CH3F3-30 Advanced Chemistry (Organic, Inorganic and Physical)

22/23

Department
: Chemistry

Level
: Undergraduate Level 3

Module leader
: Nikola Chmel

Credit value
: 30

Module duration
: 5 weeks

Assessment
: 100% exam

Study location
: Distance or Online Delivery

Description

Introductory description

N/A

[Module web page]

Module aims

This module contains the taught lecture elements of CH3F1, CH3E9 and CH3F0 combined. It does not contain any laboratory components of these modules and is designed to be taken by students undertaking placements.

PHYSICAL: This module provides an introduction to two advanced topics in physical chemistry; molecular modelling and interfacial chemistry.
First, this module will develop students' knowledge of the properties of surfaces and interfaces, and the methods available for characterising them. Here, students will be introduced to the physical chemistry of a range of surface and interfacial processes, including both solid and liquid interfaces, as well as experimental methods such as atomic force microscopy and scanning tunnelling microscopy. A significant aspect of this module is to demonstrate the importance of surfaces processes in chemistry and the borders of chemical engineering, biomedical science,

materials science and physics.
Second, students will be introduced to basic concepts in molecular modelling, focussing on molecular dynamics simulations using empirical force-fields. Starting from the Born-Oppenheimer approximation, this part of the module will cover the basics of molecular dynamics simulations, including periodic boundaries, integration algorithms, and implementation of different thermodynamic ensembles. As well as providing a firm grounding in the theoretical basis of molecular dynamics simulations, this module will also emphasize what properties can be calculated, and the connection between molecular dynamics and statistical mechanics.

ORGANIC: The objective of this module is to provide the students with the information they need to be able to determine the products from complex pericyclic reactions, intramolecular cyclisation processes, rearrangement reactions of reactive intermediates, and reactions creating new stereogenic centres by either substrate, reagent, or catalyst control.
By the end of the module students will be able to predict the products arising from reactions. Be familiar with the empirical rules and models related to concerted, cyclisation, rearrangement, and stereoselective reactions. Student should be able to use their knowledge to devise syntheses of complex molecules.
INORGANIC: The module aims to give an advanced background to the issues which impact on industrial catalytic reactions. Organometallic chemistry uses principles from organic and inorganic (particularly coordination) chemistry, and also physical chemistry (particularly kinetics). Inorganic materials chemistry uses principles from inorganic chemistry (structures of solids) and physical chemistry (electronic properties of solids). The module draws together aspects of this work developed in Year 2 and extends it to the types of reactions and catalysis used widely in chemical industries (petrochemicals, polymers, fine chemicals and pharmaceuticals).

Outline syllabus

This is an indicative module outline only to give an indication of the sort of topics that may be covered. Actual sessions held may differ.

PHYSICAL SECTION
Surfaces and interfacial chemistry:

- Introduction. Scope of surface and interfacial chemistry. Examples.
- Solid surfaces. Structures and indexing of single crystal surfaces. Miller indices. Kossel model of surfaces: steps, terraces, kink sites, Schottky and Frenkel defects. Screw dislocations. Growth modes of solid surfaces (Frank-van der Merwe; Stranski-Krastanov; Volmer-Weber). Comparison of site reactivities.
- Surface spectroscopy. Photoelectron spectroscopy (XPS). Surface infra-red spectroscopy (IRRAS).
- Scanning tunnelling microscopy (STM). Principles of tunnelling. Dependence of tunnelling current on distance and barrier height. Vertical and lateral resolution: constant current vs. constant height modes. Dependence on voltage, scanning tunnelling spectroscopy (STS).
- Applications of STM. Examples of atomic-level STM images. STM of metals, semiconductors and molecular adsorbates. Time-resolved STM. Wavefunction mapping. STM-induced manipulation: writing with atoms.
- Atomic force microscopy (AFM). Principles and instrumentation. Features in tip-approach curves. Contact, non-contact and tapping (intermittent contact) modes. Q-plus AFM.

Application of NC-AFM as new analytical technique.
- New generation STM techniques. Scanning ion-conductance microscopy (SICM). Scanning electrochemical microscopy (SECM). Combined SECM-AFM. Scanning near-field optical microscopy (SNOM).
- Fractal surfaces. Fractal geometry of surfaces. Determination of fractal dimensions of surface. Implications for surface area measurements. Contact angle measurements.
- Liquid surfaces. Surface tension. Effects of various solutes on surface tension. Surfactants. Soap bubbles. Young-Laplace equation. Surface pressure. Gibbs adsorption isotherm.
- Monolayer films and bilyaer membranes. Langmuir film balance and applications. Isotherms for gaseous, condensed and expanded films. Characterisation of monolayers by fluorescence microscopy. Lateral diffusion in monolayers. Diffusion across cell membranes.
- Chemially-functionalised surfaces. Langmuir-Blodgett films and applications. Self-assembled monolayers and films.
- Surface reactions and kinetics (1). Steps in a surface reaction. Crystal growth and dissolution.
- Surface reaction and kinetic (2). Electrode reactions and electrocatalysis.

