

Monomer spectra

At least two vibrational modes are required to reproduce the lineshapes of the spectra as well as the Stokes shift between the absorption and the emission maximum.

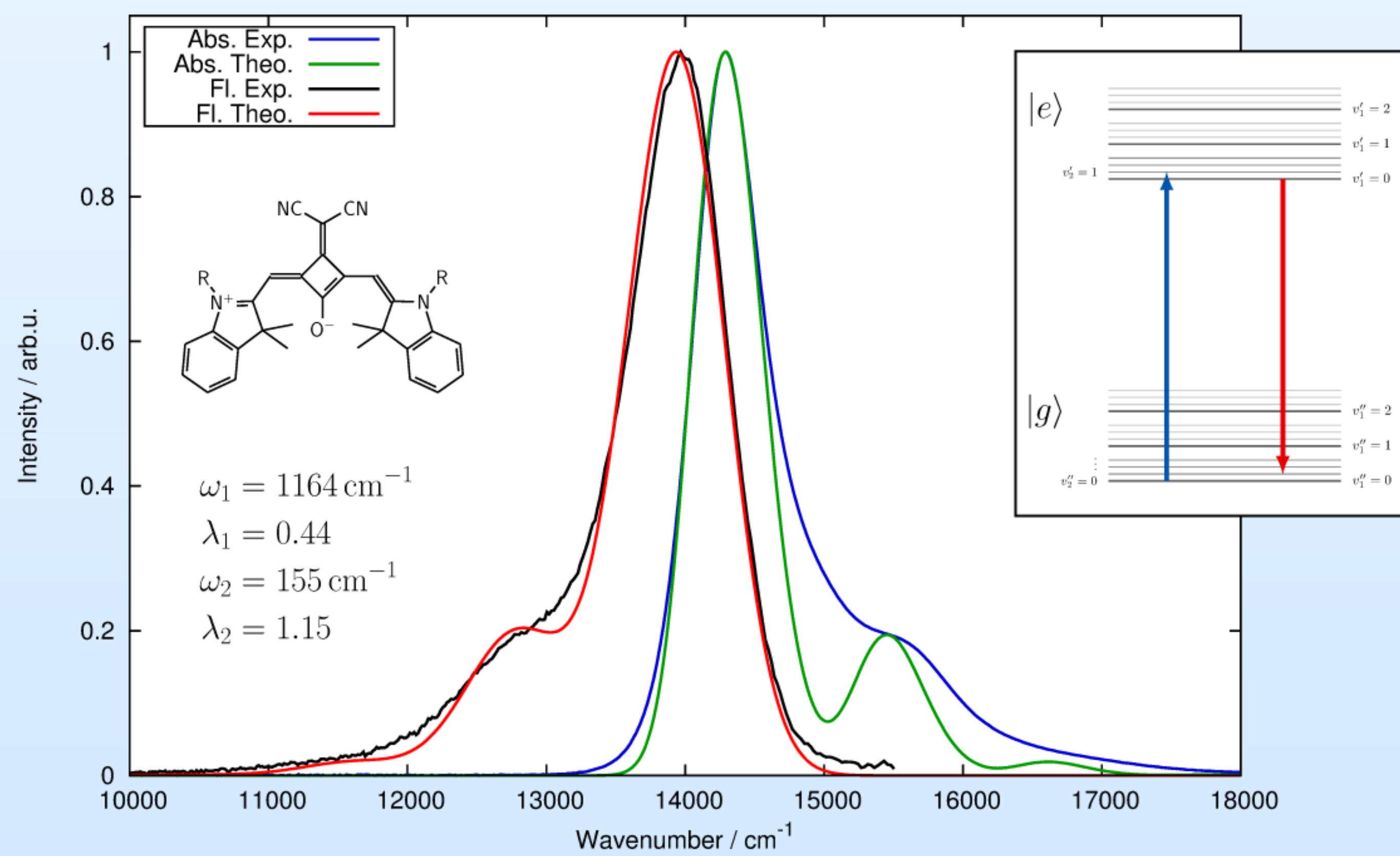


Figure 2: Measured [1] and calculated absorption and emission spectra of *cis*-Indolenine squaraine monomers. Also shown are the molecule and the parameters of the model Hamiltonian. The inset on the right shows the energy levels and transitions that correspond to the absorption and the emission maximum, respectively.

