

1.1: Linear Absorption Spectroscopy

Absorption is the simplest example of a coherent spectroscopy. In the semi-classical picture, the polarization induced by the electromagnetic field radiates a signal field that is out-of-phase with the transmitted light. To describe this, all of the relevant information is in $R(t)$ or $\chi(\omega)$.

$$\bar{P}(t) = \int_0^\infty d\tau R(\tau) E(t - \tau) \quad (1.1.1)$$

$$\bar{P}(\omega) = \chi(\omega) \bar{E}(\omega) \quad (1.1.2)$$

Let's begin with a frequency-domain description of the absorption spectrum, which we previously found was proportional to the imaginary part of the susceptibility, χ'' .¹ We consider one monochromatic field incident on the sample that resonantly drives dipoles in the sample to create a polarization, which subsequently re-radiate a signal field (free induction decay). For one input field, the energy and momentum conservation conditions dictate that $\omega_{in} = \omega_{sig}$ and $k_{in} = k_{sig}$, that is a signal field of the same frequency propagates in the direction of the transmitted excitation field.

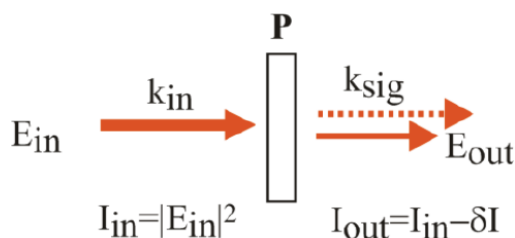


Figure 1.1.1: Linear absorption with the signal propagating in the same direction as the incident light.

In practice, an absorption spectrum is measured by characterizing the frequency-dependent transmission decrease on adding the sample $A = -\log I_{out}/I_{in}$. For the perturbative case, let's take the change of intensity $\delta I = I_{in} - I_{out}$ to be small, so that $A \approx \delta I$ and $I_{in} \approx I_{out}$. Then we can write the measured intensity after the sample as

$$\begin{aligned} I_{out} &= |E_{out} + E_{sig}|^2 \\ &= |E_{out} + (iP)|^2 \\ &= |E_{out} + i\chi E_{in}|^2 \\ &\approx |E_{in} + i\chi E_{in}|^2 \\ &= |E_{in}|^2 |1 + i(\chi' + i\chi'')|^2 \\ &= I_{in} (1 - 2\chi'' + \dots) \\ \Rightarrow I_{out} &= I_{in} - \delta I \end{aligned}$$

Here we have made use of the assumption that $|E_{in}| \gg |\chi|$. We see that as a result of the phase shift between the polarization and the radiated field that the absorbance is proportional to χ'' : $\delta I = 2\chi'' I_{in}$.

A time-domain approach to absorption draws on Eq. (2.1.1) and should recover the relationships to the dipole autocorrelation function that we discussed previously. Equating $\bar{P}(t)$ with $\mu(t)$, we can calculate the polarization in the density matrix picture as

$$\bar{P}(t) = Tr(\mu_I(t) \rho_I^{(1)}(t)) \quad (1.1.3)$$

where the first order expansion of the density matrix is

$$\rho_I^{(1)} = -\frac{i}{\hbar} \int_{-\infty}^t dt_1 [V_I(t_1), \rho_{eq}] \quad (1.1.4)$$

Substituting eq. (2.13) we find

$$\begin{aligned}\bar{P}(t) &= \text{Tr} \left(\mu_I(t) \frac{i}{\hbar} \int_{-\infty}^t dt' [-\mu_I(t') E(t'), \rho_{eq}] \right) \\ &= -\frac{i}{\hbar} \int_{-\infty}^t dt' E(t') \text{Tr} (\mu_I(t) [\mu_I(t'), \rho_{eq}]) \\ &= +\frac{i}{\hbar} \int_0^{\infty} d\tau E(t-\tau) \text{Tr} ([\mu_I(\tau), \mu_I(0)] \rho_{eq})\end{aligned}$$

In the last line, we switched variables to the time interval $\tau = t - t'$, and made use of the identity $[A, [B, C]] = [[A, B], C]$. Now comparing to Eq. (2.1.1), we see, as expected

$$R(\tau) = \frac{i}{\hbar} \theta(\tau) \text{Tr} ([\mu_I(\tau), \mu_I(0)] \rho_{eq}) \quad (1.1.5)$$

So the linear response function is the sum of two correlation functions, or more precisely, the imaginary part of the dipole correlation function.

$$R(\tau) = \frac{i}{\hbar} \theta(\tau) (C(\tau) - C^*(\tau)) \quad (1.1.6)$$

$$C(\tau) = \text{Tr} (\mu_I(\tau) \mu_I(0) \rho_{eq})$$

$$C^*(\tau) = \text{Tr} (\mu_I(\tau) \rho_{eq} \mu_I(0)) \quad (1.1.7)$$

Also, as we would expect, when we use an impulsive driving potential to induce a free induction decay (i.e., $E(t-\tau) = E_0 \delta(t-\tau)$), the polarization is directly proportional to the response function, which can be Fourier transformed to obtain the absorption lineshape.

1. Remember the following relationships of the susceptibility with the complex dielectric constant $\epsilon(\omega)$, the index of refraction $n(\omega)$, and the absorption coefficient $\kappa(\omega)$:

$$\epsilon(\omega) = 1 + 4\pi\chi(\omega)$$

$$\sqrt{\epsilon(\omega)} = \tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$

This page titled [1.1: Linear Absorption Spectroscopy](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Andrei Tokmakoff](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.