CHEM 550: Modern Molecular Spectroscopy – Part I.
Spring 2011

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Office Hours Whenever you can find me in the office, or make appointment

Lectures Tue, Thu 9:30-11:00 am, SSC 604

Texts Recommended references:
S. Mukamel "*Principles of Nonlinear Optical Spectroscopy*", (Oxford University Press, 1995).
D. Tannor "*Introduction to Quantum Mechanics: A Time-Dependent Approach*"
Y. R. Shen "*The Principles of Nonlinear Optics*"
R. Boyd "*Nonlinear Optics*"
J. I. Steinfeld "*Molecules and Radiation*"
J.L McHale "*Molecular Spectroscopy*", First Edition (Prentice Hall, 1999);
B. J. Berne, R. Pecora "*Dynamic Light Scattering*"
J.-C. Diels, W. Rudolph "*Ultrashort Laser Pulse Phenomena*"

Course outline This course is an introduction to the fundamental description of modern condensed-phase optical spectroscopy. The main goal of molecular spectroscopy is to probe structure and complex dynamics of molecular systems interacting with their environment. The relation between the spectroscopic signals and the underlying molecular dynamics is rarely straightforward, especially in the condensed phase (molecules in solution, biological systems, electronic materials, etc.). This makes interpretation of experimentally measured spectroscopic signals a challenging and nontrivial task. The art of spectroscopy is the ability to understand this link and to choose adequate spectroscopic techniques to study specific dynamical phenomena. The emphasis will be on the time-domain nonlinear spectroscopy that encompasses a rich variety of techniques capable of addressing different aspects of molecular dynamical phenomena.
In this course, we will stay within the semi-classical description of spectroscopy, where the light-matter interactions are described by classical electromagnetic theory within the electric dipole approximation, but the matter is treated quantum-mechanically. We will consider the time-dependent quantum mechanics in Hilbert (wavefunction) and Liouville (density operator) spaces. The general formalism of linear and nonlinear optical susceptibilities will be derived. Calculation of spectroscopic signals will be based on a unified language of quantum Liouville-space (density matrix) dynamics of the molecular system and the time correlation functions of the transition dipole. Interactions with the condensed-phase environment will be treated using the reduced density matrix description. This general approach

will be used to provide a unified description of various linear and nonlinear (3- and 4-wave mixing) spectroscopic techniques, including absorption, fluorescence, resonant and nonresonant Raman, pump-probe, hole burning, photon echo, 2D correlation spectroscopy, 2-photon absorption, and sum-frequency generation.

Tentative schedule of lectures

Week	Date	Topic	Reading assignment
1	1/11	Time-dependent quantum mechanics in Hilbert space: T.D. Schrodinger equation. The T.D. coupled two-state problem – exact solution. Degenerate vs. nondegenerate case. Oscillatory coupling. Rabi frequency and Rabi oscillations (optical nutation).	
	1/13	T.D. perturbation theory. Oscillatory perturbations. Fermi's Golden Rule.	
2	1/18	Overview of Spectroscopy. Semi-classical description of light-matter interactions. Multipolar expansion and the electric dipole approximation. Spectroscopic signals as optical fields emitted by oscillating polarization in a sample. Transition dipole moment. Symmetry and selection rules. Types of spectroscopic transitions: electronic, vibrational, and rotational. Resonant versus non-resonant transitions.	
	1/20	Expansion of the induced polarization in a sample in powers of the applied optical (laser) field: linear and nonlinear optical susceptibilities. Frequency- and time-domain description. Spectral densities. Tensorial nature of the susceptibilities. Kleinman symmetry.	
3	1/25	Optical linear response. Absorption of light – derivation via $P^{(1)}$ and Maxwell's equations. Generalized linear response theory. The causality principle and Kramers-Kronig relations.	
	1/27	Quantum dynamics in Hilbert space. Time evolution operator. Dyson series and time-ordered exponentials.	
4	2/1	Heisenberg, Schrödinger, and interaction representations.	
	2/3	Density operator.	
5	2/8	Quantum dynamics in Liouville space.	
	2/10	Calculation of linear and nonlinear optical response functions (susceptibilities).	
6	2/15	Description of nonlinear spectroscopy experiments: Double-sided Feynman diagrams and energy level diagrams.	
	2/17	Time-correlation functions (TCF).	
7	2/22	Irreversible relaxation by coupling to continuum. Two-level system revisited: Optical Bloch equations. Dephasing and population relaxation. Linear response for an ensemble of TLS with relaxation.	
	2/24	Spectroscopic line shapes. Homogeneous and inhomogeneous broadening.	
8	3/1	Hole burning and photon echo experiments. Spectral diffusion and motional narrowing.	
	3/3	Coupling between modes. Multidimensional (2D) correlation spectroscopy.	

9	3/8		
	3/10		
	3/14-3/19	Spring Break	
10	3/22		
	3/24		
11	3/29		
	3/31		
12	4/5		
	4/7		
13	4/12		
	4/14		
14	4/19		
	4/21		
15	4/26		
	4/28		