

Rotational spectroscopy signature of smelling allyl alcohols

Assimo Maris¹, Susana Blanco²

1) Department of Chemistry G. Ciamician, University of Bologna

2) Department of Physical Chemistry and Inorganic Chemistry, University of Valladolid

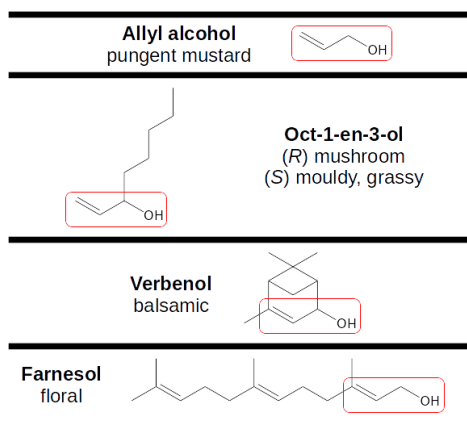
Allyl alcohol is a strong lachrymator with a pungent mustard odor. It is a fundamental building block of several smelling organic molecules. Depending on the carbon frame, they present a quite different odor, suggesting a modulation role of the molecular shape in the ligand–receptor interaction.

Rotational spectroscopy is a suitable tool to get insights on the structure of molecules and molecular complexes in the gas phase and, in combination with computational chemistry simulations, allows for exploration of high dimension conformational spaces. Here we present, for the first time, the rotational spectra and the analysis of three allyl alcohols: oct-1-en-3-ol (mushroom alcohol, C₁₀H₁₆O), 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol (verbenol, C₈H₁₆O), and 3,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol, C₁₅H₂₆O).

The spectrum of oct-1-en-3-ol has been collected in the 59.6–74.4 GHz frequency range with the free jet absorption millimeter wave spectrometer in Bologna. Two species were observed. In both of them the allyl alcohol substructure is *skew-gauche* (referring to OCC=C and HOCC dihedral angles, respectively) and the alkyl chain is all *trans*. The difference lies on the relative orientation of the alkyl and allyl alcohol subunits.

The spectrum of *cis*-verbenol has been recorded in the 2–8 GHz frequency range with the chirped-pulse Fourier transform spectrometer in Valladolid. The rotational spectra of the parent, hydroxyl deuterated, and all ¹³C-isotopologues have been assigned, allowing for structure's determination. Differently from solid state, in the gas phase the most stable conformer exhibits an *anti* HCOH arrangement. Observation of the 1:1 water complex has shown that water acts as proton donor to the hydroxyl group, forming a secondary O–H interaction with alkyl verbenol's hydrogen atoms.

With the same spectrometer, the spectrum of farnesol has been collected. Since farnesol is formed by a mixture of 4 *cis/trans*-isomers, the spectrum is quite congested and, due to the presence of 8 rotatable bonds, the assignment is not straightforward. Preliminary considerations on the conformational space will be presented.



DNA sugars: in the gas phase and in solution

Iciar Uriarte¹, Camilla Calabrese¹, Aran Insausti¹, Montserrat Vallejo-López², Francisco Corzana³, Benjamin G. Davis⁴, Emilio J. Cocinero¹

1) Department of Physical Chemistry (UPV/EHU) and Biofísica Institute (CSIC, UPV/EHU), Universidad del País Vasco (UPV/EHU), Bilbao.

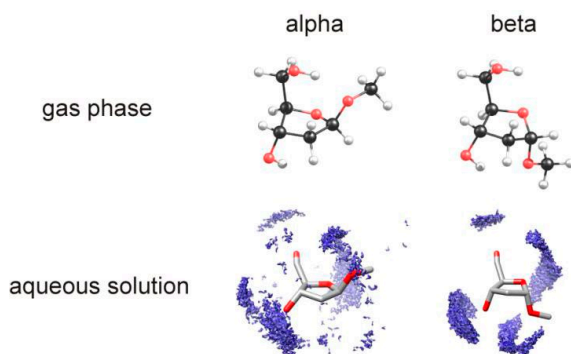
2) Department of Physical Chemistry, Universidad del País Vasco (UPV/EHU), Bilbao.

3) Department of Chemistry, Universidad de La Rioja, Logroño.

4) Chemistry Research Laboratory, University of Oxford, Oxford.