Molecular modelling:

- General concepts in molecular modelling. Coordinate systems, hardware and software.
- Empirical force-fields and interatomic potentials. Born-Oppenheimer approximation. Discussion of typical empirical force-fields, including functional forms and parameterization strategies. Periodic boundary conditions.
- Molecular dynamics. Introduction to molecular dynamics method, discussion of molecular dynamics as a route to calculating dynamic and thermodynamic properties of molecules and materials. Connection with statistical mechanics.
- Modelling applied to problems in surface and interface chemistry
- Examples of molecular modelling studies. What can and cannot be calculated using molecular dynamics simulations with empirical force-fields?

ORGANIC SECTION:

- Pericyclic reactions and the Woodward-Hoffmann rules, including photochemistry.
- Cycloadditions (including 1,3-dipolar cycloadditions), electrocyclisations and sigmatropic rearrangements. Frontier orbital theory and Woodward-Hoffmann rules will be used to explain the stereochemical observations made in pericyclic reactions.
- Polar rearrangements:Carbocation induced alkyl and hydride shifts, Wagner-Meerwein, Pinacol, Tiffeneau-Demyanov, hydride shifts, cyclisations. Nucleophilic rearrangements to carbon involving carbanions, Favorskii, Ramburg Buckland.
- Radicals: Cyclisations, ring-openings, 1,5-H translocations, radical migrations.
- Carbenes:Structure, reactivity and generation. Insertion reactions, cyclopropanation, metathesis
- Rearrangement reactions to electron deficient nitrogen and oxygen.:Nitrenes. Beckmann, Curtius, Lossen, Schmidt rearrangments. Baeyer-Villiger
- Reactions of chiral carbonyl containing compounds:Addition to -stereogenic carbonyl compounds: non-polar-Felkin model, polar Felkin model, chelation model. Addition to -stereogenic carbonyl compounds

- Reactions of chiral alkene containing compounds:Houk-type model for control of reaction stereochemistry, including steric, and chelation factors, including the reaction of chiral allyl silanes.
- Synthesis of enantiomerically enriched compounds: Chiral Pool: amino-acids, hydroxy-acids, terpenes. Evans Auxiliary:, alkylation, aldols, conjugate additions, Diels Alder reaction. Chiral reagents, BINAL-H redutions, terpene-borane reductions, hydroboration, allylation.
- Asymmetric catalysis (reagent control):Sharpless Asymmetric Epoxidation (AE), dihydroxylation (AD) and aminohydroxylation (AA).
- Additions to carbonyls, reductions (Noyori, Corey). Menthol synthesis. C-C R2Zn:Enolate chemistry, alkylations (e.g. PTC) aldol (Mukayama etc, Evans, List)
- Cycloadditions (Evans Macmillan): Modern chiral Bronstead acid catalysis
- Pd catalysed allylation includes simple catalyst based kinetic resolution and catalyst based DKR e.g. Noyori Hydrogenation ofketoesters
- Enzymes:Esterification and hydrolysis with lipases ad esterases includes Pd catalyse DKR
- Asymmetric oxidations e.g. arene dihydroxylation and Baeyer-Villiger. cyanide additions and aldol reactions

INORGANIC SECTION

- What is catalysis? Homogeneous vs Heterogeneous. Key concepts
- Recap: Electron Counting and Coordination Numbers in Organometallics; Covalent Bond Classification
- Reactivity of organometallics: Oxidative addition and Reductive Elimination
- Reactivity of organometallics: Insertion and Elimination
- Homogeneous Catalysis : Hydrogenation, activation of dihydrogen using transition metals. Mechanisms of alkene hydrogenation. Mechanisms of ketone hydrogenation (including transfer hydrogenation) . Asymmetric hydrogenation. Homogeneous vs. Heterogeneous catalysis (arene hydrogenation)
- Hydroformylation of alkenes (Co, Rh)
- Hydrocyanation (Ni)
- Carbonylation of methanol (Rh, Ir) – good industrial
- Carbonylation of alkynes (Ni)
- Wacker Process (Pd) - important to cover mechanisms of palladium catalysed reactions
- Heck olefination (Pd)
- Olefin metathesis (Co, Mo, pre Grubbs) – important. Ligand design => activity. Thermodynamics
- Ziegler catalysis (Ti, Zr, Ln)
- Hydroamination (Ln, Zr)
- Heterogeneous Catalysis: Zeolites: silicates and alumino-silicates, Structure description, Synthesis: solvothermal crystallisation, the use of templates , design of new materials
- Zeotypes: AlPOs
- Mixed tetrahedral-octahedral frameworks (transition-metal-containing)
- Mesoporous silicas
- Metal-Organic Frameworks: structures and synthesis
- Ion-exchange properties of nanoporous materials
- Separation (molecular sieving) by porous materials
- Shape-selective catalysis: Petroleum cracking, Solid-acid catalysis, Transition-metal

