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**Lecture Course Synopses**

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**LEVEL 1**

Courses A1–A4 are for one unit, courses A5 and A6 are for two units.

***A1: Inorganic I – Structure and Bonding***

This course focuses on the bonding models that are currently used to rationalise main group and transition metal inorganic complexes and how these bonding models can help us to understand their structures.

**Dr S. R. Boss: 6 lectures**

The first half of the course introduces the types of bonding models displayed by polyhedral architectures (electron-deficient, electron-precise and electron-rich bonding models). The interesting class of electron deficient compounds is discussed in depth and used to rationalise the structures of cluster molecules of the p and d block. The course will recap diborane and the failure of the 2c,2e-bond. The structures of higher boranes will be considered and the course will present Wade's rules and their limitations. Carboranes, met-alloboranes, Zintl phases, and some transition metal clusters will also be considered. The isolobal, isoelectronic and isostructural principles will be introduced as will the  $(v + x - 12)$  rule. The synthesis and reactivity of electron deficient compounds will be described and you will be introduced to the physical methods by which the structures of these species may be determined.

**Topics** Electron-deficient, -precise, and -rich cluster complexes. Electron-counting. Cluster shapes. Wade's Rules. Main Group clusters. Transition Metal clusters. Synthesis and reactivity of electron deficient compounds. Characterisation.

**Dr D. A. Beauregard and Dr M. J. Duer: 6 lectures**

The second half of this course examines the heavier transition metals and f-block elements, focusing on the availability (or otherwise) of valence d and f orbitals in bonding. A huge body of experimental data supports the more extensive participation of the d orbitals in the bonding of the second and third row transition metals. The more expanded nature of the 4d and 5d orbitals of the second and third row transition metals leads to significantly stronger covalency in bonding which leads to greater prevalence for metal–metal as well as metal–ligand multiple bonding for the heavier elements. These aspects will be investigated from a primarily structural view point, reinforced with bonding and thermodynamics arguments. Whilst the lanthanide and actinides comprise almost a quarter of the periodic table, they receive comparatively little attention despite their intrinsically interesting properties and widespread applications. A comparison of the chemistry of the lanthanide and actinides reveals strongly differing behaviour which is attributed to the extent of f orbital availability. The effect on bonding and structures is discussed: predominantly ionic bonding in lanthanides and significant covalency in actinide complexes. A good knowledge of IB coordination chemistry is desirable.

**Topics** Metal–metal multiple bonding in the d block. Metal–ligand multiple bonding in d block chemistry. Ionic vs covalent bonding in the f block. Metal–ligand multiple bonding in f block chemistry.

### *Recommended books*

- N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann Ltd, 2nd Edn.  
F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley 5th Edition, 1988.  
J. E. Huheey, *Inorganic Chemistry*, Longman, 4th Edn.  
N. C. Norman, *Periodicity in the s- and p-block Elements*, Oxford Primer, 2nd Edn.  
N. Kaltsoyannis *The elements*, OUP, 1999.  
S.A. Cotton and F.A. Hart, *The Heavy Transition Metals*, Macmillan, 1975.  
S.F.A. Kettle, *Physical Inorganic Chemistry*, Spectrum Books, 1996.

## *A2: The Foundations of Organic Synthesis*

Dr W. P. Nolan

This course will apply the basic organic chemistry courses, *Key Organic Reactions* and *Shape and Reactivity* taught in IB Chemistry B to organic synthesis. You will see how a molecule can be logically dissected into simple building blocks by working backwards (retrosynthetic analysis) and how using these tools you will be able to devise synthetic strategies towards new molecules.

- Topics** Retrosynthetic Analysis and the Language of Synthesis: Target Molecules. Disconnections. Synthetic equivalents. Criteria for Good Synthetic Planning
- C–X Disconnections: Synthesis of halides, ethers, sulphides and amines (considered as one-group –X disconnections). Two-group disconnections illustrated by the synthesis of 1,1-, 2,2- and 1,3-difunctionalised compounds.
- C–C Disconnections and Synthesis using the Carbonyl Group: Carbonyl group as an a<sup>1</sup> (acceptor) reagent. Alkene synthesis and the Wittig reaction.
- Carbonyl group as a d<sup>2</sup> (donor) reagent. Enolate alkylations. The aldol condensation. Synthetic control in carbonyl condensations.
- $\alpha,\beta$ -unsaturated carbonyl compounds as a<sup>3</sup> (acceptor) reagents. Synthesis of 1,5-dicarbonyl compounds. Construction of 1,4-difunctionalised compounds.
- Construction of 1,4-difunctionalised compounds using synthons of “unnatural” polarity.
- More Tools of the Trade: Synthesis of More Complex Systems. Control of Mixed Functionality. Use of Latent Functionality
- Concepts and Methods for Ring Synthesis: Heterocyclic. Carbocyclic

### *Recommended books*

- Warren, S., *Organic Synthesis – The Disconnection Approach*, Wiley 1982.  
Clayden J., Greeves N., Warren S. and Wothers P. *Organic Chemistry*, OUP, 2001.  
Clayden J., Greeves N. and Warren S. *Organic Chemistry*, 2nd Edn, OUP, 2012. (either edition is fine)

## *A3: High-Resolution Molecular Spectroscopy*

Dr J. H. Keeler

This course will be concerned with the high-resolution spectra of small molecules, mostly in the gas phase. We will look at rotational, vibrational and electronic spectroscopy (including the Raman effect), and the kinds of detailed structural information that can be obtained from each kind of spectrum. The course draws extensively on material previously covered in Part IB Chemistry A, showing how the concepts introduced there can be used and extended to more complex cases.

**Topics** **Electromagnetic radiation and its interaction with molecules.** Transition moments and Einstein coefficients. Linewidths. Lasers.

