

Concepts and Methods of 2D Infrared Spectroscopy

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Answer Keys: Chapter 6

Problem 6.1: With the rules from Appendix B, verify that the Hamiltonian in Eq. 6.2 translates into the Hamilton matrix in Eq. 6.5.

Solution: Lets consider for example the matrix element $H_{4,6} = \sqrt{2}\beta_{12}$, which originates from the basis functions $|11\rangle$ and $|20\rangle$:

$$\begin{aligned} H_{4,6} &\equiv \langle 11|H|20\rangle \\ &= \langle 11|\hbar\omega_1 b_1^\dagger b_1 + \hbar\omega_2 b_2^\dagger b_2 + \beta_{12}(b_1^\dagger b_2 + b_2^\dagger b_1)|20\rangle \end{aligned}$$

The first two terms don't contribute to this matrix element, because e.g. $\langle 11|\hbar\omega_1 b_1^\dagger b_1|20\rangle = 2\hbar\omega_1 \langle 11|20\rangle = 0$. The one term that does contribute is $\langle 11|\beta_{12} b_2^\dagger b_1|20\rangle = \sqrt{2}\beta_{12} \langle 11|11\rangle = \sqrt{2}\beta_{12}$.

Problem 6.2: Verify that the Hamiltonian 6.10 translates into the Hamilton matrix 6.11.

Solution: What is new in the Hamiltonian is the terms of the form e.g. $-\frac{\Delta}{2} b_1^\dagger b_1^\dagger b_1 b_1$. Its acts on the basis function $|20\rangle$ only (for example, since the ladder climbs down lead to zero for all other basis states). Then:

$$-\frac{\Delta}{2} \langle 20|b_1^\dagger b_1^\dagger b_1 b_1|20\rangle = -\Delta \langle 20|20\rangle = -\Delta \quad (0.1)$$

Problem 6.3: Show that the terms $b_i^\dagger b_i^\dagger b_i b_i$ are related to $V_{1122} q_1^2 q_2^2$ in a Taylor expansion of the potential energy surface. Why do we retain only the term $b_i^\dagger b_i^\dagger b_i b_i$, and not, e.g. $b_i b_i b_i b_i$?

Solution: To answer this problem, we need to write $q_1^2 q_2^2$ in terms of ladder operators using $q_n = 1/\sqrt{2}(b_n^\dagger + b_n)$, such that

$$q_1^2 q_2^2 = (b_1^\dagger + b_1)(b_1^\dagger + b_1)(b_2^\dagger + b_2)(b_2^\dagger + b_2)$$

One gets lots of terms, two of which are $b_i^\dagger b_i^\dagger b_i b_i$ and $b_i b_i b_i b_i$. We only retain the quantum conserving terms, such as $b_i^\dagger b_i^\dagger b_i b_i$, because they couple nearly degenerate states. The specific term $b_i^\dagger b_i^\dagger b_i b_i$ contributes to the local mode anharmonicity. The terms that couple different quantum states are neglected. $b_i b_i b_i b_i$ is one such term, which couples $\nu=0$ to $\nu=4$, for example, and thus should have a much smaller impact on the eigenstate energies than the quantum conserving terms.

Problem 6.4: Show that the Hamiltonian in Eq. 6.5 would no longer be block-diagonal if we were to include cubic anharmonicity, e.g. terms of the sort $V_{122} q_1 q_2^2$ in a Taylor expansion of the potential energy surface. Would these coupling terms create cross peaks?

Solution: As in the previous problem, when we expand $q_1 q_2^2$, we obtain in total 8 terms of the sort e.g. $b_1^\dagger b_2 b_2$ (and all possible permutations of whether there is a † or not). However, since it is an odd number, it will necessarily mean an overall excitation or de-excitation a one or three quanta. So, if $\hbar\omega_1$ and $\hbar\omega_2$ are similar, all these terms will be non-resonant, and hence will contribute only little (that is different for a Fermi resonance where $\hbar\omega_1 \approx 2\hbar\omega_2$, see Chapter 6.8). Furthermore, these terms couple e.g. basis functions $|10\rangle$ with $|02\rangle$, since the matrix element $\langle 10|b_1^\dagger b_2 b_2|02\rangle \neq 0$, so the Hamilton matrix Eq. 6.11. is no longer block diagonal.

