

## I. MOTIVATION

The concept of nuclear spin isomers is known since more than 80 years, when the two modifications of hydrogen, *ortho* and *para*, were separated for the first time[1]. In the case of hydrogen, the two nuclear spin isomers are very stable and its anomalous large rotational level spacing in comparison with its small boiling point makes the separation of its isomers possible using simple cooling techniques. However, in the case of heavier molecules, the rotational level splitting is much smaller and their boiling point much larger, and consequently, other techniques have to be employed in order to shift the isomer ratio away from its equilibrium value[2]. Since this is a very challenging process, the separation of molecular nuclear spin isomers different from hydrogen is still in its infancy.

Given the importance of spin symmetry and its implications in many fields of science, it is important to suggest theoretical concepts able to identify properties that are different for *ortho* and *para* isomers, making its discrimination and eventual separation experimentally feasible by methods complementary to those suggested to date. In the last years, some of us have proposed that it should be possible to employ the coherence of light to discriminate nuclear spin isomers by exploiting interference effects that occur when the nuclear spin isomers are electronically excited[3–6].

In contrast to systems such as hydrogen or water, where the exchange of the two hydrogens is related to an overall rotation of the molecule, in the theoretical proposals mentioned above, the molecules possess an internal torsional degree of freedom that exchanges the two hydrogen atoms, and thus relates the different classes of nuclear spin isomers[7].

## II. WORK PLAN

In our previous work we focused on the photoinduced dynamics of the nuclear spin isomers of 1,1-difluoroethylene (DFE) using wavepacket propagations in a one-dimensional model system (torsional motion). Now we plan to extend our model system to more dimensions to check if the interference effects still remain, allowing us to distinguish between the excited state dynamics of both nuclear spin isomers. For this purpose, the method of choice is the multi-configurational time-dependent Hartree, as it can treat systems up to about 1000 degrees of freedom including quantum effects[8]. Previously, we have calculated (cc-pvdz/SA(3)-MS-CASPT2(2,2)) two-dimensional potential energy surfaces for the three lowest electronic states of DFE where the two normal modes chosen were CH<sub>2</sub> pyramidalization - torsion, CF<sub>2</sub> pyramidalization - torsion and C-C stretching - torsion. These adiabatic potentials will be transformed to a suitable basis to be used by MCTDH[9] during the first week of the stay. The rest of the time will be employed learning how to set up and run the quantum dynamics using the MCTDH method.

- 
- [1] K. Bonhoeffer, P. Harteck, Weitere Versuche mit Parawasserstoff, *Naturwissenschaften* 17 (1929) 321.
  - [2] P. L. Chapovsky, Conversion of nuclear spin modifications of CH<sub>3</sub>F molecules in the gaseous phase, *J. Exp. Theor. Phys.* 70 (1990) 895.
  - [3] T. Grohmann, M. Leibscher, Nuclear spin selective alignment of ethylene and analogues, *J. Chem. Phys.* 134 (2011) 204316.
  - [4] J. Floß, T. Grohmann, M. Leibscher, T. Seideman, Nuclear spin selective laser control of rotational and torsional dynamics, *J. Chem. Phys.* 136 (2012) 084309.
  - [5] R. Obaid, D. Kinzel, M. Oppel, L. González, Discrimination of nuclear spin isomers exploiting the excited state dynamics of a quinodimethane derivative, *J. Chem. Phys.* 141 (2014) 164323.
  - [6] R. Obaid, D. Kinzel, M. Oppel, L. González, Separating nuclear spin isomers using a pump-dump laser scheme 134 (2015) 46.

- [7] S. Belz, O. Deeb, L. González, T. Grohman, D. Kinzel, M. Leibscher, J. Manz, R. Obaid, M. Oppel, G. D. Xavier, S. Zilberg, Nuclear spin selective torsional states: Implications of molecular symmetry, *Z. Phys. Chem.* 227 (2013) 1021.
- [8] M.H. Beck, A. Jäckle, G.A. Worth, H.-D. Meyer, The multiconfiguration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets, *Phys. Rep.* 324 1 (2000).
- [9] A. Jäckle, H.-D. Meyer, Product representation of potential energy surfaces, *J. Chem. Phys.* 104, 7974 (1996)