Sugars are versatile molecules that play a variety of roles in the organism. For example, they are important in energy storage processes or as structural scaffolds. Here, we focus on the monosaccharide present in DNA by addressing the conformational and puckering properties in the gas phase of α - and β -methyl-2-deoxy-ribofuranoside and α - and β -methyl-2-deoxy-ribofuranoside. Other sugars have been previously studied in the gas phase.[1,2]

The work presented here stems from a combination of chemical synthesis, supersonic expansions, quantum chemical calculations, microwave spectroscopy, NMR spectroscopy and Molecular Dynamics. Thanks to the alliance of these techniques, we have studied for the first time the conformational landscape of the sugar present in DNA in its biologically relevant form. Previous studies in the gas phase had been performed on 2-deoxyribose,[3] but only pyranose forms were detected. In this work, we isolate and characterize furanose forms of the sugar, which are the biologically active forms in DNA. Our gas phase study serves as a probe of the conformational preferences of these biomolecules under isolation conditions. Moreover, we compare the results obtained in the gas phase with data in solution thanks to a combination of NMR spectroscopy and Molecular Dynamics. In this way, we characterize the favored conformations in solution and, by comparing with the results under isolation conditions (gas phase), we extract the role of the solvent in the conformations and puckering of the monosaccharide.



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Multiresponsive Chromic Soft Materials: Formation of Macrocycles from Carbazole-based Biradicaloids

M. Carmen Ruiz Delgado

Department of Physical Chemistry, University of Malaga, Campus de Teatinos s/n, 229071, Malaga, Spain

π -conjugated biradical compounds become essential building blocks in DCC (dynamic covalent chemistry).[1] This field is based on the creation of structural scaffolds based on chemical components which interact through strong but reversible bonds. Importantly, dynamic covalent bonds will be at the center of attention because of their unique feature to become reversible under mild conditions.[2] Recently, we have demonstrated the reversible interconversion between a stable quinoid precursor based on a para-substituted carbazole with terminal dicyanomethylene groups and a macrocycle cyclophane upon soft external stimuli (temperature, pressure, light), which results on strong chromic features.[3] In this work, we investigate the interconversion of the monomer/cyclophane transformation in carbazole-based systems, both in solution and solid state, upon external stimuli. To this end, we use a combined experimental and theoretical study that links vibrational spectroscopy (Raman and IR) with DFT calculations.



Figure 1. Interconversion between 2,7-Dicyanomethylenecarbazole-based Biradicaloid (right) and Corresponding Cyclophane Tetramer (left).

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Raman spectroscopy as a versatile tool to study organic biradicals

Jose Luis Zafra Paredes¹, Juan Casado Cordon¹

1) *University of Málaga*

In recent years, there has been a renewed interest in the study of open-shell polycyclic aromatic hydrocarbons (PAHs). Among them, biradicals are characterized by a four states energetic model for the low lying electronic states. Such a distribution is related to the attractive electronic, magnetic and optical properties which make biradicals promising candidates for a wide range of applications in organic electronics, such as nonlinear optics, molecular spintronics, energy storage and organic photovoltaic devices sensitized by singlet fission. Despite all the promising properties predicted for open-shell PAHs, a common drawback still needs to be overcome: the high reactivity of radicals, which implies that most open-shell species tend to be too short-lived for practical applications and even for characterization [1]. In this regard, Raman spectroscopy has shown to be a suitable tool for studying this kind of molecular systems, able to provide valuable information that could be used in the development of new synthetic approaches [2].

Herein we report the study of different open shell PAHs with biradical character with the aim to highlight how Raman spectroscopy can help us to elucidate the molecular structure and the electronic configuration of their ground states and how the molecular information provided can be used to rationalize their properties in the context of the four states model [3–5].

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Molecular spectroscopic study on a natural uric acid type of Kidney Stone

Mustafa Kumru¹, Arkadiusz Miernik¹, Ahmet Altun², Meral Ari³, Michael Walter⁴

- 1) University of Freiburg – Medical Center, Faculty of Medicine, Department of Urology, Hugstetter Str. 55, 79106 Freiburg, Germany
- 2) Max Planck Institute for Chemical Energy Conversion, Stifstrasse 34–36, D–45470 Mülheim an der Ruhr, Germany
- 3) University of Freiburg – Physics Institute, Hermann–Herder–Str. 3a, 79104 Freiburg, Germany
- 4) FIT Freiburg Centre for Interactive Materials and Bioinspired Technologies, Georges–Köhler–Allee 105, 79110 Freiburg, Germany

The studies on kidney stone at molecular level are essential for prevention of diseases. In this study, a natural uric acid type of kidney stones was collected in the Department of Urology, Medical Centre – University of Freiburg, Germany. Uric acid is a heterocyclic compound with the formula $C_5H_4N_4O_3$. Uric acid stones may exist as uric acid monohydrate $C_5H_4N_4O_3 \times H_2O$ and uric acid dihydrate $C_5H_4N_4O_3 \times 2H_2O$. FT-IR and FT-Raman spectra of the uric acid stone have been recorded to determine its vibrational properties and molecular constitutions, including the existing tautomers. Computationally obtained vibrational spectra of several tautomers of uric acid with B3LYP and PBE density functionals were compared with experimental results. This leads to unique assignment of experimental vibrational bands and to extract information about the existing tautomers.

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Keywords: Uric acid; Kidney stone; Vibrational spectroscopy