FLUCTUATIONS AND SPECTRAL DIFFUSION

We now have a model for the interaction of one spectroscopic transition with nuclear motion treated as an undamped harmonic oscillator, which can be extended to a continuous distribution of harmonic modes with frequency $\omega$. We know from previously that coupling of a state to a continuum will lead to irreversible relaxation and line broadening, so we will want to look at this in some detail to understand the origin of lineshapes.

Coupling to a continuous distribution of harmonic modes is a static picture of what is actually a dynamic problem. In the following lectures, we will show how this frequency domain picture is equivalent to a time-domain picture in which the spectroscopic transition energy gap fluctuates about an average frequency with statistics given by the distribution coupled modes.

To begin, let’s discuss the influence on the absorption lineshape of random fluctuations in $\omega_{eg}$, which arise from intermolecular interactions. Consider the two limiting cases of line broadening:

**Homogeneous:**

Absorption lineshape is dynamically broadened by variations in the amplitude, phase, or orientation of dipoles.

Dephasing, Lifetime, Rotation $\rightarrow$ exponential decay time $T_2$

For the case of our current discussion, let’s only concentrate on pure-dephasing $T_2^*$ from rapid fluctuations in $\omega_{eg}$.

**Inhomogeneous:**

Static distribution of resonance frequencies.

Width of line represents distribution of frequencies (for instance structural environments).

More generally, every system lies between these limits. Imagine every molecule having a different “instantaneous frequency” $\omega_i(t)$ which evolves in time.
**Spectral Diffusion**

The homogeneous (pure-dephasing) and inhomogeneous limits can be described as limiting forms for the fluctuations of a frequency $\omega_i(t)$ through a Gaussian distribution of frequencies.

- If $\omega_i(t)$ evolves slowly $\rightarrow$ inhomogeneous
- If $\omega_i(t)$ evolves rapidly $\rightarrow$ homogeneous

The general behavior is well described by the transition frequency correlation function.

### Time-domain behavior

\[ C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle \]

#### Homogeneous

"Motionally narrowed"

\[ \frac{1}{\pi T_2^*} \]

#### Inhomogeneous

Static distribution

\[ \langle \omega_{eg}^2 \rangle \]

#### Time-varying freq.

\[ \omega_{eg}(t) \]

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Gaussian-Stochastic Model for Spectral Diffusion

We will begin with a classical description of how random fluctuations in frequency would be expected to influence the absorption lineshape. The absorption lineshape will again be obtained from the dipole correlation function for the electronic transition.

We will find the lineshape function $g(t)$ for a Gaussian-Stochastic model for random fluctuations in the transition frequency $\omega_{eg}$. The time dependence to the transition energy reflects random fluctuations about average value:

$$\omega(t) = \langle \omega_{eg} \rangle + \delta \omega(t)$$

$$\langle \delta \omega(t) \rangle = 0$$

The fluctuations in $\omega_{eg}$ allow the system to explore a Gaussian distribution of transitions frequencies characterized by a variance:

$$\Delta = \langle \delta \omega^2 \rangle^{1/2}$$

The time scale of the fluctuations are characterized by a correlation time:

$$\tau_c = \frac{1}{\Delta^2} \int_0^{\infty} dt \langle \delta \omega(t) \delta \omega(0) \rangle$$

Classical Description

Let’s treat the variation of the dipole moment as a classical internal variable to the system, which is coupled to the frequency fluctuations $\omega(t)$

$$\frac{\partial \mu}{\partial t} = -i \omega(t) \mu$$

$$\mu(t) = \mu(0) \exp \left[ -i \int_0^t d\tau \omega(\tau) \right]$$

This is a classical equation, but note the similarity to the quantum Heisenberg equation for the dipole operator:

$$\frac{\partial \mu}{\partial t} = \frac{i}{\hbar} \left[ H(t) \mu - \mu H(t) \right]$$

This offers some insight into how the quantum version of this problem will look.
\[
\mu(t) = \mu(0) \exp \left[ -i \int_0^t d\tau \langle \omega(\tau) \rangle \right]
\]

\[
= \mu(0) \exp \left[ -i \langle \omega \rangle t - i \int_0^t d\tau \delta \omega(\tau) \right]
\]

\[
C_{\mu \mu}(t) = \langle \mu(t) \mu(0) \rangle = |\mu|^2 e^{i\langle \omega \rangle t} F(t)
\]

where \( F(t) = \left\langle \exp \left[ -i \int_0^t d\tau \delta \omega(\tau) \right] \right\rangle. \)

