

## 15.4: Time Correlation Function Expressions for Transition Rates

The first-order E1 "golden-rule" expression for the rates of photon-induced transitions can be recast into a form in which certain specific physical models are easily introduced and insights are easily gained. Moreover, by using so-called equilibrium averaged time correlation functions, it is possible to obtain rate expressions appropriate to a large number of molecules that exist in a distribution of initial states (e.g., for molecules that occupy many possible rotational and perhaps several vibrational levels at room temperature).

### State-to-State Rate of Energy Absorption or Emission

To begin, the expression obtained earlier

$$R_{i,f} = \left( \frac{2\pi}{\hbar^2} \right) g(\omega_{f,i}) |\mathbf{E}_0 \cdot \langle \phi_f | \mu | \Phi_i \rangle|^2,$$

that is appropriate to transitions between a particular initial state  $\Phi_i$  and a specific final state  $\Phi_f$ , is rewritten as

$$R_{i,f} = \left( \frac{2\pi}{\hbar^2} \right) \int g(\omega) |\mathbf{E}_0 \cdot \langle \phi_f | \mu | \phi_i \rangle|^2 \delta(\omega_{f,i} - \omega) d\omega.$$

Here, the  $\delta(\omega_{f,i} - \omega)$  function is used to specifically enforce the "resonance condition" that resulted in the time-dependent perturbation treatment given in Chapter 14; it states that the photons' frequency  $\omega$  must be resonant with the transition frequency  $\omega_{f,i}$ . It should be noted that by allowing  $\omega$  to run over positive and negative values, the photon absorption (with  $\omega_{f,i}$  positive and hence  $\omega$  positive) and the stimulated emission case (with  $\omega_{f,i}$  negative and hence  $\omega$  negative) are both included in this expression (as long as  $g(\omega)$  is defined as  $g(|\omega|)$  so that the negative- $\omega$  contributions are multiplied by the light source intensity at the corresponding positive  $\omega$  value).

The following integral identity can be used to replace the  $\delta$ -function:

$$\delta(\omega_{f,i} - \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega_{f,i} - \omega)t} dt$$

by a form that is more amenable to further development. Then, the state-to-state rate of transition becomes:

$$R_{i,f} = \left( \frac{1}{\hbar} \right) \int g(\omega) |\mathbf{E}_0 \cdot \langle \phi_f | \mu | \phi_i \rangle|^2 \int_{-\infty}^{\infty} e^{i(\omega_{f,i} - \omega)t} dt d\omega.$$

### Averaging Over Equilibrium Boltzmann Population of Initial States

If this expression is then multiplied by the **equilibrium probability**  $\rho_i$  that the molecule is found in the state  $\Phi_i$  and summed over all such initial states and summed over all final states  $\Phi_f$  that can be reached from  $\Phi_i$  with photons of energy  $\hbar\omega$ , the **equilibrium averaged rate of photon absorption** by the molecular sample is obtained:

$$R_{\text{eq.ave.}} = \left( \frac{1}{\hbar^2} \right) \sum_{i,f} \rho_i \int g(\omega) |\mathbf{E}_0 \cdot \langle \Phi_f | \mu | \Phi_i \rangle|^2 \int_{-\infty}^{\infty} e^{i(\omega_{f,i} - \omega)t} dt d\omega.$$

This expression is appropriate for an ensemble of molecules that can be in various initial states  $\Phi_i$  with probabilities  $\rho_i$ . The corresponding result for transitions that originate in a particular state ( $\Phi_i$ ) but end up in any of the "allowed" (by energy and selection rules) final states reads:

$$R_{\text{state } i} = \left( \frac{1}{\hbar^2} \right) \sum_f \int g(\omega) |\mathbf{E}_0 \cdot \langle \Phi_f | \mu | \Phi_i \rangle|^2$$

$$\int_{-\infty}^{\infty} e^{i(\omega_{f,i}-\omega)t} dt d\omega.$$

For a canonical ensemble, in which the number of molecules, the temperature, and the system volume are specified,  $\rho_i$  takes the form:

$$\phi_i = \frac{g_i}{Q} e^{-\frac{E_i^0}{kT}}$$

where  $Q$  is the canonical partition function of the molecules and  $g_i$  is the degeneracy of the state  $\Phi_i$  whose energy is  $E_i^0$ .