**Instrumentation.** Dispersive spectrometers: diffraction gratings, sources and detectors. Fourier transform instruments: advantages. Spectroscopy with lasers.

**Rotational spectroscopy.** Classification of molecules and the resulting spectra. Intensities. Centrifugal distortion. Electric field effects (Stark effect).

**Vibrational spectroscopy.** Classification of normal modes and vibrational wavefunctions according to symmetry. Selection rules. Overtones and combination lines. Rotational fine structure: parallel and perpendicular bands.

**Raman spectroscopy.** Origin of the Raman effect. Practicalities. Rotational and vibrational Raman spectroscopy of linear molecules and symmetric tops. Rule of mutual exclusion. Molecular identification using IR and Raman spectra.

**Electronic spectroscopy.** Diatomic molecules. Electronic structure and term symbols. Selection rules and the Franck Condon principle. Vibrational structure in absorption and emission. Electronic spectroscopy of larger molecules: Jablonski diagram.

### *Recommended books*

J M Hollas, *Modern Spectroscopy, 4th edit* (Wiley, 2004).

C N Banwell and E M McCash, *Fundamentals of Molecular Spectroscopy, 4th edit*, (McGraw-Hill, 1994).

*the following texts are for reference.*

D A McQuarrie and J D Simon, *Physical Chemistry, a Molecular Approach*, (University Science Books, 1997).

J M Hollas, *High Resolution Spectroscopy, 2nd edit*, (Wiley, 1998)

P F Bernath, *Spectra of Atoms and Molecules*, (Oxford, 1995).

P W Atkins and R S Friedman, *Molecular Quantum Mechanics, 3rd. edit*, (Oxford, 1997).

## **A4: Theoretical Techniques**

### **Prof. M. Sprik**

Rationalising molecular properties such as reactivity is a central goal of theoretical chemistry. Much qualitative insight can be obtained from molecular orbital theory, which you have already encountered in the Part IB *Symmetry and Bonding* lectures. In this course we expand on this topic introducing some theoretical techniques and ideas, such as perturbation theory, applied to MO calculations, which enable one to extract chemical insight.

The interaction between electrons is ignored in this qualitative treatment or implicitly assumed when experimental input is used, for example, when orbital energies are approximated by ionization energies and electron affinities measured by experiment. However, for more quantitative understanding electron–electron repulsion must be taken into account and we therefore also continue the more rigorous treatment of the Part IB *Quantum Mechanics* course with a brief introduction of self consistent field (SCF) theory.

**Topics** Recap of Hückel theory; symmetry; linear and ring systems; population and bond-order analysis; alternant hydrocarbons; perturbation theory and heteroconjugated systems; Hartree–Fock theory of two and three electron systems; electron correlation and molecular dissociation; molecular vibrations.

### *Recommended books*

Atkins, P.W. and Friedman, R.S., *Molecular Quantum Mechanics, 3rd edit.*, OUP, 1997 (other editions are fine)

Cotton, F.A., *Chemical Applications of Group Theory*, Wiley, 1990.

Leach, A. R., *Molecular Modelling: Principles and Applications*, Prentice Hall, 2001 (Longmans edition of 1996 is acceptable).

House, J. E., *Fundamentals of Quantum Chemistry*, Elsevier.

Murrell, J. M., Kettle, S. F. A. and Tedder, J. M., *Valence theory*, (Wiley).

### *A6: Concepts in physical chemistry*

Dr P. T. Griffiths and Dr J. H. Keeler

This course is aimed at giving you a more detailed understanding of chemical bonding than was possible in the Part IA course. This will require us to introduce some quantum mechanics, which we will do by taking an approach which is always firmly rooted in your chemical understanding and avoids excessive formality or mathematical detail. We will develop the key principles of quantum mechanics using simple model systems, which involve relatively easy mathematics, and then go on to see how these ideas can be applied in atoms and molecules.

The course concludes by showing how molecular symmetry, in the form of *group theory*, can be used to great effect in drawing up MO diagrams of simple molecules.

**Topics** **Revision of some basic mathematics.** Functions and curve sketching (polynomials and trigonometric functions). The exponential function and logarithms. Differentiation: the chain rule; differentiation of a product. Integration. Introduction to complex numbers and the complex exponential.

**Introducing quantum mechanics.** What is quantum mechanics and why is it useful? Wave-functions, operators and energy levels. Exemplifying these ideas for two simple systems.

**Atomic orbitals.** Review of AOs, their shapes and energies. Multi-electron atoms: the energies of singlets and triplets. Term symbols.

**Molecular orbitals.** The two orbital problem. Homo- and hetero-nuclear diatomics. Extended arrangements of orbitals ( $\pi$  systems) in rings and chains. Computational aspects.

**Symmetry.** The description of symmetry. Symmetry elements operations. Point groups. Character tables. Representations and reduction of representations. Constructing molecular orbital diagrams using symmetry as an aid. Transition metal complexes.

### *Recommended books*

P W Atkins, *Concepts in Physical Chemistry*, any edition, Oxford University Press.

A Vincent, *Molecular Symmetry and Group Theory*, 2nd edition, Wiley 2001.

## LEVEL 2

### *B1: Inorganic II – Transition Metal Reactivity and Organometallic Catalysis*

Dr P. T. Wood: 6 lectures

In the first part of this course we examine the mechanisms of substitution, electron-transfer and photochemical reactions in coordination compounds. In the second half of the course we extend our arguments to examine metal-promoted organic transformations which play a fundamental role in catalytic processes such as alkene polymerization and enantioselective synthesis. Well-defined transition metal systems are particularly effective homogeneous catalysts due to the ability of the metal to adopt different geometries, coordination numbers,

and oxidation states. By considering a variety of catalytic processes, we shall examine the exact role of the metal in such cycles and discuss how it is possible to 'tune' the metal centre by varying both the steric and electronic properties of its ancillary ligands in order to favour a specific reaction outcome. The course will also consider several stoichiometric metal-assisted organic transformations and again examine the particular traits of the metal that allow such reactions to occur.

