Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 5

Problem 5.1: Derive Eq. 5.26.

Solution: As stated in the text, there are several ways to solve this problem. One way is the following. The integral that we need to compute is Eq. 5.19, which is

$$\langle (\hat{Z} \cdot \hat{\alpha})(\hat{Z} \cdot \hat{\alpha})(\hat{Z} \cdot \hat{\beta})(\hat{Z} \cdot \hat{\beta}) \rangle = \frac{1}{4\pi} \int d\Omega \cos^2 \theta_{Z\alpha}^2 \cos^2 \theta_{Z\beta}$$

where $\int d\Omega$ is the integral of the molecule over all possible orientations. Let's consider the case when we use $\theta_{Z\alpha}$ as the variable to integrate over so that we get

$$= \frac{1}{4\pi} \int_0^{2\pi} d\phi_\alpha \int_0^\pi d\theta_{Z\alpha} \sin \theta_{Z\alpha} \cos^2 \theta_{Z\alpha} \cos^2 \theta_{Z\beta}$$

However, when $\theta_{Z\alpha}$ rotates, it also changes $\theta_{Z\beta}$. Thus, we need to rewrite $\theta_{Z\beta}$ in terms of $\theta_{Z\alpha}$ and the relative angle $\theta_{\alpha\beta}$ that is set by the molecular conformation. One way to do this is to use the Spherical Harmonic Addition theorem from Eq. 5.25. When written in trigonometric terms, it is

$$\cos \theta_{Z\beta} = \frac{4\pi}{3} \Big[\frac{3}{8\pi} \sin \theta e^{-i\phi} \sin \theta_{\alpha\beta} e^{i\phi_{\alpha\beta}} + \frac{3}{4\pi} \cos \theta \cos \theta_{\alpha\beta}$$
$$+ \frac{3}{8\pi} \sin \theta e^{i\phi} \sin \theta_{\alpha\beta} e^{-i\phi_{\alpha\beta}} \Big]$$

where $\theta \equiv \theta_\alpha$ and $\phi \equiv \phi_\alpha$. When substituted into the integral above, there are only two terms that survive the integration of $\int d\phi$, which leaves

$$= \frac{4\pi}{9} \int_0^{2\pi} d\phi \int_0^\pi d\theta \left\{ \left(\frac{3}{2\pi} \right)^2 \sin^3 \theta \cos \theta \sin^2 \theta_{\alpha\beta} + \left(\frac{3}{4\pi} \right)^2 \sin \theta \cos^4 \theta \cos^2 \theta_{\alpha\beta} \right\}$$

$$= \frac{1}{15} \sin^2 \theta_{\alpha\beta} + \frac{1}{5} \cos^2 \theta_{\alpha\beta}$$

$$= \frac{1}{15} \left(2\cos^2\theta_{\alpha\beta} + 1 \right)$$

Problem 5.2: Derive the ratio analogous to Eq. 5.31 but for a 2D IR spectrum measured using a narrow band pump method like an etalon (Sect. 4.4).

Solution: Fig. 4.16 shows the Feynman diagrams for the cross peaks created in the narrow band pump method. In these diagrams, the laser pulses interact twice with j and then twice with i. Thus, we need $\langle Z_j Z_j Z_i Z_i \rangle$ and $\langle Z_j Z_j X_i X_i \rangle$, which are given in Table 5.1,

$$\langle Z_j Z_j Z_i Z_i \rangle = (4P_2 + 5)/45 \tag{0.1}$$

$$\langle Z_j Z_j X_i X_i \rangle = (5 - 2P_2)/45 \tag{0.2}$$

so that the ratio

$$\frac{S_{ZZZZ}}{3S_{ZZXX}} = \frac{(4P_2 + 5)}{3(5 - 2P_2)} \tag{0.3}$$

Problem 5.3: Using spherical harmonics, derive Eq. 5.53.