Trimer and Tetramer spectra

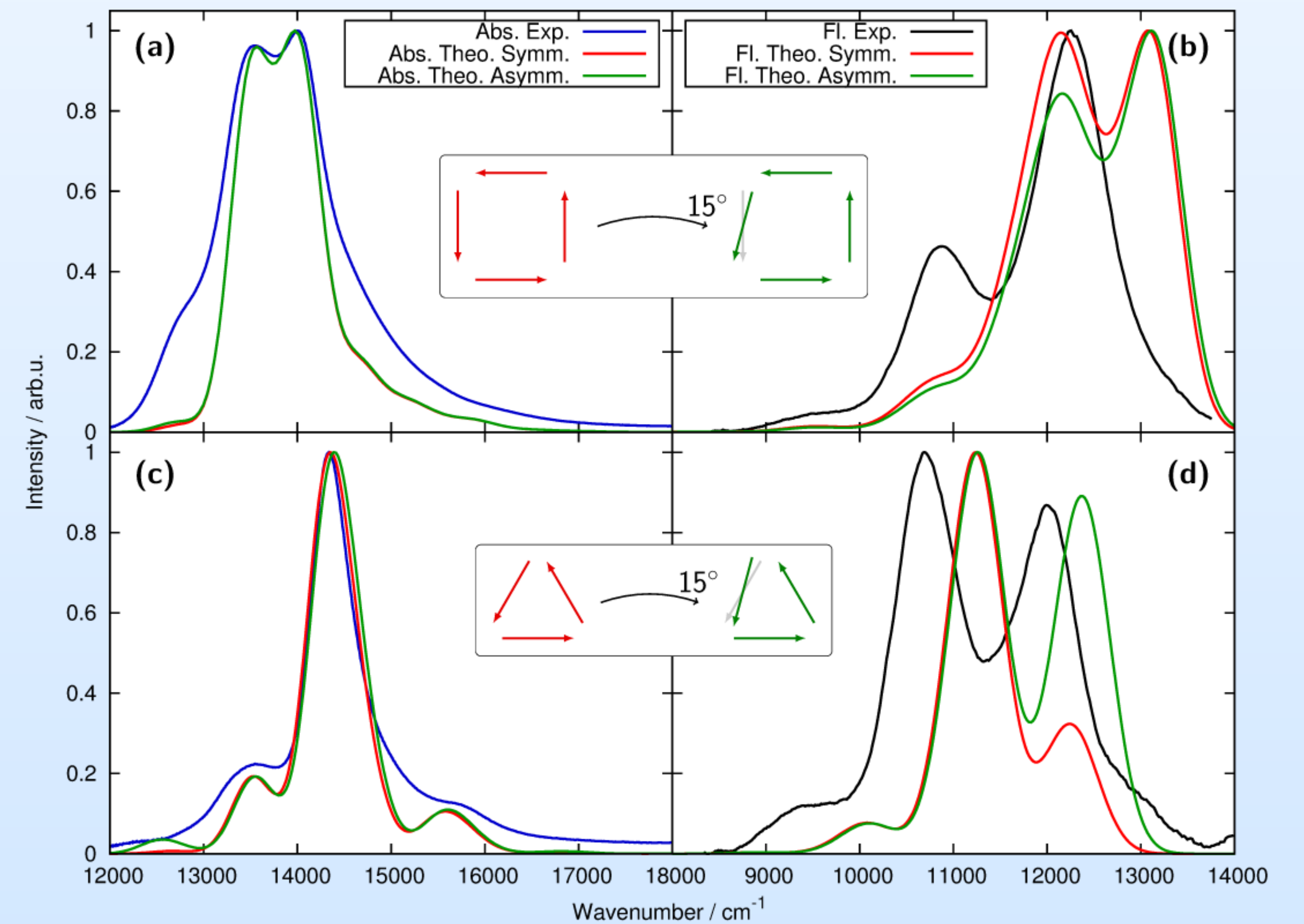


Figure 3: Comparison of measured [1] and calculated spectra for cyclic *cis*-Indolenine squaraine oligomers: (a) Tetramer Absorption, (b) Tetramer Emission, (c) Trimer Absorption, (d) Trimer Emission. The relative orientation of the transition dipole moments in the symmetric (red) and asymmetric (green) case are indicated in the insets.