A good knowledge of both the IB courses *Coordination Chemistry* and *Organometallic Chemistry* is assumed.

**CO Reactions.** Alkene carbonylation, hydroformylation; alcohol carbonylation; the Monsanto and BP Cativa processes.

**H<sub>2</sub> & HX reactions.** Hydrogenation; hydrosilylation; hydrocyanation.

**Alkene reactions.** Isomerization; polymerization with heterogeneous and metallocene catalysts; chain-end and ligand control in stereospecific propene polymerizations; late transition metal catalysts; alkene dimerization and trimerization; ethene oligomerization; SHOP process; alkene oxidation.

**Metathesis reactions.** Alkene and alkyne metathesis; Ring-Opening Metathesis Polymerisation (ROMP), Ring-Closing Metathesis (RCM) *etc.*

**Selective Catalysis.**  $\alpha\beta$ -unsaturated aldehyde hydrogenation; epoxidation/aziridination with SALEN- & Sharpless-type catalysts.

**Modern Hybrid Systems.** Examples of single-site heterogeneous catalysts with enhanced turnover rates, product selectivities and recovery.

### Dr E. Reisner: 6 lectures

Inorganic coordination chemistry can be broadly typified by the following types of reactions: substitution chemistry, redox chemistry and photochemistry. We initially focus on the two extrema substitution chemistry (associative and dissociative reaction mechanisms) although experimental evidence often suggests the role of the outer coordination sphere is significant leading to so-called interchange processes. The roles of the inner and outer coordination spheres are also important in electron-transfer processes and we consider factors affecting the rate of electron transfer in both inner sphere and outer sphere mechanisms. The last lecture will focus on uni- and biomolecular photochemistry of coordination compounds.

**Topics** Dissociative reaction mechanisms in octahedral complexes; crystal field stabilization energy: inert and labile complexes; the influence of auxiliary ligands on transition state geometry and the geometric outcome of the reaction.

Associative reaction mechanisms in square-planar complexes; the trans-influence and trans-effect.

Outer-sphere electron-transfer between substitutionally inert complexes; Marcus-Hush theory.

Inner-sphere electron-transfer: rate determining steps.

Uni- and biomolecular photochemistry, photo-induced redox chemistry.

### Recommended books

- D. F. Schriver, P. W. Atkins and C. H. Langford, *Inorganic Chemistry*, 2<sup>nd</sup> Edn., OUP, 1995  
I. S. Butler and J. F. Harrod, *Inorganic Chemistry: Principles and Applications*, Benjamin Cummings, 1989.  
S. F. A. Kettle, *Inorganic Chemistry: A Coordination Chemistry Approach*, Spektrum, 1996.  
K. F. Purcell and J. C. Kotz, *Inorganic Chemistry*, Holt & Saunders., 1977.  
M. L. Tobe and J. Burgess, *Inorganic Reaction Mechanisms*, Longman, 1999.

- C. Elschenbroich and A. Salzer, *Organometallics*, 2nd Edn, VCH, 1992.  
R. H. Crabtree. *The Organometallic Chemistry of the Transition Metals*, 3rd Edn, Wiley, New York, 2001.  
G. W. Parshall, *Homogeneous Catalysis*, 2nd Edn, Wiley, New York, 1992.  
F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6th Edn, Wiley, New York, 1988.  
G. O. Spessand, and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, New Jersey, 1996

## **B2: Structure and Reactivity**

**Dr W. R. J. D. Galloway and Prof. I. Paterson**

In the first half of this lecture series (Dr Galloway), molecular orbital theory will be applied, without mathematics, to explain the preferred structures and conformations of organic molecules, and then extended to explain the reactivity and stereochemistry of a wide range of organic reactions. New reactions having interesting features will be added, greatly extending the range from those already presented in Part IB (Chemistry B) and building upon some of the ideas presented in the Part II course *The Foundations of Organic Synthesis*.

The focus will shift during the second part (Prof. Paterson) to build on last year's work on NMR spectroscopy and on the relationship between molecular geometry and reactivity. It will introduce powerful new methods for structure determination that have revolutionised NMR spectroscopy. These will be applied to problems of conformation and configuration, both in simple ring systems and bicyclic structures.

- 1–6 The fundamental ideas of molecular orbital theory are used as the basis for understanding reactivity. Through space and through-bond (HOMO/LUMO) interactions, hard/soft nucleophiles and electrophiles are explored in detail, as applied to ambident systems and nucleophilic substitution reactions.
- Stereoelectronic effects on fundamental organic reactions are thoroughly examined, as applied to the following: cyclisation (Baldwin's rules and the Thorpe-Ingold effect), elimination, fragmentation, rearrangement (migration). Electronic strain and the topic of carbene chemistry are also introduced.
- An introduction to pericyclic reactions is given: cycloadditions and electrocyclic reactions are examined in detail in the context of the Woodward-Hoffman Rules.
- 7–12 NMR Spectroscopy. Pulsed NMR. Chemical exchange. Shift reagents. Nuclear Overhauser effect. Two-dimensional spectra.
- Conformational Analysis. Conformation of six-membered rings, including ketones, alkenes and heterocycles. Larger and smaller rings. Fused ring systems including steroids. Cis- and trans-ring-fusion. Axial and planar chirality.
- Structure determination. How to determine absolute configuration and enantiomeric excess. Combined use of spectroscopic techniques to determine structure and conformation.

