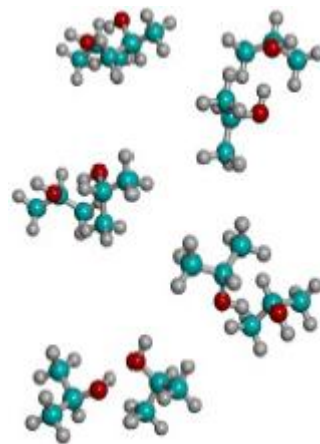


## ROTATIONAL SPECTROSCOPY OF HYDROGEN-BONDED MOLECULAR CLUSTERS

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The information obtained by pulsed jet rotational spectroscopy on some kind of hydrogen bonded molecular complexes will be presented and discussed. Among them, we will present the features of the internal dynamics of adducts of water with organic molecule, such as the combined motion of the alcoholic group and of the water molecule in *tert*-butanol-water, and the Ubbelohde effect observed in some dimers involving heavy alcohols molecules and ethers.

In addition, we will show how the transient chirality of gauche isopropanol (two mirror images are connected through a low energy barrier of the OH torsion potential energy surface becomes a permanent chirality upon hydrogen bond assisted dimerisation. We assigned the rotational spectra of five conformers of the dimer of isopropanol, all of them involving at least one gauche monomer (see the Figure to the right). The inertial effects quench the tunneling and, in the time scale of MW spectroscopy, all these systems appear as made of a pair of "classical" enantiomers. From the relative intensities of the rotational transitions of the various conformers it has been possible to estimate their relative abundances.



Some interesting features related to the molecular recognition, dynamic of formation of the dimers in the supersonic expansion and sizing of the Ubbelohde effect will be discussed.

## SPECTROSCOPY OF CHIRAL SOLUTE-WATER INTERACTIONS: FROM THE GAS PHASE TO SOLUTION

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Hydrogen bonding interactions between chiral molecules and water molecules play an essential role in life sciences since nearly all important biomolecules are chiral and most biological events take place in an aqueous environment. The structural aspects of water surrounding a chiral molecule and the fundamental roles of water in many important biological processes remain subjects of intense debate. In our laboratory, we apply the two-pronged approach to obtain the structural information of water surrounding a chiral molecule using both high resolution spectroscopy and vibrational circular dichroism (VCD) spectroscopy. We observed that some vibrational bands of an achiral molecule, such as water, can show significant VCD strength through hydrogen bonding to a chiral molecule. These chirality transfer VCD features can provide detailed insight into the specific hydrogen bonding configurations taken on by the surrounding water molecules. This, together with the step wise solvation studies using high resolution spectroscopy and the complementary ab initio calculations, will allow one to map out the solvation process in unprecedented details.

**Presentation mode:** lecture

**Time required:** 15min min

**Comment:** *Session on chirality and chirality recognition*

## PROGRESS TOWARD A FIRST OBSERVATION OF PARITY VIOLATION IN CHIRAL MOLECULES BY HIGH-RESOLUTION LASER SPECTROSCOPY

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Parity violation (PV) effects have so far never been observed in molecules. Originating from the weak interaction, PV should lead to frequency differences in the rovibrational spectrum of the enantiomers of a chiral molecule. However the weakness of the effect represents a very difficult experimental challenge. To take up this challenge, a consortium of physicists and chemists has been established. This talk will review the latest results towards a first experimental PV observation<sup>1</sup>. We have proposed to take advantage of the very high resolution spectroscopy technique of Doppler-free two-photon Ramsey fringes in a supersonic molecular beam. With an alternate beam of left- and right-handed molecules and the ability to perform absolute frequency measurement, we could reach a fractional sensitivity better than  $10^{-15}$ . The key point is to target a chiral molecule which is stable and easy to synthesize, exhibits a high enough PV effect and could lead to an intense and cold supersonic molecular beam. Chemists are now concentrating on methyltrioxorhenium (MTO), which seems to fulfill all the requirements of the ideal achiral parent molecule. Experimentalist chemists are working on synthesizing chiral derivatives of MTO, while calculations from quantum chemists are currently under progress. High resolution spectroscopy of the MTO antisymmetric Re-O stretching band ( $\nu_8$ ) has been performed on a Fourier Transform InfraRed spectrometer with a resolution of  $0.005\text{ cm}^{-1}$ . Consequently, the experimental conditions for an intense molecular beam were obtained. Finally, we recorded the first spectra of MTO around  $975\text{ cm}^{-1}$  on the set up dedicated to the observation of PV, with a moderately high resolution of  $4 \times 10^{-5}\text{ cm}^{-1}$ .

1. B. Darquié et al, to be published in Chirality, 2010.

**Presentation mode:** lecture

**Time required:** 15 min

**Comment:**

## HIGH RESOLUTION LASER SPECTROSCOPY OF SrOCH<sub>3</sub>

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The  $\tilde{A}^2E - \tilde{X}^2A_1$  transition of SrOCH<sub>3</sub> was first studied at high resolution by O'Brien et al.<sup>7</sup> using a Broida oven; however lines with  $J \leq 20$  were not observed; and congestion prevented them from resolving the  $\Omega = 1/2$  component. We have studied the  $\tilde{B}^2A_1 - \tilde{X}^2A_1$  and the  $\tilde{A}^2E - \tilde{X}^2A_1$  transitions of SrOCH<sub>3</sub> in a laser ablation molecular jet source, where jet cooling and low Doppler widths greatly simplified the spectra. An optical-optical double resonance technique facilitated definite assignments in a number of the transition observed. Our analysis of the  $\tilde{A}^2E - \tilde{X}^2A_1$  transition was straightforward, but a perturbation was observed in the  $\tilde{B}^2A_1 K' = 1 F_2$  levels. A satisfactory fit was achieved for the  $\tilde{B}^2A_1 - \tilde{X}^2A_1$  transition when a separate  $B$  parameter was used to fit the perturbed levels.

1. L. C. O'Brien, C. R. Brazier and P. F. Bernath, *J. Mol. Spectrosc.* 130 (1988) 33-45.

**Presentation mode:** lecture

**Time required:** 15 min

**Comment:** *Session on electronic spectra*