Universida de Vigo

IDENTIFYING DATA				
Physical Chemistry IV: Molecular Structure and Spectroscopy				
Subject	Physical Chemistry IV: Molecular Structure and Spectroscopy			
Code	V11G201V01307			
Study programme	Grado en Química			
Descriptors	ECTS Credits	Choose	Year	Quadmester
	6	Mandatory	3rd	2nd
Teaching language	Spanish Galician			
Department				
Coordinator	Flores Rodríguez, Jesús Ramón			
Lecturers	Flores Rodríguez, Jesús Ramón Giráldez Martínez, Jesús Mandado Alonso, Marcos			
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General description	In the present subject Quantum Mechanics is applied to the study of molecules and the fundamentals of molecular spectroscopy. First, the Born-Oppenheimer approximation is introduced and the concept of potential energy surface presented, so a relatively detailed study of the rotation and vibration-rotation spectroscopies can later be done. The molecular orbital (MO) and valence bond (VB) methods for the analysis of the electronic structure of molecules are presented, so that of simple molecules can be studied and some basic aspects discussed. The concepts needed for studying the electron and photoelectron spectroscopies are, therefore, given. The most important computational methods for the study of the electronic structure, which form the basis of Computational Chemistry, are also presented in a simple way. The analysis of the spectroscopic methods includes the fundamentals of the magnetic resonance techniques, which is done from a theoretical perspective, as well as those of some other methods, including those based on the use of the laser. The theoretical developments studied in this subject rely on the fundamentals of Quantum Mechanics and the models for translation, vibration and rotation as presented in Química Física III: Química Cuántica. The introduction to Group Theory provided in that subject is completed in the present one by the first theme. Some elements of Statistical Mechanics are used to analyze the intensity and width/shape of the spectral lines for instance. By its theoretical and experimental contents, it provides some support to Química Física V: Cinética Química.			

Training and Learning Results	
Code	
A1	Students can apply their knowledge and understanding in a manner that indicates a professional approach to their work or vocation, and have competences typically demonstrated through devising and sustaining arguments and solving problems within their field of study
A5	Students have developed those learning skills that are necessary for them to continue to undertake further study with a high degree of autonomy
B1	Ability for auronomous learning
B2	Organization and planning capacity
B4	Ability for analysis and synthesis
C2	Use correctly chemical terminology, nomenclature, conversions and units
C4	Use computer tools properly to obtain information, process data, perform computational calculations and calculate matter properties
C14	To know the principles of quantum mechanics and its application in the description of the structure and properties of atoms and molecules
C15	Know the main techniques of structural research, including spectroscopy
D1	Ability to solve problems

Expected results from this subject

Expected results from this subject	Training and Learning Results			
To apply the group theory in the context of the chemistry	A1 A5		C4	D1
To formulate the molecular Hamiltonian taking into account the Born-Oppenheimer approximation and to know about potential energy surfaces	A1 A5	B4	C2 C4 C14	D1
To describe the MO and VB methods and to apply the MO method to simple molecules.	A1 A5	B1 B2 B4	C2 C4 C14	D1
To describe some important computational methods and apply them to molecular electronic structure calculations.	A1 A5	B1 B2 B4	C2 C4 C14	D1
To apply the basic concepts of molecular spectroscopy.	A1 A5	B1 B2 B4	C2 C4 C14 C15	D1
To interpret distinct types of molecular spectra (microwave, infrared and visible-ultraviolet) in order to obtain structural information.	A1 A5	B1 B2 B4	C2 C4 C14 C15	D1
To describe the foundations of resonance spectroscopies	A1 A5	B1 B2 B4	C2 C4 C14 C15	D1

Contents

Topic	
Subject I. The Group Theory in Chemistry.	1. Matrix representations. 2. Character tables. Degeneracy. 3. Basis functions. 4. Direct product representations. 5. Vanishing integrals. 6. Symmetry adapted linear combinations and projection operators. 7. Group Theory and Quantum Chemistry.
Subject II. Molecular electronic structure I.	1. The molecular hamiltonian: the Born-Oppenheimer approximation. 2. Potential energy surfaces. 3. The hydrogen molecule ion H2+: the MO method. 4. The hydrogen molecule H2: the VB method 5. Comparison of the MO and VB methods. 6. The validity of the Born-Oppenheimer approximation.
Subject III. Molecular electronic structure II.	1. Electronic configurations and electronic terms in diatomic molecules. 2. The effect of the spin-orbit interaction. 3. Electron density and bond polarity. 4. The MO and VB methods applied to diatomic molecules. 5. Polyatomic molecules: classification of the electronic states. 6. Application of the MO method to simple polyatomic molecules. 7. Electron population analysis. 8. Localized MOs. 9. Molecules with conjugate bonds: the sigma-pi separation. The free electron MO method. 10. The Hückel MO method. 11. Electron delocalization and aromatic stability. 12. Application of the VB method to polyatomic molecules: types of hybridization. 13. Resonance.
Subject IV. Electronic structure and Computational Chemistry.	1. The Hartree-Fock SCF method applied to molecules. 2. Basis functions in molecular calculations. 3. The Roothaan-Hall and Pople-Nesbet equations. 4. Limitations of the Hartree-Fock SCF method. 5. Post-Hartree-Fock methods. 6. Density Functional Theory (DFT). 7. Relativity in molecular calculations. 8. Semi-empirical methods.

