IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	Understanding weak intermolecular interactions: a combined experimental and theoretical study	
Project Number	**IMURA0340**	
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Research Academy Themes:

Highlight which of the Academy's Theme(s) this project will address? 1

(*Feel free to nominate more than one. For more information, see www.iitbmonash.org)*

1. **Advanced computational engineering, simulation and manufacture**
2. Infrastructure Engineering
3. Clean Energy
4. Water
5. Nanotechnology
6. Biotechnology and Stem Cell Research

The research problem

Define the problem

Weak intermolecular interactions such as hydrogen bonding and π-π stacking are known to affect the structure and reactivity of simple organic compounds to complex systems such as polymers. These interactions also play a vital role in the determining the crystal structure and polymorphism in the crystals. The extent of this effect is specific to a particular class of compounds. In order to tailor chemical reactivity, the ability to predict fundamental components of interaction energies such as electrostatics, dispersion, induction, exchange repulsion and charge transfer is important. These components usually hold a key to indentifying energetic factors responsible for the crystal packing and also affect their chemical reactivity. In this context the chemical systems with soft potentials are a challenging proposition both in terms of experiment and theory. Phenylacetylene and its substituted analogues are interesting due to the lack of strongly interacting functional groups, thus resulting in shallow potential energy surfaces. Using these sets of molecules it is possible to probe a wide variety of molecular systems exhibiting weak intermolecular interactions, otherwise not possible in molecular systems with stronger interactions.

Project aims

Define the aims of the project

The aims of this project are to understand which fundamental components that play an important role in the structure and chemical reactivity of phenylacetylene and some of its substituted analogues. This will be achieved by combing experimental measurements with *ab-initio* and molecular dynamics methods. The experimental methods will comprise of infrared-optical double resonance spectroscopy and velocity map imaging of photo-fragments. These two complimentary experimental techniques are based on the time-of-flight mass spectrometer. The first technique allows us to probe the intermolecular interactions based on the perturbations relative to the un-interacting molecule, while the second technique determines the binding energy based on the fragmentation pathways. First principles methods will include symmetry adapted perturbation theory (SAPT) and effective fragment potential (EFP) to accurately predict the fundamental components of interaction energies. Methods of perturbation theory (e.g. MP2) and coupled cluster (e.g. CCSD(T)) will be used to accurately calculate 1) the binding energies as a function of the size of molecular system and 2) molecular and spectroscopic properties such as dipole moments, polarizabilities, IR vibrations and electronic excitations. The solvent effects will also be investigated through implicit solvent (polarisable continuum models) and explicit solvent (inclusion of actual solvent molecules as clusters) approaches. The computational results will be correlated with experimental data to establish a computer-aided design of the structural arrangement and chemical reactivity for this class of compounds.

Expected outcomes

Highlight the expected outcomes of the project

The outcomes of this project will be:

1. A thorough understanding of which fundamental components affect the structural arrangement, polymorphism and chemical reactivity of phenylacetylene and its substituted analogues.
2. Size dependent structural transitions
3. Effects of solvent on chemical reactivity in these systems

How will the project address the Goals of the above Themes?

Describe how the project will address the goals of one or more of the 6 Themes listed above.

High-level *ab initio*-based methods will be applied to predict energetics, structure and chemical reactivity of molecular aggregates of phenylacetylene and its substituted analogues, thus further advancing our understanding of how the structure and chemical reactivity of similar systems with weak intermolecular interactions can be tailored. The experiments will be carried out at IIT Bombay using two complimentary techniques (i) infrared-optical double resonance spectroscopy and (ii) velocity map imaging. The experimental results on these systems will be underpinned by computational results. This project will address the Advanced computational engineering, simulation and manufacture theme. *Ab initio*-based calculations will be conducted using the computational facilities available to Dr Pas at Monash University and the National Facilities in Canberra, Australia.

Capabilities and Degrees Required

List the ideal set of capabilities that a student should have for this project. Feel free to be as specific or as general as you like. These capabilities will be input into the online application form and students who opt for this project will be required to show that they can demonstrate these capabilities.

A student should have basic understanding of quantum chemistry and physical chemistry and should have aptitude towards advanced experimental techniques.