To simplify \( F(t) \), we can expand it: **cumulant expansion of averages** (see Appendix)

\[
F(t) = \exp \left[ -i \int_0^t d\tau_1 \langle \delta \omega(\tau_1) \rangle + \frac{i^2}{2!} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta \omega(\tau_1) \delta \omega(\tau_2) \rangle + \cdots \right]
\]

First term = 0 \quad Stationary: \( \langle \delta \omega(\tau' - \tau'') \delta(0) \rangle \)

Only the second term survives for a system with Gaussian statistics to the fluctuations. This is a classical description, so there is no time-ordering to the exponential.

\[
F(t) = \exp \left[ -\frac{i}{2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta \omega(\tau_1) \delta \omega(\tau_2) \rangle \right]
\]

\( F(t) \) can be rewritten through a change of variables (\( \tau = \tau' - \tau''' \)):

\[
F(t) = \exp \left[ -\int_0^t d\tau (t - \tau) \langle \delta \omega(\tau) \delta(0) \rangle \right]
\]

So the frequency fluctuations are described by a correlation function

\[
C_{\delta \omega \delta}(t) = \langle \delta \omega(t) \delta(0) \rangle
\]

\[
\Delta = \langle \delta \omega^2 \rangle^{1/2}, \quad \tau_c = \frac{1}{\Delta^2} \int_0^\infty d\tau \ C_{\delta \omega \delta}(\tau)
\]
Now, we will calculate the lineshape assuming that the $C_{\delta\omega\delta\omega}$ decays exponentially

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp[-t/\tau_c]$$

Then

$$F(t) = \exp\left[-\Delta^2 \tau_c^2 \left(\exp\left(-t/\tau_c\right) + t/\tau_c - 1\right)\right]$$

or

$$g(t) = \Delta^2 \tau_c^2 \left(\exp\left(-t/\tau_c\right) + t/\tau_c - 1\right) \quad \text{with } F(t) = \exp(-g(t)).$$

Let’s look at the limiting forms of $g(t)$.

1) **Long correlation times** (or short $t$): $t \ll \tau_c$. This corresponds to the inhomogeneous case where $C_{\delta\omega\delta\omega}(t) = \Delta^2$ (a constant). For $t \ll \tau_c$ we do short time expansion of exponential

$$e^{-t/\tau_c} \rightarrow 1 - t/\tau_c + \frac{t^2}{2\tau_c^2} + \ldots$$

$$g(t) = \Delta^2 t^2 / 2$$

At short times, our correlation function will have a Gaussian decay

$$F(t) = \exp\left(-\Delta^2 t^2 / 2\right)$$

with a rate $\propto \Delta$. This has the proper behavior for a classical correlation function: even in time $C_{\mu\nu}(t) = C_{\mu\nu}(-t)$.

Now the absorption lineshape is:

$$\sigma_{abs}(\omega) \propto \int_{-\infty}^{\infty} dt \, e^{i\omega t} e^{-i(\omega)\tau - g(t)}$$

$$\propto \int_{-\infty}^{\infty} dt \, e^{i(\omega-\langle\omega\rangle)t} e^{-\Delta^2 t^2 / 2}$$

$$\approx \exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \quad \text{Gaussian shape}$$

Inhomogeneous lineshape.
2) **Very short correlation times** $t >> \tau_c$. This corresponds to the homogeneous case where $C_{\delta\delta}(t) = \Delta^2 \delta(t)$. For $t >> \tau_c$ we set $e^{-t/\tau_c} \rightarrow 0$ and $t/\tau >> 1$. Then

$$g(t) = -\Delta^2 \tau_c t$$

$$F(t) = \exp[-\Delta^2 \tau_c t] \quad \text{An exponential decay!}$$

Or

$$F(t) \propto \exp[-t/T_2] \quad \Delta^2 \tau_c \equiv \frac{1}{T_2}$$

Lineshape: For very short correlation times (or very fast fluctuations)

$$\sigma_{abs}(\omega) \propto \text{Re} \int_{-\infty}^{\infty} dt e^{i(\omega-\langle\omega\rangle)t} e^{-t/T_2}$$

$$\propto \frac{1}{(\omega-\langle\omega\rangle)^2 + \frac{1}{T_2^2}} \quad \text{Lorentzian shape}$$

Homogeneous limit!

