Absorption and Emission coefficients

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There are lots of different ways to define absorption and emission coefficients. Here I describe one way which is simple to relate to experimental parameters and detail how it can be related to other definitions used in previous simulations/papers/reports. To me, the conceptual difficulty arises when defining constants in the absence of spatial resolution and then trying to later introduce spatial resolution. Therefore, I start from the spatially resolved case.

1 Total absorption

The total absorption rate of a single photon is trivial to find, from dimensionful experimental measurements of absorption of Rhodamine 6G. More spatially focussed photon modes interact more strongly with fewer dye molecules such that the only relevant adjustable parameter for absorption rate per photon is the dye concentration in number$/m^3$.

The total rate of absorption rate per photon from mode i is therefore given by:

$$A_i = c^* \times \rho \times \sigma(\lambda_i) \tag{1}$$

where c^* is the speed of light in the medium, ρ is the 3D number density of molecules, and $\sigma(\lambda_i)$ is the absorption cross section of the dye, for which experimental data is available.

I vote in favour of taking these values A_i as the standard coefficients which can be compared across different simulations, insensitive of many of the other simulations parameters. With knowledge of the dye concentration, these can be compared to experiment.

2 Kennard-Stepanov relation

We make the assumption that the Kennard-Stepanov relation holds, meaning that the emission rate from a single excited dye molecule is related to the absorption rate of a single photon by a single molecule via a Boltzmann factor.

3 Spatial resolution

We discretise the molecules into groups of $n_{mol,j}$ molecules at different positions, j. We know the total rate of absorption of photons from mode i as described above. The rate of absorption per photon from mode i by molecules in group j,

$A_{i,j}$ is related to A_i via the intensity of the photon wavefunction of mode i at position j.

$$A_{i,j} = A_i \times g_{ij} \tag{2}$$

where

$$g_{ij} = \frac{|\psi_i(r_j)|^2}{\sum_k |\psi_i(r_k)|^2} \tag{3}$$

where the normalisation ensures we retain the correct total rate of absorption from mode i.

The rate of emission per molecule into mode i from group j is therefore given by

$$E_{i,j} = \frac{A_{i,j}}{n_{mol,j}} \times \exp\{-\hbar\Delta/k_B T\} \tag{4}$$

4 Putting into equations of motion

In order to more easily see the simplest way to define our coefficients, it makes sense to look at our equations of motion:

$$\dot{n}_i = -\kappa n - \sum_j A_{i,j} n_i (1 - f_j) + \sum_j E_{i,j} n_{mol,j} f_j (n_i + 1) \tag{5}$$

$$\dot{m}_j = \Gamma_\uparrow n_{mol,j}(1 - f_j) - \Gamma_\downarrow m_j + \sum_i A_{i,j}(1 - f_j) n_i - \sum_i E_{i,j} m_j (n_i + 1) \tag{6}$$

where I have introduced the values f_j and m_j, the fraction of excited molecules and the number of excited molecules in group j respectively ($m_j = f_j \times n_{mol,j}$ – a redundancy to be resolved later). f_j is used to modify the absorption rate into group j by the factor (1-f_j). $\Gamma_\uparrow$ is the pump rate per ground state molecule, and $\Gamma_\downarrow$ is the rate of spontaneous emission into free space per excited molecule.

Some rearrangement and substitution gives:

$$\dot{n}_i = -\kappa n - \sum_j A_i g_{ij} n_i (1 - f_j) + \sum_j \frac{A_i g_{ij}}{n_{mol,j}} \times \exp\{-\hbar\Delta/k_B T\} n_{mol,j} f_j (n_i + 1) \tag{7}$$

$$\dot{m}_j = \Gamma_\uparrow n_{mol,j}(1 - f_j) - \Gamma_\downarrow m_j + \sum_i A_i g_{ij}(1 - f_j) n_i - \sum_i \frac{A_i g_{ij}}{n_{mol,j}} \times \exp\{-\hbar\Delta/k_B T\} m_j (n_i + 1) \tag{8}$$

It now appears to be helpful to define

$$E_i = A_i \exp\{-\hbar\Delta/k_B T\} \tag{9}$$

where E_i is the rate of emission into mode i.[1]

This then gives

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[1] If the rate of emission from each molecule is related to the rate of absorption by that molecule by a Boltzmann factor, then it follows that the total rate of absorption from a mode is related to the total rate of emission into that mode by a Boltzmann factor.

