

The Plíva Prize Session K

Lecture Hall AII

September 1, Thursday, 9:00 – 10:30

REMPI and IDIRS spectroscopy of Glucose-Derivative Dimers in Gas Phase

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Glucose is the most abundant carbohydrate in nature and it is used by living beings in many different contexts, such as for energy storage in vacuoles, structural support in plants cell walls and in glycoproteins working as docking centers. All these functions are governed by weak intermolecular forces. Here, we explore the intermolecular interactions between sugars, and more precisely of glucose-derivative dimers, in order to investigate their characteristic intermolecular interactions, by means of laser spectroscopy and quantum mechanical calculations. Glucose derivatives, Phenyl/Methyl/ α / β -Glucopyranose, were vaporized using laser ablation and coupled to a supersonic jet expansion. The cold environment of the beam allows the molecules to form aggregates. A fine tune of the experimental conditions was carried out to favor the formation of glucose-derivatives dimers, that were probed using a combination of lasers. The experiment was carried out inside the ionization chamber of a modified T.O.F. mass spectrometer, which allowed us to do mass-resolved experiments. Using REMPI and IR/UV double resonance,^[1-2] structural information of the dimers was obtained and compared with molecular mechanics and DFT calculations. To better analyse and explain the assignments, Gibbs free energies were calculated in the overall temperature range. The results clearly demonstrate that the binding energy of the complexes strongly depend on the anomer of the monomers and that the interaction between beta anomers is significantly stronger than between alpha anomers or between alpha-beta aggregates.

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Internal rotation potential and pure rotational spectroscopy of 3-nitrotoluene

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Nitrotoluene compounds are semi-volatile organic molecules of environmental and military interest. They are widely used in dyestuff, pesticides, rubber and pharmaceutical manufacturing¹. Persistent in natural conditions, they are difficult to oxidize due to the strong electron-withdrawing effect of the nitro group². Moreover, they are derivative products and taggants of the very well-known explosive TNT.

In a previous study, gas phase Far-IR vibrational cross-sections have been measured using FT-FarIR spectroscopy based on the AILES beamline of the SOLEIL synchrotron facility³. Even at the maximum resolution of the interferometer, it was not possible to resolve rotationally the Far-IR spectra at room temperature. In this study, we present the first high resolution analysis of 3-nitrotoluene (3-NT).

Pure rotational measurements were performed in jet-cooled conditions and at room temperature using the Fourier Transform MicroWave (FTMW) spectrometer⁴ located at the PhLAM (2-20 GHz range) and the submm/THz frequency multiplication chain⁵ located at the LPCA (70-220 GHz range), respectively.

The FTMW data have been analyzed using the BELGI-Cs program⁶. 440 rotational transitions with $J''_{\max}=11$ have been assigned and included in the fitting procedure, allowing the determination of the rotational constants, the quartic centrifugal distortion constants, the hyperfine structure constants due to the nuclear quadrupole coupling of nitrogen and the internal rotation parameters characterized by a very low barrier height (calculated at about 6 cm^{-1}).

In the submillimeter domain, a weak and very congested spectrum is observed because of the very low vapour pressure of the sample (8.6 Pa at room temperature), the photosensitivity of the compound and the presence of many pure rotation lines in low-frequency vibrational excited states. Its analysis is in progress by combining Kisiel's (ASCP and SVIEW) and Pickett's (SPFIT SPCAT) programs in support to the use of the BELGI-Cs program taking into account both the internal rotation motion and the hyperfine structure.

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Accurate and sensitive molecular spectroscopy with a virtually imaged phased array spectrometer and an optical frequency comb

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An optical frequency comb (OFC) consists of tens of thousands of narrow laser lines, separated by the repetition rate frequency, f_{rep} , and shifted from the zero frequency by the offset frequency f_0 . The comb line positions are determined by the formula $\nu_n = n \times f_{rep} + f_0$. Both of the frequencies can be referenced and stabilized to a frequency reference such as an Rb reference, an H-maser or an optical atomic clock. Additionally, when the comb light is resonantly coupled into an optical enhancement cavity, the optical path length is increased up to a few tens of kilometers and weak molecular transitions in dilute gases can be measured with high signal-to-noise ratio.

Frequency comb spectroscopy (FCS) can be an excellent tool for rapid, broadband, sensitive and frequency accurate measurements. An important issue in FCS is how to efficiently discriminate different spectral elements without losing any of these merits. By introducing the OFC into a spectrometer based on a virtually imaged phased array (VIPA) etalon with resolution higher than f_{rep} , we can rapidly and sensitively retrieve broadband spectra. The calibration of the spectrometer with a stabilized OFC allows us to retain some of the frequency accuracy¹. On the other hand, by decimating the comb of laser lines, we can resolve the lines and make full use of the frequency accuracy². This necessitates tuning of the system to fill in the gaps in the spectra and to the best of our knowledge has not been demonstrated with a VIPA spectrometer in a cavity-enhanced scheme.