Problem 6.5: With the rules from Appendix B, verify that we obtain for the transition dipoles of an harmonic oscillator: $\langle 1|\hat{\mu}|2\rangle = \sqrt{2}\langle 0|\hat{\mu}|1\rangle$. To that end, keep in mind that we have for a vibrational transition dipole operator $\hat{\mu} = d\mu/dq \cdot \hat{q}$, where $d\mu/dq$ is the change of the molecular dipole with coordinate q .

Solution: Start by writing the transition dipole operator using ladder operators, which gives

$$\hat{\mu} = d\mu/dq \cdot \hat{q} = \frac{d\mu}{dq} \frac{1}{\sqrt{2}}(b^\dagger + b)$$

We then evaluate the two matrix elements

$$\langle 1|\hat{\mu}|2\rangle = \langle 1|\frac{d\mu}{dq}\frac{1}{\sqrt{2}}(b^\dagger + b)|2\rangle = \frac{d\mu}{dq}\langle 1|1\rangle$$

$$\langle 0|\hat{\mu}|1\rangle = \langle 0|\frac{d\mu}{dq}\frac{1}{\sqrt{2}}(b^\dagger + b)|1\rangle = \frac{d\mu}{dq}\frac{1}{\sqrt{2}}\langle 0|0\rangle$$

so that we arrive at our equality

$$\langle 1|\hat{\mu}|2\rangle = \sqrt{2}\langle 0|\hat{\mu}|1\rangle$$

Problem 6.6: Diagonalize the two exciton matrix of the Hamiltonian in Eq. 6.11 with $\omega_1 = \omega_2 \equiv \omega$ to get Eq. 6.13. Hint: Do a coordinate transformation into a basis set defined by $|2\pm\rangle = 1/\sqrt{2}(|02\rangle \pm |20\rangle)$, which will create a block diagonal 2-exciton Hamiltonian that can then be analytically diagonalized.

Solution: Using the hint, we can calculate the matrix elements we need to rewrite the 2-quantum Hamiltonian in the new basis set of $|11\rangle, |2+\rangle$, and $|2-\rangle$.

$$\begin{aligned}\langle 11|H|2+\rangle &= (\langle 11|H|02\rangle + \langle 11|H|20\rangle)1/\sqrt{2} \\ &= (\sqrt{2}\beta + \sqrt{2}\beta)1/\sqrt{2} = 2\beta\end{aligned}$$

$$\begin{aligned}\langle 11|H|2-\rangle &= (\langle 11|H|02\rangle - \langle 11|H|20\rangle)1/\sqrt{2} \\ &= 0\end{aligned}$$

$$\begin{aligned}\langle 2+|H|2+\rangle &= (\langle 02|H|02\rangle + \langle 20|H|20\rangle + \langle 20|H|02\rangle + \langle 02|H|20\rangle)1/2 \\ &= 2\hbar\omega - \Delta\end{aligned}$$

The 2-quantum portion of the matrix in Eq. 6.11 now becomes

$$\begin{pmatrix} 2\hbar\omega & 2\beta & 0 \\ 2\beta & 2\hbar\omega - \Delta & 0 \\ 0 & 0 & 2\hbar\omega - \Delta \end{pmatrix} \quad (0.2)$$

where the columns are written in the order of $|11\rangle, |2+\rangle$, and $|2-\rangle$. By doing this coordinate transformation, we have block diagonalized the 2-quantum Hamiltonian so that the "asymmetric" stretch mode $|2-\rangle \equiv |a\rangle$ is decoupled

from the other two. The matrix is now fully diagonalized by diagonalizing the remaining 2x2 Hamiltonian using

$$\begin{aligned} |S_+\rangle &= \cos \frac{\theta}{2} |11\rangle + \frac{1}{2} \sin \frac{\theta}{2} (|02\rangle + |20\rangle) \\ |S_-\rangle &= -\sin \frac{\theta}{2} |11\rangle + \frac{1}{2} \cos \frac{\theta}{2} (|02\rangle + |20\rangle) \end{aligned} \quad (0.3)$$

where $\tan \theta = 4|\beta|/\Delta$.