Calculation of spectra

The spectrum is obtained by a Fourier Transformation of an autocorrelation function:

$$c_{abs}(t) = \langle \psi_{0,g} | (\vec{\varepsilon} \cdot \vec{\mu}) e^{-i\hat{H}t} (\vec{\varepsilon} \cdot \vec{\mu}) | \psi_{0,g} \rangle$$

$$c_{em}(t) = \langle \psi_{0,e} | (\vec{\varepsilon} \cdot \vec{\mu}) e^{-i\hat{H}t} (\vec{\varepsilon} \cdot \vec{\mu}) | \psi_{0,e} \rangle$$

↓ Fourier ↓

$$\sigma_{abs}(E) \sim \int_{-\infty}^{+\infty} e^{+i(E+E_0)t} c_{abs}(t) w(t) dt$$

$$\sigma_{em}(E) \sim \int_{-\infty}^{+\infty} e^{-i(E-E_0)t} c_{em}(t) w(t) dt$$

The spectrum is convoluted with a Gaussian – i. e. multiplied with a Gaussian-shaped window function $w(t)$ in time-domain – with an FWHM adjusted such that the linewidth of experimental spectra is reproduced.

Method

Numerical calculations are carried out with the MCTDH method [2], using the Heidelberg program package.

Overview

Using a vibronic coupling model we analyse measured absorption and emission spectra of cyclic polymeric *cis*-Indolenine squaraine dyes. From theory, features in the absorption spectra are identified as vibronic structures.

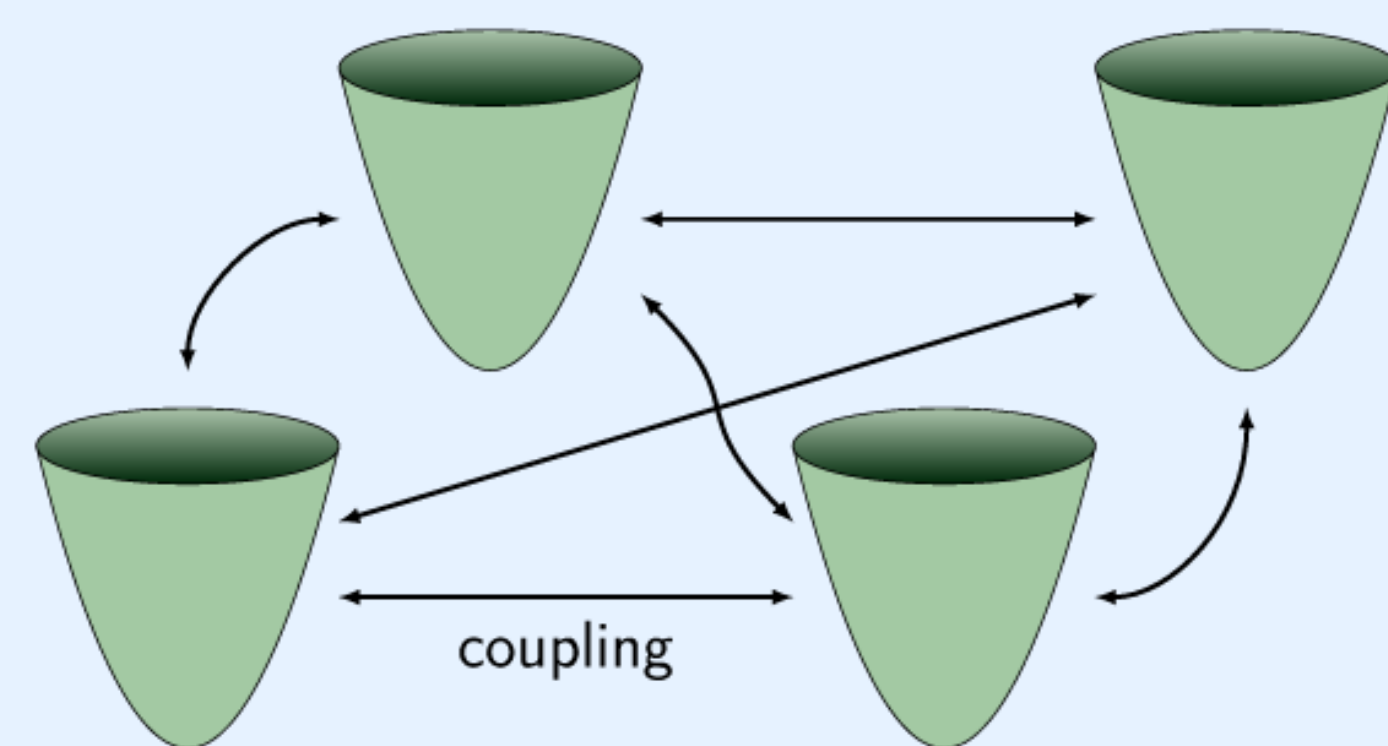


Figure 1: Schematic visualization of the vibronic coupling Hamiltonian.