We will present the results of rapid, accurate and sensitive OFC spectroscopy and a scheme to obtain such measurements. We will also present the work done with the aim of obtaining cavity-enhanced, high signal-to-noise ratio, comb-mode-resolved spectra. The experimental system consists of a near-infrared Er: fiber-based OFC, referenced to an Rb frequency standard. The optical cavity used offers finesse of ~ 21500 , which translates to an optical path length equal to approx. 4 km, for the swept locking scheme³, or 8 km, for the Pound-Drever-Hall scheme⁴. The VIPA spectrometer offers 38-nm spectrum bandwidth with a minimum acquisition time of 2×16 ms.

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Double Resonance Measurement of Acetylene Symmetric States with Optical Frequency Comb Referenced Cavity Ring-down Spectroscopy

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Symmetric vibrational states of acetylene are inaccessible by a single-photon excitation from the vibrational ground state. These states can be observed using multiphoton methods, such as those based on laser induced fluorescence or stimulated emission.^{1,2} Here, we present a novel double resonant absorption setup for accessing high-energy symmetric vibrational states of acetylene.

Our experiment uses a continuous-wave optical parametric oscillator (OPO) to pump a strong vibrational transition to an intermediate anti-symmetric state in the mid-infrared region. The transition from the intermediate state to the target symmetric state is probed using continuous-wave cavity ring-down spectroscopy (CRDS). The light source for the CRDS is a near-infrared external cavity diode laser (ECDL). The ECDL wavelength is stabilized with an optical frequency comb by locking their beat note with an optical phase-locked loop. The frequency comb is fully stabilized and provides an absolute wavelength reference.

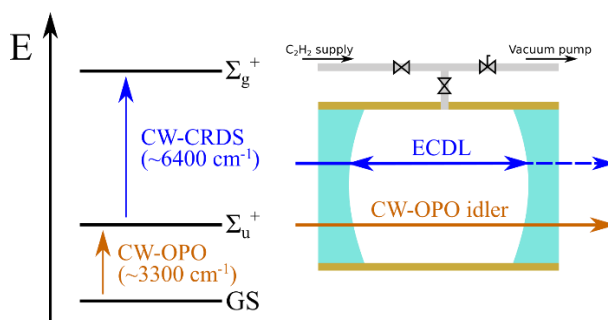


Figure 1: The principle of the measurement setup. A mid-infrared OPO continuously pumps a transition to an anti-symmetric (Σ_u^+) intermediate state. CRDS is used to probe a secondary transition to a symmetric (Σ_g^+) state.

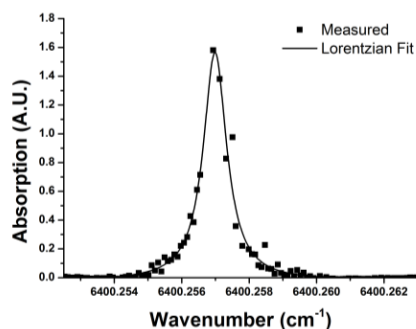


Figure 2: A preliminary measurement of the R(14) line of the transition $\nu_1+2\nu_3$ (Σ_g^+) \leftarrow ν_3 (Σ_u^+). The data points are least-squares fitted with a Lorentzian profile.

The strength of the mid-infrared transition and the high output power of the OPO ensure efficient population transfer to the intermediate state. This, combined with the sensitivity of CRDS in the near-infrared region, allows measuring weak secondary transitions with a high signal-to-noise ratio. The frequency comb locking decreases the effect of the ECDL linewidth on the measured transition profile and allows the determination of the transition energy with high precision and accuracy. The final transition is measured with sub-Doppler resolution due to the narrow linewidths of the laser sources used for the excitations.

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Coupled Internal Rotations in Five-Membered Rings

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From previous microwave spectroscopic studies on monomethyl substituted five-membered heterocyclic aromatic rings, it is known that the structures of such molecules are quite rigid. The conjugated double bonds force the molecule to planarity. On the other hand, the internal dynamics arising from internal rotation of the methyl group in these molecules is unpredictable. Currently, no definitive statement exists for predicting the barrier heights. Chemical intuition often fails and quantum chemical calculations are still rather inaccurate.

