

## Modern Spectroscopy: a graduate course.

### Chapter 0. Introduction

#### 0.1 The spectroscopy paradigm

Spectroscopy, generally speaking, is a way to study matter (structure and dynamics) using electromagnetic field *as an interrogation tool*. This strategy works because of the interactions between the charges (matter) and electromagnetic (EM) field. In the classical picture, EM field perturbs the trajectories of the charged particles (e.g., electrons and nuclei), which leads to accelerated motion of charged particles, which in turn results in emission of EM radiation that can be detected experimentally. Some information about the motion (dynamics) of the electrons, atoms, and molecules can therefore be obtained by measuring the resulting EM radiation (signals field) as a function of the input perturbing EM field. Note that the more parameters characterize the input and output field, the more information about the molecular system can be extracted from the measurement, at least in principle. A continuous wave (cw) input field has three basic characteristics: its frequency, amplitude, and polarization. Using pulsed fields adds a few more parameters: the pulse width and chirp (i.e., how the frequency content of the EM field changes with time under the pulse envelope). Finally, using a sequence of pulses gives more parameters – time delays between pulses – which, as we shall see, can be very informative about the microscopic dynamics. In general, the polarization state of the input/signal EM fields (in the lab frame) carries information on the instantaneous orientation of the molecules with respect to the lab frame, whereas parameters describing frequencies and/or time dependence of the EM fields reflect the dynamics of the charged particles.

Using the full quantum mechanical description for both the matter and the EM field, the language and concepts are different, but the overall scheme is the same: the EM field interacts with the system of charged particles, perturbing their motion, which in turn leads to detectable changes in the EM field.

In spectroscopic measurement, a light source (a lamp, glowbar, laser, or a collection of lasers) is used to create a controlled input EM field that perturbs the sample under investigation, ‘kicking’ it out of its equilibrium state. In the semiclassical electric dipole approximation assumed in this course (discussed in Chapters 1 and 2), this creates time-dependent polarization  $\vec{P}(t)$  in the sample. This polarization  $\vec{P}(t)$  in turn results in radiation of a signal EM field by the sample, which is registered by a detector. The main goal of spectroscopy is to “decode” thus recorded spectroscopic signals, in order to obtain information about the structure and complex dynamics of the atomic or molecular system, e.g. a molecule in a condensed phase interacting with its environment. The relation between the signals and the underlying molecular dynamics is rarely straightforward, especially in the condensed phase (solids, glasses, molecules in solutions and at interfaces, 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 the most adequate spectroscopic techniques to study specific dynamical phenomena.

Because of the aforementioned difficulty in interpreting the spectroscopic data in terms of the molecular structure and dynamics, modern spectroscopy is a 50-50 mix of experimental and theoretical effort.

## 0.2 The relation between Spectroscopy and Optics

Optics and Spectroscopy are related areas, since they both study light-matter interactions. However, there is a conceptual difference in the approach. In optics, *materials are used to create and manipulate optical fields* with desired properties – e.g., for light sources, optical data storage, optical telecommunications, etc. In contrast, a spectroscopist *uses optical fields to learn about the properties of matter*.

In optics, the relationship between the EM fields applied to the material and the material's response (the time-dependent polarization) is described by phenomenological optical susceptibilities  $\chi^{(n)}$  (linear for  $n=1$  and  $n^{\text{th}}$  order nonlinear). These are considered “material properties” which are assumed to be known (e.g., measured previously) and are in themselves of no interest. They are used to solve Maxwell equations and calculate the EM field propagating through optical elements.

In spectroscopy, researchers try to *measure* these optical susceptibilities  $\chi^{(n)}$  and *interpret* them in terms of the underlying microscopic dynamics (e.g., photodynamics of an excited electronic state, vibrational relaxation and/or dephasing dynamics, electron or proton transfer, orientational dynamics, decoherence, etc.). Such microscopic processes usually require quantum-mechanical description. Therefore, spectroscopy necessarily involves quantum dynamics as the basis for interpretation of the measurements.

There are a number of excellent texts on linear and nonlinear optics (e.g., *Principles of Optics* by M. Born and E. Wolf, *Nonlinear Optics* by N. Bloembergen; *Nonlinear Optics* by R. Boyd; *The Principles of Nonlinear Optics* by Y. R. Shen). In comparison, there are relatively few modern texts on the nonlinear optical spectroscopy, other than the superb and comprehensive book by S. Mukamel *Principles of Nonlinear Optical Spectroscopy*. However, due to its rigorous treatment (which makes it mathematically heavy by necessity) and breadth of coverage, it is difficult to use in a one semester course.

## 03. The general scheme

The art of spectroscopy is in choosing specific spectroscopic technique to study specific dynamical phenomena. We outline the following steps in the design of a spectroscopic measurement and interpretation of spectroscopic signals:

- (i) By studying the light-matter interactions, the signals can be related to spectroscopic response functions  $R^{(n)}$  (linear for  $n=1$  and  $n^{\text{th}}$  order nonlinear), or, equivalently, optical susceptibilities  $\chi^{(n)}$ .
- (ii)  $R^{(n)}$  and  $\chi^{(n)}$  are further expressed via time-correlation functions of the polarization  $\vec{P}(t)$ . These time-correlation functions are computed within the general theoretical framework of quantum dynamics of the material system alone, uncoupled from the EM field.
- (iii) Several relatively simple yet adequate models exist that describe the molecular dynamics in the condensed phase. These describe the basic processes in the condensed phase such as decoherence, relaxation, and energy transfer, and allow calculation of the response functions and their

interpretation in terms of the underlying microscopic dynamics (e.g., vibrational relaxation model that yields a vibrational population and dephasing lifetimes).

