

11. TIME-DOMAIN DESCRIPTION OF SPECTROSCOPY

11.1. A Classical Description of Spectroscopy

The traditional quantum mechanical treatment of spectroscopy is a static representation of a very dynamic process. An oscillating light field acts to drive bound charges in matter, which under resonance conditions leads to efficient exchange of energy between the light and matter. This dynamical picture emerges from a time-domain description, which shares many similarities to a classical description. Since much of the physical intuition that is helpful in understanding spectroscopy naturally emerges from the classical view, we will describe it first.

The classical view begins with the observation that atoms and molecules are composed of charged particles, and these charges are the handle by which an electromagnetic field exerts a force on the atom or molecule. The force exerted on the molecules depends on the form of the potential binding the charges together, the magnitude of the charges, and the strength of the external field.

The simplest elements of a model that captures what happens in absorption spectroscopy require us to consider a charged particle in a bound potential interacting with an oscillating driving force. The matter can be expressed in terms of a particle with charge z in a harmonic potential (the leading term in any expansion of the potential in the coordinate Q):

$$V_{res}(t) = \frac{1}{2} \kappa Q^2 \quad (11.1)$$

Here k is the restoring force constant. For the light field, we use the traditional expression

$$V_{ext}(t) = -\bar{\mu} \cdot \bar{E}(t) \quad (11.2)$$

for an external electromagnetic field interacting with the dipole moment of the system, $\bar{\mu} = zQ$. We describe the behavior of this system using Newton's equation of motion $F=ma$, which we write as

$$m \frac{\partial^2 Q}{\partial t^2} = F_{res} + F_{damp} + F_{ext} \quad (11.3)$$

On the right hand side of eq. (11.3) there are three forces: the harmonic restoring force, a damping force, and the driving force exerted by the light. Remembering that $F = -(\partial V / \partial Q)$, we can write eq. (11.3) as

$$m \frac{\partial^2 Q}{\partial t^2} = -\kappa Q - b \frac{\partial Q}{\partial t} + F_0 \cos(\omega t) \quad (11.4)$$

Here, b describes the rate of damping. For the field, we have only considered the time-dependence $\bar{E}(t) = \bar{E}_0 \cos(\omega t)$ and the amplitude of the driving force

$$F_0 = \left(\frac{\partial \bar{\mu}}{\partial Q} \right) \cdot \bar{E}_0 \quad (11.5)$$

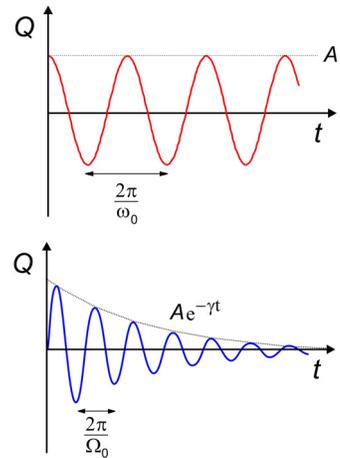
Eq. (11.5) indicates that increasing the force on the oscillator is achieved by raising the magnitude of the field, increasing how much the charge is displaced, or improving the alignment between the electric field polarization and the transition dipole moment.

We can rewrite eq. (11.4) as the driven harmonic oscillator equation:

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{F_0}{m} \cos(\omega t) \quad (11.6)$$

Here the damping constant $\gamma = b/2m$ and the harmonic resonance frequency $\omega_0 = \sqrt{\kappa/m}$.

Let's look at the solution to eq. (11.6) for a couple of simple cases. First, for the case that there is no damping or driving force ($\gamma = F_0 = 0$), we have simple harmonic solutions in which oscillate at a frequency ω_0 : $Q(t) = A \sin(\omega_0 t) + B \cos(\omega_0 t)$. Let's just keep the *sin* term for now. Now if you add damping to the equation: $Q(t) = A e^{-\gamma t} \sin \Omega_0 t$. The coordinate oscillates at a reduced frequency $\Omega_0 = \sqrt{\omega_0^2 - \gamma^2}$. As we continue, let's assume a case with weak damping for which $\Omega_0 \approx \omega_0$.