Subject V. Interaction of the electromagnetic radiation with matter and molecular spectroscopy.	1. Interaction of the electromagnetic radiation with matter. 2. Diffusion. 3. Absorption: transition moments and selection rules. 4. The Lambert-Beer law. 5. Broadening of the spectral lines. 6. Raman effect. 7. Laser. 8. Fourier transform. 9. General aspects of the experimental techniques
Subject VI. Molecular rotation and rotational spectroscopies.	1. The polyatomic rigid rotor: results of the classical and quantum treatments. 2. Rotational spectra. 2.1. Selection rules, populations and line intensities 2.2. Stark effect. 2.3. Hyperfine structure and nuclear quadrupole moment. 2.4. Molecules with non-zero electronic angular momentum. 2.5. Type-l doubling. 3. Microwave spectroscopy (MW) and its applications. 4. Rotational Raman spectra. 5. Obtaining the molecular geometry from the rotational constants. 6. Nuclear spin and rotational states.
Subject VII. Molecular vibration and vibrational spectroscopies.	1. Vibration in diatomics. 2. Anharmonicity, vibration-rotation interaction and centrifugal distortion. 3. Vibration and vibration-rotation spectra in diatomic molecules. 4. Line intensity and nuclear spin. 5. Vibration in polyatomic molecules. 6. Vibration-rotation spectra in polyatomic molecules. 7. Analysis based on the symmetry: IR and Raman activities. 8. Anharmonicity and potential energy surfaces. 9. Normal modes with more than a minimum.
Subject VIII. Electronic spectra.	1. Electronic spectra. 2. Diatomic molecules. 2.1 Selection rules. 2.2 Franck-Condon principle and fine structure. 2.3 Dissociation and predissociation. 3. Electronic spectra in polyatomic molecules. 4. Fluorescence and phosphorescence. 5. Non-radiative transitions. 6. Photoelectron spectroscopies 7. Optically active molecules. Circular dicroism. 8. Laser techniques.
Subject IX. Resonance spectroscopies	1. Introduction. 2. Foundations of the RMN and RSE spectroscopies : Chemical shift. 3. Interpretation of the shielding constants. 4. Interpretation of the fine structure. 5. RMN and nuclear exchange processes. 6. RMN for the solid state. 7. Foundations of the pulse techniques and spin relaxation. 8. RSE spectroscopy: hyperfine structure. 9. Quadrupole resonance spectroscopy. 10. Mössbauer spectroscopy.

Planning

	Class hours	Hours outside the classroom	Total hours
Lecturing	23	57.6	80.6
Problem solving	12	26.4	38.4
Laboratory practical	14	14	28
Objective questions exam	2	0	2
Objective questions exam	1	0	1

*The information in the planning table is for guidance only and does not take into account the heterogeneity of the students.

Methodologies

	Description
Lecturing	Discussion of the basic aspects of each topic and description of those to be addressed in the seminars. Discussion of the specific issues raised by students. The student will be provided with the necessary study material to follow the lessons through the Moovi (Moodle) platform.

Problem solving	Solution to numerical problems and theoretical questions as well as test-type exercises. Numerical and theoretical problems will be solved by the teacher in the seminars with the participation of the students. The results will be analyzed and interpreted. On a voluntary basis, the student may solve some of these exercises in the seminar, with the assistance of the teacher and the participation of the other students. They may, voluntarily as well, present a written resolution to an exercise and debate it with the teacher in tutoring time.
Laboratory practical	Every student is expected to perform a well-balanced set of experiments which exemplifies and develops the basic topics. The experiments will be carried out by couples of students for agility. Scripts describing every experiment, references to bibliography and instructions for the use of computers, programs and instrumentation, as well as others related to laboratory safety, will be made available as needed. The student must produce the figures and do the necessary calculations to obtain the final results, as well as analyze and discuss them.

Personalized assistance

Methodologies	Description
Lecturing	The student may raise specific questions in the lectures and ampler ones in the teacher's tutoring time.
Problem solving	The solution to the exercises will be discussed with the students in connection with the development of the theoretical aspects. The additional questions students may raise will be answered during the teacher's tutoring time.
Laboratory practical	The practical problems or doubts the students may raise regarding the theoretical foundation of the experiments, their development or the key aspects of the calculations needed to obtain the result will be discussed during the practical sessions. Additional issues may be addressed in tutoring hours.
Tests	**Description**
Objective questions exam	Any doubts regarding the exams, in particular those related to their scope and configuration, will be clarified. In the case of the short exams, the solutions to the exercises will be briefly presented and discussed in a seminar after the short exam. During tutoring hours, the answers provided by the student will be discussed with him/her at his/her request.