containing microporous catalysts for oxidation, Mesoporous solids to tether molecular catalysts
- MOFs – limitations on their use
- Other industrially relevant solid-state catalysts: three-way catalytic convertors, Haber-Bosch, water-gas shift (WGS) reaction, steam reforming, sulphuric acid production
- SUMMARY: Homo vs Hetero Fischer-Tropsch (Fe, Co, analogy with homogeneous processes)

Learning outcomes

By the end of the module, students should be able to:

- PHYSICAL SECTION: After taking this module, students will have a firm understanding of core topics in both molecular modelling and surface chemistry. With regards to molecular modelling, students who complete this module will have a good understanding of the theory behind molecular dynamics simulations and empirical force-fields, as well as an appreciation of what sorts of research questions can be addressed by molecular simulation. Students will also gain hands-on experience of running molecular dynamics simulations in order to further reinforce these learning outcomes. Students will also gain a strong appreciation of the importance and scope of interfacial chemistry, including wet interfaces and surfaces in ultrahigh vacuum, as well as the experimental methods which are used to study such systems; both foundational material and contemporary topics will be covered. The aim is to develop a broad understanding of the chemistry of surfaces and interfaces, so that students will be able to follow-up any particular topic if they wish to in the future.
- ORGANIC SECTION: The objective of this module is to provide the students with the information they need to be able to determine the products from complex pericyclic reactions, intramolecular cyclisation processes (particularly radical processes), and rearrangement reactions of reactive intermediates and to understand how reactive intermediates can used in organic synthetic transformations. In addition this course extends this knowledge to the more complex and challenging area of stereoselective and asymmetric synthesis, which refers to the specific three dimensional shape and structure of specific target molecules. By the end of this course, students shall understand how to control the absolute and relative configuration of organic molecules during their synthesis.By the end of the module students will be able to predict the products arising from reactions mediated by these reactive intermediates. Identify the type of reactive intermediate mediating a particular organic transformation. Be familiar with the empirical rules and models related to concerted, cyclisation and rearrangement reactions. Understand the key issues of stereochemical control associated with organic synthesis. Use their knowledge to devise syntheses of complex molecules.
- INORGANIC SECTION: Building on their knowledge of inorganic chemistry from Yr 1 and Yr2, students will understand how results from academic research in catalysis, including organometallic chemistry and solid-state materials chemistry, are used in industrial applications.

Indicative reading list

INORGANIC SECTION: Shriver and Atkins' Inorganic Chemistry, 5th Edition, Chapter 24 & 25 (in

part for heterogeneous) and 26.
Organometallic Chemistry by Spessard and Miessler (Prentice Hall) – several copies in library.
Applied Organometallic Chemistry and Catalysis (Oxford Chemistry Primers) Robin Whyman
Homogeneous Catalysis: Understanding the Art. Piet van Leuven. Superb, expensive, used in development of module materials. Good for kinetics.
Metal-Catalysis in Industrial Organic Processes (RSC) Gian Paolo Chiusoli (Editor), Peter M. Maitlis (Editor) – expensive, used in development of module materials.
Inorganic Chemistry 4ed by Shriver and Atkins (OUP) – standard text book for earlier years.
The Organometallic Chemistry of the Transition Metals (Wiley) Robert H. Crabtree – expensive, used in the development of the module materials
The f Elements (Oxford Chemistry Primers), Nikolas Kaltsoyannis and Peter Scott – inexpensive but not necessary to purchase. Useful for basic f element chemistry principles.
Principles and Applications of Organotransition Metal Chemistry, James P. Collman, Louis S. Hegedus, Jack R. Norton, and Richard C. Finke (University Science Books,U.S.; 2nd Revised edition) – expensive, was used in development of course materials.
Organotransition Metal Chemistry: From Bonding to Catalysis, John F. Hartwig (Univeristy Science Books) – expensive, was used in the development of course materials.
Smart and Moore Solid-State Chemistry (in part for heterogeneous)

ORGANIC SECTION: Much of the material for this module is taken from compulsory organic chemistry text by Clayden et al.; “Organic Chemistry” by Clayden, Greeves, Warren and Wothers, Oxford 2001.
The following books will also be compulsory. “Reactive Intermediates” C. J. Moody and G. H. Whitham, Oxford University Press, 2001. “Polar Rearrangements” L. M. Harwood, Oxford University Press, 1992. “Organic Synthesis – Strategy and Control” Wyatt and Warren, Wiley, 2007
The following texts may be consulted for further information on the contents of the module: Review on Woodward-Hoffmann rules: R. B. Woodward and R. Hoffmann in Angew. Chem., Int Ed. Engl., 1969, 8, 781.“Organic Reactions and Orbital Symmetry”, T. L Gilchrist and R. Storr, Cambridge Academic Press, 1979.