The solution to eq. (11.6) takes the form

$$Q(t) = \frac{F_0/m}{\sqrt{(\omega_0^2 - \omega^2)^2 + 4\gamma^2 \omega^2}} \sin(\omega t + \beta) \quad (11.7)$$

Where the phase factor is

$$\tan \beta = (\omega_0^2 - \omega^2) / 2\gamma\omega \quad (11.8)$$

So this solution to the displacement of the particle says that the amplitude certainly depends on the magnitude of the driving force, but more importantly on the resonance condition. The frequency of the driving field should match the natural resonance frequency of the system, $\omega_0 \approx \omega$...like pushing someone on a swing. When you drive the system at the resonance frequency there will be an efficient transfer of power to the oscillator, but if you push with arbitrary frequency, nothing will happen. Indeed, that is what an absorption spectrum is: a measure of the power absorbed by the system from the field.

Notice that the coordinate oscillates at the driving frequency ω and not at the resonance frequency ω_0 . Also, the particle oscillates as a *sin*, that is, 90° out-of-phase with the field when driven on resonance. This reflects the fact that the maximum force can be exerted on the particle

when it is stationary at the turning points. The phase shift β , depends varies with the detuning from resonance.

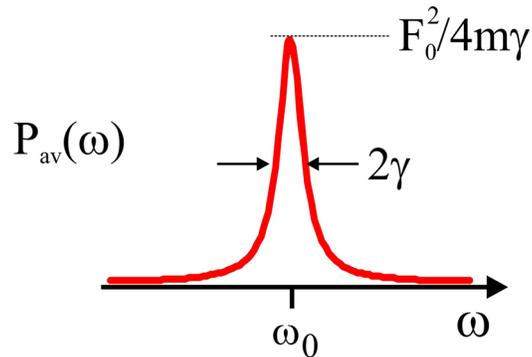
Now we can make some simplifications to eq. (11.7) and calculate the absorption spectrum. For weak damping $\gamma \ll \omega_0$ and near resonance $\omega_0 \approx \omega$, we can write

$$(\omega_0^2 - \omega^2)^2 = (\omega_0 - \omega)^2 (\omega_0 + \omega)^2 \approx 4\omega_0^2 (\omega_0 - \omega)^2 \quad (11.9)$$

The absorption spectrum is a measure of the power transferred to the oscillator, so we can calculate it by finding the power absorbed from the force on the oscillator times the velocity, averaged over a cycle of the field.

$$\begin{aligned} P_{avg} &= \left\langle F(t) \cdot \frac{\partial Q}{\partial t} \right\rangle_{avg} \\ &= \frac{\gamma F_0^2}{2m} \frac{1}{(\omega - \omega_0)^2 + \gamma^2} \end{aligned} \quad (11.10)$$

This is the Lorentzian lineshape, which is peaked at the resonance frequency and has a line width of 2γ (full width half-maximum, FWHM). The area under the lineshape is $\pi F_0^2 / 4m$.



11.2. Time-Correlation Function Description of Absorption Lineshape

The interaction of light and matter as we have described from Fermi's Golden Rule gives the rates of transitions between discrete eigenstates of the material Hamiltonian H_0 . The frequency dependence to the transition rate is proportional to an absorption spectrum. We also know that interaction with the light field prepares a superposition of the eigenstates of H_0 , and this leads to the periodic oscillation of amplitude between the states. Nonetheless, the transition rate expression really seems to hide any time-dependent description of motions in the system. An alternative approach to spectroscopy is to recognize that the features in a spectrum are just a frequency domain representation of the underlying molecular dynamics of molecules. For absorption, the spectrum encodes the time-dependent changes of the molecular dipole moment for the system, which in turn depends on the position of electrons and nuclei.

A time-correlation function for the dipole operator can be used to describe the dynamics of an equilibrium ensemble that dictate an absorption spectrum. We will make use of the transition rate expressions from first-order perturbation theory that we derived in the previous section to express the absorption of radiation by dipoles as a correlation function in the dipole operator. Let's start with the rate of absorption and stimulated emission between an initial state $|\ell\rangle$ and final state $|k\rangle$ induced by a monochromatic field

$$w_{k\ell} = \frac{\pi E_0^2}{2\hbar^2} \left| \langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right] \quad (11.11)$$