Assessment

	Description	Qualification	Training and Learning Results
Problem solving	The resolution of one or more exercises by the student and their presentation in the seminar will be rated. Short tests taken in the seminar will be rated as well. In both cases on a voluntary basis. The weight in the global grade lies between 0-10%.	10	A1 A5 B1 B2 B4 C2 C4 C14 C15 D1
Laboratory practical	Lab practices are compulsory. They will be rated by the assessment of their development (5%) as well as by that of the corresponding practice reports (15%), one per practice. Those reports have to be elaborated individually, must contain tables, figures and graphics and the calculations needed to obtain the results, as well as an analysis of them. Students must upload them to the Moovi platform before the deadline.	20	A1 A5 B1 B2 B4 C2 C4 C14 C15 D1
Objective questions exam	For the written exams the subject is divided into two parts (I and II), which have a relative weight of 50% in the mark. The written exams consist in the resolution of questions and problems. First short exam ("Primera prueba corta", Part I). Voluntary. It will take place by about half of the lecturing period. If its mark is equal or greater than 5 points over 10, part I will be considered as passed by the student. If it is lower than 5 but equal or greater than 3.75, it may represent 50% of the mark of part I, the other 50% coming from part I of the Final Exam, if that leads to improvement; otherwise the latter prevails. Its weight on the global mark depends on the results of other items and lies in the range: 0-40%.	35	A1 A5 B1 B2 B4 C2 C14 C15 D1

Objective questions exam	Second short exam (Part II). Voluntary. It will take place near the end of the lecturing period. Independently of the mark, the students must take part II in the Final Exam (see below). Its mark is only valid for calculating an average for part II with corresponding mark of the Final Exam, not independently of the latter. It may represent 25% of part II if that leads to an improvement, otherwise the mark obtained for part II in the Final Exam will prevail. Its weight on the global mark, depending on that other sections is: 0-10%. Final Exam. Compulsory. It will take place shortly after the lecturing period (May/June). Those students who have not passed the first short exam (mark>=5) will have to take all the exercises. Those who passed it can still take the exercises of part I to improve the corresponding mark. Its weight on the global mark depends on that of other sections and lies within 26.5%-80%. The combined mark of the exams (not including the tests of the first item) has to be of at least 3.75 on the 10-point scale for the subject to be passed. The lab practices and the final exam are compulsory. See also the second and third points of the next section (Other Comments on the Evaluation) The assessment rules of the second call (late June or early July) to those students who have not passed the subject, are given in the first point of the next section.	35	A1 B1 C2 D1 A5 B2 C14 B4 C15

Other comments on the Evaluation

- In the *second-opportunity evaluation* ("July's exam") the corresponding Final Exam is also compulsory, otherwise the mark will be the same as in the first opportunity. In any case, the mark cannot be lower than that of the first-opportunity evaluation. Lab practices represent 20% of the mark. The marks corresponding to "Problem Solving", second short exam and also that of the first short exam if >= 3.75, will be kept and used to calculate the average by the weights given in the last section, but only if their use gives a higher grade. Otherwise the mark of the Final Exam, including all exercises, will prevail, being 80% of the global grade.
- The average mark corresponding to the exams, third and fourth items of the last section, has to be >=3.75 on a 10 point scale for the other items to be considered in the global average. Such global average must be >=5 on the 10 point scale for the subject to be passed. Lab Practices and the Final Exam are compulsory.
- Taking two or more tests or presenting one exercise (Problem Solving), or attending one Lab session or any of the short exams, makes it impossible to get "No Presentado" as a grade.

Sources of information

Basic Bibliography

Atkins, P.W.; de Paula, J.; Keeler, J., **Atkins Physical Chemistry**, 11th, Oxford University Press, 2018

Levine, I. N, **Physical Chemistry**, 6th ed., McGraw Hill, 2009

Complementary Bibliography

Levine, I. N, **Quantum Chemistry**, 7th, Pearson, 2014

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

Levine, I.N., **Molecular Spectroscopy**, 1st ed., John Wiley & Sons, 1975

Banwell, C. N., **Fundamentals of Molecular Spectroscopy**, 4th, McGraw-Hill, 1994

Requena, A. ; Zúñiga, J., **Espectroscopía**, 1, Pearson, 2004

Gil Criado, M.; Núñez Barriocanal, J.L., **Espectroscopía Molecular**, 1, Garceta, 2018

Bernath, P.J., **Spectra of Atoms and Molecules**, 4th, Oxford University Press, 2020

Atkins, P. W. ; Friedman, R., **Molecular Quantum Mechanics**, 4th ed., Oxford University Press, 2005

Atkins, P. W., **Quanta : a handbook of concepts**, 2nd ed., Oxford University Press, 1991

Recommendations

Subjects that are recommended to be taken simultaneously

Physical Chemistry V: Chemical Kinetics/V11G201V01308

Subjects that it is recommended to have taken before

Physical chemistry I: Chemical thermodynamics/V11G201V01203