The system becomes much more complicated if two or more methyl substituents exist on the ring because of the possible coupling between the internal rotations. In this talk, we will report on the microwave spectra of five rings, which are 2,5-dimethylthiophene¹ and -furan (**1**, two equivalent methyl rotors), 2-acetyl-5-methylfuran (**2**) and 4,5-dimethylthiazole (**3**, two inequivalent methyl rotors), and tetramethylthiophene (**4**, four-rotor molecule with two pairs of equivalent methyl groups). We will compare the barrier heights of different rotors in a molecule with each other and with those of monomethyl substituted systems. The internal rotation coupling is determined experimentally and theoretically using potential energy surfaces.

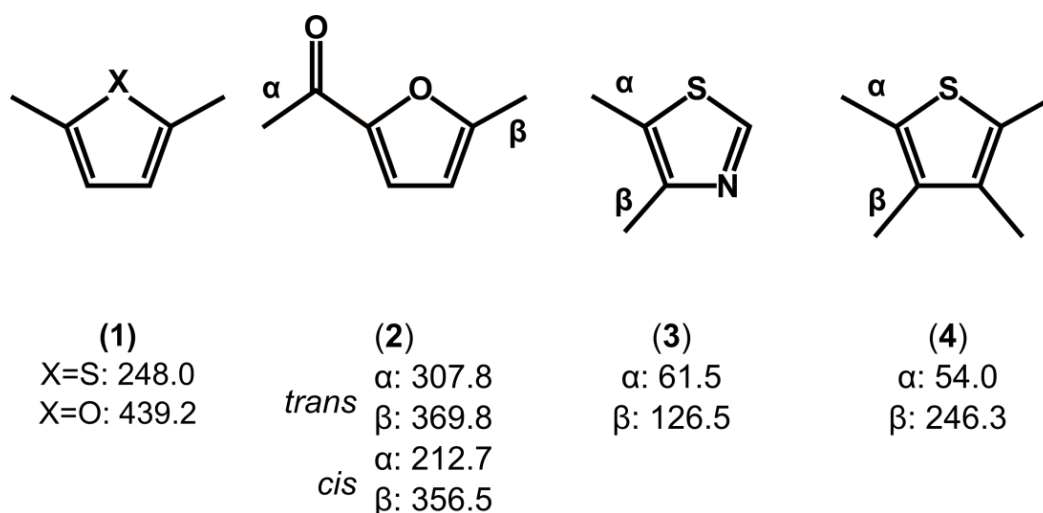


Fig. 1: Torsional barriers in five-membered rings (in cm^{-1}). 2,5-dimethylthiophene and -furan (**1**),¹ 2-acetyl-5-methylfuran (**2**), 4,5-dimethylthiazole (**3**), tetramethylthiophene (**4**).

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The conformational landscape of rose ketones in the gas phase

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Ionones and damascone belong to the group of rose ketones (a family of odorant molecules) and share a common structural motif of a cyclohexene ring and an enone chain. They are responsible for scents such as rose or violets in essential oils and are derived from the degradation or metabolization of carotenoids. From a structural point of view, they are flexible molecules with a rich conformational landscape. In order to assess their preferred conformations and their possible implications in biological activity, accurate structural studies are needed. Some studies were performed in 1974 on α - and β -ionones in the gas phase using microwave spectroscopy¹. However, the results were not conclusive on the overall conformation of the molecules due to the low resolution of the experiment.

We hereby present a structural study performed in the gas phase of α - and β -ionones and β -damascone using the chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer at the Universidad del País Vasco (UPV-EHU). The use of a supersonic expansion provides an “interaction-free” environment where these molecules can be probed without solvent or crystal packing effects. The rotational spectrum (6-18 GHz) reveals the presence of 5 conformers for α -ionone, 4 for β -ionone and 3 for β -damascone, proving the richness of the conformational landscape of these substances. Hyperfine structures arising from internal rotation of the methyl top(s) have also been characterized. The experimental results are complemented by an exploration of the *ab initio* potential energy surface of these substances.

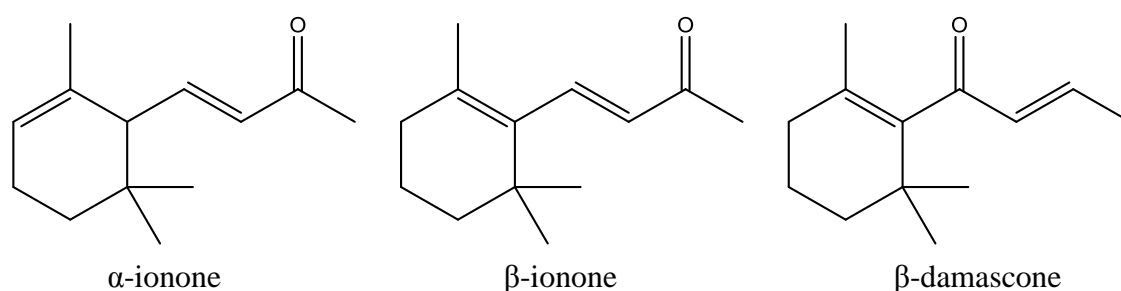


Fig. 1: Chemical structure of α - and β -ionones and β -damascone.