In the above expression for  $R_{\text{eq.ave.}}$ , a double sum occurs. Writing out the elements that appear in this sum in detail, one finds:

$$\sum_{i,f} \phi_i \mathbf{E}_0 \cdot \langle \Phi_i | \mu | \Phi_f \rangle \mathbf{E}_0 \cdot \langle \Phi_f | \mu | \Phi_i \rangle e^{i(\omega_{f,i})t}.$$

In situations in which one is interested in developing an expression for the intensity arising from transitions to **all** allowed final states, the sum over these final states can be carried out explicitly by first writing

$$\langle \Phi_f | \mu | \Phi_i \rangle e^{i(\omega_{f,i})t} = \langle \Phi_f | e^{\frac{iHt}{\hbar}} \mu e^{-\frac{iHt}{\hbar}} | \Phi_i \rangle$$

and then using the fact that the set of states  $\{\Phi_k\}$  are complete and hence obey

$$\sum_k |\Phi_k\rangle \langle \Phi_k| = 1.$$

The result of using these identities as well as the **Heisenberg definition** of the time dependence of the dipole operator

$$\mu(t) = e^{\frac{iHt}{\hbar}} \mu e^{-\frac{iHt}{\hbar}},$$

is:

$$\sum_i \rho_i \langle \Phi | \mathbf{E}_0 \cdot \mu \mathbf{E}_0 \cdot \mu(t) | \Phi_i \rangle.$$

In this form, one says that the time dependence has been reduce to that of an equilibrium averaged (n.b., the  $\sum_i \rho_i \langle \Phi_i | | \Phi_i \rangle$ ) **time correlation function** involving the component of the dipole operator along the external electric field at  $t = 0$  ( $\mathbf{E}_0 \cdot \mu$ ) and this component at a different time  $t$  ( $\mathbf{E}_0 \cdot \mu(t)$ ).

## Photon Emission and Absorption

If  $\omega_{f,i}$  is positive (i.e., in the photon absorption case), the above expression will yield a non-zero contribution when multiplied by  $e^{-i\omega t}$  and integrated over positive  $\omega$  values. If  $\omega_{f,i}$  is negative (as for stimulated photon emission), this expression will contribute, again when multiplied by  $e^{-i\omega t}$ , for negative  $\omega$ -values. In the latter situation,  $\rho_i$  is the equilibrium probability of finding the molecule in the (excited) state from which emission will occur; this probability can be related to that of the lower state  $\rho_f$  by

$$\begin{aligned} \rho_{\text{excited}} &= \rho_{\text{lower}} e^{-\frac{(E_{\text{excited}}^0 - E_{\text{lower}}^0)}{kT}} \\ &= \rho_{\text{lower}} e^{-\frac{\hbar\omega}{kT}}. \end{aligned}$$

In this form, it is important to realize that the excited and lower states are treated as individual **states**, not as levels that might contain a degenerate set of states.

The absorption and emission cases can be combined into a single **net** expression for the rate of photon absorption by recognizing that the latter process leads to photon production, and thus must be entered with a negative sign. The resultant expression for the **net rate of decrease of photons** is:

$$R_{\text{eq.ave.net}} = \left( \frac{1}{\hbar^2} \right) \sum_i \rho_i \left( 1 - e^{-\frac{\hbar\omega}{kT}} \right) \iint g(\omega) \langle \Phi_i | (\mathbf{E}_0 \cdot \boldsymbol{\mu}) \mathbf{E}_0 \cdot \boldsymbol{\mu}(t) | \Phi_i \rangle e^{-i\omega t} d\omega dt.$$

## The Line Shape and Time Correlation Functions

Now, it is convention to introduce the so-called "line shape" function  $I(\omega)$ :

$$I(\omega) = \sum_i \rho_i \int \langle \Phi_i | (\mathbf{E}_0 \cdot \boldsymbol{\mu}) \mathbf{E}_0 \cdot \boldsymbol{\mu}(t) | \Phi_i \rangle e^{-i\omega t} dt$$

in terms of which the net photon absorption rate is

$$R_{\text{eq.ave.net}} = \left( \frac{1}{\hbar^2} \right) \left( 1 - e^{-\hbar\omega/kT} \right) \int g(\omega) I(\omega) d\omega.$$

As stated above, the function

$$C(t) = \sum_i \rho_i \langle \Phi_i | \mathbf{E}_0 \cdot \boldsymbol{\mu} \mathbf{E}_0 \cdot \boldsymbol{\mu}(t) | \Phi_i \rangle$$

is called the equilibrium averaged **time correlation function** of the component of the electric dipole operator along the direction of the external electric field  $\mathbf{E}_0$ . Its Fourier transform is  $I(\omega)$ , the **spectral line shape** function. The convolution of  $I(\omega)$  with the light source's ( $g(\omega)$ ) function, multiplied by  $\left( 1 - e^{-\frac{\hbar\omega}{kT}} \right)$ , the correction for stimulated photon emission, gives the net rate of photon absorption.

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