Solution: We need to solve the equation

$$\langle (\hat{\alpha} \cdot \hat{E}_a(0)) \ (\hat{\alpha} \cdot \hat{E}_a(t_1)) \ (\hat{\alpha} \cdot \hat{E}_a(t_2)) \ (\hat{\alpha} \cdot \hat{E}_a(t_3)) \rangle$$
$$= \int d\Omega_3 \int d\Omega_2 \int d\Omega_1 \int d\Omega_0 (\hat{E}_a(t_3) \cdot \hat{\alpha}) G(\Omega_3 t_3 | \Omega_2)$$
$$(\hat{E}_a(t_2) \cdot \hat{\alpha}) G(\Omega_2 t_2 | \Omega_1)(\hat{E}_a(t_2) \cdot \hat{\alpha}) G(\Omega_1 t_1 | \Omega_0)(\hat{E}_a(0) \cdot \hat{\alpha}) p_0(\Omega_0)$$

Since all the pulses are polarized along the Z-axis and it is the same transition dipole for each interaction, we can write this equation in terms of spherical harmonics using (see Appendix D)

$$(\hat{Z} \cdot \hat{\alpha}) = \cos\theta$$
$$= \left(\frac{4\pi}{3} \right)^{1/2} Y_{10}(\Omega)$$

and the definition of the normalization constant $p_0(\Omega_0)$ to get

$$= \left(\frac{4\pi}{3}\right)^2 \frac{1}{4\pi} \int d\Omega_3 \int d\Omega_2 \int d\Omega_1 \int d\Omega_0 Y_{10}(\Omega_3) G(\Omega_3 t_3|\Omega_2)$$
$$Y_{10}(\Omega_2) G(\Omega_2 t_2|\Omega_1) Y_{10}(\Omega_1) G(\Omega_1 t_1|\Omega_0) Y_{10}(\Omega_0)$$

Using the definition of $G(\Omega_1 t_1|\Omega_0)$ from Eq. 5.46, we can then solve the first integral, which becomes

$$\int d\Omega_0 Y_{10}(\Omega_0) \sum_{\ell m} Y_{\ell m}^*(\Omega_1) Y_{\ell m}(\Omega_0) e^{-\ell(\ell+1)Dt_1} \qquad (0.4)$$

$$= Y_{10}^*(\Omega_1) e^{-2Dt_1}$$

since

$$\int d\Omega_0 Y_{10}(\Omega_0) Y_{\ell m}(\Omega_0) = \delta_{\ell 1}\delta_{m0} \qquad (0.5)$$

The next integral can now be solved

$$e^{-2Dt_1} \int d\Omega_1 Y_{10}^*(\Omega_1) \sum_{\ell m} Y_{\ell m}^*(\Omega_2) Y_{\ell m}(\Omega_1) e^{-\ell(\ell+1)Dt_2} Y_{10}(\Omega_1) \qquad (0.6)$$

$$= e^{-2Dt_1} \left[(4\pi)^{-1/2} Y_{00}(\Omega_2) + (5\pi)^{-1/2} e^{-6Dt_2} Y_{20}(\Omega_2) \right]$$

since (see Appendix D)

$$\int d\Omega_1 Y_{10}^*(\Omega_1) Y_{\ell m}(\Omega_1) Y_{10}(\Omega_1) = (4\pi)^{-1/2}\delta_{\ell 0}\delta_{m0} + (5\pi)^{-1/2}\delta_{\ell 2}\delta_{m0} \quad (0.7)$$

The next two integrals are done in a similar fashion to get the final answer. Note that the terms that survive alternate between e^{-2Dt} and e^{-6Dt} for each integral. Similarly, most pulse sequences alternate between vibrational responses that are coherences and population decays. So e^{-2Dt} usually correlates to a vibrational coherence time and e^{-6Dt} to a vibrational population time. Can you write a pulse sequence that is an exception to this generality?

Problem 5.4: Derive Eq. 5.57 for a diagonal peak. At magic angle ($\theta = 54.7°$), one only measures population relaxation during t_2. Is that also true for the cross peaks?

Solution: To derive Eq. 5.57, just plug the quantities from Table 5.3 into Eq. 5.55. By setting $\theta=54.7°$, the rotational contribution dissappears, because $P_2(\cos\theta) = 0$. However, the analogous equation for the cross peaks has a

more complicated relationship because one has to use terms in Table 5.3 that include both i and j transitions. As a result, rotational dynamics will still be present in the response even when θ=54.7°.

Problem 5.5: When switching between $\langle ZZZZ \rangle$ and $\langle ZXXZ \rangle$ with a rephasing 2D IR pulse sequence the ratio of the peaks on the diagonal should be 3. Explain why this is not the case for (a) non-rephasing and (b) absorptive 2D IR spectra collected with impulsive pulses in a collinear beam geometry.

