

Spectroscopy

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Spectroscopy

- Spectroscopy is the study of the interaction of radiation and matter.
- It can be used to study atomic and molecular structure, but also to measure thermodynamic state properties and species concentrations.
- There are several forms of spectroscopy including:
 - Absorption, Emission, Fluorescence, and Scattering
- We start with discussing the absorption and emission of radiation.

The Absorption and Emission of Radiation

- At the most basic level spectroscopy is concerned with how light is absorbed or emitted by atoms and molecules.
- Here we explore the Einstein picture.

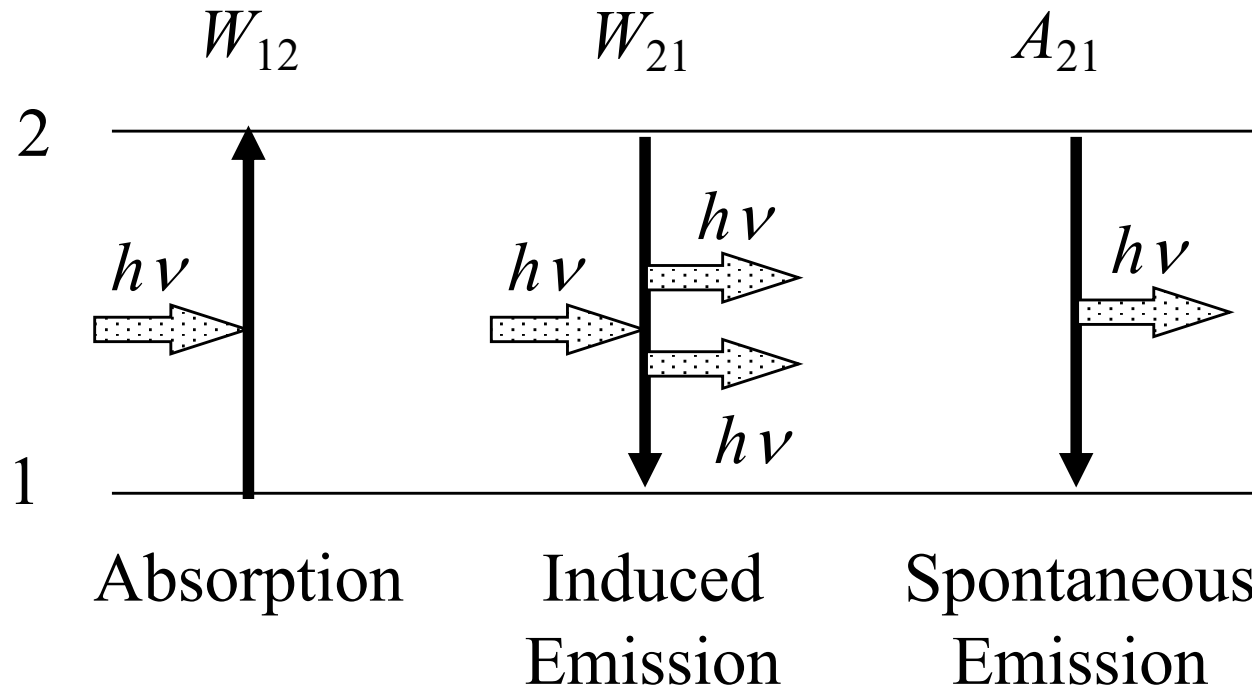
The Einstein Radiative Processes

- In 1916, Einstein published a seminal paper on the subject of the absorption and emission of radiation.
- In the paper, he outlined an extremely simple theory and introduced what are now called the A and B “Einstein Coefficients.”
- Interestingly, he use detailed balance arguments to relate the different coefficients.

Einstein, A. (1916). "Strahlungs-Emission und -Absorption nach der Quantentheorie". Verhandlungen der Deutschen Physikalischen Gesellschaft. **18**: 318–323.



The Einstein Radiative Processes



$$W_{12} = \int_0^{\infty} B_{12} E_{\nu}(\nu) \phi(\nu) d\nu$$

E_{ν} is Spectral Irradiance

$$\frac{A_{ij}}{B_{ij}} = 8\pi h \nu^3 / c^2$$

$$g_i B_{ij} = g_j B_{ji}$$

Transition Probabilities

- The Einstein coefficients can be calculated from the relation

$$B_{ij} = \frac{8\pi^3 R^2}{3ch^2 g_i}$$

- R^2 is the probability for the transition from state i to j and is given by the square of the electric dipole moment

$$R^2 = \left| \int \psi_i \vec{\mu} \psi_j dV \right|^2$$

- where

$$\vec{\mu} = \sum e\vec{r}$$

Oscillator Strength

- Transition probability data is sometimes expressed in terms of the non-dimensional oscillator strength, f_{ij} .
- This is the ratio of the actual transition probability to the transition probability predicted by the classical harmonic oscillator model.

$$f_{ij} = \frac{32R^2\pi^3\epsilon_0 m_e c}{3e^2 h \lambda_m g_i}$$

Data Tabulations

- From Radzig and Smirnov: A coefficient is inverse of lifetime.

Atom or Molecule	Ground State	Excited State	Lifetime (ns)
Na	$3s -^2 S_{1/2}$	$3p(^2 P_{1/2}^0)$	16.4
O	$2p^4 -^3 P_2$	$3s(^1 D_2^0)$	2.0
OH	$X^2\Pi_i$	$A^2\Sigma^+$	0.00069
CH	$X^2\Pi_r$	$A^2\Delta$	0.0005
C_2	$X^1\Sigma_g^+$	$C^1\Pi_g$	0.000031
NO	$X^2\Pi_r$	$B^2\Pi_r$	0.0031