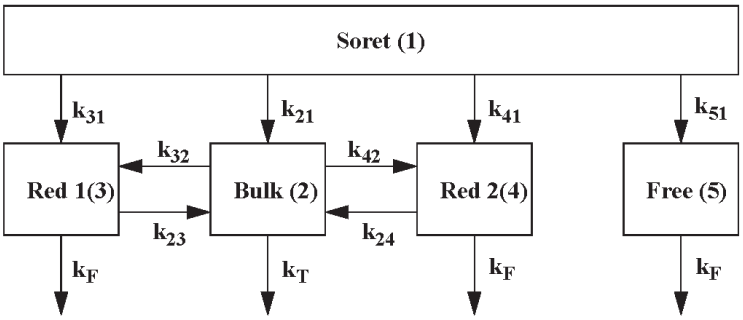
Cyanobacterial PSI compartmental model



Compartmental model describing the kinetics of cyanobacterial PS I core particles upon excitation at 400 nm.

The concentrations of all compartments are collated in a vector $c(t) = \begin{bmatrix} c_1(t) & c_2(t) & \dots & c_{n_{comp}}(t) \end{bmatrix}^T = \begin{bmatrix} S(t) & B(t) & R_1(t) & R_2(t) & F(t) \end{bmatrix}^T$ (where S, B, R_1, R_2 and F stand for Soret, Bulk, Red1, Red2, and Free, respectively) which obeys the differential equation

$$\frac{d}{dt}c(t) = Kc(t) + j(t)$$

where the transfer matrix *K* contains off-diagonal elements k_{pq}, representing the microscopic rate constant to compartment *p* from compartment *q*. The diagonal elements contain the total decay rates of each compartment. The input to the compartments is $j(t) = i(t)\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \end{bmatrix}^T$. Using the k_{tofrom} notation, the K matrix reads:

$$K = \begin{bmatrix} -(k_{21}+k_{31}+k_{41}+k_{51}) & & & & \\ k_{21} & -(k_{T}+k_{32}+k_{42}) & k_{23} & k_{24} & \\ k_{31} & k_{32} & -(k_{F}+k_{23}) & & \\ k_{41} & k_{42} & & -(k_{F}+k_{24}) & \\ k_{51} & & & & -k_F \end{bmatrix}$$

Note that charge separation starts from the PSI reaction center which is considered to be a subset of the bulk Chl, with an effective rate constant k_T where the T stands for photochemical Trapping of the excitation energy. The natural decay rate of free Chl is k_F where the F stands for Fluorescence, although part of the decay is of course nonradiative. Typically, the natural Chl lifetime (the reciprocal of k_F) is several ns. The trapping lifetime (the reciprocal of k_T) in a PSI core with about 90 bulk Chl is typically 18 ps. Therefore the loss through fluorescence is less than 1%, and the efficiency of the PSI reaction center is better than 99%.

Reduced K matrix

In Glotaran, only the net loss rates have to be specified on the diagonal, without a minus sign. The reduced K matrix thus reads:

$$K = \begin{bmatrix} & & & & \\ k_{21} & k_T & k_{23} & k_{24} & \\ k_{31} & k_{32} & k_F & & \\ k_{41} & k_{42} & & k_F & \\ k_{51} & & & & k_F \end{bmatrix}$$

Then implicitly the programme deduces the total loss rates from a compartment by summing all rates in a column and adding the minus sign.

Disregarding the inputs to the Red1 and Red2 species (since they contain just a few pigments, whereas the Bulk Chl consists of over 90 pigments, this K matrix can be implemented in Glotaran as

$$Kscal = \begin{bmatrix} & & & & \\ 1 & 3 & 4a1 & 5a2 & \\ & 4 & 6 & & \\ & 5 & & 6 & \\ 2 & & & & 6 \end{bmatrix}$$

Where 4a1 means that the fourth element of the *kinpar* vector is to be multiplied by the first element of the *kinscal* vector. The indices of the *kinscal* vector are indicated in the *Scaling parameters* matrix.