Solution: (a) The non-rephasing pathways have both "off-diagonal" and "on-diagonal" cross peaks (see Fig. 4.13). As a result, the intensity along the diagonal is a sum of both the standard diagonal peaks and the "on-diagonal" cross peaks. Thus, unless the cross peaks arise from transitions which are perfectly parallel, the intensity of the 2D IR spectrum along the diagonal will no longer decrease by a factor of 3. (b) The same answer applies, because in the collinear geometry one also measures the non-rephasing spectrum.

Problem 5.6: Show that the angles between two transition dipoles can be measured using the ratio of $\langle 45°, -45°, 0°, 0° \rangle$ and $\langle 75°, -75°, 0°, 0° \rangle$ in a non-rephasing spectrum. Is this ratio preferable to $\langle 90°, 90°, 0°, 0° \rangle$ and $\langle 0°, 0°, 0°, 0° \rangle$ used in pump-probe style 2D IR methods?[153]

Solution: The $\langle 45°, -45°, 0°, 0° \rangle$ and $\langle 75°, -75°, 0°, 0° \rangle$ responses can be written more generally as

$$\langle \theta, -\theta, 0°, 0° \rangle = \langle (Z\cos\theta + X\sin\theta)(Z\cos\theta + X\sin\theta)ZZ \rangle \qquad (0.8)$$
$$= \cos^2\theta \langle ZZZZ \rangle - \sin^2\theta \langle XXZZ \rangle$$

The cross peaks in the non-rephasing spectrum follow the ordering $jjii$, so that we get the equation (using Table 5.1)

$$\langle \theta, -\theta, 0°, 0° \rangle_{jjii} = \cos^2\theta \{ \frac{4P_2 + 5}{45} \} - \{ \sin^2\theta \langle \frac{5 - 2P_2}{45} \} \qquad (0.9)$$

and for the diagonal peaks the ordering is $iiii$, which gives

$$\langle \theta, -\theta, 0°, 0° \rangle_{iiii} = \cos^2\theta \{ \frac{1}{5} \} - \{ \sin^2\theta \langle \frac{1}{15} \} \qquad (0.10)$$

Thus, the orientational response of the diagonal peaks is $\langle 45°, -45°, 0°, 0° \rangle_{iiii} = 0.07$ and $\langle 75°, -75°, 0°, 0° \rangle_{iiii} = -0.045$, so that when we switch between the

two the signal changes by a factor of -1.39. Therefore, the ratio for the cross peaks that we want is

$$\frac{\langle 45°, -45°, 0°, 0° \rangle_{jjii}}{-1.39 \langle 75°, -75°, 0°, 0° \rangle_{jjii}} \qquad (0.11)$$

which is plotted in the figure below.

$$\frac{\langle 45,-45,0,0 \rangle}{-1.55 \langle 75,-75,0,0 \rangle}$$
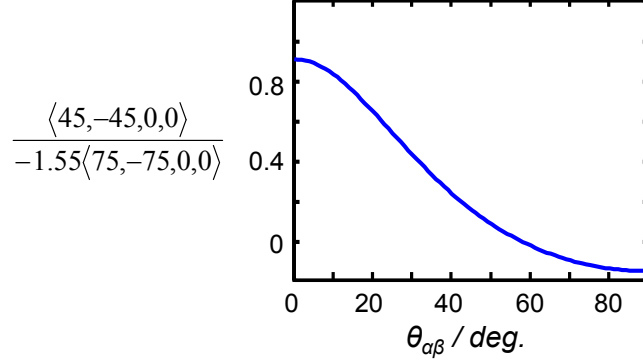
Is this ratio preferable to the $\langle 90°, 90°, 0°, 0° \rangle$ and $\langle 0°, 0°, 0°, 0° \rangle$ used in to measure the angles in a collinear absorptive spectrum? Compare this graph to that in Fig. 5.5b. In Fig. 5.5b, the dynamic range of the measurement is about (1 - 0.3)=0.7, whereas the dynamic range for the ratio derived in this problem is about (0.88+0.18)=1.06. So, in that regard it is much more accurate at measuring angles. However, the absolute signal strengths are also much smaller, since $\langle ZZZZ \rangle$=0.3 whereas $\langle 45°, -45°, 0, 0 \rangle$=0.07, for instance.

Problem 5.7: Explain how one experimentally measures the 5th-order orientational response $\langle XXYYZZ \rangle$.

Solution: In order to get a projection along a third polarization axis, the beams need to impinge on the sample from different spatial directions. e.g. they cannot be collinear.