Dynamics of water interacting with biomolecules

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4.1 Isotropic transient spectrum

The isotropic transient absorption spectrum measured by vibrational pump-probe spectroscopy reflects the dynamics of excited vibrations as they relax back to the ground state. These dynamics can be quite complicated; vibrations might relax via different intermediate states before the vibrational energy is finally converted into heat. In case the system is inhomogeneous, the dynamics are further complicated by the presence of multiple vibrational species, as each species might have a different spectral response and relaxation pathway.

To extract physical information from the transient spectrum, we usually decompose the transient spectrum into a number of different spectral components. Each spectral component can be assigned to a different state of our system, and the number of molecules in each state is proportional to the time-dependent amplitude of the spectral component. The transient absorption spectrum \( \Delta \alpha_{mdl} \) is thus described as

\[
\Delta \alpha_{mdl}(\omega,t) = \sum_i N_i(t) \cdot \sigma_i(\omega)
\]  

(4.1)

where \( N_i(t) \) is the time-dependent amplitude, or population, of component number \( i \) and \( \sigma_i(\omega) \) is its spectral signature. Note that in this notation, the subscript of \( \sigma_i \) does not refer to the \( i^{th} \) vibrational state (as in chapter 2), but to the entire response of component number \( i \), which includes both \( 0 \rightarrow 1 \) and \( 1 \rightarrow 2 \) transitions.

4.1.1 Relaxation models

The best model to describe the transient spectrum is in general based on trends that are observed in the spectrum directly, and the properties of the system (for example, knowledge of the system composition). Two models that are commonly used to describe vibrational relaxation are shown in fig. 4.1. In the cascade model, the excited vibration relaxes via an intermediate state to a thermalized ground state, and the populations are described by

\[
\frac{d}{dt} N_1(t) = -k_1 N_1(t)
\]  

(4.2)

\[
\frac{d}{dt} N_0^*(t) = +k_1 N_1(t) - k_h N_0^*(t)
\]  

(4.3)

\[
\frac{d}{dt} N_0'(t) = +k_h N_0'(t)
\]  

(4.4)
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4.1

where \( k_1 \) is the vibrational decay rate, which is the inverse of the vibrational lifetime, and \( k_h \) is the thermalization rate, i.e. the rate at which the excitation energy is converted into heat. The above set of differential equations can conveniently be written in matrix notation as

\[
\frac{d}{dt} \begin{pmatrix} N_1(t) \\ N_0^*(t) \\ N_0'(t) \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ +k_1 & -k_h & 0 \\ 0 & +k_h & 0 \end{pmatrix} \begin{pmatrix} N_1(t) \\ N_0^*(t) \\ N_0'(t) \end{pmatrix} \tag{4.5}
\]

Solving these equations leads to a description of the transient signal:

\[
\Delta \alpha_{mdl}(\omega, t) = \sigma_1(\omega) N_1(0) e^{-k_1 t} + \sigma_* (\omega) N_1(0) \left( \frac{k_1}{k_h - k_1} (e^{-k_1 t} - e^{-k_h t}) \right) + \sigma_h(\omega) N_1(0) \left( \frac{k_1 e^{-k_1 t} - k_h e^{-k_h t}}{k_h - k_1} + 1 \right) \tag{4.6}
\]

It has been demonstrated that the vibrational relaxation of the OD stretch vibration in isotopically diluted water\(^{74}\) is very well described by the cascade model. The excited OD stretch vibrations relax via an intermediate state to a thermalized ground state. This thermalized ground state accounts for the temperature rise that occurs as the energy of the excited vibrations is transferred into heat: the associated spectrum corresponds to the difference spectrum of a slightly heated sample and the original, unexcited sample. The intermediate state accounts for the fact that the thermalization is delayed, and has no spectral signature of its own (\( \sigma_* = 0 \)), which means that the population of the intermediate state does not alter the spectral response of the OD vibration. As such, the intermediate state is unlikely to correspond to a specific vibrational mode, because the excitation of lower energy vibrational modes such as the HOD bend vibration would lead to an anharmonic shift of the OD stretch vibration. Instead, it might reflect a relatively slow adaptation of the low-energy degrees of freedom (hydrogen-bond stretch and bend) to the new equilibrium positions that correspond to the higher energy content.

For other molecular systems, the transient signal can be modelled using the parallel model, which describes the independent relaxation of two species of
excited vibrations to a common thermalized ground state. In this case

\[
\Delta \alpha_{mdl}(\omega, t) = \sigma_a(\omega) N_{1a}(0) e^{-k_{1a}t} + \sigma_b(\omega) N_{1b}(0) e^{-k_{1b}t} + \sigma_h(\omega) \left( 1 - N_{1a}(0) e^{-k_{1a}t} - N_{1b}(0) e^{-k_{1b}t} \right)
\] (4.7)

This model, and variants thereof, have been used to describe the relaxation of the OD stretch vibration of HOD molecules in different mixtures\textsuperscript{75–77}. Here the two excited states correspond to distinct water hydrogen-bond configurations. Of course, more complicated models can be defined by expanding the number of states and/or redefining the rate matrix of eq. 4.5.