For shorthand we have written $|\bar{\mu}_{k\ell}|^2 = \left| \langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle \right|^2$. We would like to use this to calculate the experimentally observable absorption coefficient (cross-section) which describes the transmission through the sample

$$T = \exp[-\Delta N \alpha(\omega) L] \quad (11.12)$$

The absorption cross section describes the rate of energy absorption per unit time relative to the intensity of light incident on the sample

$$\alpha = \frac{-\dot{E}_{rad}}{I} \quad (11.13)$$

The incident intensity is

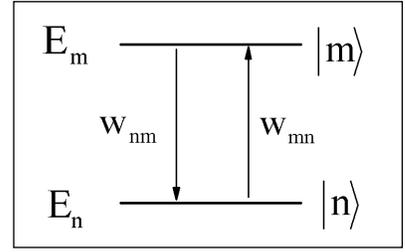
$$I = \frac{c}{8\pi} E_0^2 \quad (11.14)$$

If we have two discrete states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$, the rate of energy absorption is proportional to the absorption rate and the transition energy

$$-\dot{E}_{rad} = w_{nm} \cdot \hbar \omega_{nm} \quad (11.15)$$

For an ensemble this rate must be scaled by the probability of occupying the initial state.

More generally, we want to consider the rate of energy loss from the field as a result of the difference in rates of absorption and stimulated emission between states populated with a thermal distribution. So, summing all possible initial and final states $|\ell\rangle$ and $|k\rangle$ over all possible upper and lower states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$



$$-\dot{E}_{rad} = \sum_{\ell, k \in \{m, n\}} p_{\ell} w_{k\ell} \hbar \omega_{k\ell} \quad (11.16)$$

$$= \frac{\pi E_0^2}{2\hbar} \sum_{\ell, k \in \{m, n\}} \omega_{k\ell} p_{\ell} |\bar{\mu}_{k\ell}|^2 [\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega)]$$

The cross section including the net change in energy as a result of absorption $|n\rangle \rightarrow |m\rangle$ and stimulated emission $|m\rangle \rightarrow |n\rangle$ is:

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \sum_{n, m} [\omega_{mn} p_n |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) + \omega_{nm} p_m |\bar{\mu}_{nm}|^2 \delta(\omega_{nm} + \omega)] \quad (11.17)$$

To simplify this we note:

- 1) Since $\delta(x) = \delta(-x)$, $\delta(\omega_{nm} + \omega) = \delta(-\omega_{nm} + \omega) = \delta(\omega_{mn} - \omega)$.
- 2) The matrix elements squared in the two terms are the same: $|\bar{\mu}_{mn}|^2 = |\bar{\mu}_{nm}|^2$.
- 3) $\omega_{mn} = -\omega_{nm} = \omega$ as a result of the delta function enforcing this equality.

So,

$$\alpha(\omega) = \frac{4\pi^2 \omega}{\hbar c} \sum_{n, m} (p_n - p_m) |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) \quad (11.18)$$

Here we see that the absorption coefficient depends on the population difference between the two states. This is expected since absorption will lead to loss of intensity, whereas stimulated emission leads to gain. With equal populations in the upper and lower state, no change to the incident field would be expected. Since $p_{\ell} = \exp[-\beta E_{\ell}] / Z$

$$p_n - p_m = p_n (1 - \exp[-\beta \hbar \omega_{mn}]) \quad (11.19)$$

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sum_{n, m} p_n |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) \quad (11.20)$$

Again the ω_{mn} factor has been replaced with ω . We can now separate α into a product of factors that represent the field, and the matter, where the matter is described by $\sigma(\omega)$, the absorption lineshape.

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta\hbar\omega}) \sigma(\omega) \quad (11.21)$$

$$\sigma(\omega) = \sum_{n,m} p_n |\bar{\mu}_{mn}|^2 \delta(\omega_{mn} - \omega) \quad (11.22)$$

To express the lineshape in terms of a correlation function we use one representation of the delta function through a Fourier transform of a complex exponential:

$$\delta(\omega_{mn} - \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i(\omega_{mn} - \omega)t} \quad (11.23)$$

to write

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \sum_{n,m} p_n \langle n | \bar{\mu} | m \rangle \langle m | \bar{\mu} | n \rangle e^{i(\omega_{mn} - \omega)t} \quad (11.24)$$

Now equating $U_0 |n\rangle = e^{-iH_0 t/\hbar} |n\rangle = e^{-iE_n t/\hbar} |n\rangle$, and recognizing that our expression contains the projection operator $\sum_m |m\rangle \langle m| = 1$, we can write

$$\begin{aligned} \sigma(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \sum_{n,m} p_n \langle n | \bar{\mu} | m \rangle \langle m | U_0^\dagger \bar{\mu} U_0 | n \rangle e^{-i\omega t} \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \sum_{n,m} p_n \langle n | \bar{\mu}_I(0) \bar{\mu}_I(t) | n \rangle e^{-i\omega t} \end{aligned} \quad (11.25)$$