$$\dot{n}_i = -\kappa n - \sum_j A_i g_{ij} n_i (1 - f_j) + \sum_j E_i g_{ij} f_j (n_i + 1) \tag{10}$$

$$\dot{m}_j = \Gamma_\uparrow n_{mol,j}(1-f_j) - \Gamma_\downarrow m_j + \sum_i A_i g_{ij}(1-f_j)n_i - \sum_i \frac{E_i g_{ij}}{n_{mol,j}} m_j(n_i+1) \tag{11}$$

$$\dot{f}_j = \Gamma_\uparrow (1-f_j) - \Gamma_\downarrow f_j + \sum_i \frac{A_i g_{ij}}{n_{mol,j}}(1-f_j)n_i - \sum_i \frac{E_i g_{ij}}{n_{mol,j}} f_j(n_i+1) \tag{12}$$

5 Comparison to other definitions

I compare the definitions above to other definitions used in photon BEC theory

5.1 Kirton and Keeling

In doing this comparison to Kirton and Keeling, I have skipped over all the master equation parts and jumped straight to the rate equation part (which I know how to read off more easily).

2015: Non spatially resolved. "Absorption rate from cavity mode m" $\Gamma(\delta_m)$. In words, it looks the same as what I have, but should read in 'per molecule' given the equations in the paper. This leads to:

$$\frac{\partial n_m}{\partial t} = \ldots - N\Gamma(\delta_m)n_m(1-p_e) \tag{13}$$

which means

$$\Gamma_{15}(\delta_m) = c^* \times \rho_{3D} \times \sigma(\delta_m)/N \tag{14}$$

where the '15' subscript refers to the 2015 paper.

2016: Continuous excitation $f(\mathbf{r})$. ρ_0 appears. Units of l_{HO}^{-2}.

$$\frac{\partial n_m}{\partial t} = \ldots - \rho_0 \Gamma(\delta_m)(1-f_m)n_m \tag{15}$$

$$f_m = \int d^d\mathbf{r} f(\mathbf{r})|\psi_m(\mathbf{r})|^2 \tag{16}$$

What are the units of ψ? If l_{HO}^{-2} then:

$$\int d^d\mathbf{r} \rho_0 |\psi_m(\mathbf{r})|^2 = \rho_0 \tag{17}$$

If dimensionless, then

$$\int d^d\mathbf{r} \rho_0 |\psi_m(\mathbf{r})|^2 = N_{eff} \tag{18}$$

where N_{eff} is the effective number of dye molecules.[2]

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[2]Note that some neat/annoying things happen (depending on your perspective) when using units of l`HO, such as the effective number of dye molecules having the same numerical value as the 2D dye concentration (with different units of course).

However, they say that "Similarly, since $\Gamma(\pm\delta)$ are multiplied by ρ_0 or $|\psi_m(\mathbf{r})|^2$, this means Γ_{max} also has dimensions $[T]^{-1}[L]^d$." This, along with equation 15 implies that ψ has dimensions of l_{HO}^{-2}.

If $f(\mathbf{r})$ is constant, then $f_m = p_e$, and we recover the 2015 equation but with a factor of ρ_0. This then gives

$$\Gamma_{16}(\delta_m) = \frac{c^* \times \sigma(\delta_m)}{d_0} \tag{19}$$

where d_0 is the cavity length.

In both cases, the emission rate is the emission rate per molecule, related to the absorption rate per molecule exactly by a Boltzmann factor (in fact, they don't define two separate variables, instead have $\Gamma(\delta_m)$ and $\Gamma(-\delta_m)$).

These definitions make relating the absorption and emission rates by a Boltzmann factor easy, but make connection to real experimental parameters slightly harder.

5.2 Hesten simulations

$$\frac{\partial n_m}{\partial t} = ... - n_m Ab_m \sum_j g_{mj} n_{mol,j}(1 - f_j) \tag{20}$$

where g_{mj} is a Hermite Gauss squared multiplied by the size of reservoir j. If f_j and $n_{mol,j}$ are constant, then we have

$$\frac{\partial n_m}{\partial t} = ... - n_m Ab_m n_{mol,j}(1 - f) \tag{21}$$

the same as equation 13. *i.e.*

$$Ab_{HH}(\delta_m) = c^* \times \rho_{3D} \times \sigma(\delta_m)/n_{mol,j} \tag{22}$$

5.3 Nyman

Parameters used by Rob for the simulations in the Nature Physics paper. Takes $cfg["peak_X sectn"] = 2.45e - 20$. Zenodo says the peak should be $1.4e - 20 m^2$. Not sure why the discrepancy. Then convert to $cfg["Gamma\_max\_m^2\_Hz"]$ using equation 19. Then simply convert to units of l_{HO}^2. Unsurprisingly, Rob implemented a wholly sensible method for linking experimental parameters with the formalism from the Kirton and Keeling papers. Not sure where the $2.45e-20$ max cross-section came from though...