- (iv) The analysis of the spectroscopic signals outlined above can be used to select the spectroscopic technique most appropriate for the dynamical process one is interested in studying (or design a new technique to answer a specific question about the dynamics). That is, the information content of the chosen technique must match the questions that we are trying to answer about the system.

#### 0.4 The scope of this course

This course is an introduction to the fundamentals of modern optical spectroscopy, in particular linear and nonlinear optical spectroscopy as applied to condensed phase systems. It is intended as a supplement – either a follow-up or a parallel course, but not a replacement – to a more traditional “gas-phase” spectroscopy course. Spectroscopic issues important for isolated (gas phase) atoms and molecules, such as angular momentum, point group symmetry, stationary quantum states of atoms and molecules, and various approximations for atomic/molecular Hamiltonians, etc., are not considered in this course. There are a number of excellent texts on the gas-phase spectroscopy (e.g., the classic *Molecular Spectroscopy* by G. Herzberg, *Angular Momentum* by R. Zare, *Molecules and Radiation* by J. Steinfeld, *Fundamentals of Molecular Spectroscopy* by W. S. Struve, etc.).

The emphasis here is placed on the *time-domain description* of the spectroscopic processes, which provides an intuitive and unified framework for a variety of linear and nonlinear modern spectroscopic techniques, including absorption, fluorescence, resonant and nonresonant Raman, pump-probe, transient grating, photon echoes, 2D-IR, and surface-selective even-order techniques such as sum-frequency and second-harmonic generation, which are capable of addressing different aspects of molecular dynamical phenomena.

We will begin (Chapter 1) by considering the semi-classical picture for the light-matter interaction and the electric dipole approximation. This will allow us to write the light-matter interaction Hamiltonian that perturbs the motion of the system. It is this perturbation that set in motion the nonequilibrium dynamics of the charged particles in the system, causes the time-dependent polarization in the sample that gives rise to the spectroscopic signal, and thus allows us to learn about the dynamics. In this chapter, we will also consider the general phenomenology of describing the response of a material system to external perturbation through the linear and nonlinear response function formalism, and talk about the general properties of the optical response functions such as causality and Kramers-Kronig relations, and their tensorial nature.

We will then consider (Chapter 2) the quantum dynamics in the Hilbert space (where the quantum system is described by a wavefunction) and use the time-dependent perturbation theory to find the time-evolution of the system under a time-dependent perturbation. This will then be used to calculate the expectation value of the polarization and thus the spectroscopic signal. We will show how the linear and nonlinear optical response functions are connected to the different order terms in the perturbative series for the quantum evolution, in powers of applied perturbation.

In Chapter 3, we will consider an alternative description of quantum dynamics, describing evolution of the density operator in Liouville space (instead of the wavefunction in Hilbert space). This will allow us to treat dynamics of statistical ensembles of quantum systems, such as an ensemble of atoms or molecules in a macroscopic sample. It will also allow simplified description of the molecules' interactions with their condensed-phase environment using the reduced density matrix. Another advantage of working in Liouville space is the use of two-sided Feynman diagrams, which, along with the energy level diagrams, connect the response functions with the frequencies and wavevectors of the interacting (incoming and outgoing) light fields. For coherent nonlinear optical spectroscopy, this allows one to easily predict the frequency and direction of the various nonlinear signals (based on the energy conservation and the phase-matching conditions) and which terms in the perturbative series contribute to the response function for that particular signal.

Examples of modern time- and frequency-domain spectroscopies will be considered in Chapter 4 in light of the theory developed in the previous chapters. We will consider some important experimental aspects (such as description of short femtosecond laser pulses and methods of their generation, techniques for detection of optical signals, etc.), but mostly focus on the information content of particular measurements. We will discuss

- (1) Absorption/Fluorescence/spontaneous Raman spectra and line shapes;
- (2) Free Induction Decay (FID) measurements, the total dephasing, and the connection with the absorption line shape;
- (3) Pump-probe spectroscopy using absorption, fluorescence, or Raman for the probe step, and the population relaxation;
- (4) Polarization-selected pump-probe (anisotropy decay) and the orientational dynamics;
- (5) Spectral hole-burning spectroscopy, homogeneous and inhomogeneous broadening, and spectral diffusion;
- (6) Photon echo techniques, line narrowing, and selective elimination of inhomogeneous broadening;
- (7) 2D correlation spectroscopy, measurements of coupling between chromophores, spectral dynamics, and chemical exchange;
- (8) Surface-selective second-order spectroscopy: sum frequency generation (SFG) and second-harmonic generation (SHG), and their information content in terms of the molecular orientation at interfaces.