But this last expression is just a dipole moment correlation function: the equilibrium thermal average over a pair of time-dependent dipole operators:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\mu}_I(0) \bar{\mu}_I(t) \rangle \quad (11.26)$$

The absorption lineshape is given by the Fourier transform of the dipole correlation function. The correlation function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of E field and contains information on states of system and broadening due to relaxation. Additional manipulations can be used to switch the order of operators by taking the complex conjugate of the exponential

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \bar{\mu}_I(t) \bar{\mu}_I(0) \rangle \quad (11.27)$$

and we can add back the polarization of the light field to the matrix element

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \hat{\varepsilon} \cdot \bar{\mu}_I(t) \hat{\varepsilon} \cdot \bar{\mu}_I(0) \rangle \quad (11.28)$$

to emphasize the orientational component to this correlation function.

Here we have written operators emphasizing the interaction picture representation. As we move forward, we will drop this notation, and take it as understood that for the purposes of

spectroscopy, the dipole operator is expressed in the interaction picture and evolves under the material Hamiltonian H_0 .

Readings

1. McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
2. McQuarrie, D. A., *Statistical Mechanics*. Harper & Row: New York, 1976; Ch. 21.
3. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006.
4. Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; Section 6.2.

11.3. Different Types of Spectroscopy Emerge from the Dipole Operator

So the absorption spectrum in any frequency region is given by the Fourier transform over the dipole correlation function that describes the time-evolving charge distributions in molecules, solids, and nanosystems. Let's consider how this manifests itself in a few different spectroscopies, which have different contributions to the dipole operator. In general the dipole operator is a relatively simple representation of the charged particles of the system:

$$\bar{\mu} = \sum_i q_i (\bar{r}_i - \bar{r}_0) \quad (11.29)$$

The complexity arises from the time-dependence of this operator, which evolves under the full Hamiltonian for the system:

$$\bar{\mu}(t) = e^{iH_0 t/\hbar} \bar{\mu}(0) e^{-iH_0 t/\hbar} \quad (11.30)$$

$$\begin{aligned} H_0 = & H_{elec} + H_{vib} + H_{rot} + H_{trans} + H_{spin} + \dots + H_{bath} + \dots \\ & + \sum_{i,j \in \{e,v,r,t,s,b,EM\}} H_{i-j} + \dots \end{aligned} \quad (11.31)$$

The full Hamiltonian accounts for the dynamics of all electronic, nuclear, and spin degrees of freedom. It is expressed in eq. (11.31) in terms of separable contributions to all possible degrees of freedom and a bath Hamiltonian that contains all of the dark degrees of freedom not explicitly included in the dipole operator. We could also include an electromagnetic field. The last term describes pairwise couplings between different degrees of freedom, and emphasizes that interactions such as electron-nuclear interactions H_{e-v} and spin-orbit coupling H_{e-s} . The wavefunction for the system can be expressed in terms of product states of the wavefunctions for the different degrees of freedom,

$$|\psi\rangle = |\psi_{elec} \psi_{vib} \psi_{rot} \dots\rangle \quad (11.32)$$

When the H_{i-j} interaction terms are neglected, the correlation function can be separated into a product of correlation functions from various sources:

$$C_{\mu\mu}(t) = C_{elec}(t) C_{vib}(t) C_{rot}(t) \dots \quad (11.33)$$

which are each expressed in the form shown here for the vibrational states

$$C_{vib}(t) = \sum_{n=vib} p_n \langle \Phi_n | e^{iH_{vib}t} \mu e^{-iH_{vib}t} \mu | \Phi_n \rangle \quad (11.34)$$

Φ_n is the wavefunction for the n^{th} vibrational eigenstate. The net correlation function will have oscillatory components at many frequencies and its Fourier transform will give the full absorption spectrum from the ultraviolet to the microwave regions of the spectrum. Generally speaking the

highest frequency contributions (electronic or UV/Vis) will be modulated by contributions from lower frequency motions (...such as vibrations and rotations). However, we can separately analyze each of these contributions to the spectrum.

