University of Washington
Department of Chemistry
Chemistry 553
Spring Quarter 2011

Lecture 24: Kubo Theory of Spectral Line Shapes
05/20/10
Text Reading: Ch 21,22
R. Kubo "A Stochastic Theory of Line Shape and Relaxation" in Fluctuation, Relaxation, and Resonance in Magnetic Systems, D. Ter Haar, Ed. 1962, Oliver & Boyd, Edinburgh.

A. Kubo's Stochastic Line Shape Theory

- Assume a property that we will call A(t). A can be any of the propertiesdiscussed earlier including a electric or magnetic dipole moment. Assume as a result of a periodic motion A(t) varies according to the simple equation

$$\frac{dA}{dt} = i\omega(t)A \qquad (24.1)$$

where ω is a frequency of the system . The time dependence of the system is assumed to result from a random process that modulates the frequency such that

$$\omega(t) = \omega_0 + \delta\omega(t) \qquad (24.2)$$

where $\omega_0 = \overline{\omega(t)} = \underset{T\to\infty}{Lim}\frac{1}{T}\int_0^T \omega(s)\,ds$ and $\overline{\delta\omega(t)} = \langle \delta\omega(t)\rangle = 0$.

- Now integrate (24.1):

$$A(t) = A(0)\exp\left\{i\int_0^t \omega(s)\,ds\right\} = A(0)e^{i\omega_0 t}\exp\left\{i\int_0^t \delta\omega(s)\,ds\right\} \qquad (24.3)$$

- Multiply both sides of (24.3) by A*(0) and take the ensemble average:

$$C(t) = \langle A(t)A^*(0)\rangle = |A(0)|^2 e^{i\omega_0 t}\left\langle \exp\left\{i\int_0^t \delta\omega(s)\,ds\right\}\right\rangle = |A(0)|^2 e^{i\omega_0 t}\phi(t) \qquad (24.4)$$

where $\phi(t) = \left\langle \exp\left\{i\int_0^t \delta\omega(s)\,ds\right\}\right\rangle$ is the relaxation function. The relaxation function is nothing more than the characteristic function of the lineshape function I(w). These two functions constitute a Fourier pair, i.e.

$$I(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} C(t) dt = |A(0)|^2 \int_{-\infty}^{+\infty} e^{-i\omega t} e^{i\omega_0 t} \phi(t) dt = |A(0)|^2 \int_{-\infty}^{+\infty} e^{-it(\omega-\omega_0)} \phi(t) dt \quad (24.5)$$

Recall that the characteristic function can be expanding in a "cumulant" series

$$\ln \phi(t) = \ln \phi(0) + t \left.\frac{\partial \ln \phi}{\partial t}\right|_{t=0} + \frac{t^2}{2} \left.\frac{\partial^2 \ln \phi}{\partial t^2}\right|_{t=0} + \dots \quad (24.6)$$

Given that $\phi(t) = \left\langle \exp\left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle$ we have previously shown that the first two terms in the cumulant expansion are:

$$\phi(t) = \left\langle \exp\left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle = \exp\left[i \int_0^t \langle \delta\omega(s) \rangle ds - \frac{1}{2} \int_0^t ds_1 \int_0^t ds_2 \langle \delta\omega(s_1) \delta\omega(s_2) \rangle + \dots \right] (24.7)$$

- For a Gaussian process the first term in the argument of the exponent on the right is zero. For a stationary process we additionally obtain:

$$\begin{aligned} \phi(t) &= \left\langle \exp\left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle = \exp\left[-\frac{1}{2} \int_0^t ds_1 \int_0^t ds_2 \langle \delta\omega(s_1) \delta\omega(s_2) \rangle \right] \\ &= \exp\left[-\frac{1}{2} \int_0^t ds_1 \int_0^t ds_2 \psi(s_1 - s_2) \right] = \exp\left[-\int_0^t ds (t-s) \psi(s) \right] \end{aligned} \quad (24.8)$$

where $s=s_1-s_2$. For a stationary, Gaussian process the third, fourth, etc cumulants are zero.

- To evaluate (24.9) further we assume a form for the correlation function of the stationary random process

$$\psi(s) = \langle \delta\omega(s) \delta\omega(0) \rangle = \Delta^2 e^{-s/\tau} \quad (24.9)$$

where $\Delta = |\delta\omega|$ is the amplitude of the random modulation and τ is the relaxation time. Substitute this form into (24.9):

$$\begin{aligned} \phi(t) &= \exp\left\{ -\int_0^t (t-s) \psi(s) ds \right\} \\ &= \exp\left\{ -\Delta^2 \int_0^t (t-s) e^{-s/\tau} ds \right\} = \exp\left\{ -\Delta^2 \tau \left(t - \tau \left(1 - e^{-t/\tau} \right) \right) \right\} \end{aligned} \quad (24.10)$$

- The relaxation function ϕ(t) is a super-exponential, but can be Fourier transformed analytically in certain limiting cases.
  - Assume the random modulation of the system's frequency is slow such that $t \ll \tau$. Then the exponential can be expanded:

$$\phi(t) \approx \exp\left\{ -\Delta^2 \tau \left(t - \tau \left(1 - \left(1 - \tfrac{t}{\tau} + \tfrac{t^2}{2\tau^2} \right) \right) \right) \right\} = \exp\left\{ -\Delta^2 t^2 / 2 \right\} \quad (24.11)$$

- If we Fourier transform C(t) using (24.12):

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, C(t)e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-\Delta^2 t^2/2} e^{-i(\omega-\omega_0)t} = \frac{\sqrt{2\pi}}{\Delta} e^{-(\omega-\omega_0)^2/2\Delta^2} \qquad (24.12)$$

- When the random modulation is slow, the correlation function and the line shape are Gaussian. In this limit the line is inhomogeneously broadened.
- Now assume the random modulation is fast such that t>>τ. In this limit the exponential decays almost to zero so

$$C(t) \approx e^{i\omega_0 t} \exp\left\{-\Delta^2\tau(t-\tau)\right\} \approx e^{i\omega_0 t} \exp\left\{-\Delta^2 \tau t\right\} \qquad (24.13)$$

- Taking the Fourier transform of the correlation function in (24.14) yields:

$$\begin{aligned} I(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, C(t)e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-\Delta^2\tau t} e^{-i(\omega-\omega_0)t} \\ &= \frac{2}{\Delta^2\tau}\frac{\left(\Delta^2\tau\right)^2}{\left(\Delta^2\tau\right)^2 + \left(\omega-\omega_0\right)^2} = \frac{2\Delta^2\tau}{\left(\Delta^2\tau\right)^2 + \left(\omega-\omega_0\right)^2} \end{aligned} \qquad (24.14)$$

- When the modulation is fast the correlation function C(t) is exponential and the line shape in (24.15) is Lorenzian. This is called the motionally narrowed limit and is commonly observed in solution NMR, for example. The line is said to be homogeneously broadened in this limit.