The absorption spectra of monomers, cyclic trimers and cyclic tetramers are well described using a model with only one intra-monomer vibrational degree of freedom. However, to reproduce both the Stokes shift in the emission spectrum of the monomer and the lineshapes of the monomer absorption and emission spectra, the model has to be extended to a second intra-molecular vibrational mode with a significantly smaller frequency. Additionally, the emission spectra of the trimer and the tetramer exhibit unusual features that can be qualitatively explained by taking a geometry distortion into account which disturbs the symmetry of the molecule.

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In a symmetric – i. e. in-plane, regular polygon arrangement of the transition dipole moments – configuration,

- the absorption spectra of both the trimer and the tetramer are excellently reproduced,
- the lineshapes of the emission spectra, however, are not.

If the symmetry is broken, a vibronic band at the high-energy side of the emission spectrum rises in intensity.

- In the trimer case, twisting the orientation of one monomer by 15° reproduces the lineshape of the emission spectrum.
- The tetramer shows the same behaviour, although less pronounced.
- In both cases, the absorption spectrum is nearly unaffected.

The experimental emission spectra show an energy shift which is not reproduced within the model.

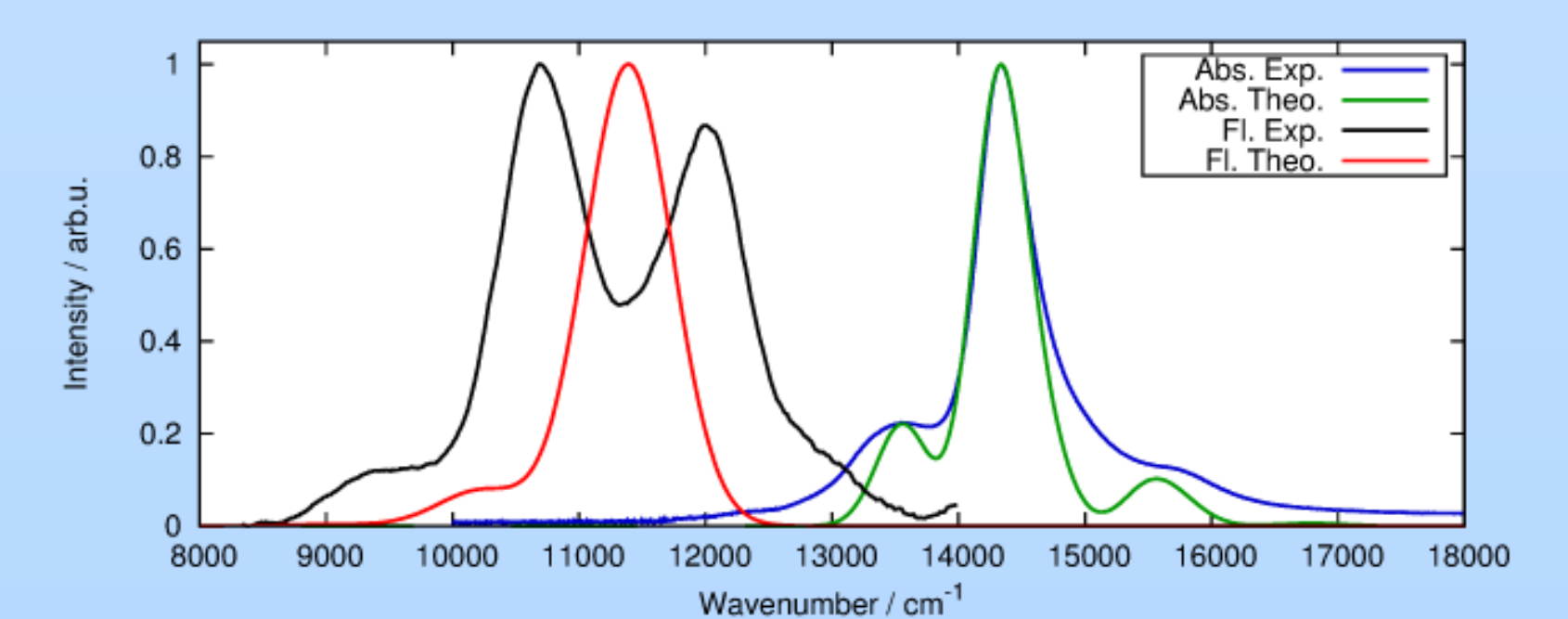


Figure 4: Trimer absorption and emission spectrum taking into account the higher frequency mode into account.