Spectral constraints

A natural spectral constraint is that the SAS of the Soret species (absorbing near 400 nm) is zero in the Q_y Chl emission region (> 650 nm). Furthermore, the SAS of the Red1 and Red2 species are assumed to be zero below ≈680 and ≈690 nm, respectively, since they are red shifted relative to Bulk Chl. The SAS of Free and Bulk Chl have their maximum at ≈675 and ≈685 nm, respectively.

How to estimate equilibria and branching

From a global analysis the eigenvalues of the K matrix can be estimated. However, spectral constraints are needed to estimated more than *ncomp* kinetic parameters. As a rule of thumb, the SAS area should be similar for the different Chl species. This allows to estimate that the fraction of free Chl is about 5%. The constraint that the SAS area of the two Red Chl species should be similar to that of the Bulk Chl allows to estimate that the ratio of the backward and forward rate constants expressed through the *Scaling parameters* should be about 1.87 and 1.37. This cannot be easily estimated with Glotaran, and different software is needed. However, by trial and error you could also find these values.

Gibbs free energy difference

When two compartments *i* and *j* are at equilibrium, we have

$$k_{ij}c_j(t) = k_{ji}c_i(t) \quad (1)$$

and we can compute the Gibbs free energy difference between compartments *i* and *j* as

$$\Delta G_{ij} = k_B T \ln(k_{ji} / k_{ij}) \quad (2)$$

Near 700 nm a wavelength difference of 10 nm corresponds roughly to $k_B T$ =207 cm^{-1} at RT (25ºC). More precisely, assume that the wavelength of maximum emission of the bulk Chl SAS is 690 nm and that of the Red 1 SAS is 710 nm, then the enthalphy difference is $\frac{10^7}{690} - \frac{10^7}{710} = 408\,cm^{-1}$. Then from the estimated microscopic rate constants the observed $\Delta G_{32} = k_B T \ln(k_{23} / k_{32})$.

Consequently, the entropy difference between the bulk Chl and the Red 1 compartments can be computed using $\Delta G = \Delta H - T\Delta S = \Delta H - k_B T \ln(N_3 / N_2)$. Thus although the enthalpy difference favours Red 1, at RT this is more than compensated by the huge entropy difference.

Glotaran demo projects

The Glotaran demo projects contain three new icons: Dispersion, WeightPar and CohSpec.

Dispersion means that the location of the maximum of the IRF $\mu(\lambda)$ is wavelength dependent. Typically it is described with a polynomial function:

$$\mu(\lambda) = \mu(\lambda_c) + \sum_{i=1}^{npoly} d_i \left(\frac{\lambda - \lambda_c}{100}\right)^i$$

Where λ_c is the center wavelength of the polynomial. Typically the mid wavelength of the measurements is used, or the excitation wavelength λ_{exc} when it is observed in the data. Then $\mu(\lambda_c)$ can easily be "read" from the data image. For streak camera data uncorrected for the dispersion typically the order of polynomial is two, or sometimes three. For difference absorption data uncorrected for the dispersion typically the order of polynomial is between one (if only a small wavelength region is analysed) and three (like in the Glotaran demo projects).

With WeightPar a weight (typically less than 1) can be applied to the data, in order to take into account that some of the data is more noisy. The order is (1) min-max time, and then (2) min-max wavelength.

CohSpec has several options to model a coherent artefact. Most often it is assumed that it is proportional to the IRF shape.

Notes

Always work within a single project

Save model by clicking the floppy icon before you can copy it.

The sum of the jvec inputs **must** sum to 1.0

Spectral equality constraints: there are three cells on top of each other: min-max wavelength (and parameter number three is a scaling parameter involved, but this is not used, it is by definition 1, e.g. normal equality of the SA(D)S). Multiple constraints must be in the same column, e.g. if both SAS2 and SAS3 are equal to SAS1, you should put both constraints in column 1.

Color and line convention. See http://glotaran.org/wiki.html