University of Washington
Department of Chemistry
Chemistry 553
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Lecture 23: Spectroscopic Lineshapes and Linear
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A. Application: Energy Absorption from a Field

- Here we show that spectroscopic line shapes and autocorrelation functions are related by a Fourier transform. We show that this fact is a manifestation of the quantum mechanical fluctuation dissipation theorem.
- Energy absorbed from a weak field is dissipated by fluctuations that are characteristic of the system at equilibrium. In the following analysis we assume that A=B=u, where u is the electric or magnetic dipole moment. We assume the field has the form $E(t)=E_0\cos\omega t$, theaverage energy $U = \frac{1}{2}\varepsilon_0 E_0^2$ where ε_0 is the free space permittivity.
- Suppose a spectral system absorbs energy from a resonant field (electric or magnetic). The net dissipation of energy from the radiation field is

$$-\frac{dU}{dt} = -\dot{U} = \sum_{i,f} p_i W_{i\to f}\left(\hbar\omega_{f,i}\right) \tag{23.1}$$

where V is the irradiated sample volume, N is the number of absorbing dipoles in V, p_i is the probability that energy level i is occupied, $W_{i,f}$ is the probability of a transition from energy state i to f, and $\hbar\omega_{f,i}$ is the energy absorbed by the i-f transition.

Note the probability p_i is given by a Boltzmann distribution

$$p_i = \frac{1}{Q}e^{-\hbar\omega_{i0}} \tag{23.2}$$

where $\omega_{i,0}=\omega_i-\omega_0$ and ω_0 is the ground state energy.

- The transition probability per unit time $W_{i,f}$ is given by Fermi's Golden Rule

$$W_{i\to f} = \frac{\pi}{2\hbar^2}\left|\langle f\,|u\cdot E_0|\,i\rangle\right|^2\left\{\delta\left(\omega_{f,i}-\omega\right)+\delta\left(\omega_{f,i}+\omega\right)\right\} \tag{23.3}$$

where u is the x component of the dipole moment and the time dependent field is $\vec{E}(t)=\left(\vec{E}_0\cos\omega t,0,0\right)=E_0\hat{\mu}_x\cos\omega t$. Combining (23.3) and (23.1) we obtain

$$-\dot{U} = \frac{\pi}{2\hbar}\sum_{i,f}\left\{p_i\omega_{f,i}\left|\langle f\,|u\cdot E_0|\,i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)+p_i\omega_{f,i}\left|\langle f\,|u\cdot E_0|\,i\rangle\right|^2\delta\left(\omega_{f,i}+\omega\right)\right\}$$

(23.4)

- Note in the second term in (23.4) the indices i and f can be interchanged i.e. $p_i \to p_f$ *and* $\omega_{f,i} \to \omega_{i,f}$. Then using the fact that $\omega_{if} = -\omega_{fi}$ (23.9) becomes

$$
\begin{aligned}
-\dot{U} &= \frac{\pi}{2\hbar}\sum_{i,f}\left\{p_i\omega_{f,i}\left|\langle f|u\cdot\vec{E}_0|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)+p_f\omega_{i,f}\left|\langle f|u\cdot E_0|i\rangle\right|^2\delta\left(\omega_{i,f}+\omega\right)\right\}\\
&= \frac{\pi}{2\hbar}\sum_{i,f}\left\{p_i\omega_{f,i}\left|\langle f|u\cdot\vec{E}_0|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)-p_f\omega_{f,i}\left|\langle f|u\cdot E_0|i\rangle\right|^2\delta\left(-\omega_{f,i}+\omega\right)\right\}\\
&= \frac{\pi}{2\hbar}\sum_{i,f}\left\{\left(p_i-p_f\right)\omega_{f,i}\left|\langle f|u\cdot\vec{E}_0|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)\right\}\\
&= \frac{\pi E_0^2}{2\hbar}\sum_{i,f}\left\{p_i\left(1-e^{-\hbar\omega_{fi}\beta}\right)\omega_{f,i}\left|\langle f|u\cdot\hat{e}_x|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)\right\}
\end{aligned}
$$

(23.5)

where in the final step of (23.5) we used the fact that $\frac{p_f}{p_i} = e^{-\hbar\omega_{fi}\beta}$.