Examples

Atomic transitions

$H_0 = H_{atom}$. For hydrogenic orbitals, $|n\rangle \rightarrow |n \ell m_\ell\rangle$.

Rotational spectroscopy

From a classical perspective, the dipole moment can be written in terms of a permanent dipole moment with amplitude and direction

$$\bar{\mu} = \mu_0 \hat{u} \quad (11.35)$$

$$\sigma(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \mu_0^2 \langle \hat{\varepsilon} \cdot \hat{u}(0) \hat{\varepsilon} \cdot \hat{u}(t) \rangle \quad (11.36)$$

The lineshape is the Fourier transform of the rotational motion of the permanent dipole vector in the laboratory frame. μ_0 is the magnitude of the permanent dipole moment averaged over the fast electronic and vibrational degrees of freedom. The frequency of the resonance would depend on the rate of rotation—the angular momentum and the moment of inertia. Collisions or other damping would lead to the broadening of the lines.

Quantum mechanically we expect a series of rotational resonances that mirror the thermal occupation and degeneracy of rotational states for the system. Taking the case of a rigid rotor with cylindrical symmetry as an example, the Hamiltonian is

$$H_{rot} = \frac{\bar{L}^2}{2I} \quad (11.37)$$

and the wavefunctions are spherical harmonics $Y_{J,M}(\theta, \phi)$ which are described by

$$\begin{aligned} \bar{L}^2 |Y_{J,M}\rangle &= \hbar^2 J(J+1) |Y_{J,M}\rangle & J = 0, 1, 2, \dots \\ L_z |Y_{J,M}\rangle &= M\hbar |Y_{J,M}\rangle & M = -J, -J+1, \dots, J \end{aligned} \quad (11.38)$$

J is the rotational quantum number. M (or M_J) refers to its projection onto an axis (z), and has a degeneracy of $g_M(J) = 2J+1$. The energy eigenvalues for H_{rot} are

$$E_{J,M} = \bar{B}J(J+1) \quad (11.39)$$

where the rotational constant, here in units of joules, is

$$\bar{B} = \frac{\hbar^2}{2I} \quad (11.40)$$

If we take a dipole operator in the form of eq. (11.35), then the far-infrared rotational spectrum will be described by the correlation function

$$C_{rot}(t) = \sum_{J,M} p_{J,M} |\mu_0|^2 \langle Y_{J,M} | e^{iH_{rot}t/\hbar} (\hat{u} \cdot \hat{\epsilon}) e^{-iH_{rot}t/\hbar} (\hat{u} \cdot \hat{\epsilon}) | Y_{J,M} \rangle \quad (11.41)$$

The evaluation of this correlation function involves an orientational average, which is evaluated as follows

$$\langle Y_{J',M'} | f(\theta, \phi) | Y_{J,M} \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{J',M'}^* f(\theta, \phi) Y_{J,M} \quad (11.42)$$

Recognizing that $(\hat{u} \cdot \hat{\epsilon}_Z) = \cos\theta$, we can evaluate eq. (11.41) using the reduction formula

$$\cos\theta | Y_{J,M} \rangle = c_{J+} | Y_{J+1,M} \rangle + c_{J-} | Y_{J-1,M} \rangle \quad (11.43)$$

$$c_{J+} = \sqrt{\frac{(J+1)^2 - M^2}{4(J+1)^2 - 1}} \quad c_{J-} = \sqrt{\frac{J^2 + M^2}{4J^2 - 1}} \quad (11.44)$$

and the orthogonality of spherical harmonics

$$\langle Y_{J',M'} | Y_{J,M} \rangle = 4\pi \delta_{J',J} \delta_{M',M} \quad (11.45)$$

The factor $p_{J,M}$ in eq. (11.41) is the probability of thermally occupying a particular J, M level. For this we recognize that $p_{J,M} = g_M(J) e^{-\beta E_J} / Z_{rot}$, so that eq. (11.41) leads to the correlation function

