

University of Washington
Department of Chemistry
Chemistry 553
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Lecture 26: Kubo Theory of Spectral Line Shapes

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Text Reading: Ch 21,22

A. Introduction

- In lecture 25 the spectroscopic lineshape function $I(\omega)$ was derived as the Fourier transform of the correlation function $C(t)$. This was done as shown below.

$$\begin{aligned}
 I(\omega) &= \frac{1}{2\pi} \sum_{i,f} \int_{-\infty}^{+\infty} dt p_i \langle i|u|f\rangle \langle f|u(t)|i\rangle e^{-i\omega t} \\
 &= \frac{1}{2\pi} \sum_i \int_{-\infty}^{+\infty} dt p_i \langle i|u \cdot u(t)|i\rangle e^{-i\omega t} \\
 &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \langle u \cdot u(t) \rangle e^{-i\omega t} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt C(t) e^{-i\omega t}
 \end{aligned}$$

$$\text{where } C(t) = \langle u \cdot u(t) \rangle = \sum_i p_i \langle i|u \cdot u(t)|i\rangle$$

(26.1)

- As noted below, the property $u(t)$ depends upon the spectroscopy involved
 - Microwave Spectroscopy: $u = u_0$, the permanent dipole moment.
 - i. Infrared: $u = \left(\frac{\partial u}{\partial Q} \right)_0 \cdot Q$, where Q is a normal coordinate
 - ii. Rayleigh Scattering: $u = u_{ind} = \hat{e}_i \cdot \alpha \cdot \hat{e}_s$ where α is the polarizability tensor, and $\hat{e}_{i,s}$ are the unit vectors in the direction of the incident and scattered radiation.
 - iii. Raman Scattering: $u = u_{ind} = \hat{e}_i \cdot \alpha' \cdot \hat{e}_s$ where $\alpha' = \left(\frac{\partial \alpha}{\partial Q} \right)_0$
 - iv. Magnetic Resonance: correlation functions in magnetic resonance involve the magnetic dipole moment of the particle. Relaxation rates in magnetic resonance involve spectral densities that are Fourier transforms of correlation functions
- More generally, in the definition of the correlation function we should allow for the fact that the operator is complex... $C(t) = \langle A^*(0) A(t) \rangle$
- (26.1) shows that the spectral lineshape and the correlation function $C(t)$ are related by a Fourier transform. (26.1) can be inverted

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt C(t) e^{-i\omega t} \Rightarrow C(t) = \int_{-\infty}^{+\infty} d\omega I(\omega) e^{i\omega t} \quad (26.2)$$

B. Kubo Line Shape Theory

- It remains to determine a form for the correlation function that determines the line shape. Assume a property that we will call A(t). Assume A(t) varies according to the simple equation

$$\frac{dA}{dt} = i\omega(t) A \quad (26.3)$$

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

$$\omega(t) = \omega_0 + \delta\omega(t) \quad (26.4)$$

where $\omega_0 = \overline{\omega(t)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \omega(s) ds$ and $\overline{\delta\omega(t)} = 0$.

- Now integrate (26.3):

$$A(t) = A(0) \exp \left\{ i \int_0^t \omega(s) ds \right\} = A(0) e^{i\omega_0 t} \exp \left\{ i \int_0^t \delta\omega(s) ds \right\} \quad (26.5)$$

- Multiply both sides of (26.5) by $A^*(0)$ and take the ensemble average:

$$\langle A(t) A^*(0) \rangle = |A(0)|^2 e^{i\omega_0 t} \left\langle \exp \left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle \quad (26.6)$$

- We define the correlation function as

$$C(t) = \frac{\langle A(t) A^*(0) \rangle}{|A(0)|^2} = e^{i\omega_0 t} \left\langle \exp \left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle \quad (26.7)$$

- Now we use the cumulant expansion introduced in Lecture 2 section A:

$$\begin{aligned} C(t) &= e^{i\omega_0 t} \left\langle \exp \left\{ i \int_0^t \delta\omega(s) ds \right\} \right\rangle \\ &= e^{i\omega_0 t} \exp \left\{ it \langle \delta\omega(t) \rangle - \int_0^t (t-s) \langle \delta\omega(s) \delta\omega(0) \rangle ds \right\} \\ &= e^{i\omega_0 t} \exp \left\{ - \int_0^t (t-s) \langle \delta\omega(s) \delta\omega(0) \rangle ds \right\} \end{aligned} \quad (26.8)$$

- Now assume a form for the correlation function

$$\langle \delta\omega(t) \delta\omega(0) \rangle = \Delta^2 e^{-t/\tau} \quad (26.9)$$

where $\Delta = |\delta\omega|$ is the amplitude of the random modulation and τ is the relaxation time. Substitute this form into (26.9):

$$\begin{aligned}
C(t) &= e^{i\omega_0 t} \exp \left\{ -\int_0^t (t-s) \langle \delta\omega(s) \delta\omega(0) \rangle ds \right\} \\
&= e^{i\omega_0 t} \exp \left\{ -\Delta^2 \int_0^t (t-s) e^{-s/\tau} ds \right\} = e^{i\omega_0 t} \exp \left\{ -\Delta^2 \tau \left(t - \tau \left(1 - e^{-t/\tau} \right) \right) \right\}
\end{aligned} \tag{26.10}$$

- The correlation function $C(t)$ 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:

$$\begin{aligned}
C(t) &= e^{i\omega_0 t} \exp \left\{ -\Delta^2 \tau \left(t - \tau \left(1 - \left(1 - \frac{t}{\tau} + \frac{t^2}{2\tau^2} \right) \right) \right) \right\} \\
&= e^{i\omega_0 t} \exp \left\{ -\Delta^2 t^2 / 2 \right\}
\end{aligned} \tag{26.11}$$

- If we Fourier transform (26.11):

$$\begin{aligned}
I(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt C(t) e^{-i\omega t} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-\Delta^2 t^2 / 2} e^{-i(\omega - \omega_0)t} \\
&= \frac{\sqrt{2\pi}}{\Delta} e^{-(\omega - \omega_0)^2 / 2\Delta^2}
\end{aligned} \tag{26.12}$$

- 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 $t \gg \tau$. In this limit the exponential decays almost to zero so

$$C(t) \approx e^{i\omega_0 t} \exp \left\{ -\Delta^2 \tau (t - \tau) \right\} \approx e^{i\omega_0 t} \exp \left\{ -\Delta^2 \tau t \right\} \tag{26.13}$$

- Taking the Fourier transform of the correlation function in (26.13) yields:

$$\begin{aligned}
I(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt C(t) e^{-i\omega t} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-\Delta^2 \tau t} e^{-i(\omega - \omega_0)t} \\
&= \frac{2}{\Delta^2 \tau} \frac{(\Delta^2 \tau)^2}{(\Delta^2 \tau)^2 + (\omega - \omega_0)^2} = \frac{2\Delta^2 \tau}{(\Delta^2 \tau)^2 + (\omega - \omega_0)^2}
\end{aligned} \tag{26.14}$$

- When the modulation is fast the correlation function $C(t)$ is exponential and the line shape in (26.14) is Lorentzian. 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.