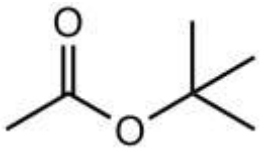
Work plan of Dr. Mouhib, Halima:
The work plan is to foster collaboration between two groups, which are very active research groups in MOLIM participating. At the RWTH University in Aachen (Germany), they develop a state-to-the-art experimental microwave experiments using Fourier transform spectrometers combined with molecular jet with outstanding accuracy [1]. At LISA in Créteil (France), the spectroscopy group is specialized in theoretical modeling of the rotational and vibration-rotational spectra of various medium-sized molecular systems especially those containing large amplitude motions (internal rotation of methyl groups hindered by a three-fold potential barrier and out-of-plane inversion [2-3]). **Recently, the two groups have established a new collaboration which showed the complementarities of the two groups for better understanding the nuclear motions within these medium sized molecular species** (2 common publications between the Applicant H. Mouhib and I. Kleiner, see publication list of the applicant). This collaboration will be reinforced by the visit of Dr H. Mouhib.

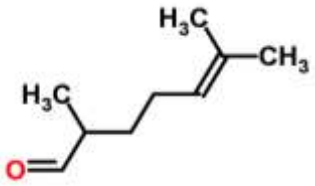
During the two months of her visit, the **Applicant H. Mouhib will learn the theoretical modeling of large amplitude motions and use of the BELGI code** [2], which is developed in LISA (France). This code uses an effective Hamiltonian to describe the effects present in molecules containing one or two internal rotors, as well as rotation and centrifugal distortion. Due to the presence of a finite internal rotation potential barrier, each rotational transition is split by a quantum chemical tunneling effect which complicates the microwave spectra. Therefore, traditional Hamiltonians cannot be used. Such spectra are non-conventional and are complicated to analysis without the help of theoretical inputs. The BELGI code allows reproducing the rotational data at their experimental accuracy (a few kHz). **Dr H. Mouhib will also take advantage of her visit to increase her knowledge on quantum chemical calculations** with the colleagues at U. Paris-Est. Indeed if the *ab initio* techniques are now commonly used to produce initial values for the rotational constants which often can serve as guesses for the first assignments of the rotational spectra [4]. State-of-the-art techniques to actually calculate precisely and carefully various molecular parameters (potential barriers and structural parameters) are commonly left out. This is a highly specialized area where the groups in the East of Paris at U. Paris-Est are World leaders [5]. The idea is to validate the high level quantum chemical with high resolution experimental data.

The visit of Dr H. Mouhib will also aims at begin a new research theme. Indeed Dr H. Mouhib has acquired in Germany (and at the VU in Amsterdam) competences in molecular dynamics simulation, especially in order to understand the interactions between an odorant molecule and the ligand in an olfactory binding protein or in an olfactory receptor [6]. Very recently we have made some contacts with a team of the Institute of Ecology and Environmental Sciences in Paris (IEES) which are specialized in the olfaction phenomenon and chemical transmission signals (including pheromones) in insects.

The molecular targets we are planning to study are: **First Dr. H. Mouhib will treat the *tert*-butyl acetate** (Figure 1) and then she will study another organic molecule which is more complex, the **Melonal** (2,6-Dimethyl-5-heptenal, Figure 1). The *tert*-butyl acetate compound is a small volatile compound with a camphor or blueberry like smell, often used for industrial purposes, as it is an important dissolver for organic fats. The major application of TBA is as a component in cleaning and degreasing reagents. It is also often used as a solvent for synthesis in organic chemistry. **Melonal** is involved in both flavors and fragrances due to its fresh, green, melon and cucumber note.



tert-Butyl acetate molecule



Melonal molecule

Figure 1

There is significant interest in characterizing the various conformers of organic molecules, e.g., in terms of relative energies, structures, and dipole moments. *tert*-Butyl acetate is a small enough molecule so we can validate our methodologies, both experimentally and theoretically, but large enough so we can have interesting structure and dynamics results. This will serve as a "benchmark" molecular system.

Usually, we are not able to observe *cis*-conformations of esters in a supersonic jet, as the beam temperature is close to 1 K and *cis*-esters are about 40 kJ/mol higher in energy than the corresponding *trans*-conformations [7]. However, the existence of the *cis*-conformer of some carboxylic acids and esters was studied by Oki *et al.* at room temperature in the infrared range [8]. They suggested an interaction between the methyl and the *tert*-butyl group that might result in an energetic stabilization of the *cis*-conformer. We are thus curious to verify this assumption under molecular beam conditions.

First, Dr H. Mouhib will learn the theoretical modeling of internal rotation and the use of the software developed in the LISA group. She will use it to the ***tert*-butyl acetate** to study the conformational landscape of this molecule. This information is of great importance to assign the microwave data which she already recorded at the RWTH University of Aachen. She will also get familiar with *ab initio* calculations on this system. Then, Dr H. Mouhib will also compare the results obtained for the molecular parameters obtained using the effective Hamiltonian and the BELGI code with the parameters calculated using *ab initio* techniques. The potential energy surface to explore the conformational landscape of *tert*-butyl acetate will be calculated at the MP2/6-311++G(d,p) level by rotating the *tert*-butyl group and the acetyl methyl group against each other. Afterwards, Dr. H. Mouhib will investigate the **Melonal** molecule. This molecule was never studied before using high resolution gas phase spectroscopy. Thus we plan perform first quick MP2 *ab initio* calculations or B3LYP calculations to identify the molecule conformers. For the lowest ones, we will derive a first guess for the values of the rotational constants and potential barriers hindering the internal rotation of the methyl groups. Then preliminary assignments will be made on the high resolution microwave data of this molecule. We will then use the BELGI code to refine the data. The molecular parameters provided by the BELGI code will then be compared to the *ab initio* parameters.

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