PHYSICAL SECTION: The chapter entitled "Processes at solid surfaces" in Physical Chemistry, Peter Atkins and Julio de Paula, OUP (Ch 28, in 7th edition) provides reasonably good coverage of some aspects of the course.
More specialised texts include:
"Modern Techniques of Surface Science", D.P. Woodruff (Cambridge, 2016)
"Solid Surfaces, Interfaces and Thin Films", H. Lüth (Springer, 2010)
"Surface Science Techniques", G. Bracco and H. Bodil eds. (Springer, 2010)
“Physical Chemistry of Surfaces", A.W. Adamson (Wiley, 5th or 6th edition).
“Surface Science: Foundations of Catalysis and Nanoscience” Kurt W. Kolasinski, 2002, Wiley, 2nd edition
“Colloid and Surface Chemistry", D. J. Shaw (Butterworth, 3rd or 4th edition).
There are numerous papers that will help with parts of the course. These are given to students in lectures to emphasise particular aspects and updated each year.
Essentials of computational chemistry, C. J. Cramer (Wiley 2005)
Understanding molecular simulation, D. Frenkel and B. Smit (Academic press 2002)
Molecular quantum mechanics, P. W. Atkins and R. S. Freedman (Oxford 2001)

Subject specific skills

Numeracy
Problem solving
Critical thinking

Transferable skills

Numeracy
Problem solving
Critical thinking

Study

Study time

Type	Required
Lectures	60 sessions of 1 hour (20%)
Practical classes	17 sessions of 1 hour (6%)
Other activity	3 hours (1%)
Private study	220 hours (73%)
Total	300 hours

Private study description

Self Study and Directed Reading: 220 hours

Other activity description

Computer workshops

Costs

No further costs have been identified for this module.

Assessment

You do not need to pass all assessment components to pass the module.

Assessment group B3

	Weighting	Study time
In-person Examination 1 - Organic	34%	
In-person Examination 2 - Inorganic	33%	
In-person Examination 3 - Physical	33%	

Feedback on assessment

Cohort level examination feedback provided via Moodle.

Informal feedback automatically generated by online quizzes associated with "Molecular modelling". Informal feedback also to be provided online for "Molecular modelling" computer workshop.

Past exam papers for CH3F3

Availability

Pre-requisites

To take this module, you must have passed:

- All of
  - CH267-15 Transition Metal Chemistry: Structure, Reactivity & Organometallic Chemistry
  - CH270-15 Selective Organic Synthesis
  - CH271-15 Mechanistic and Biological Chemistry
  - CH272-15 Materials and Polymers
  - CH273-15 Properties of Solutions and Foundations of Electrochemistry and Statistical Mechanics
  - CH274-15 Electrons in Molecules and Solids

Post-requisite modules

If you pass this module, you can take:

- CH412-15 Advanced Biophysical Chemistry
- CH408-15 Advanced Medicinal and Biological Chemistry
- CH406-15 Electrochemistry and Nanotechnology
- CH413-15 Advanced Computational Chemistry
- CH402-15 Synthetic Chemistry I (Organic)
- CH403-15 Synthetic Chemistry II (Metallo-organic)
- CH401-60 Research Project & Methodology

Courses

This module is Core for:

- UCHA-F109 Undergraduate Master of Chemistry (with International Placement)
    - Year 3 of F109 MChem Chemistry (with International Placement)
    - Year 3 of F111 MChem Chemistry with Medicinal Chemistry (with International Placement)
- UCHA-4M Undergraduate Master of Chemistry Variants
    - Year 3 of F109 MChem Chemistry (with International Placement)
    - Year 3 of F126 MChem Chemistry with Med Chem (with Prof Exp)
    - Year 3 of F106 MChem Chemistry with Professional Experience

This module is Core optional for:

- Year 4 of UCHA-4 Undergraduate Chemistry (with Intercalated Year) Variants
- UCHA-3 Undergraduate Chemistry 3 Year Variants
    - Year 3 of F100 Chemistry
    - Year 3 of F100 Chemistry
- Year 3 of UCHA-F110 Undergraduate Master of Chemistry (with Industrial Placement)
- Year 3 of UCHA-4M Undergraduate Master of Chemistry Variants