### **Recommended books**

- Kirby, A. J., *Stereoelectronic Effects*, OUP 1996.  
Moody, C. J. and Whitham, G. H., *Reactive Intermediates*, OUP, 1992.  
Eliel, E. L., Wilen S.H. and Mander, L.N., *Stereochemistry of Organic Compounds*, Wiley, 2nd Edn. 1994.  
Fleming, I., *Pericyclic Reactions*, OUP, 1999.  
Fleming, I., *Frontier Orbitals and Organic Chemical Reactions*, Wiley, 1996.  
Fleming, I., *Molecular Orbitals and Organic Chemical Reactions*, Wiley, 2009.  
Available online via Newton catalogue:  
<http://linux02.lib.cam.ac.uk:2048/login?url=http://dx.doi.org/10.1002/9780470689493>  
Clayden, J., Greeves, N., Warren, S. and Wothers, P., *Organic Chemistry*, OUP, 2001.  
Williams, D. H. and Fleming, I. *Spectroscopic methods in Organic Chemistry*, McGraw-Hill, 5th Edn 1995.  
Sanders, J, K, M. and Hunter, B. K., *Modern NMR Spectroscopy*, OUP, 2nd Edn., 1993

### **B3: Chemical Biology I – Biological Catalysis**

**Prof. C. Abell and Prof. D. R. Spring**

Enzymes are the main catalysts in the cell. They catalyse an amazing array of reactions, with high chemo-, regio- and stereoselectivity and at rate enhancements of up to  $10^{15}$ ! Consequently, about half of the drugs currently being developed in the pharmaceutical industry are targeted at enzymes. It is therefore very important for us to understand how enzymes achieve catalysis, and how to use this information to design specific inhibitors.

In IB some of the basic concepts behind enzymatic catalysis were introduced. Now we will build on that foundation and explain the diversity of chemical reactions that enzymes catalyse. The examples are chosen to illustrate how enzymes are studied and to introduce concepts that you will need for subsequent biological courses in Part III.

**Prof. C. Abell**

**Topics** Enzymes basics (a reprise); carbon-carbon bond forming reactions: the biological SN1 reaction, the biological aldol reaction; decarboxylation and elimination reactions; one carbon transfer; activation of oxygen.

**Prof. D. R. Spring**

**Topics** Enzymes and Coenzymes. Vitamins; Reduction and Oxidation, NAD(P)H and Flavins; Thiamine Pyrophosphate (TPP)-Dependent Enzymes; Enzymatic Transformations of Amino Acids, PLP; Glucose Metabolism, Enzymes Work Together.

#### **Recommended books**

T D H Bugg, *An Introduction to Enzyme and Coenzyme Chemistry* Blackwell Science 2004.  
the following texts are for reference

R B Silverman, *Organic Chemistry of Enzyme-Catalysed Reactions* Academic Press 2002.

R B Silverman, *The Organic Chemistry of Drug Design and Drug Action* Academic Press 1992.

A Fersht, *Structure and Mechanism in Protein Science*, Freeman 1999

### **B4: Diffraction Methods in Chemistry**

*This course is given entirely in the Michaelmas Term*

**Dr D. A. Jefferson**

This course provides the background knowledge for the main use of diffraction methods in chemistry, namely the solution of structures by single-crystal x-ray diffraction. It is not intended to be a course in formal crystallography, and no prior knowledge is assumed, but instead it illustrates the basic principles of diffraction, the fundamental relationship between diffracted x-ray amplitudes and the crystal structure, and the problems arising from the measurement of x-ray intensities rather than amplitudes, together with the manner in which these may be circumvented.

All the main methods of structure determination will be dealt with, ranging from the relatively simple approach used in structures containing heavy atoms, through the so-called "Direct Methods" used for medium sized molecules in Organic and Inorganic Chemistry, to the advanced isomorphous replacement methods used in the determination of protein structures. In all these cases the aim is to provide, via selected worked examples, the underlying principles behind the techniques.

The course concludes with an introduction to methods of crystal structure refinement, an assessment of what constitutes a “correct” structure, and an outline of some of the additional information which may be gained from the use of neutron diffraction.

### *Recommended books*

- Dunitz, J.D., *X-ray Analysis and the Structure of Inorganic Solids*, Cornell Univ. Press.  
Guinier, A., *X-ray Diffraction*, W.H. Freeman and Co.  
Cowley, J.M., *Diffraction Physics*, North Holland Publishers  
Giacovazzo, C., *Fundamentals of Crystallography*, O.U.P.  
Woolfson, M.M., *X-ray Crystallography*, C.U.P.  
Stout, G.H. and Jensen, L.H., *X-ray Structure Determination – A Practical Guide*, John Wiley & Sons

## ***B5: The Chemistry of Materials***

**Prof. W. Jones and Dr M. J. Duer**

So far you have not had any specific lectures on materials (at least not within Chemistry Department courses). We are surrounded, however, by (and indeed ourselves composed of) materials that function because of their specific solid state structures. Importantly, the properties of these solids are not just a result of the molecular structure of their constituents but more significantly the ‘collective’ solid state effects.

This course will examine a range of organic, metal-organic and inorganic materials and demonstrate their varied uses. We will, in particular, identify important structural features relevant to such areas as the pharmaceutical and petrochemical industries and to naturally occurring biomaterials such as bone. The underlying chemistry and properties will be shown to be often sensitive to the way that the constituent atoms and molecules are packed together. This aspect of solid state control will be examined in some detail. The development and design of new materials, incorporating structural characteristics of inorganic solids and functionality of organic molecules will be described.

Leading on from this, biological materials, such as bone, hair, skin etc. present an opportunity to learn from Nature how to build functional materials that have different functions on different lengthscales. For instance, on a macroscopic lengthscale, bone provides structural support whilst on a nanoscopic lengthscale, it provides a home for cells and on an even smaller lengthscale, the molecules that make up the tissue are key in providing a communication system between cells.