The energies are

$$\begin{aligned} E_{S\pm} &= \frac{1}{2}(4\hbar\omega - \Delta) \pm \Omega \\ E_a &= 2\hbar\omega - \Delta \end{aligned}$$

with

$$\Omega = \frac{1}{2}\sqrt{(\Delta^2 + 16\beta^2)}$$

It is interesting to look at the results in various coupling limits. For example, if $\beta^2 \gg \Delta^2$, then $\Omega \approx 2\beta$ so that $E_{S\pm} = 2\hbar\omega - \Delta/2 \pm 2\beta$ and $E_a = 2\hbar\omega - \Delta$. If instead $\Delta^2 \gg \beta^2$, then $\Omega \approx \Delta/2$ so that $E_{S+} = 2\hbar\omega$ and $E_{S-} = E_a = 2\hbar\omega - \Delta$.

Problem 6.7: Calculate the dispersion relation of an exciton in a 3_{10} -helix which has 3.2 residues per turn and $\beta_{i,i+1} = 0.9 \text{ cm}^{-1}$, $\beta_{i,i+2} = -2.5 \text{ cm}^{-1}$, $\beta_{i,i+3} = -2.8 \text{ cm}^{-1}$, $\beta_{i,i+4} = -0.8 \text{ cm}^{-1}$ [128], and vanishing coupling for larger distances. Calculate the expected splitting between the A and E modes.

Solution: The dispersion relation is given by Eq. 6.35, which for this problem only has 4 terms:

$$E_k = \hbar\omega_0 + 2 \left[0.9 \cos \left(\frac{2\pi k}{N} \right) - 2.5 \cos \left(\frac{4\pi k}{N} \right) - 2.8 \cos \left(\frac{6\pi k}{N} \right) - 0.8 \cos \left(\frac{8\pi k}{N} \right) \right]$$

where the number of peptide units N is a large number. The A and E terms are given by Eqs. 6.34 and 6.35, respectively. Thus, their frequencies are given by

$$E_A - \hbar\omega_0 = 2(0.9 - 2.5 - 2.8 - 0.8) = -10.4$$

$$E_E - \hbar\omega_0 = 2 \left[0.9 \cos \left(\frac{2\pi}{3.2} \right) - 2.5 \cos \left(\frac{4\pi}{3.2} \right) - 2.8 \cos \left(\frac{6\pi}{3.2} \right) - 0.8 \cos \left(\frac{8\pi}{3.2} \right) \right] = -2.3$$

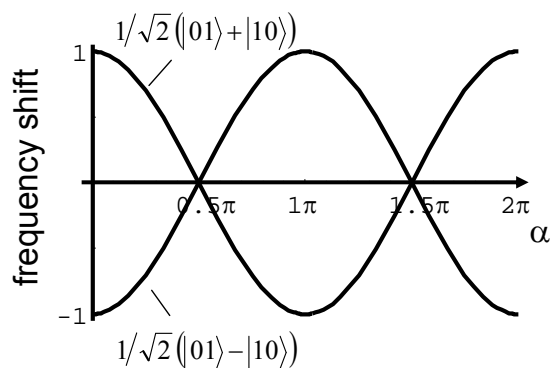
so that the splitting is 8 cm^{-1} .

Problem 6.8: Consider two coupled oscillators in a plane, like the two carbonyl groups in Fig. 6.1a. Using transition dipole coupling, determine the sign of the coupling and the intensities of the two peaks in a linear infrared spectra when one carbonyl is rotated out of the plane. Do the same for a 2D IR spectrum, predicting both the diagonal and cross peak intensities.

Solution: We define unit-less transition dipoles and a vector separating both sites:

$$\begin{aligned}\vec{\mu}_1 &= \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\ \vec{\mu}_2 &= \begin{pmatrix} 0 \\ \cos \alpha \\ \sin \alpha \end{pmatrix} \\ \vec{r}_{12} &= \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}\end{aligned}$$

One easily sees that we then have for the transition dipole coupling $\beta_{12} = \cos \alpha$ (Eq. 6.16). We assume that the monomers are identical, so $\hbar\omega_1 = \hbar\omega_2$. The frequency shift relative to a monomer will then be β_{12} for the symmetric solution $1/\sqrt{2}(|01\rangle + |10\rangle)$ and $-\beta_{12}$ for the antisymmetric solution $1/\sqrt{2}(|01\rangle - |10\rangle)$, see figure below:

