

Introduction

Spectroscopy comes from the Latin “spectron” for spirit or ghost and the Greek “σκοπεῖν” for to see. These roots are very telling, because in molecular spectroscopy you use light to interrogate matter, but you actually never see the molecules, only their influence on the light. Different spectroscopies give you different perspectives. This indirect contact with the microscopic targets means that the interpretation of spectroscopy in some manner requires a model, whether it is stated or not. Modeling and laboratory practice of spectroscopy are dependent on one another, and therefore a spectroscopy is only as useful as its ability to distinguish different models. The observables that we have to extract microscopic information in traditional spectroscopy are resonance frequencies, spectral amplitudes, and lineshapes. We can imagine studying these spectral features as a function of control variables for the light field (amplitude, frequency, polarization, phase, etc.) or for the sample (for instance a systematic variation of the physical properties of the sample).

In complex systems, those in which there are many interacting degrees of freedom and in which spectra become congested or featureless, the interpretation of traditional spectra is plagued by a number of ambiguities. This is particularly the case for spectroscopy of disordered condensed phases, where spectroscopy is the primary tool for describing molecular structure, interactions and relaxation, kinetics and dynamics, and tremendous challenges exist on understanding the variation and dynamics of molecular structures. This is the reason for using nonlinear spectroscopy, in which multiple light-matter interactions can be used to correlate different spectral features and dissect complex spectra. We can resonantly drive one spectroscopic feature and see how another is influenced, or we can introduce time delays to see how properties change with time.

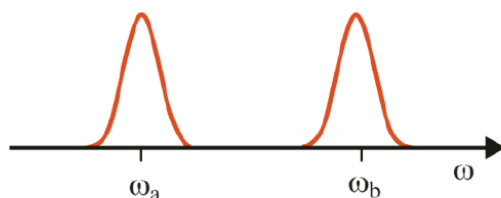


figure 1: graph of spectral features over time

Absorption or emission spectroscopies are referred to as linear spectroscopy, because they involve a weak light-matter interaction with one primary incident radiation field, and are typically presented through a single frequency axis. The ambiguities that arise when interpreting linear spectroscopy can be illustrated through two examples:

1) Absorption spectrum with two peaks. Do these resonance arise from different, non-interacting molecules, or are these coupled quantum states of the same molecule? (One cannot resolve couplings or spectral correlations directly).

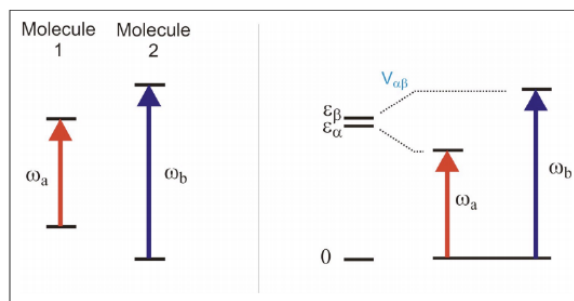


Figure 2 absorption spectrums for two elements

2) Broad lineshapes. Can you distinguish whether it is a homogeneous lineshape broadened by fast irreversible relaxation or an inhomogeneous lineshape arising from a static distribution of different frequencies? (Linear spectra cannot uniquely interpret line-

broadening mechanism, or decompose heterogeneous behavior in the sample).

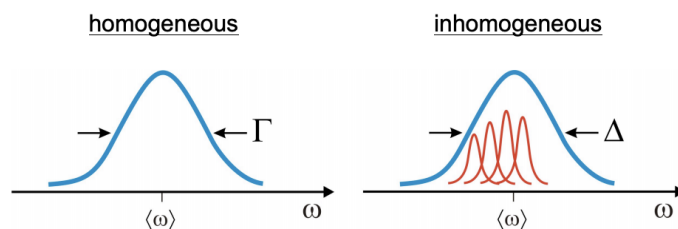


Figure 3 linear Spectra of molecules

In the end effect linear spectroscopy does not offer systematic ways of attacking these types of problems. It also has little ability to interpret dynamics and relaxation. These issues take on more urgency in the condensed phase, when lineshapes become broad and spectra are congested. Nonlinear spectroscopy provides a way of resolving these scenarios because it uses multiple light fields with independent control over frequency or time-ordering in order to probe correlations between different spectral features. For instance, the above examples could be interpreted with the use of a double-resonance experiment that reveals how excitation at one frequency ω_1 influences absorption at another frequency ω_2 .