Chapter 1. Introduction

What is spectroscopy?

Study of matter through interaction of electromagnetic radiation with matter. The strength of radiation can be minimized to affect the matter as little as possible (Exception: strong field spectroscopy or quantum control). In most cases, time dependent perturbation theory in Quantum Mechanics provides sufficient theoretical description.

Spectroscopy provides information on energy levels

Due to energy conservation, the following relation holds:

$$h\nu_i + E_i = h\nu_f + E_f$$

absent for emission ↑ ↑ absent for absorption

Spectroscopy gives the difference of energy levels only. Thus, its correct interpretation requires some background quantum mechanical information on the matter or molecule (This becomes simplified if we know that the initial or final state corresponds to the ground state of the molecule).

Selection Rules are important for assigning the energy levels.

Photon is a boson with spin 1. When it is absorbed or emitted, the total angular momentum of matter plus radiation should be conserved. This in general leads to the general selection rule that the total angular momentum quantum number of the matter changes by 1 or remain invariant under special circumstances.

Other symmetry requirements may lead to selection rules specific for each molecule. Group theory is very useful for understanding these selection rules.

Types of Spectroscopy

Type	ν(Hz)	$\tilde{\nu}(\mathrm{cm}^{-1})$	kJ/mol	Transition	Information
Microwave	$10^9 \sim 10^{11}$	$0.03 \sim 3$	4×10^{-4} $\sim 4 \times 10^{-2}$	Rotation (heavy molec.)	Interatom. distances Dipole moments
Far IR	$10^{11} \sim 10^{13}$	$3 - 300$	4×10^{-2} ~ 4	Rotation (light molec.) Bending vibs.	Interatom. distances Force constants
IR	$10^{13} \sim 10^{14}$	$300 \sim 3000$	$4 \sim 40$	Vibrations	Force constants
Raman	$10^{11} \sim 10^{14}$	$3 \sim 3000$	4×10^{-2} ~ 40	same as above	same as above
Visible UV	$10^{14} \sim 10^{16}$	3×10^3 $\sim 3 \times 10^5$	40 ~ 4000	Electronic Transitions	All above Electronic energies Bond dissoc.
Vacuum UV	$> 10^{16}$	$> 3 \times 10^5$	> 4000	Same as above	Same as above

Visible: λ=4,000 -7,000 Å; UV: λ=2,000 -4,000 Å; Vacuum UV: $\lambda < 2,000$ Å

Spectroscopy provides information on the dynamics of molecules

Analysis of vibrational and rotational energy levels, lineshape analysis, and time resolved spectroscopy provides information on the quantum and classical dynamics of the molecule and environments.

Most spectroscopy is a result of interaction between electric field component of radiation and dipole (or transition dipole) moment.

$$\hat{H}_{tot} = \hat{H}_M + \hat{H}'(t)$$

$$\hat{H}'(t) = -\hat{\mathbf{d}} \cdot \mathbf{E}(t)$$

$$\hat{\mathbf{d}} = \hat{\mathbf{d}}_p + \hat{\mathbf{d}}_{ind} = \hat{\mathbf{d}}_p + \hat{\alpha}\mathbf{E}(t)$$