Model Hamiltonian

Monomer

- Two electronic states
- Two vibrational degrees of freedom
- Harmonic oscillators, shifted in the excited state

$$\hat{H}^M = |g\rangle \hat{H}_g^M \langle g| + |e\rangle \hat{H}_e^M \langle e|$$

$$H_g^M = -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} + \frac{\omega_1^2}{2} x_1^2 - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} + \frac{\omega_2^2}{2} x_2^2$$

$$H_e^M = -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} + \frac{\omega_1^2}{2} \left(x_1 - \lambda_1 \sqrt{\frac{2}{\omega_1}} \right)^2 - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} + \frac{\omega_2^2}{2} \left(x_2 - \lambda_2 \sqrt{\frac{2}{\omega_2}} \right)^2 + \bar{\Delta}^M$$

Oligomer

N monomer units

- N localized one-exciton states $|n\rangle$:
Monomer n is in the electronically excited state, all others in the electronic ground state
- Dipole-dipole coupling between localized one-exciton states
- Separable ground state

$$\hat{H}_e = \sum_{n,m} |n\rangle \left\{ \delta_{nm} \left(H_e^{M,n} + \sum_{l \neq n} H_g^{M,l} + \Delta \right) + (1 - \delta_{nm}) J_{nm} \right\} \langle m|$$

$$\hat{H}_g = |g\rangle \left(\sum_n H_g^{M,n} \right) \langle g|$$

with

$$J_{nm} = \frac{\vec{\mu}_n \cdot \vec{\mu}_m}{|\vec{R}_{nm}|^3} - 3 \frac{(\vec{R}_{nm} \cdot \vec{\mu}_n)(\vec{R}_{nm} \cdot \vec{\mu}_m)}{|\vec{R}_{nm}|^5} \quad (1)$$