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Internal Rotation in Methyl methacrylate

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Methyl methacrylate (MMA, C₅H₈O₂) is a colorless, at room temperature and atmospheric pressure liquid substance with a characteristic smell. MMA is vastly used in the plastics industry and is known for its tendency to self-polymerization at high temperatures.

The rotational spectra of two conformers of MMA were measured at high resolution and the internal dynamics was accurately analyzed. The spectral data were collected using the coaxially oriented beam resonator arrangement (COBRA) Fourier transform microwave spectrometer.¹ MMA is a molecule with two nonidentical methyl groups. The rotational constants *A*, *B*, *C*, quartic centrifugal distortion coefficients in the Watson S reduction² *D_J*, *D_k*, *D_{JK}*, *d₁*, *d₂* and internal rotation parameters such as the barrier to internal rotation *V₃* for both internal rotors were obtained using the XIAM³ program.

An additional splitting, likely to be caused by spin-rotational coupling of the hydrogen nuclei, is observed but remains unanalyzed so far.

The parameters obtained from the experimental data were rationalized in comparison to calculations with the B3LYP method and aug-cc-pVTZ basis set as implemented in the Gaussian 09 program package.⁴

References

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Sub-Millimeter Wave Rotational Spectroscopy of HOCO^+ and DOCO^+

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Carbon dioxide is an important proxy for oxygen chemistry in the interstellar medium (ISM). However, it lacks a permanent dipole moment and thus the best tracer for this compound is HOCO^+ . Together with its deuterated variant, DOCO^+ , it has been recently detected in a number of protostellar environments.

Previous spectroscopic studies of these species were carried out in the late 80s by Bogey *et al.*^{1,2} who measured their rotational spectra up to 420 GHz.

We have extended the measurements of HOCO^+ and DOCO^+ up to 1 THz, obtaining improved rotational and centrifugal distortion constants. The target ion has been produced via magnetically enhanced glow discharge³ of a mixture of CO_2 , H_2 (D_2), and Argon.

Our results provide very accurate rest-frequencies in the ALMA spectral windows for the purpose of extended astronomical searches.

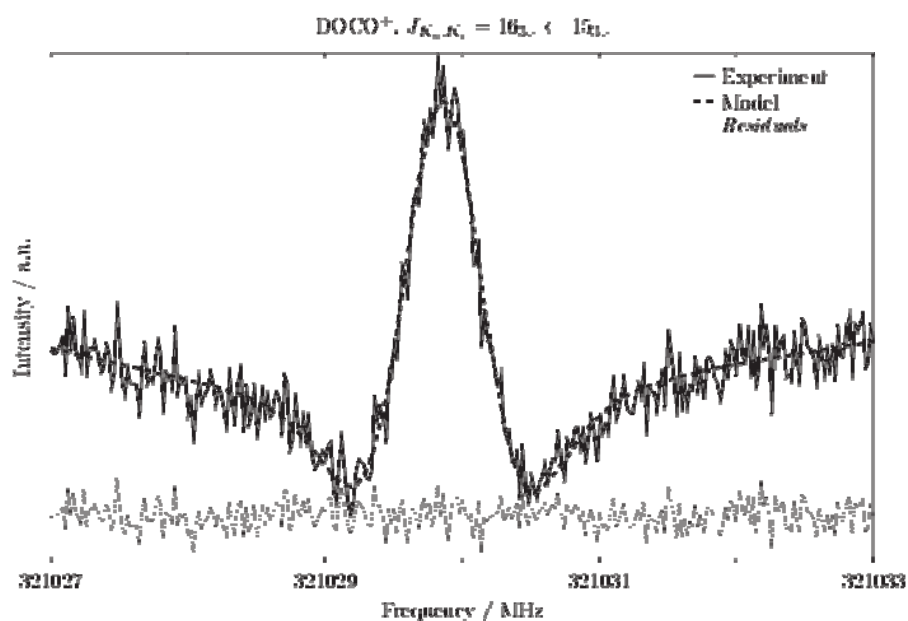


Fig. 1: Recording of the DOCO^+ $16_{3,13} - 15_{3,12}$ and $16_{3,14} - 15_{3,13}$ overlapped transitions at 160 K. The solid trace is the experimental measurement; the dashed one is obtained with the proFFit code employing a Voigt profile with $\nu_0=321029.866(13)$ MHz and $\Gamma_L=0.380(12)$ MHz. The gray solid line represents the fit residuals.

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