenge. For these reasons, the study of the structural arrangements of large clusters of halocarbons can still be considered an interesting topic.

In this work, the structure of large clusters of difluoromethane (CH<sub>2</sub>F<sub>2</sub>) is presented combining state-of-the-art rotational spectroscopy and quantum chemical calculations. The development in the last years of chirp pulsed Fourier transform microwave (CP-FTMW) spectrometers intensified the studies of oligomers of relatively large asymmetric rotors, opening to the observation of greater molecular cluster difficult to detect.[1] This extensive study is a collaboration between different laboratories both for the measurements (CP-FTMW spectrometers of Bilbao (ES) and Virginia (USA)) and for the theoretical part (USA).

In particular, the challenging assignments of one pentamer, two hexamers, and one heptamer homoclusters of CH<sub>2</sub>F<sub>2</sub> were carried out, highlighting the high sensitivity of the technique. The ability to create a dense network of different weak interactions is the main driving force for the stabilization of each system. These kinds of studies of relatively large molecular aggregates can be considered a bridge between microsystems and molecular bulk.[2,3] In this regard, the results obtained for CH<sub>2</sub>F<sub>2</sub> heteroclusters with water molecules will be also mentioned.

Despite a considerable gap remains between cluster and bulk properties, the last advances of rotational spectroscopy opening to the identification of larger clusters in an isolated environment, represent a step toward detailed structural understanding of first stage of nucleation and aggregation processes.



[1] Angew. Chemie – Int. Ed. 2017, 56, 6289.

[2] Science 2002, 297, 2030.

[3] Science 2012, 336, 897.

# The nitrogen–nitrogen noncovalent interaction in the gas phase

Lorenzo Spada<sup>1</sup>, Weixing Li<sup>2</sup>, Nicola Tasinato<sup>1</sup>, Luca Evangelisti<sup>2</sup>, Sergio Rampino<sup>1</sup>, Andrea Gualandi<sup>2</sup>, Pier Giorgio Cozzi<sup>2</sup>, Sonia Melandri<sup>2</sup>, Vincenzo Barone<sup>1</sup>, Cristina Puzzarini<sup>2</sup>

1) *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa (Italy)*

2) *Dipartimento di Chimica "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna (Italy)*

B7.3.

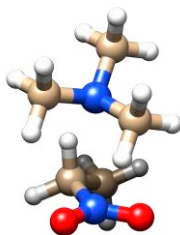
The N–N noncovalent interaction, along with weak C–H...O and secondary C–H...N hydrogen bonds, has been characterized in the gas-phase in the 1:1 nitroethane–trimethylamine complex by using state-of-the-art quantum-chemical computations combined with pulsed-jet Fourier-transform microwave spectroscopy.

The conformational potential energy surface has been deeply investigated by means of quantum chemical calculations rooted in density functional theory. In particular, three different minima and the corresponding connecting transition states have been identified. As for minima, rotational spectroscopic parameters, including rotational and centrifugal distortion constants as well as nitrogen nuclear quadrupole coupling constants, have been worked out by also accounting for vibrational effects by means of the generalized vibrational perturbation machinery [1] implemented in the Gaussian quantum chemical package [2]. The two most stable conformers are energetically nearly equivalent, and they present very similar structures and hence rotational parameters.

Experimentally, rotational transitions belonging to two different isologues, namely the main isotopic species and that containing <sup>15</sup>N–trimethylamine, have been measured and fitted by using the VMS-ROT module [3] of the virtual multifrequency spectrometer [4,5].

The nature and weight of the different contributions to the interaction in terms of charge rearrangement have been probed and quantitatively described by means of the "Natural Orbitals for Chemical Valence/Charge-Displacement" (NOCV/CD) scheme [6].

Given the small energy difference between the two lowest-lying minima (about 0.2 kcal/mol) combined with the low energy transition state (about 0.3 kcal/mol) ruling their interconversion as well as their almost equivalent rotational behaviour, the observed spectrum is consistent with either that of the global minimum or that of a structure continuously interconverting between the nearly equivalent conformers.



[1] *J. Chem. Theory Comput.*, 2012, 8 (3), 1015.

[2] *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

[3] *J. Chem. Theory Comput.*, 2017, 13 (9), 4382.