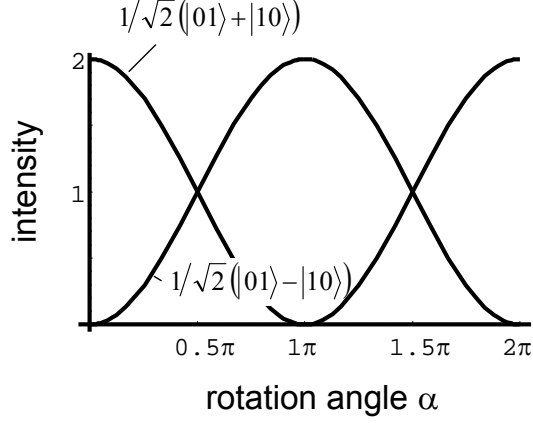


The intensities of the two transitions scale as:

$$I_s = 1/2|\vec{\mu}_1 + \vec{\mu}_2|^2$$

$$I_{as} = 1/2|\vec{\mu}_1 - \vec{\mu}_2|^2,$$

see below:



For $\alpha = 0$, the intensity of the symmetric state is two times that of a monomer, while the antisymmetric state is dark. For $\alpha = \pi/2$, where the coupling vanishes, both transitions are equally strong and they appear at the same frequency. For $\alpha = \pi$, the antisymmetric solution is the higher frequency one and carries all oscillator strength.

The 2D IR spectrum is essentially that of Fig. 6.3c. The separation between both peaks is $2\beta_{12}$, as in the linear spectrum, the intensities of the diagonal peaks scale as:

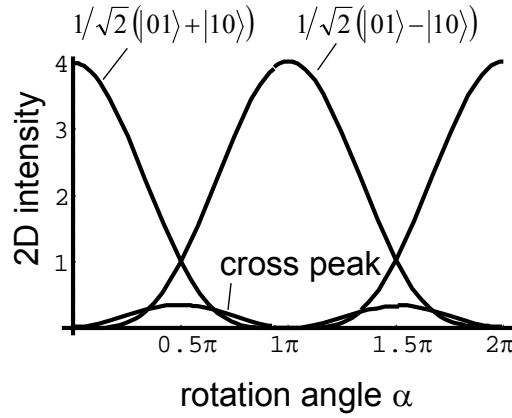
$$I_s = 1/4|\vec{\mu}_1 + \vec{\mu}_2|^4$$

$$I_{as} = 1/4|\vec{\mu}_1 - \vec{\mu}_2|^4,$$

and those of the cross peaks as

$$I_{cross} = 1/4|\vec{\mu}_1 + \vec{\mu}_2|^2|\vec{\mu}_1 - \vec{\mu}_2|^2(2\cos^2\theta_{s,as} + 1)/3 \quad (0.4)$$

The last term is an orientational factor, and we assume here parallel polarization of all laser pulses (Eq. 5.26). However, in this particular case, the transition dipoles of both eigenstates, $1/\sqrt{2}(\vec{\mu}_1 + \vec{\mu}_2)$ and $1/\sqrt{2}(\vec{\mu}_1 - \vec{\mu}_2)$, are always mutually perpendicular, so there is no α -dependence of the orientational term. The intensities of the diagonal peaks and the cross peak is shown in the figure below.



Problem 6.9: The transition dipole strength of a vibrational mode can be determined from its infrared spectrum. The integrated absorption coefficient A is the integral of the molar absorption coefficient, ϵ over the band[6]

$$A = \int \epsilon(\nu) d\nu \quad (0.5)$$

which is related to the transition dipole by

$$|\mu_{01}|^2 (m^2 C^2) = \frac{3\hbar n c \epsilon_0 \ln 10}{\pi \nu_0 N_A} A = 1.02 \times 10^{-61} \times \frac{A (M^{-1} cm^{-2})}{\nu_0 (cm^{-1})} \quad (0.6)$$

where the units are given in the parenthesis, ϵ_0 is the permittivity of free space, n is the index of refraction, N_A is Avogadro's number, and $\nu_0 = \omega_0/2\pi$ is the center frequency of the band. (a) Do a unit analysis and verify the constant (constants are given in Appendix C). (b) Given that a protein with 18 residues has a maximum ϵ of $8000 M^{-1} cm^{-1}$ and a spectral width of $40 cm^{-1}$ for the amide I band, estimate the transition dipole strength $|\mu_{01}|$ for a single residue in Debye.