Currently, man-made materials generally are designed to perform on one lengthscale only, so studying biological materials gives us insight into designing a new generation of materials. We will study these materials to gain perspective on how they perform their various material roles.

Dealing with complex materials like these however means that we have to investigate different ways of examining their structure from the more conventional diffraction techniques. Thus this part of the course will begin with an overview of solid-state NMR and how it can be applied to determine molecular structures, then lead on to a detailed examination of keratin tissues (hair, nails etc.), and collagenous tissues (bone, tendon, skin, muscle, etc.), to focus throughout being on understanding how the underlying molecular structures and dynamics lead to the required material properties.

From paracetamol to petrol to proteins to bone – the importance of *the Chemistry of Materials* will be explored in these lectures.



- gen bond; implications for crystal structure. Crystal engineering. Supramolecular chemistry. Methods of studying materials I: XRD
- 5–6 Introduction to inorganic-organic composites. Intercalation and formation of inorganic-organic composites. Ion exchange materials. Microporous aluminosilicates and zeolites. Applications of zeolites, especially in catalysis and shape selective control.
- 7–8 Solid-state NMR spectroscopy; applications to studying molecular structure and dynamics.
- 9–10 Keratin (“dead”) tissues; basic protein structures, primary and secondary structures. Composite structure of keratin tissues. The importance of fibril structures for mechanical strength; the role of the  $\alpha$ -helix protein structure in mechanical properties
- 11–12 Collagen tissues; their composite structure, and self-assembly of collagen fibrils; the role of proteoglycans in organizing collagen fibrils. Mineralization of collagen matrices.

### **Recommended books**

- Basic Solid State Chemistry*, A R West, John Wiley and Sons Ltd. (2nd Edition)
- Molecular Crystals*, J D Wright, Cambridge University Press. (1st or 2nd Edition).
- Reactions and Characterisation of Solids*, S E Dann, RSC, Tutorial Chemistry Texts.
- Structural Biomaterials*, Julian Vincent, Princeton University Press, 1990.
- Biom mineralization*, S. Mann, Oxford Chemistry Masters, OUP, 2001.
- Organic Molecular Solids: Properties and Applications*, Edited by W Jones, CRC Press.
- An Introduction to Solid-State NMR*, M.J. Duer, Blackwell Science Ltd, 2004.
- Core Concepts in Supramolecular Chemistry and Nanochemistry*, J. W. Steed, D. R. Turner & K.J. Wallace. Wiley, 2007.

## **B6: Statistical Mechanics**

### **Prof. D. Frenkel**

The IB Course *Molecular Energy Levels and Thermodynamics* showed how the thermodynamic properties of a macroscopic sample of matter can be expressed in terms of the energy levels of individual molecules and the interactions between them. To move on from here, we need to introduce the concept of Gibbs ensembles, and then we can express the thermodynamic and transport properties of a macroscopic sample of matter in terms of the basic interactions between molecules. Except for some limiting situations like the ideal gas, approximations must be introduced to allow explicit calculations. One of the generic approximations is mean-field theory, which provides a reasonable description of many systems and phenomena, such as phase transitions, magnetism and electrical double layers around membranes. The course will provide an introduction to ensemble theory, classical statistics, mean field methods and the basic theory of transport phenomena. The concepts will be illustrated by applications to Physical Chemistry and Condensed Matter Science.

### **Recommended books**

- McQuarrie, D.A, and Simon, J.D, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.
- Dill, K.A., and Bromberg, S., *Molecular Driving Forces: Statistical Mechanics in Chemistry and Biology*, Garland Science, 2002.
- For reference
- Chandler, D., *Introduction to Modern Statistical Mechanics*, O.U.P., 1987.
- Huang, K., *Statistical Mechanics*, John Wiley, 1987.
- McQuarrie, D., *Statistical Mechanics*, Harper and Rowe, 1976.

## ***B7: Symmetry and Perturbation Theory***

Dr G. H. Booth and Prof. A. Alavi

Perturbation theory is an important technique in quantum chemistry. Although few systems can be solved exactly, we can study the effects of a small change to the Hamiltonian of a system, and using this technique we can predict, for example, how a molecule responds to an applied electric field or to the presence of a neighbouring molecule. The method provides a framework for understanding anharmonic effects in vibrational spectra, intensities in spectra generally, and many other phenomena.

The methods by which symmetry can be used to simplify calculations have been introduced in earlier courses. Here we shall examine some of the theory that underlies these methods, and extend it to further applications.

Dr G. H. Booth

- 1–6 Nondegenerate perturbation theory. The first order wavefunction. Polarisability of the hydrogen atom. Rayleigh–Schrödinger perturbation theory. Variation perturbation theory. Degenerate perturbation theory e.g. the H atom in an electric field. Molecular vibrations. Anharmonic vibrations. Fermi resonance for CO<sub>2</sub>. Time dependent perturbation theory. Transition probabilities. Frequency dependent polarisabilities. Dispersion forces.

Prof. A. Alavi

- 7–12 Introduction and basic ideas. Representations. What is a representation? Equivalent representations. Characters and classes. The Great Orthogonality Theorem. The symmetric representation. Symmetry and physical properties of molecules. The projection formula. Spherical harmonics and the full rotation group. Direct product representations. Calculation of integrals. The symmetrized and antisymmetrized square. The Jahn Teller theorem. Choosing the symmetry group. What symmetries can be ignored? Approximate symmetries. Selection rules. Rotational spectroscopy. Vibration–rotation spectroscopy. Electronic spectroscopy.

### ***Recommended books***

Atkins, P.W. and Friedman, R.S., *Molecular Quantum Mechanics*, OUP,  
Johnson, C.S. and Pedersen, L.G., *Problems and Solutions in Quantum Chemistry and Physics*,  
Dover, 1986.