### 4.1.2 Least-squares fit

To estimate how well a given model describes the measured transient spectrum we can calculate the error-weighted square error:

\[
\chi^2 = \int \int \left( \frac{\Delta \alpha(\omega, t) - \Delta \alpha_{mdl}(\omega, t)}{\epsilon(\omega, t)} \right)^2 d\omega dt
\] (4.8)

where \(\epsilon(\omega, t)\) is the standard deviation of the measured transient spectrum \(\Delta \alpha(\omega, t)\). The model \(\Delta \alpha_{mdl}\) in general contains a number of free parameters. In the formalism of the previous section, the free parameters are the vibrational relaxation rates \(k\) and the spectral signatures of each state \(\sigma_i\). To find the optimal parameter values, we have to minimize the square error

\[
\chi^2(k) = \int \int \left( \frac{\Delta \alpha(\omega, t) - \sum_i N_i(k, t) \sigma_i(\omega)}{\epsilon(\omega, t)} \right)^2 d\omega dt
\] (4.9)

The minimization can be carried out numerically using an automated fitting routine: starting out with an estimate for the vibrational decay rates \(k\), the best-fitting spectra are obtained analytically by calculating the minimum of \(\chi^2\) with respect to the spectrum \(\sigma_i\) at every measured frequency \(\omega_j\) (singular value decomposition):

\[
\frac{d}{d\sigma_i(\omega_j)} \int \left( \frac{\Delta \alpha(\omega_j, t) - \sum_i N_i(k, t) \sigma_i(\omega_j)}{\epsilon(\omega_j, t)} \right)^2 dt = 0
\] (4.10)

after which the square error is calculated using eq. 4.9. The loop is iterated using different values of \(k\) until the optimal \(k\) is reached.

### 4.2 Anisotropy dynamics

The anisotropy of the transient spectrum reflects the depolarization dynamics of excited vibrations as they reorient or transfer their energy to other vibrations by resonant Förster energy transfer. However, if the transient spectrum
contains multiple spectral components, as discussed in the previous section, the anisotropy decay of the total spectral response is not so easy to interpret. This is due to the fact that the different spectral components do not contribute equally to the anisotropy at all times. Short-lived components contribute mostly at early time delays, while long-lived components dominate at later time delays.

In the case of isotopically diluted water, the OD stretch vibration decays via a dark intermediate state to a thermalized ground state. To calculate the anisotropy associated with the OD stretch vibration, the transient spectra have to be corrected for the isotropic heating contribution:

\[
\Delta \alpha_{\parallel,\text{corr}}(\omega,t) = \Delta \alpha_{\parallel}(\omega,t) - N_h(t)\sigma_h(\omega) \quad (4.11)
\]

\[
\Delta \alpha_{\perp,\text{corr}}(\omega,t) = \Delta \alpha_{\perp}(\omega,t) - N_h(t)\sigma_h(\omega) \quad (4.12)
\]

before calculating the anisotropy according to

\[
R(\omega,t) = \frac{\Delta \alpha_{\parallel,\text{corr}}(\omega,t) - \Delta \alpha_{\perp,\text{corr}}(\omega,t)}{\Delta \alpha_{\parallel,\text{corr}}(\omega,t) + 2\Delta \alpha_{\perp,\text{corr}}(\omega,t)} \quad (4.13)
\]

In case two species of excited vibrations relax to a common thermalized ground state, as described by eq. 4.7, we do not only want to correct for the isotropic heating contribution, but wish to extract the component-specific anisotropy decays as well. If we know the spectral signatures \(\sigma_i\) of each component from a fit to the isotropic data, we can calculate the component-specific anisotropy decays \(R_i\) by singular value decomposition of the parallel and perpendicular absorption signals. This means describing the parallel and perpendicular signals as

\[
\Delta \alpha_{\text{mdl,}\parallel}(\omega,t) = \sum_i N_i,\parallel(t) \cdot \sigma_i(\omega) \quad (4.14)
\]

\[
\Delta \alpha_{\text{mdl,}\perp}(\omega,t) = \sum_i N_i,\perp(t) \cdot \sigma_i(\omega) \quad (4.15)
\]

and solving for each measured delay time \(t_j\)

\[
\frac{d}{dN_i,\parallel(t_j)} \int \left( \frac{\Delta \alpha_{\parallel}(\omega,t_j) - \sum_i N_i,\parallel(t_j)\sigma_i(\omega)}{\epsilon(\omega,t_j)} \right)^2 d\omega = 0 \quad (4.16)
\]

\[
\frac{d}{dN_i,\perp(t_j)} \int \left( \frac{\Delta \alpha_{\perp}(\omega,t_j) - \sum_i N_i,\perp(t_j)\sigma_i(\omega)}{\epsilon(\omega,t_j)} \right)^2 d\omega = 0 \quad (4.17)
\]

This yields the time-dependent amplitudes \(N_i,\parallel\) and \(N_i,\perp\) of each component, after which the component-specific anisotropy can be calculated according to

\[
R_i(t) = \frac{N_i,\parallel - N_i,\perp}{N_i,\parallel + 2N_i,\perp} \quad (4.18)
\]