Concepts and Methods of 2D Infrared Spectroscopy

Peter Hamm and Martin T. Zanni

Answer Keys: Chapter 7

Problem 7.1: Use the stationary property of a time-correlation function to show that it is an even function. That is, prove

$$\langle A(0)A(t)\rangle = \langle A(0)A(-t)\rangle$$

Solution: Time-stationary means that we can evaluate the correlation function starting from any arbitrary time point t', and it depends only on the time interval t, so:

$$\langle A(0)A(t)\rangle = \langle A(t')A(t+t')\rangle$$

Now, chose $t' = -t$, so:

$$\langle A(0)A(t)\rangle = \langle A(-t)A(0)\rangle = \langle A(0)A(-t)\rangle$$

Problem 7.2: Prove that

$$g(t) = \frac{1}{2}\int_0^t\int_0^t d\tau' d\tau'' \langle \delta\omega_{01}(\tau')\delta\omega_{01}(\tau'')\rangle$$

$$= \int_0^t\int_0^{\tau'} d\tau' d\tau'' \langle \delta\omega_{01}(\tau'-\tau'')\delta\omega_{01}(0)\rangle$$

$$= \int_0^t\int_0^{\tau'} d\tau' d\tau'' \langle \delta\omega_{01}(\tau'')\delta\omega_{01}(0)\rangle$$

Hint: break the integral of $\int_0^t d\tau''$ into two terms, one of which goes from 0 to τ' and the other from τ' to t, and then show that the second term is equal to the first. Hint 2: To get the final step in the derivation, do a coordinate

transformation of the integral by defining $x = \tau' - \tau''$.

Solution: In a first step, we use the stationary condition:

$$g(t) = \frac{1}{2} \int_0^t \int_0^t d\tau' d\tau'' \langle \delta\omega_{01}(\tau')\omega_{01}(\tau'') \rangle$$

$$= \frac{1}{2} \int_0^t \int_0^t d\tau' d\tau'' \langle \delta\omega_{01}(\tau' - \tau'')\delta\omega_{01}(0) \rangle$$

Then, we realize that the function $\langle \delta\omega_{01}(\tau' - \tau'')\delta\omega_{01}(0) \rangle$, which is a function of two coordinates τ' and τ'', is integrated over a square-shaped area with $0 \le t \le \tau'$ and $0 \le t \le \tau''$. We separate the integration area into two triangles:
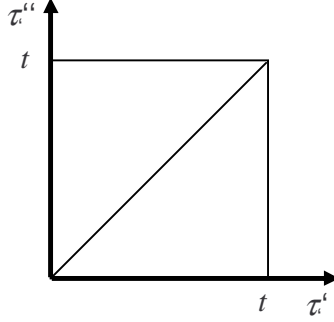
Each point in the lower right-triangle has an corresponding point in the upper-left triangle point with the sign of $\tau' - \tau''$ inverted. Hence, due to the time-reversal symmetry of the correlation function (see Problem 7.1), integration over the two triangles gives identical results (cancelling the factor $1/2$), so we restrict the calculation to the lower-right triangular:

$$g(t) = \int_0^t \int_0^{\tau'} d\tau' d\tau'' \langle \delta\omega_{01}(\tau' - \tau'')\delta\omega_{01}(0) \rangle$$

We set $\tau''' = \tau' - \tau''$ (with $d\tau''' = -d\tau''$):

$$g(t) = -\int_0^t \int_{\tau'}^0 d\tau' d\tau''' \langle \delta\omega_{01}(\tau''')\delta\omega_{01}(0) \rangle$$

Inverting the integration borders of the inner integral, we obtain the final result:

$$g(t) = \int_0^t \int_0^{\tau'} d\tau' d\tau''' \langle \delta\omega_{01}(\tau''')\delta\omega_{01}(0) \rangle$$

Problem 7.3: Starting from the Kubo lineshape function Eq. 7.25, prove Eqs. 7.26 and 7.28 in the homogeneous and inhomogeneous limits, respectively.