Geometry

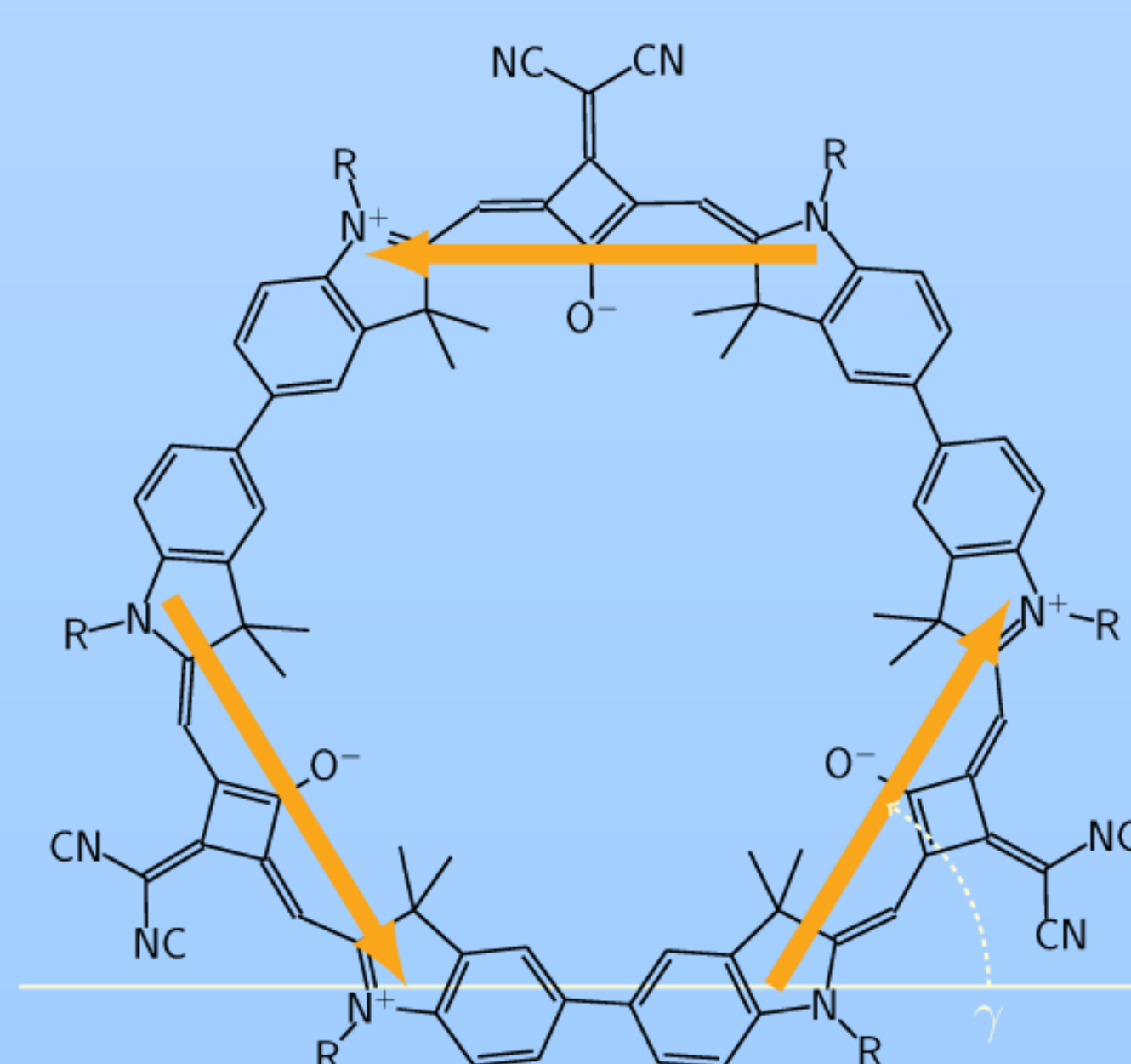


Figure 5: Structure of the cyclic trimer with a proposed arrangement of the transition dipole moments

The relative orientation of the transition dipole moments enters the coupling term – cf. eqn. (1) – as well as the correlation function:

$$c_{abs}(t) = \sum_{n,m} \langle m, \psi_{0,g} | e^{-i\hat{H}t} | n, \psi_{0,g} \rangle \cos(\gamma_n - \gamma_m)$$

$$c_{em}(t) = \sum_{n,m} \langle m, \psi_{0,e} | e^{-i\hat{H}t} | n, \psi_{0,e} \rangle \cos(\gamma_n - \gamma_m)$$

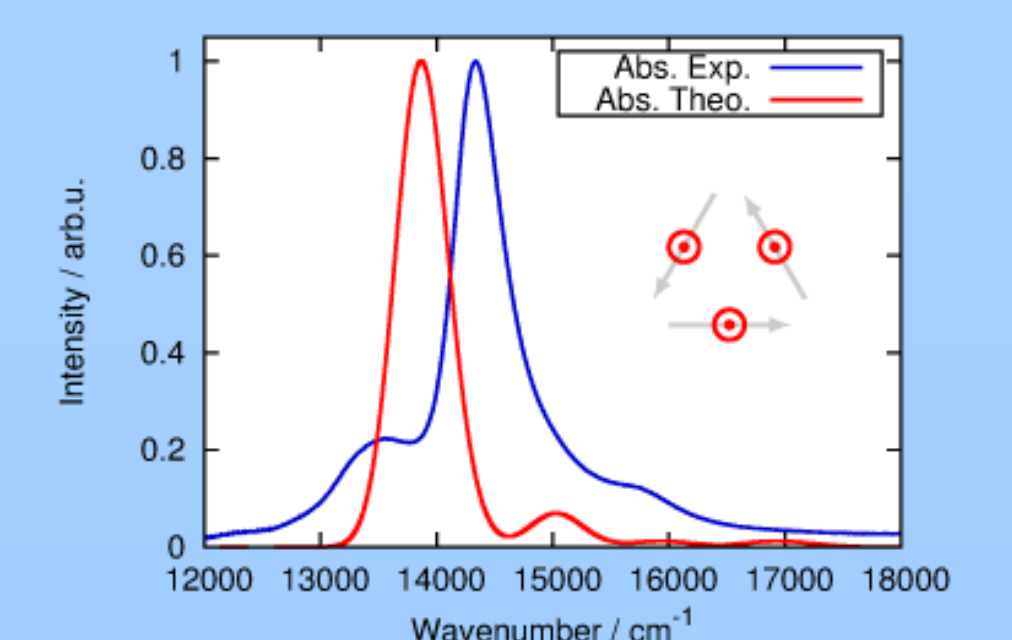


Figure 6: Trimer absorption spectrum with the transition dipole moments pointing out of plane.

Acknowledgement

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References

- [1] S. F. Völker and C. Lambert, Chem. Mater., 2012, 24, 2541 - 2553
- [2] M. H. Beck et al., Phys. Rep. 324, 1-105 (2000)