

Advanced radiation and remote sensing

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December 29, 2016

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1 Rotational spectra

This section on absorption is based on a script for a radiation course, written by Björn Martin Sinnhuber.

1.1 Energy states and photons

Absorption and emission of a photon can happen if the internal energy of a molecule changes. The difference in two energy states E and the frequency of the photon ν are connected through the Planck constant h .

$$E_f - E_i = \Delta E = h\nu \quad (1)$$

The transition between different energy levels can be divided into three types, corresponding to different states of the molecule. Each transition type is characteristic for a specific region of the electro-magnetic spectra. One can distinguish changes in a molecule's rotation (microwave), vibration (infrared) and electronic transitions (UV/visible).

Molecules consist of different atoms. There are diatomic molecules with two atoms (O_2 , N_2 , NO , HCl , CO) and polyatomic molecules with three or more atoms (O_3 , NO_2 , CO_2). We will mainly discuss diatomic molecules, because they are easier to understand.

One can distinguish between three types of interaction between a photon and a molecule: absorption, spontaneous emission and stimulated emission. There are three conditions to be fulfilled for a molecule to absorb a photon:

1. The frequency of the photon has to match one of the molecule's energy transitions.

$$\Delta E = h\nu \quad (2)$$

2. The net absorption has to be proportional to the difference of occupation probabilities of states i and f : $p_i - p_f$. Where p_i is given by the Boltzmann distribution (in local thermodynamic equilibrium).

$$p_i = \frac{q_i e^{-E_i/(kT)}}{\sum_{j=1}^{\infty} q_j e^{-E_j/(kT)}} \quad (3)$$

The denominator is often referred to as $Q(T)$. It has various names like total internal partition sum, partition function, or Zustandssumme.

3. Absorption is proportional to the electric dipole matrix element μ_{if} between states i and f .

$$\mu_{if} = \mu \iiint \psi_f^*(x, y, z) \psi_i(x, y, z) dx dy dz \quad (4)$$

Where μ is the magnitude of the dipole operator. μ_{if} is a constant for each transition.

Combining all conditions, one can define the absorption coefficient α .

$$\alpha(\nu) = n \sum_{f,i} S_{fi}(T) \delta(\nu_{fi} - \nu) \quad (5)$$

With number density n , line strength S_{fi} , difference of state energies $h\nu_{fi}$ and Dirac's delta function δ (physical not true, will be replaced later by a so called "line shape" function).

The line strength is different for each transition and defined as follows.

$$S_{fi} = \frac{8\pi^3 \nu_{fi} |\mu_{fi}|^2 q_i}{3hcQ(T)} \left(e^{E_i/(kT)} - e^{E_f/(kT)} \right) \quad (6)$$

Although this equations looks complicated, there is only one true independent variable, the temperature T . All other variables are constants of the transition, or fundamental constants.

Spectral line catalogues are collections of these transition parameters. There is one line in the catalogue for each spectral line (thousands for each molecule). The most well-known is the HITRAN catalogue.

1.2 Rotational transitions

2 Vibrational spectra

3 Line shape

4 Thermal radiation

5 Radiative transfer equation