## ***B8: Investigating Organic Mechanisms***

*This course is given entirely in the Lent Term*

Dr P. D. Wothers

How do we know how a reaction proceeds? How much faith should we put in the mechanisms we so readily draw? In this course we will investigate the different methods available to the chemist in order to understand exactly how species react in solution. We will look at the ways of determining and manipulating the reaction pathways from starting materials, through transition states and intermediates to products. The crucial role of the solvent in controlling the outcome of a reaction is also examined.

**Topics** Kinetics, potential energy surfaces for reactions, interpretation of enthalpy, entropy and volume of activation, interpretation of kinetic isotope effects, acid and base catalysis, linear free energy relationships (Brønsted and Hammett equations). Noncovalent interactions, solvation, water as a solvent and hydrophobic effects and solvent effects on organic reactivity.

Please note that all of the lectures for this course will be given in the Lent Term.

### **Recommended books**

*Organic and Bio-organic Mechanisms*, M. Page and A. Williams, Longman, 1997.

*Structure and Reactivity in Organic Chemistry*, Howard Maskill, Oxford Chemistry Primer 81, 1999.

*Modern Physical Organic Chemistry*, E. V. Anslyn and D. A. Dougherty, University Science Books, 2004.

## LEVEL 3

### **C1: Inorganic III – Characterisation Methods**

**Prof. C. P. Grey, Dr E. Reisner and Dr D. A. Beauregard**

The range of atoms encompassed by inorganic chemistry presents opportunities for characterisation and analysis with techniques that are not always employed in organic chemistry. In this course we focus on electron paramagnetic resonance spectroscopy, electrochemical techniques, and multinuclear NMR spectroscopy. The use of EPR spectroscopy to probe the electronic structure of paramagnetic complexes of the d- and f-block elements will be explored. Electrochemical measurements underpin our understanding of redox processes and the stability of different oxidation states. Basic electrochemical methods and some applications will be described. Multinuclear NMR spectroscopy will be investigated, particularly for the characterisation of main group compounds and diamagnetic transition metal complexes. This set of lectures complements the IB Structure Determination and Part II organic (spectroscopy) courses and the Part II C8 course dealing with the physical basis of NMR spectroscopy, while introducing new techniques that apply more specifically to inorganic systems. It is likely that a combination of classes and supervisions, will be offered for this course.

**Prof. C. P. Grey: 4 lectures**

These lectures examine a technique that is used to characterize the electronic structure of a paramagnetic complex, namely EPR spectroscopy. Magnetic responses of (isolated) paramagnetic molecules are briefly reviewed.

**Topics** Paramagnetism and diamagnetism: Spin ( $S$ ), orbital ( $L$ ) and total angular momentum ( $J$ ) contributions to magnetism.  
Magnetism of the free ion: Term symbols and magnetism of the lanthanides.  
Quenching of orbital angular momentum; Term symbols for common Oh and Td complexes; the Van Vleck formula and spin-only magnetic moment for d-block metals.  
Basics of EPR spectroscopy focusing on  $S = \frac{1}{2}$  systems: electron-Zeeman, nuclear-Zeeman interactions and electron-nuclear interactions.  
The g-value and hyperfine coupling.  
Information that can be extracted from EPR spectra: localized and delocalized magnetic orbitals; spin-polarisation.

### **Recommended books**

*Magnetochemistry*, A. F. Orchard, Oxford Chemistry Primers, 2003.

*Introduction to Magnetic Resonance*, A. Carrington and A. D. McLachlan, Harper International Edition, 1967.

*Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, M. Symons, Van Nostrand Reinhold Co. Ltd, 1978.

General Inorganic text books such as: *Inorganic Chemistry*, Shriver and Atkins, *Inorganic Chemistry: Principles of Structure and Reactivity*, Huheey, Keiter and Keiter and *Chemical Applications of Group Theory*, Cotton.

#### Dr E. Reisner: 4 lectures

The lectures will give an introduction to electrochemistry and its use to study inorganic redox processes in solution and the solid state.

**Topics** Overview of electrode processes. Potentials and thermodynamics of cells. Kinetics of electrode reactions. Techniques: Cyclic voltammetry, Film voltammetry, Chrono-amperometry, spectroelectrochemistry. Applications: Electrode reactions with coupled homogeneous chemical reactions, Protein film voltammetry.

#### Recommended books

*Electrochemical Methods, Fundamentals and Applications*, 2nd Edition. A. J. Bard and L. R. Faulkner, Wiley, 2001.

*Understanding Voltammetry*, 2nd Edition. R. G. Compton, C. E. Banks, ICP, 2011.

*Inorganic Electrochemistry, Theory, Practice and Application*, 2nd Edition. P. Zanello, F. Fabrizi de Biani, C. Nervi, RSC Publ., 2012.

*Electrode Dynamics*. A. C. Fisher, Oxford Chemistry Primers, 1996.

#### Dr D. A. Beauregard: 4 lectures

The focus is on the characterisation of inorganic compounds through multinuclear NMR spectroscopy.

**Topics** Pulse sequences.  
Structural information from relaxation times.  
NMR using nuclei other than  $^1\text{H}$  and  $^{13}\text{C}$  for inorganic structure determination.  
Chemical shifts: shielding, extended chemical shift ranges in inorganic systems.  
Scalar coupling magnitudes for structure determination.  
Two-dimensional NMR spectroscopy techniques for inorganic chemistry.

#### Recommended books

*NMR Spectroscopy in Inorganic Chemistry*, J.A. Iggo, Oxford University Press, 1999.

## C2: Chemical Biology II – Proteins and Metalloproteins

#### Dr S. E. Jackson and Dr P. D. Barker

Proteins are the most diverse of biological macromolecules from both a structural and functional point of view. Starting with just the twenty naturally occurring amino acids it is possible to form massive structures such as the 34,350 residue long, 2M Da giant muscle protein titin, in addition to small but potent structures such as the 60-residue long Textilinin-1 snake venom.