- Now in the last line of (23.10) we let the delta function operate to convert all instances of ω_{fi} to ω. Then we obtain

$$
\begin{aligned}
-\dot{U} &= \frac{\pi E_0^2}{2\hbar}\sum_{i,f}\left\{p_i\left(1-e^{-\hbar\omega\beta}\right)\omega\left|\langle f|u_x|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)\right\}\\
&= \frac{\pi\omega E_0^2}{2\hbar}\left(1-e^{-\hbar\omega\beta}\right)\sum_{i,f}\left\{p_i\left|\langle f|u_x|i\rangle\right|^2\delta\left(\omega_{f,i}-\omega\right)\right\}
\end{aligned}
\tag{23.6}
$$

B. The Spectral Line Shape

- Equation (23.6) can be combined with the expression for the intensity of radiation absorbed at frequency w:

$$
I(\omega)=\sum_{i,f}p_i\langle f|u|i\rangle\langle i|u|f\rangle\delta\left(\omega_{f,i}-\omega\right)=-\frac{2\hbar}{\pi\omega\left(1-e^{-\hbar\omega\beta}\right)}\dot{U}
\tag{23.7}
$$

- Recall the integral definition of the delta function:

$$
\delta(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\;and\;so\;\delta\left(\omega_{f,i}-\omega\right)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{i\left(\omega_{f,i}-\omega\right)t}
\tag{23.8}
$$

and equation (23.7) becomes

$$
I(\omega)=\sum_{i,f}p_i\langle f|u|i\rangle\langle i|u|f\rangle\left\{\frac{1}{2\pi}\int_{-\infty}^{+\infty}\exp\left[it\left(\frac{E_f-E_i}{\hbar}-\omega\right)\right]\right\}
\tag{23.9}
$$

Where $\hbar\omega_{f,i} = E_f - E_i$

- (23.9) may be further reduced using standard methods…

$$I(\omega)=\frac{1}{2\pi}\sum_{i,f}\int_{-\infty}^{+\infty}dt\, p_i \langle f|u|i\rangle\langle i|u|f\rangle e^{iE_f t}e^{-iE_i t}e^{-i\omega t}$$

$$=\frac{1}{2\pi}\sum_{i,f}\int_{-\infty}^{+\infty}dt\, p_i \langle f|e^{iHt}ue^{-iHt}|i\rangle\langle i|u|f\rangle e^{-i\omega t}=\frac{1}{2\pi}\sum_{i,f}\int_{-\infty}^{+\infty}dt\, p_i \langle i|u|f\rangle\langle f|u(t)|i\rangle e^{-i\omega t}$$

(23.10)

where $u(t)=e^{iHt}ue^{-iHt}$

- We then use the closure property $\sum_k |k\rangle\langle k|=1$ to collapse the double summation to a single summation

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

$$=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,\langle u\cdot u(t)\rangle e^{-i\omega t}=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,C(t)e^{-i\omega t} \qquad (23.11)$$

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

- Equation (23.11) shows that the spectral lineshape and the auto-correlation function C(t) are related by a Fourier transform. More generally, in the definition of the correlation function we should allow for the fact that the operator is complex… $C(t)=\langle A^*(0)A(t)\rangle$
- Equation (23.11) can be inverted

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\,C(t)e^{-i\omega t}\Rightarrow C(t)=\int_{-\infty}^{+\infty}d\omega I(\omega)e^{i\omega t} \qquad (23.12)$$

- Recall that result can be obtained from lijnear response theory. Recall from the last lecture

$$\chi_{BA}(\omega)=\int_0^{+\infty}dte^{-i\omega t}\phi_{BA}(t)=\frac{\pi}{i\hbar Q}\left(1-e^{-\beta\hbar\omega}\right)\sum_{m,n}e^{-\beta\hbar\omega_m}A_{mn}B_{nm}\delta(\omega-\omega_{nm})$$

$$=\frac{\pi}{i\hbar}\left(1-e^{-\beta\hbar\omega}\right)\sum_{m,n}p_m A_{mn}B_{nm}\delta(\omega-\omega_{nm}) \qquad (23.13)$$

  - Now let A=B= μ_x and again use the integral definition of the delta function

$$\chi_{BA}(\omega) = \frac{\pi}{i\hbar}\left(1-e^{-\beta\hbar\omega}\right)\sum_{m,n} p_m \mu_{xmn}\mu_{xnm} \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt e^{it(\omega_{nm}-\omega)}$$

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = -\frac{i\pi}{\hbar}\left(1-e^{-\beta\hbar\omega}\right)\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt e^{-i\omega t}\left(\sum_{m,n} p_m \mu_{xmn} e^{iE_n t/\hbar}\mu_{xnm} e^{-iEmt/\hbar}\right)$$

$$\therefore \chi''(\omega) = \frac{\pi}{\hbar}\left(1-e^{-\beta\hbar\omega}\right)\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \left\langle \mu_x \mu_x(t)\right\rangle e^{-i\omega t}$$

$$\approx \frac{\omega}{2k_B T}\int_{-\infty}^{+\infty} dt \left\langle \mu_x \mu_x(t)\right\rangle e^{-i\omega t} = \frac{\pi\omega}{k_B T} I(\omega)$$

(23.14)

- There is a direct relationship between the absorption line shape and the imaginary part of the complex susceptibility

$$I(\omega) = \frac{\hbar}{\pi}\frac{\chi''(\omega)}{1-e^{-\beta\hbar\omega}} \approx \frac{k_B T}{\pi}\frac{\chi''(\omega)}{\omega} \qquad (23.15)$$