Solution: (a) Verifying units:

$$\begin{aligned} \frac{3\hbar n c \epsilon_0 \ln 10}{\pi N_A} &= 3(1.054 \cdot 10^{-34} Js)(3 \cdot 10^{10} cms^{-1})(8.854 \cdot 10^{-12} C^2 s^2 kg^{-1} m^{-3}) \\ &\quad \times (100^{-3} m^3 cm^{-3}) \ln 10 \\ &= 1.02 \cdot 10^{-61} (m^2 C^2) mmol cm^{-2} = 1.02 \cdot 10^{-61} (m^2 C^2) M cm \end{aligned}$$

(b) Given that the amide I band has a frequency of about $1600 cm^{-1}$, we

get

$$\begin{aligned}
 |\mu_{01}|^2 &= 1.02 \times 10^{-61} M c m m^2 C^2 \frac{8000 M^{-1} c m^{-1} 40 c m^{-1}}{1600 c m^{-1}} \frac{1}{18 \text{ oscillators}} \\
 &= 1.13 \cdot 10^{-60} C^2 m^2 \\
 |\mu_{01}| &= 1.06 \cdot 10^{-30} C m \times \frac{D}{3.33 \cdot 10^{-30} C m} = 0.32 D \quad (0.7)
 \end{aligned}$$

Problem 6.10: When calculating transition dipole strengths and couplings, units must be done properly, which is not always straightforward. For instance, the transition dipole moment, μ_{01} (debyes (D), Eq.6.36), is often written[112]

$$\mu_{01} = \left(\frac{\hbar}{8\pi^2 c \nu_{01}} \right)^{1/2} \frac{\partial \mu}{\partial q} = \left(\frac{4.1058}{\nu_{01}^{1/2}} \right) \frac{\partial \mu}{\partial q} \quad (0.8)$$

where ν_{01} (cm^{-1}) is the observed frequency, $\partial \mu / \partial q$ is in units of $\text{D} \text{ \AA}^{-1} u^{-1/2}$ where u is the reduced mass, and the constant has units of $\text{D} \text{ \AA}^{1/2} \text{ cm}^{-1/2}$. q is written in units of $\text{D} \text{ \AA}^{1/2}$ so that the coordinate system is mass-weighted, which is often used in normal mode analysis[174]. Derive the constant in Eq. 0.8 by solving the integral for the transition dipole moment $\mu_{01} = d\mu/dq \langle 0|\hat{q}|1 \rangle$. Hint: Use the following wavefunctions for a harmonic oscillator to evaluate the integral: $\psi_0(q) = (\frac{\alpha}{\pi})^{1/4} e^{-\alpha q^2/2}$ and $\psi_1(q) = (\frac{\alpha}{4\pi})^{1/4} 2\alpha^{1/2} q e^{-\alpha q^2/2}$ where $\alpha = \sqrt{k u / \hbar^2}$ (in SI units). Replace the force constant, k , with a conversion to ν_{01} .

Solution: We need to solve the integral

$$\begin{aligned}
 \mu_{01} &= \frac{d\mu}{dq} \langle 0|\hat{q}|1 \rangle = \frac{d\mu}{dq} \int \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} x \left(\frac{\alpha}{4\pi}\right)^{1/4} 2\alpha^{1/2} x e^{-\alpha x^2/2} dx \\
 &= \frac{1}{4^{1/4}} \frac{\hbar^{1/2}}{(ku)^{1/4}} \frac{d\mu}{dq}
 \end{aligned}$$

We now substitute in for k by relating it to the frequency of a harmonic oscillator

$$\nu_{01} = \frac{1}{2\pi c} \left(\frac{k}{u}\right)^{1/2}$$

so that

$$k^{1/4} = (2\pi c \nu_{01})^{1/2} u^{1/4}$$

and

$$\mu_{01} = \frac{1}{4^{1/4}} \frac{\hbar^{1/2}}{(ku)^{1/4}} \frac{d\mu}{dq} = \frac{1}{u^{1/2}} \left(\frac{h}{8\pi^2 c \nu_{01}} \right)^{1/2} \frac{d\mu}{dq}$$

We now convert to mass weighted coordinates by multiplying by $u^{1/2}$ to get

$$\mu_{01}^Q = u^{1/2} \mu_{01} = \left(\frac{h}{8\pi^2 c \nu_{01}} \right)^{1/2} \frac{d\mu}{dq}$$

Problem 6.11: The amide I mode of N-methylacetamide has $\partial\mu/\partial q = 3.466$ D $\text{\AA}u^{1/2}$. What is its transition dipole strength? Hint: Use the conversion factor from Problem 6.10.