Even with a broad distribution of accessible frequencies, if the system explores all of these frequencies on a time scale fast compared to the inverse of the distribution ($\Delta \tau_c > 1$), then the resonance will be “motionally narrowed” into a Lorentzian line. We can see this by looking at the general behavior of F(t)….

**General Behavior:**

More generally, the envelope of the dipole correlation function will look Gaussian at short times and exponential at long times. The correlation time is the separation between these regimes. The behavior for varying time scales of
the dynamics ($\tau_c$) are best characterized with respect to the distribution of accessible frequencies ($\Delta$). So we can define a factor $\kappa=\Delta \cdot \tau_c$, where $\kappa<<1$ is the fast modulation limit and $\kappa>>1$ is the slow modulation limit.

Let’s look at how $C_{\delta \omega \delta \omega}$, $F(t)$, and $\sigma_{abs}(\omega)$ change as a function of $\kappa$.

\[
\begin{align*}
\Delta &= 1 \\
\tau_c &= \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \\
\kappa &= \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix}
\end{align*}
\]
We see that for a fixed distribution of frequencies $\Delta$ the effect of increasing the time scale of fluctuations through this distribution (decreasing $\tau_c$) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM) of $2.35 \cdot \Delta$ to a “motionally narrowed” Lorentzian lineshape with width (FWHM) of $\Delta^2 \tau_c / \pi$.

This is analogous to the motional narrowing effect first described in the case of temperature dependent NMR spectra of two exchanging species. Assume we have two resonances at $\omega_A$ and $\omega_B$ associated with two chemical species that are exchanging at a rate $k_{AB}$

$$A \xleftrightarrow[k_{AB}]{k_{BA}} B$$

If the rate of exchange is slow relative to the frequency splitting, $k << \omega_A - \omega_B$, then we expect two resonances, each with a linewidth dictated by the molecular relaxation processes ($T_2$) and transfer rate of each species. On the other hand, when the rate of exchange between the two species becomes faster than the energy splitting, then the two resonances narrow together to form one resonance at the mean frequency.\(^1\)

**Appendix: The Cumulant Expansion**

For a statistical description of the stochastic (random) variable $x$, we need to know the momenta of $x$: $\langle x \rangle, \langle x^2 \rangle, \ldots$. We want to express the statistical average of

$$\langle e^{ikx} \rangle = \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle$$

which is an expansion in moments of $x$. An alternate way of expressing this expansion is in terms of cumulants $c_n(x)$

$$\langle e^{ikx} \rangle = \exp \left( \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right)$$

where the first few cumulants are:

- $c_1(x) = \langle x \rangle$ mean
- $c_2(x) = \langle x^2 \rangle - \langle x \rangle^2$ variance
- $c_3(x) = \langle x^3 \rangle - 3 \langle x \rangle \langle x^2 \rangle + 2 \langle x \rangle^3$ skewness

An expansion in cumulants converges much more rapidly than an expansion in moments. For a system that obeys Gaussian statistics, all cumulants with $n > 2$ vanish!

We can show this as follows. For the expansion of an exponential operator

$$F = \exp[-fH] = 1 - f_1H + f_2H^2 + \cdots \quad (1)$$

We obtain the cumulants by postulating that we can expand the exponential argument in powers of the operator $H$

$$F = \exp[-c] \quad (2)$$

$$c = c_1H + c_2H^2 + c_3H^3 + \cdots$$

expanding the exponential in eq. 2:

$$F = 1 - \left( c_1H + c_2H^2 + \cdots \right) + \frac{1}{2} \left( c_1H + c_2H^2 + \cdots \right)^2$$

$$= 1 - H(c_1) + H_2(-c_2 + \frac{1}{2}c_1^2) + \cdots \quad (3)$$
By comparing (1) and (3), we can see

\[ c_1 = f_1 \]
\[ c_2 = f_2 - \frac{1}{2} f_1^2 \]

Now if we perform this for our time ordered exponential operator we obtain:

\[ F = \left\langle \exp \left[ -i \int_0^t dt \omega(t) \right] \right\rangle \]
\[ c_1 = -i \int_0^t d\tau \langle \omega(\tau) \rangle \]
\[ c_2 = -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \omega(\tau_2) \omega(\tau_1) \rangle - \langle \omega(\tau_2) \rangle \langle \omega(\tau_1) \rangle \]
\[ = -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega(\tau_2) \delta\omega(\tau_1) \rangle \]

For Gaussian statistics, all higher cumulants vanish.