5.4 Maximum values

For reference, derived values based on 2.4 mMol and dye mirror separation of $0.8\mu m$. We have 1.4e6 molecules.

Maximum absorption cross-section: 1.4 e-20 m^2

Maximum absorption rate BTW: 4.2 e12 s^{-1}

Maximum absorption rate KK15: 2.9 e6 $s^{-1}(mol^{-1})$

Maximum absorption rate KK16: 3.6 e-6 $s^{-1}m^2$

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Maximum absorption rate KK_16_LHO: 2.9 e6 $s^{-1}l_{HO}^2$
Maximum absorption rate HH thesis: 1.2 e-9 κl_{HO}^2
Maximum HH simulation: gmax=1e-12

5.5 Ben's Conclusion

The absorption cross-section as a function of wavelength or detuning is really a property of the dye molecules, so makes sense as the common starting point. However, it does sometimes make sense to build in some experimental parameters such as concentration and cavity length to our defined absorption and emission rates so that theorists don't need to worry about dirty experimental things like cavity length and dye concentration. To me, it seems odd to build the cavity length into our rates, but not the dye concentration.

5.5.1 Why it took so long

My original approach when trying to determine the correct absorption and emission coefficients corresponding to the experiment had been to start from the non-spatially resolved picture and then later generalise to the spatially resolved picture. This lead to the following conceptual problem:

1. Define an emission function $\Gamma(-\delta_m)$ for every detuning.

2. Consider a cavity with 10 modes, so that the total emission rate of a given molecule is:
$$Em_{tot}^{(1)} = \sum_m^{10} \Gamma(-\delta_m) \tag{23}$$

3. Now consider a cavity with 1/100 of the mode spacing of the first and hence 100 times as many relevant cavity modes as the first. Total emission rate of a molecule is now:
$$Em_{tot}^{(2)} = \sum_m^{1000} \Gamma(-\delta_m) \sim 100 \times Em_{tot}^{(1)} \tag{24}$$

   We should not be able to make the emission rate of a given molecule arbitrarily large by adding more cavity modes.

The problem resolves itself straightforwardly when we move to the spatially resolved picture. This then gives

$$Em_{tot}^{(1)} = \sum_m^{10} \Gamma(-\delta_m) \left|\psi_m^{(1)}(\mathbf{r})\right|^2 \tag{25}$$

$$Em_{tot}^{(2)} = \sum_m^{1000} \Gamma(-\delta_m) \left|\psi_m^{(2)}(\mathbf{r})\right|^2 \tag{26}$$

Cavities with closer spaced modes in energy also have a larger spatial extent meaning

$$\left|\psi_m^{(2)}(\mathbf{r})\right|^2 \sim \left|\psi_m^{(1)}(\mathbf{r})\right|^2/100 \tag{27}$$

giving

$$Em_{tot}^{(1)} \sim Em_{tot}^{(2)} \tag{28}$$

In fact, this does all still work out in the Kirton and Keeling picture. What we need to do when adding more cavity modes is to update the molecular density in units of l_{HO}.

energy level	Ab_{BTW} s^{-1}	Ab_{KK15} $s^{-1}(mol^{-1})$	Ab_{KK16} $s^{-1}m^2$	$Ab_{KK16,LHO}$ $s^{-1}l_{HO}^2$	Ab_{RAN} $s^{-1}l_{HO}^2$	$Ab_{HH,sim}$ s^{-1}
0	1.7e10	110	7.8e-9	6.3e3	1.0e4	3.9e-3
1	2.1e10	135	9.9e-9	7.7e3	1.4e4	5.4e-3
2	2.8e10	180	1.3e-8	1.0e4	1.9e4	7.4e-3
3	3.7e10	243	1.7e-8	1.4e4	2.6e4	1.0e-2
4	4.9e10	315	2.2e-8	1.8e4	3.6e4	1.4e-2
5	6.5e10	419	3.8e-8	2.4e4		2.0e-2

Some typical figures, all based on 580 nm cutoff, 1.6 nm or 1.7 THz mode spacing. RAN values have a different maximum absorption cross-section. Where explicitly needed, a mirror dye separation of 0.8 μm and dye concentration of 2.4 mMol were used. HH values are based off the gmax value of 1e-12 encoded in m_2018_04_19_functions, but should be the same as Ab_{KK15}. gmax will be a function of dye concentration and number of molecules (which are dependent variables in units of l_{HO}).