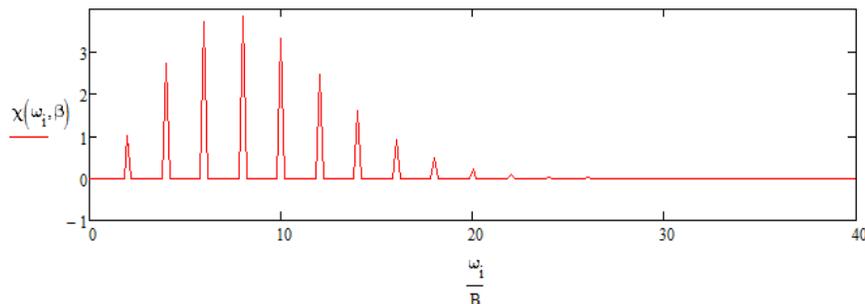
$$C_{rot}(t) = \frac{|\mu_0|^2}{Z_{rot}} \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)/\hbar} \left[e^{-i(J+1)2\bar{B}t/\hbar} + e^{iJ2\bar{B}t/\hbar} \right] \quad (11.46)$$

Fourier transforming eq. (11.46) leads to the lineshape

$$\sigma_{rot}(\omega) = \frac{|\mu_0|^2}{Z_{rot}} \hbar \sum_J (2J+1) e^{-\beta \bar{B}J(J+1)/\hbar} \left[\delta(\hbar\omega - 2\bar{B}(J+1)) + \delta(\hbar\omega + 2\bar{B}J) \right] \quad (11.47)$$

The two terms reflect the fact that each thermally populated level with $J > 0$ contributes both to absorptive and stimulated emission processes, and the observed intensity reflects the difference in populations.

Set temperature: $\beta := \frac{0.05}{B}$



IR vibrational spectroscopy

Vibrational spectroscopy can be described by taking the dipole moment to be weakly dependent on the displacement of vibrational coordinates q

$$\bar{\mu} = \bar{\mu}_0 + \left. \frac{\partial \bar{\mu}}{\partial q} \right|_{q=q_0} q + \dots \quad (11.48)$$

Here the first expansion term is the permanent dipole moment and the second term is the transition dipole moment. If we are performing our ensemble average over vibrational states, the lineshape becomes the Fourier transform of a correlation function in the vibrational coordinate

$$\sigma(\omega) = \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle q(0)q(t) \rangle \quad (11.49)$$

The vector nature of the transition dipole has been dropped here. So the time-dependent dynamics of the vibrational coordinate dictate the IR lineshape.

This approach holds for the classical and quantum mechanical cases. In the case of quantum mechanics, the change in charge distribution in the transition dipole moment is replaced with the equivalent transition dipole matrix element $|\partial \bar{\mu} / \partial q|^2 \Rightarrow |\bar{\mu}_{k\ell}|^2$. If we take the vibrational Hamiltonian to be that of a harmonic oscillator,

$$H_{vib} = \frac{1}{2m} p^2 + \frac{1}{2} m \omega_0^2 q^2 = \hbar \omega_0 \left(a^\dagger a + \frac{1}{2} \right) \quad (11.50)$$

then the time-dependence of the vibrational coordinate, expressed as raising and lowering operators is

$$q(t) = \sqrt{\frac{\hbar}{2m\omega_0}} \left(a^\dagger e^{i\omega_0 t} + a e^{-i\omega_0 t} \right) \quad (11.51)$$

The absorption lineshape is then obtained from eq. (11.49).

$$\sigma_{vib}(\omega) = \frac{1}{Z_{vib}} \sum_n e^{-\beta n \hbar \omega_0} \left[|\bar{\mu}_{(n+1)n}|^2 (\bar{n} + 1) \delta(\omega - \omega_0) + |\bar{\mu}_{(n-1)n}|^2 \bar{n} \delta(\omega + \omega_0) \right] \quad (11.52)$$

where $\bar{n} = (e^{\beta \hbar \omega_0} - 1)^{-1}$ is the thermal occupation number. For the low temperature limit applicable to most vibrations under room temperature conditions $\bar{n} \rightarrow 0$ and

$$\sigma_{vib}(\omega) = |\bar{\mu}_{10}|^2 \delta(\omega - \omega_0) \quad (11.53)$$

Raman spectroscopy

Technically, we need second-order perturbation theory to describe Raman scattering, because transitions between two states are induced by the action of two light fields whose frequency difference equals the energy splitting between states. But much the same result is obtained if we replace the dipole operator with an induced dipole moment generated by the incident field: $\bar{\mu} \Rightarrow \bar{\mu}_{ind}$. The incident field E_i polarizes the molecule,

$$\bar{\mu}_{ind} = \bar{\alpha} \cdot \bar{E}_i(t) \quad (11.54)$$

($\bar{\alpha}$ is the polarizability), and the scattered light field results from the interaction with this induced dipole

$$\begin{aligned} V(t) &= -\bar{\mu}_{ind} \cdot \bar{E}_s(t) \\ &= \bar{E}_s(t) \cdot \bar{\alpha} \cdot \bar{E}_i(t) \\ &= E_s(t) E_i(t) (\hat{\epsilon}_s \cdot \bar{\alpha} \cdot \hat{\epsilon}_i) \end{aligned} \quad (11.55)$$