Solution:

$$\mu_{01} = \left(\frac{4.1058 \text{\AA}u^{1/2} \text{cm}^{-1/2}}{(1650 \text{cm}^{-1})^{1/2}} \right) 3.466 \frac{D}{\text{\AA}u^{1/2}} = 14.2D$$

Problem 6.12: In some theory papers it is common to report couplings between vibrational groups in units of $\text{mdyn}/(\text{\AA} u)$ where u is the reduced mass. These units are used because $\beta_{12} = \partial^2 V / \partial q_1 \partial q_2$, and so should have units of a force constant (N/m) in mass weighted coordinates ($1/u^{1/2}$). For example, in one particular geometry Torii and Tasumi reported a coupling constant of $\beta = 0.02$ $\text{mdyn}/(\text{\AA} u)$ between two amide I stretches of trialanine[179]. Compute the coupling term in the Hamiltonian, namely $\beta_{12} q_1 q_2$, in cm^{-1} . Use the conversion factor in Problem 6.10 to convert β into units of $\text{mdyn}\text{\AA}$, which is energy. Then convert to cm^{-1} . (Overview of units in Appendix C.)

Solution:

$$\begin{aligned} & \frac{0.02 \text{mdyn}}{\text{\AA}u} \left(\frac{4.1058 \text{\AA}u^{1/2} \text{cm}^{-1/2}}{(1650 \text{cm}^{-1})^{1/2}} \right)^2 \times \frac{\text{dyn}}{1000 \text{mdyn}} \times \frac{1N}{10^5 \text{dyn}} \times \frac{m}{10^{10} \text{\AA}} \times \frac{J}{Nm} \frac{5.035 \cdot 10^{22} \text{cm}^{-1}}{J} \\ & = 10.6 \text{cm}^{-1} \end{aligned} \tag{0.9}$$

Problem 6.13: Generate the normal mode Hamiltonian in Eq. 6.46 using

the Dunham Expansion and the Darling-Dennison coupling terms.

Solution: We use Eq. 6.41 and 6.45 to generate the energies of the eigenstates:

$$\begin{aligned}
 |00\rangle &= \hbar\omega + \frac{3}{4}x \\
 |01\rangle &= 2\hbar\omega - \beta + \frac{11}{4}x \\
 |10\rangle &= 2\hbar\omega + \beta + \frac{11}{4}x \\
 |11\rangle &= 3\hbar\omega + \frac{27}{4}x \\
 |02\rangle &= 3\hbar\omega - 2\beta + \frac{23}{4}x \\
 |20\rangle &= 3\hbar\omega + 2\beta + \frac{23}{4}x
 \end{aligned}
 \tag{0.10}$$

We then subtract $|00\rangle$ which shifts everything to

$$\begin{aligned}
 |00\rangle &= 0 \\
 |01\rangle &= \hbar\omega + 2x - \beta \\
 |10\rangle &= \hbar\omega + 2x + \beta \\
 |11\rangle &= 2\hbar\omega + 6x \\
 |02\rangle &= 2\hbar\omega - 2\beta + 5x \\
 |20\rangle &= 2\hbar\omega + 2\beta + 5x
 \end{aligned}
 \tag{0.11}$$

We then get the final answer by setting $\nu = \hbar\omega + 2x$ and $\Delta = -2x$.

Problem 6.14: In Chapt. 1 we stated that 2D IR spectroscopy is not needed to measure the coupling if one can isotope label the local modes. Given the linear spectra in Fig. 6.14, two of which are from isotope labeled oscillators, (a) find the unknowns ω_1, ω_2 and β . (b) Find the relative angles between the transition dipoles. (c) Explain why the intensities of the isotope labeled peaks are different.