The first part of the course describes in detail the three-dimensional structures of proteins and how it is determined, and lays a strong foundation for the rest of this and other Part III lecture courses. A very wide range of examples will be used to illustrate how the structure and function of proteins are linked, and the underpinning non-covalent chemistry. The importance and widespread use of protein engineering techniques, including recently developed methods for the incorporation of non-natural amino acids into proteins, will be discussed including the engineering of antibodies for use as therapeutic agents to the engineering of haem-containing proteins for nano-electrical circuitry! The marginal

thermodynamic stability of the native states of many proteins will be highlighted in addition to the chemical methods that have been used to study it. The consequences of protein instability and the link with disease will be illustrated with a few key examples.

The second half of the course will discuss the interplay between protein structure/stability and metal binding from fundamental inorganic perspective, exploring how metal binding can be used to determine protein structure and conversely how protein structure determines metal function. After a brief overview of the principles for which biology has selected metals for different functions, we will examine in more detail, the cases of zinc, iron and copper as structural elements and catalysts.

lectures 1–6 Introduction to protein structure, Probes of protein structure: NMR, x-ray crystallography, CD and fluorescence; Manipulating protein structure and function: protein engineering techniques; Measuring protein stability; Factors that govern protein stability; The importance of protein stability: instability, misfolding and disease.

lectures 7–12 Metals in biology - binding selectivity and thermodynamics; Zinc proteins; Iron enzymes - harnessing dioxygen chemistry; Copper proteins; Electron transfer in biology.

### ***Recommended books***

- A. R. Fersht, *Structure and Mechanism in Protein Science*, Freeman  
T. Creighton, *Proteins: Structures and Molecular Properties*, Freeman  
S. J. Lippard and J. M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books  
T. D. H. Bugg, *An introduction to Enzyme and Coenzyme Chemistry*, Blackwell Science

### ***C3: Control in Organic Chemistry***

**Dr J. M. Goodman and Prof. D. R. Spring**

What controls organic reactions? Is it the reagent, the functional group, the catalyst? Questions like this will be explored in the course leading to an analysis of the different types of control - chemo- regio- and stereo- (not enantio-). Reactions you have met earlier this year will be examined in a new light. Building on these more familiar examples, the mechanisms of new reactions will be introduced.

This course will involve a fundamental analysis of organic chemistry and have a strong mechanistic content. This analysis is vital for a mature understanding of the whole of Part II organic chemistry.

### ***Recommended books***

- Clayden, J., Greeves, N., Warren, S. and Wothers, P., *Organic Chemistry*, OUP 1st Edn, 2000 or 2nd Edn, 2012.

### ***C4: Chemistry in the Atmosphere***

**Dr A. T. Archibald and Dr M. Kalberer**

This course will introduce key ideas about the chemistry of the atmosphere. It will discuss the chemical processes which control the abundances of ozone, and other trace constituents in the troposphere, and the rather different chemistry of the stratospheric ozone layer. We will use examples to reinforce ideas about reaction rates, gas and solution phase kinetics and spectroscopy.

**Topics** The physical and chemical structure of the atmosphere: composition and temperature as a function of pressure. Sources, sinks and variability. The concept of lifetimes and steady state. The role of ozone in the atmosphere.

Chemistry of the stratospheric ozone layer. The Chapman reactions. Catalytic cycles for ozone destruction and the idea of 'families', including NO<sub>x</sub>, HO<sub>x</sub>, ClO<sub>x</sub>.

Chemistry of the troposphere. Local air quality. Oxidizing and reducing smogs, photochemical oxidants. The role of nitrogen oxides and volatile organics. The global troposphere. Production and destruction of ozone. The role of OH. Sulphur compounds and acid rain

Reactions of atmospheric interest. Some important gas phase atmospheric reactions will be considered in detail. Heterogeneous reactions of important gas phase compounds on atmospherically relevant aerosol particles surfaces will be discussed. Sources, formation processes and chemical composition of tropospheric aerosol particles.

Measurements of atmospheric composition and their applications. Remote sensing. Raman spectroscopy. Ultraviolet spectroscopy. Laser studies of the atmosphere. Chemical methods: chemiluminescence, laser induced fluorescence. Electrochemical methods. Chromatographic techniques. Online and offline aerosol sampling and characterization techniques.

### *Recommended books*

*Chemistry of atmospheres*, Wayne, R P, OUP

Further reading/reference:

*Atmospheric change – an earth system perspective*, Graedel, T and Crutzen, P Freeman and Co, NY

*The physics of atmospheres*, Houghton, J T, OUP

*Chemistry of the upper and lower atmospheres*, Finlayson-Pitts and Pitts, Academic Press

*Aeronomy of the middle atmosphere*, Solomon and Brasseur, Reidel

*Reaction kinetics*, Pilling and Seakins, OUP

## **C6: Electronic Structure**

Dr A. J. Cohen

The aim of this course is to provide an introduction to Electronic Structure theory, and in particular to go beyond the non-interacting, one-electron picture which has been implicitly assumed in the molecular orbital theory used in nearly all earlier courses. The inclusion of electron–electron repulsion is crucial for the quantitative prediction of molecular properties. Self-consistent field theory provides a way to include e–e repulsion, albeit at an approximate level maintaining a one-electron picture. Two varieties of SCF theory exist: wavefunction-based methods based on Hartree–Fock and density-functional methods. The former provides the traditional starting point to more systematic theories of electron correlation, and is the bedrock of quantum chemistry. The latter have proven a highly popular and efficient alternative to Hartree–Fock, but unlike Hartree–Fock, still account for electron correlation in an approximate way. Both topics will be covered.