Solution: In the inhomogeneous limit, we have $\tau_c \to \infty$, or $\tau_c \gg t$, hence the exponent in the exponential function is very small, and we can Taylor-expand it up to second order:

$$e^{-\frac{t}{\tau_c}} = 1 - \frac{t}{\tau_c} + \frac{t^2}{\tau_c^2} + ...$$

The first two terms of that expansion cancel with the other terms in Eq. 7.25, hence in leading (quadratic) order of t, we obtain Eq. 7.28.

In the homogeneous limit, τ_c is very small, so the exponential function in Eq. 7.25 vanishes. Furthermore, $t/\tau_c \gg 1$, so the 1 in Eq. 7.25 can be neglected, and we obtain Eq. 7.26. Of course, all this is only true for not too small t. In fact, for very small t, $g(t)$ starts out as t^2 (as above), not linearly. The important point is that by the time it enters into a linear regime, $g(t)$ is still very small, so $e^{-g(t)} \approx 1$. For larger times, when $e^{-g(t)}$ starts to decay, then Eq. 7.26 is already in a linear regime.

Problem 7.4: Show that in the slow modulation limit a lineshape is produced that matches the frequency distribution of the molecules, whether or not it is Gaussian. Hint: Start with Eq. 7.9. Rewrite in terms of $\omega_{01}(t)$ using Eq. 7.6. Let $\omega_{01}(t) = \omega_{01}(0)$. Take the Fourier transform to get the spectrum.

Solution: Since the frequency of a given molecule is constant in time, $\omega_{01}(t) = const = \omega_{01}(0)$, we can write for the response function:

$$R^{(1)}(t) = \left\langle \exp\left(-i\int_0^t \omega_{01}(\tau))d\tau\right)\right\rangle \approx \left\langle \exp\left(-i\omega_{01}(0)t\right)\right\rangle$$

When writing the ensemble average explicitly as an integral over a distribution $p(\omega)$:

$$R^{(1)}(t) \approx \left\langle \exp\left(-i\omega_{01}(0) \cdot t\right)\right\rangle \equiv \int_{-\infty}^{\infty} p(\omega)\exp\left(-i\omega_{01}t\right)d\omega$$

we see that the response in the time domain is the Fourier-transformation of that distribution. The absorption spectrum, in turn, is the inverse Fourier transformation of the response function (Eq. 4.8), hence, the distribution $p(\omega)$ is retrieved. Note that the Cumulant expansion was not used in this

argument, so the result holds independent on whether the frequency fluctuations follow Gaussian statistics or not.

Problem 7.5: Imagine a carbonyl vibration on the surface of a protein. The timescale of protein structural fluctuations are typically much slower than that of solvent fluctuation. What ansatz might you use for the frequency fluctuation correlation function.

Solution: The carbonyl vibration feels both the solvent and the protein environment. The solvent response is typically described as an inertial part, which is in the motional narrowing limit, plus an spectral diffusion part on a typical 1 ps timescale (see e.g. 7.9d). Structural dynamics of a protein is significantly slower, so, on the timescale of an IR experiment, might be modelled as quasi-static. Taken together, a reasonable ansatz for the FFCF could be:

$$\langle \omega(0)\omega(t) \rangle = \delta(t)/T_2^* + \Delta\omega_1^2 e^{-t/\tau_c} + \Delta\omega_2^2$$

Problem 7.6: Not all molecules have frequency fluctuation correlation function that decay monotonically. For example for the OH stretch vibration of water, one observes a partial recurrence at about 150 fs. Discuss what this implies for the frequency trajectory, and what could be the structural cause of it.

Solution: The frequency trajectory would not be just a random walk, but to a certain extent oscillatory. In the case of water, the recurrence at 150 fs (see Fig. 10.3c) reflects the not completely over-damped vibration of the OH$\cdots$O hydrogen bond distance. However, the oscillatory behavior typically is very hard to see in the trajectory (Fig. 10.3a) unless it is strongly under-damped (actually the way to make such an oscillatory contribution visible is exactly to calculate a correlation function).