[4] *WIREs Comput Mol Sci* 2016, 6, 86

[5] *J. Comput. Chem.* 2015, 36, 321

[6] *J. Chem. Phys.* 2015, 142, 084112.

# Understanding structural similarities in the Homodimers of Fluorene, Dibenzofuran and Diphenylether via broadband rotational spectroscopy

Mariyam Fatima<sup>1</sup>, Cristóbal Pérez<sup>2</sup>, Anja Poblitzki<sup>3</sup>, Amanda Steber<sup>4</sup>, Sabrina Zinn<sup>4</sup>, Martin Suhm<sup>3</sup>, Melanie Schnell<sup>5</sup>

- 1) *Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany and Max Planck Institute for the Structure and Dynamics of Matter (MPSD) at the Center for Free Electron Laser Science, Hamburg, Germany*
- 2) *Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Leioa, Spain and Ikerbasque, Basque Foundation for Science, Bilbao, Spain*
- 3) *Institut für Physikalische Chemie, Universität Göttingen, Göttingen, Germany*
- 4) *The Hamburg Centre for Ultrafast Imaging (CUI) at the Universität Hamburg, Hamburg, Germany*
- 5) *Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany and Christian-Albrechts-Universität zu Kiel, Kiel, Germany*

B7.4.

The role of inter and intramolecular interactions, such as hydrogen bonding and dispersion interactions, in stabilizing biological molecules is of great interest to many scientific communities. A detailed understanding of these interactions can be used as a design principle for stabilizing unusual molecules and molecular architectures. Therefore, a quantitative understanding of the various types of intermolecular interactions and their impact on the preferred molecular structure is an interesting topic.

In our group, we investigate these interactions using the high-resolution chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer COMPACT under the isolated conditions of a molecular jet in the gas phase. This technique provides accurate molecular parameters for developing a broad understanding of the underlying processes at the molecular level. To understand these weak interactions, we report here our studies on the homodimers of fluorene ( $C_{13}H_{10}$ ), dibenzofuran ( $(C_6H_4)_2O$ ), and diphenylether ( $(C_6H_5)_2O$ ) using rotational spectroscopy in the region of 2–8 GHz. While their structures show overall similarities, they also have some differences: Fluorene is a polycyclic aromatic hydrocarbon that does not contain a polar group (Figure 1). Dibenzofuran replaces one  $CH_2$  group in fluorene with oxygen, thus making it polar. In diphenylether, the C–C bond connecting the two rings in dibenzofuran is absent, therefore, increasing the flexibility of the molecule. We will present the results of our systematic structural study of the series highlighting the differences and similarities in the observed homodimers.

Figure 1



# Investigation of the products of thermal self-polymerization of Methyl methacrylate by means of microwave spectroscopy – the rotational spectrum of the dimer

Sven Herbers<sup>1</sup>, Daniel Obenchain<sup>1</sup>, Peter Kraus<sup>1</sup>, Kevin Lengsfeld<sup>1</sup>, Henning Kuper<sup>1</sup>, Jörg Becker<sup>1</sup>, Jens-Uwe Grabow<sup>1</sup>

1) Leibniz Universität Hannover

After the previous analysis of the monomer ( $C_5H_8O_2$ ) of methyl methacrylate (MMA) by molecular beam Fourier transform microwave spectroscopy, this study is about the investigation of the dimer ( $C_{10}H_{16}O_4$ , figure below) of thermal self-polymerization. Segments of the spectrum from 3.3 to 21.2 GHz were recorded using the narrow band Fabry-Perot

resonator based COBRA-FTMW-spectrometer. 1508 molecular transitions were identified, of which 545 were assigned to a conformer of the dimer. Using the XIAM fitting program, rotation constants, Watson's S centrifugal distortion coefficients, and internal rotation parameters were obtained from the spectrum. The dimer contains three methyl rotors but only the two methoxy rotors cause resolvable ( $> 5$  kHz) splittings of the rotational transition lines. The experimental results are compared with the results of ab initio calculations to find a suitable prediction method for the methyl methacrylate system.

The methyl methacrylate self-polymerization system is intended as an easy to access model system for polymerization processes and the analysis of the dimer presented in this study contributes to the stepwise understanding of the system by microwave spectroscopy and ab initio methods.