Here we have written the polarization components of the incident (i) and scattered (s) light projecting onto the polarizability tensor $\bar{\alpha}$. Equation (11.55) leads to an expression for the Raman lineshape as

$$\begin{aligned} \sigma(\omega) &= \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon}_s \cdot \bar{\alpha}(0) \cdot \hat{\epsilon}_i \hat{\epsilon}_s \cdot \bar{\alpha}(t) \cdot \hat{\epsilon}_i \rangle \\ &= \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\alpha}(0) \bar{\alpha}(t) \rangle \end{aligned} \quad (11.56)$$

To evaluate this, the polarizability tensor can also be expanded in the nuclear coordinates

$$\bar{\alpha} = \bar{\alpha}_0 + \left. \frac{\partial \bar{\alpha}}{\partial q} \right|_{q=q_0} q + \dots \quad (11.57)$$

where the leading term would lead to Rayleigh scattering and rotational Raman spectra, and the second term would give vibrational Raman scattering.

Also remember that the polarizability tensor is a second rank tensor that tells you how well a light field polarized along i can induce a dipole moment (light-field-induced charge displacement) in the s direction. For cylindrically symmetric systems which have a polarizability component α_{\parallel} along the principal axis of the molecule and a component α_{\perp} perpendicular to that axis, this usually takes the form

$$\bar{\alpha} = \begin{pmatrix} \alpha_{\parallel} & & \\ & \alpha_{\perp} & \\ & & \alpha_{\perp} \end{pmatrix} = \alpha \mathbf{I} + \frac{1}{3} \beta \begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} \quad (11.58)$$

where α is the isotropic component of polarizability tensor and β is the anisotropic component.

11.4. Ensemble Averaging and Line-Broadening

We have seen that an absorption lineshape can represent the dynamics of the dipole or be broadened by energy relaxation, for instance through coupling to a continuum. However, there are numerous processes that can influence the lineshape. These can be separated by dynamic processes intrinsic to the molecular system, which is termed homogeneous broadening, and static effects known as inhomogeneous broadening, which can be considered an ensemble averaging effect. To illustrate, imagine that the dipole correlation function has an oscillatory, damped form

$$C_{\mu\mu}(t) = \sum_{g,e} p_g |\mu_{eg}|^2 \exp[-i\omega_{eg}t - \Gamma t] \quad (11.59)$$

Then the Fourier transform would give a lineshape

$$\text{Re}[\tilde{C}_{\mu\mu}(\omega)] = \sum_{g,e} p_g \frac{|\mu_{eg}|^2 \Gamma}{(\omega - \omega_{eg})^2 + \Gamma^2} \quad (11.60)$$

Here the homogeneous effects are reflected in the factor Γ , the damping rate and linewidth, whereas inhomogeneous effects arise from averaging over the ensemble.

Homogeneous broadening

Several dynamical mechanisms can potentially contribute to damping and line-broadening. These intrinsically molecular processes, often referred to as homogeneous broadening, are commonly assigned a time scale $T_2 = \Gamma^{-1}$.

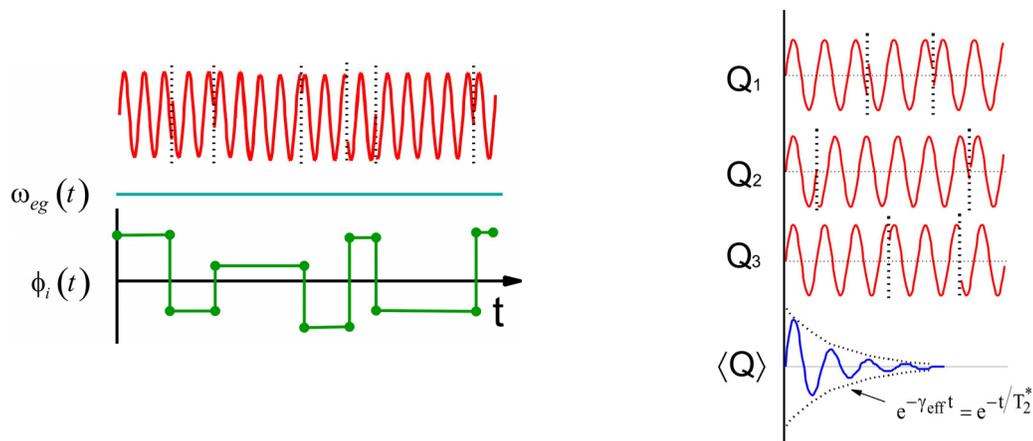
Population Relaxation. Population relaxation refers to decay in the coherence created by the light field as a result of the finite lifetime of the coupled states, and is often assigned a time scale T_1 . This can have contributions from radiative decay, such as spontaneous emission, or non-radiative processes such as relaxation as a result of coupling to a continuum.