Solution: The frequencies of a coupled set of oscillators is given by diago-

nalizing the 2x2 Hamiltonian

$$\begin{pmatrix} \hbar\omega_1 & \beta \\ \beta & \hbar\omega_2 \end{pmatrix}$$

which has solutions

$$\begin{aligned} E_{\pm} &= \frac{1}{2}(\hbar\omega_1 + \hbar\omega_2) \pm \frac{1}{2}\sqrt{(\hbar\omega_1 - \hbar\omega_2)^2 + 4\beta^2} \\ |\Psi_+\rangle &= \cos(\theta/2)|\phi_1\rangle + \sin(\theta/2)|\phi_2\rangle \\ |\Psi_-\rangle &= -\sin(\theta/2)|\phi_1\rangle + \cos(\theta/2)|\phi_2\rangle \end{aligned}$$

where

$$\tan \theta = \frac{2\beta}{\hbar\omega_1 - \hbar\omega_2} \quad (0.12)$$

(a) From the 3 spectra, we measure that the unlabeled spectra has transitions at 1642 and 1674 cm^{-1} , one of the labels gives frequencies 1590 and 1666 cm^{-1} and the other at 1599 and 1657 cm^{-1} . The coupling will probably be $\pm 20 \text{cm}^{-1}$ since the spectrum of the non-isotope labeled peptide is split by $\pm 40 \text{cm}^{-1}$. Thus, it would seem natural to assume that the isotope labeled shift of $\sim 60 \text{cm}^{-1}$ enables one to directly measure $\hbar\omega_1$ and $\hbar\omega_2$ since it is much larger than β , which would give $\hbar\omega_1 = 1666 \text{cm}^{-1}$ and $\hbar\omega_2 = 1657 \text{cm}^{-1}$. Let's check to see if that is consistent with the unlabeled spectra:

$$\begin{aligned} E_+ &= 1674 = 1651.5 + \frac{1}{2}\sqrt{9^2 + 4\beta^2} \\ E_- &= 1642 = 1651.5 - \frac{1}{2}\sqrt{9^2 + 4\beta^2} \end{aligned}$$

which gives $\beta = 11.7 \text{cm}^{-1}$ and $\beta = 19 \text{cm}^{-1}$ for the E_+ and E_- modes, respectively, which is horrible agreement. Thus, the isotope labels must not completely "decouple" the two modes.

Instead, one could iteratively solve all 3 Hamiltonians to match data:

$$\begin{pmatrix} \hbar\omega_1 & \beta \\ \beta & \hbar\omega_2 \end{pmatrix}$$

$$\begin{pmatrix} \hbar\omega_1 - \delta & \beta \\ \beta & \hbar\omega_2 \end{pmatrix}$$

$$\begin{pmatrix} \hbar\omega_1 & \beta \\ \beta & \hbar\omega_2 - \delta \end{pmatrix}$$

which gives $\hbar\omega_1=1653$, $\hbar\omega_2=1663$, $\beta=15$, and $\delta=60 \text{ cm}^{-1}$, with eigenvectors

$$\begin{aligned} |-\rangle &= -0.81|\phi_1\rangle + 0.58|\phi_2\rangle \\ |+\rangle &= 0.58|\phi_1\rangle + 0.81|\phi_2\rangle \end{aligned}$$

(b) We can now use the eigenvectors and the ratio of the two peak intensities (about 5:2) to get the relative angle θ between the transition dipole. Start by projecting the transition dipole vectors into a coordinate system (placing them in the xy-plane with reflection symmetry about the y-axis)

$$\begin{aligned} \vec{\mu}_1 &= -\sin\theta\hat{\mu}_x + \cos\theta\hat{\mu}_y \\ \vec{\mu}_2 &= \sin\theta\hat{\mu}_x + \cos\theta\hat{\mu}_y \end{aligned}$$

and then calculate the ratio

$$\begin{aligned} \frac{2}{5} &= \frac{|\mu_-|^2}{|\mu_+|^2} = \frac{|-0.81\vec{\mu}_1 + 0.58\vec{\mu}_2|^2}{|0.58\vec{\mu}_1 + 0.81\vec{\mu}_2|^2} \\ &= \frac{|1.39\sin\theta\hat{\mu}_x - 0.23\cos\theta\hat{\mu}_y|^2}{|0.23\sin\theta\hat{\mu}_x + 1.39\cos\theta\hat{\mu}_y|^2} \end{aligned} \quad (0.13)$$

Try a few angles and get $\theta=20^\circ$ so that the relative angles between the two is 40° . (c) The intensities of the two peaks in the isotope labeled spectra indicate that the two oscillators are not completely decoupled by the isotope labeling. If they were decoupled, they would be equal so long as they had the same local mode oscillator strengths (for instance, the two oscillators were equivalent protein modes). It is interesting that even though the isotope labeled shift is much larger than the coupling, it is still not large enough to fully neglect.