**Topics** Basis functions, hydrogenic (Slater) orbitals, atomic orbitals, Gaussian functions, and contracted functions; the secular equations from which orbitals are determined; self-consistent field theory, and its numerical implementation; beyond Hartree–Fock, electron correlation; the energy functional, the importance of electron density, Hohenberg–Kohn theorems; The Kohn–Sham equations and orbitals; comparison with Hartree–Fock theory; the exchange correlation functional; electronic structure calculations as research tool.

### *Recommended books*

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, 2000, Dover publications.

W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2001, Wiley-VCH.

### **C7: Chemical Biology III – Nucleic Acids**

**Prof. S. Balasubramanian, Prof. J. Chin and Dr G. Bernardes**

Nucleic acids are fundamental to life and to the study and exploitation of the life sciences. Understanding the chemistry of nucleic acids is as important now as it has ever been given the recent groundbreaking discoveries that relate to DNA, RNA and genome function. These lectures will provide detailed insights into the chemistry of nucleic acids and how this relates to their structure and function in living systems.

Specific themes will include: DNA/RNA structure; the chemical synthesis of DNA and RNA Nucleic acids analogues as therapeutics; the recognition of nucleic acids by organic (drug) molecules, and by natural proteins; chemical modification of DNA; the chemical biology of enzymes that mediate DNA- or RNA-related transactions (e.g. synthesis, cleavage and repair); the chemistry of DNA sequencing; and nucleic acids-based molecular medicine.

- Lecture 1 (GB) Introduction to nucleic acids
- Lecture 2 (GB) Chemical synthesis of nucleic acids
- Lecture 3 (GB) Chemical analogues of DNA/RNA therapeutics
- Lecture 4 (GB) Recognition of DNA by synthetic organic molecules
- Lecture 5 (JC) RNA secondary structure and protein recognition
- Lecture 6 (JC) Chemical and enzymatic cleavage of nucleic acids
- Lecture 7 (JC) RNA enzymes
- Lecture 8 (JC) Ribosomes and translation
- Lecture 9 (SB) Chemical reactions on DNA, DNA damage and repair
- Lecture 10 (SB) Enzymatic synthesis of DNA – Polymerases
- Lecture 11 (SB) DNA replication and medicinal chemistry
- Lecture 12 (SB) Chemistry of DNA sequencing

#### ***Recommended books***

Eds G. M. Blackburn, M. J. Gait, D. Loakes and D. M. Williams, *Nucleic Acids in Chemistry and Biology*, 3rd edition, RSC Publishing Cambridge, 2006.

R. B. Silverman, *The Organic Chemistry of Drug Design and Drug Action*, 2nd edition, Elsevier Academic Press 2004.

### **C8: Surfaces**

**Dr S. Clarke, Dr S. M. Driver and Dr V. Fiorin**

The behaviour of atoms and molecules at surfaces has a central role in many areas of great academic and industrial importance from everyday problems (such as corrosion, lubrication and detergency) to high added value technologies (such as oil recovery, heterogeneous catalysis and novel sensors). Many biological systems also have behaviour that is ultimately dominated by interactions at, or across interfaces. Therefore it is clearly essential that we understand surfaces and interfaces if we are to optimise and control these important processes.

In this course we aim to provide an insight into the key issues that underpins current understanding and characterization of surfaces. We will describe the structure and

properties of interfaces, both ‘wet’ (solid–liquid and liquid–vapour interfaces) and ‘dry’ (solid–vapour interfaces). We will consider the behaviour over a range of lengthscales, from the atomistic mechanisms involved in surface mediated reactions to the macroscopic, thermodynamic description of adsorption. The material will be of use in its own right and as a firm foundation for those considering a deeper study of surfaces and related topics such as nanoscience, bioscience, colloids and catalysis.

### *Recommended books*

- G. Attard and C. Barnes, *Surfaces*, Oxford Chemistry Primer No 59, Oxford Science Publications, 1998.
- R. J. Hunter, *Introduction to Modern Colloid Science*, Oxford Science Publications, 1996.
- D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, 3rd Ed, Butterworth (out of print).
- E. M. McCash, *Surface Chemistry*, Oxford University Press, 2001.
- M. Bowker, *The Basis and Applications of Heterogeneous Catalysis*, Oxford Chemistry Primer No 53, Oxford Science Publications 1998.
- P. W. Atkins, *Physical Chemistry*, Oxford University Press, 7th Ed, 2001.

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## Continuously assessed work

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You are required to complete a portfolio of continuously assessed work taken from a range of options on offer. Naturally, conventional practical work features heavily as chemistry is above all an experimentally based subject, and to describe yourself as a chemist you need to know how to design and carry out experiments.

Chemists also need to develop a wider range of skills, such as how to find out and sift information, how to write, how to use computers in different contexts and how to communicate your ideas. You will have to opportunity to develop these skills as part of your portfolio of continuously assessed work. It is important to realise that even if you are not intending to carry on as a professional chemist, these skills will nevertheless be very useful to you in your future career. The continuously assessed work you need to complete is made up in the following way:

- The two core practical courses which consist of *Techniques in Modern Synthetic Chemistry* (organic and inorganic) and the joint *Physical & Theoretical Chemistry* course.
- The three exercises associated with the *Chemical Informatics* course.
- Six ‘advanced’ experiments.

Other continuously assessed work can be substituted for some of the advanced experiments as follows:

- The Language Option (substitutes for **four** advanced experiments)
- The Computing Option (substitutes for **two** advanced experiments)
- The Mathematical Methods course (substitutes for **three** advanced experiments)

Only *one* of these substitutions can be made i.e. you can only take one out of the three listed above.

To produce a final mark for the continuously assessed work, each component will be weighted as follows: