

Simple Spectrum Simulation

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General Idea:

This small python program has a purpose to simulate simple spectrum. By giving a list of vertical excitation energies E_{0i}^v and oscillation strengths f_{0i} , a spectrum can be obtained by solving this equation:

$$\sigma(E) = 0.619n \sum_i \frac{f_{i0}}{\Gamma_i} e^{-(E-E_i^v+\delta_i)^2/\Gamma_i^2} \quad (1)$$

Where n is the refractive index, Γ_i is the width of band i , δ_i is the energy shift between the vertical excitation and the band maximum.

E is the domain of values, where E_{min} is a minimum value of E , E_{max} is a maximum value of E and dE is a size of the interval

Each parameter has a default value in the program as shown, used in some cases:

Parameters	Unit	Default value
gamma	eV	0.4
delta	eV	0.0
n	-	1.0
Emin	eV	2.0
Emax	eV	10.0
dE	eV	0.1

After execution of the program, a spectrum is obtained by plotting energies (E) given in (eV) $\times \sigma(E)$ with units of absorption cross section $\text{\AA}^2 \cdot \text{mol}^{-1}$.

Theory:

Experimentally, the oscillator strength of an absorption band ε_i is given as:

$$f_{0i} = \frac{10^3 \ln(10) mc}{\pi N_A e^2 n} \int \varepsilon_i(\nu) d(\nu)$$

Where m_e is the mass of the electron, c is the speed of the light, ε_0 is the vacuum permittivity, N_A is the Avogadro's number, and e is the electron charge (CGS units) and ε_i is the molar absorptance.

Integrating over the absorption frequency ν and supposing that the band has a gaussian shape with maximum ε_i^{max} at ν_i^{max} and width γ_i , the integral gives:

$$\int \varepsilon_i(\nu) d(\nu) = \int \varepsilon_i^{max} e^{-(\nu - \nu_i^{max})^2 / \gamma_i^2} = \sqrt{\pi} \varepsilon_i^{max} \gamma_i$$

Thus, the oscillator strength is

$$f_{0i} = \frac{10^3 \ln(10) mc}{\pi N_A e^2 n} \varepsilon_i^{max} \gamma_i$$

Following these definitions, the total simulated spectrum can be written as the sum of all bands

$$\begin{aligned} \varepsilon(\nu) &= \sum_i \varepsilon_i(\nu) \\ &= \sum_i \varepsilon_i^{max} e^{-(\nu - \nu_i^{max})^2 / \gamma_i^2} \\ &= \frac{\sqrt{\pi} N_A e^2 n}{10^3 \ln(10) mc} \sum_i \frac{f_{0i}}{\gamma_i} e^{-(\nu - \nu_i^{max})^2 / \gamma_i^2} \end{aligned}$$

The absorption cross section is given by

$$\begin{aligned} \sigma(\nu) &= \ln(10) \frac{10^3}{N_A} \varepsilon(\nu) \\ &= \frac{\sqrt{\pi} e^2 n}{mc} \sum_i \frac{f_{0i}}{\gamma_i} e^{-(\nu - \nu_i^{max})^2 / \gamma_i^2} \end{aligned}$$

It is convenient to express the absorption cross section in terms of the absorption energy

$$\sigma(E) = \frac{2\pi^{2/3} \hbar e^2 n}{mc} \sum_i \frac{f_{0i}}{\Gamma_i} e^{-(E-E_i^{max})^2/\Gamma_i^2} \quad (2)$$

where Γ_i is the energy width of the band, E_i^{max} its energy maximum and \hbar is the reduce Planck constant

Usually, the energy of the band maximum E_i^{max} is red-shifted in relation to the vertical excitation E_i^ν . Thus, an energy-shift parameter δ_i is added to account for its effect expressed as:

$$E_i^{max} = E_i^\nu - \delta_i$$

Replacing this equation in Eq (2) gives (in CGS unit):

$$\sigma(E) = \frac{2\pi^{2/3} \hbar e^2 n}{mc} \sum_i \frac{f_{0i}}{\Gamma_i} e^{-(E-E_i^{max} + \delta_i)^2/\Gamma_i^2}$$

For energies in eV and absorption cross section in $\text{\AA}^2 \cdot \text{mol}^{-1}$, it gives the main equation (1)

How to run it?

Input:

1-An input file called “inp.py” is prepared containing all the parameters:
(gamma, delta, n, Emin, Emax, dE)

Each parameter has a default value as shown:

Parameters	Unit	Default value
gamma	eV	0.4
delta	eV	0.0
n	-	1.0
Emin	eV	2.0
Emax	eV	10.0
dE	eV	0.1

Where Emin is the minimum value of E
Emax is the maximum value of E
dE is the interval size of E

Two conditions are applied for all parameter:

- If the parameter exists in the inp.py file, the value is used for the excitation energies.
- If the parameter does not exist in the file, the default value is used.

For gamma:

- If the parameter exists and the value > 0 , this value is used for all the bands
- If the parameter exists and the value $= 0$, gamma should be read from a “gamma.dat” file where it contains a list of values corresponding to each excitation energy.

For delta:

- If the parameter exists and the value $> \text{or} = 0$, this value is used for all the bands
- If the parameter exists and the value $= -1$, delta should be read from a “delta.dat” file where it contains a list of values corresponding to each excitation energy.

2-energies_forces.py file is prepared containing two lists, E_i^v and f_i

3-Run the program by: python spectra_simulation.py

Output:

1-After execution , an “Output.dat” file is created containing four columns:
(E(eV) $\lambda(\text{nm})$ $\sigma(\text{\AA}^2.\text{mol}^{-1})$ $\epsilon(\text{M}^{-1}\text{cm}^{-1})$)

Where:

λ is the wavenumber corresponding to $(1240/E)$

ϵ is the molar absorbance or extinction coefficient ($\epsilon = \sigma/3.82353 \times 10^{-5}$)

2- To plot $\sigma(E) \times E$:

- a) Install “matplotlib” library and uncomment the plotting part (last four lines in the code)
- b) Use a graphical program as gnuplot or Excel