$$\frac{1}{T_1} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}} \quad (11.61)$$

The observed population relaxation time depends on both the relaxation times of the upper and lower states (m and n) being coupled by the field: $1/T_1 = w_{mn} + w_{nm}$. When the energy splitting is high compared to $k_B T$, only the downward rate contributes, which is why the rate is often written $1/2T_1$.

Pure Dephasing. Pure dephasing is characterized by a time constant T_2^* that characterizes the randomization of phase within an ensemble as a result of molecular interactions. This is a dynamic effect in which memory of the phase of oscillation of a molecule is lost as a result of

intermolecular interactions that randomize the phase. Examples include collisions in a dense gas, or fluctuations induced by a solvent. This process does not change the population of the states involved.



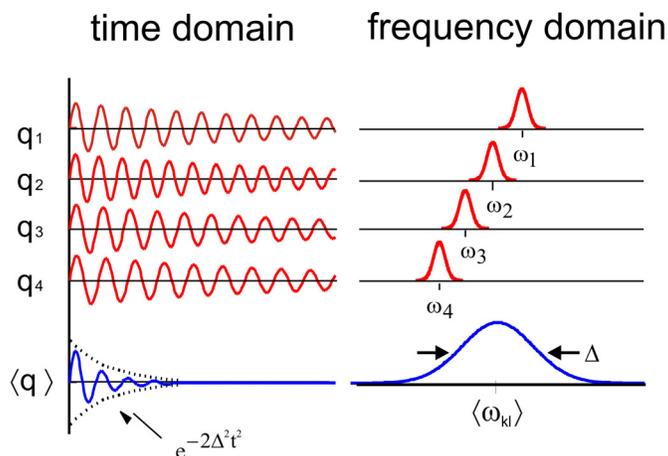
Orientalional relaxation. Orientalional relaxation (τ_{or}) also leads to relaxation of the dipole correlation function and to line-broadening. Since the correlation function depends on the projection of the dipole onto a fixed axis in the laboratory frame, randomization of the initial dipole orientations is an ensemble averaged dephasing effect. In solution, this process is commonly treated as an orientational diffusion problem in which τ_{or} is proportional to the diffusion constant.

If these homogeneous processes are independent, the rates for different processes contribute additively to the damping and line width:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{\tau_{or}} \quad (11.62)$$

Inhomogeneous broadening

Absorption lineshapes can also be broadened by a static distribution of frequencies. If molecules within the ensemble are influenced static environmental variations more than other processes, then the observed lineshape reports on the distribution of environments. This inhomogeneous broadening is a static ensemble averaging effect, which hides the dynamical content in the homogeneous linewidth. The origin of the inhomogeneous broadening can be molecular (for instance a distribution of defects in crystals) or macroscopic (i.e., an inhomogeneous magnetic field in NMR).



The inhomogeneous linewidth is dictated the width of the distribution Δ .

Total linewidth

The total observed broadening of the absorption lineshape reflects the contribution of all of these effects:

$$C_{\mu\mu} \propto \exp \left[-i\omega_{eg}t - \left(\frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{\tau_{or}} \right) t - \frac{\Delta^2}{2} t^2 \right] \quad (11.63)$$

These effects can be wrapped into a lineshape function $g(t)$. The lineshape for the broadening of a given transition can be written as the Fourier transform over the oscillating transition frequency damped and modulated by a complex $g(t)$:

$$\sigma(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg}t - g(t)} \quad (11.64)$$

All of these effects can be present simultaneously in an absorption spectrum.