

## The Research Group General Chemistry

has the honor to invite you to the public defense of the Joint PhD thesis of

# Yannick GEBOES

to obtain the degree of Doctor of Sciences

## Joint PhD with University of Antwerp

Title of the PhD thesis:

Halogen Bonds, Hydrogen Bonds and Beyond: A Cryospectroscopic Study into Competitive Noncovalent Interactions

#### Promotors:

Prof. dr. Frank De Proft Prof. dr. Wouter A. Herrebout (UAntwerp)

The defence will take place on Friday September 22 2017 at 14.00h

at the Universiteit Antwerpen, Campus Groenenborger - room V.008

#### Members of the jury:

Prof. Dr. Sabine Van Doorslaer (chair, UAntwerp) Prof. Dr. Steven Ballet (secretary) Prof. Dr. Dominique Maes Prof. Dr. Christian Johannessen (UAntwerp) Prof. Dr. Pierangelo Metrangolo (Politechnico di Milano, I.) Dr. Dieter Hauchecorne (Atlas Copco Airpower)

#### Curriculum vitae

10/2012-09/2017 Joint PhD in Sciences at UAntwerp (MolSpec) and VUB (ALGC) as aspirant FWO.

Research stays at University of Bologna (I) and University of Newcastle (UK) 9 peer reviewed papers, 6 of which as lead author

10/2010-07/2012 MSc in chemistry at University of Antwerp. Incl. Erasmus stay at KFU Graz (AT)

10/2007-09/2010 Bachelor in chemistry, University of Antwerp.

### Abstract of the PhD research

A halogen bond (XB) is a noncovalent interaction between a covalently bonded halogen atom and an electron rich site in the same or another molecule. The existence of halogen bonds is explained theoretically by the anisotropic charge distribution around the halogen atom which gives rise to a region with a more positive electrostatic potential opposite to the covalent bond, also known as the  $\sigma$ -hole. Since these noncovalent interactions are guite similar in strength and nature to the ubiquitous hydrogen bonds, they can coexist and compete with them. To strengthen hydrogen and halogen bonds, the bond donor molecules often contain electron-withdrawing groups, such as fluorine atoms. When these locally electron deficient molecules are unsaturated, they can exhibit a region of positive electrostatic potential perpendicular to the molecular plane, a so-called  $\pi$ -hole. In recent years, attractive noncovalent interactions between these  $\pi$ -holes and electron rich sites in Lewis bases, called lone pair $\cdots \pi$  (lp $\cdots \pi$ ) interactions, have also been observed in theoretical and experimental studies.

In this PhD thesis, we have investigated the competition between halogen bonding, hydrogen bonding and  $lp\cdots\pi$  interactions experimentally by studying a series of donor molecules, which are (theoretically) able to form more than one type of noncovalent interaction with a Lewis base. To this end, Fourier Transform infrared (FTIR) and Raman measurements on liquid noble gas solutions containing the combined bond donor molecule and a Lewis base are performed. The complex(-es) present in solution are identified by comparing the experimental complexation shifts with those obtained from *ab initio* calculations. As these measurements are performed at thermodynamic equilibrium, the complexation stoichiometry and complexation enthalpy can also be obtained experimentally. To enable comparison between experimental and computational results, CCSD(T)/CBS energy extrapolations, statistical thermodynamics calculations and Monte Carlo-Free Energy Perturbation simulations are performed.

The observed bond strengths are then further rationalized using conceptual quantum chemical calculations, including the Noncovalent Index (NCI), Natural Orbital for Chemical Valence (NOCV) and an energy decomposition scheme (EDA). Finally, some of the complexes have also been studied using Fourier Transform microwave (FTMW) spectroscopy to obtain direct experimental geometrical data of the formed complexes.