# Chapter 19
The Displaced Harmonic Oscillator

In this chapter, we discuss a more specific model for the transition between the vibrational manifolds using parallel displaced harmonic normal modes, for which the time-correlation function can be evaluated explicitly. We consider the limit of high frequency modes (or low temperature) where vibrational progressions appear and the limit of low frequencies (or high temperature) where the lineshape becomes Gaussian where position and width only depend on the total reorganization energy.

19.1 The Time-Correlation Function in the Displaced Harmonic Oscillator Approximation

We apply the harmonic approximation (17.11) for the nuclear motion to the zero-order Hamiltonian (18.31)

$$H_0 = |\psi_e> \left(E_e^0 + \sum_r \hbar\omega_r^e b_r^{e\dagger} b_r^e \right) < \psi_e| + |\psi_g> \left(E_g^0 + \sum_r \hbar\omega_r^g b_r^{g\dagger} b_r^g \right) < \psi_g|.$$

(19.1)

In a simplified but popular model, we neglect mixing of the normal modes (parallel mode approximation, the eigenvectors (u_j^r in 17.13) are the same) and frequency changes ($\omega_r^g = \omega_r^e = \omega_r$) in the excited state but allow for a shift of the equilibrium
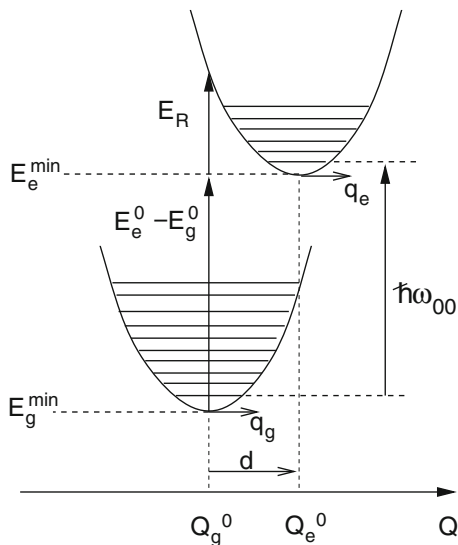
Fig. 19.1 Displaced oscillator model. The displaced oscillator model assumes that the normal mode eigenvectors are the same in both electronic states involved. Then the different modes are still independent. The figure shows the potential energy along one such normal mode Q. The minima at Q_g^0 and Q_e^0 are shifted relative to each other by a distance $d = Q_e^0 - Q_g^0$. The elongation of the normal mode is denoted as $q_{g(e)} = Q - Q_{g(e)}^0$. The curvature of the two parabolas is the same. Thus neglecting frequency changes in the excited state, the vibrationless transition energy $\hbar\omega_{00}$ equals the pure electronic transition energy $E_e^{min} - E_g^{min}$. The reorganization energy $E_R = \frac{1}{2}\omega^2 d^2$ is the amount of energy which can be released in the excited state after a vertical transition from the vibronic groundstate

position ($q_r^e = q_r^g + d_r$).[1] The potential energy for the two states then is approximated by (Fig. 19.1)

$$E_g = E_g^{min} + \frac{1}{2}\sum_r \omega_r^2 q_r^2 \tag{19.2}$$

$$E_e = E_e^{min} + \frac{1}{2}\sum_r \omega_r^2 (q_r^e)^2 = E_e^{min} + \frac{1}{2}\sum_r \omega_r^2 (q_r + d_r)^2. \tag{19.3}$$

The vertical excitation energy is[2]

$$E_e(q_r = 0) - E_g(q_r = 0) = E_e^{min} + \frac{1}{2}\sum_r \omega_r^2 d_r^2 - E_g^{min} = \hbar\omega_{00} + E_R \tag{19.4}$$

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[1] We retain only the lowest order of the potential difference.

[2] Without frequency changes the zero point energies are the same and $E_e^{min} - E_g^{min} = E_e^0 - E_g^0 = \hbar\omega_{00}$.

with the reorganization energy

$$E_R = \frac{1}{2} \sum_r \omega_r^2 d_r^2. \tag{19.5}$$

We introduce the ladder operators by substituting

$$q_r = \sqrt{\frac{\hbar}{2\omega_r}} \left(b_r^g + b_r^{g\dagger} \right) \tag{19.6}$$

$$q_r^e = \sqrt{\frac{\hbar}{2\omega_r}} \left(b_r^e + b_r^{e\dagger} \right) = \sqrt{\frac{\hbar}{2\omega_r}} \left(b_r^g + b_r^{g\dagger} \right) + d_r. \tag{19.7}$$

Since d_r is real valued we find

$$b_r^e = b_r^g + \frac{1}{2}\sqrt{\frac{2\omega_r}{\hbar}} d_r = b_r^g + \sqrt{\frac{\omega_r}{2\hbar}} d_r = b_r^g + g_r$$

with the vibronic coupling parameter

$$g_r = \sqrt{\frac{\omega_r}{2\hbar}} d_r.$$

From

$$\hbar\omega_r \left(b_r^{e\dagger} b_r^e + \frac{1}{2} \right) = \hbar\omega_r \left((b_r^{g\dagger} + g_r)(b_r^g + g_r) + \frac{1}{2} \right)$$

$$= \hbar\omega_r \left(b_r^{g\dagger} b_r^g + \frac{1}{2} \right) + \hbar\omega_r g_r \left(b_r^g + b_r^{g\dagger} \right) + \hbar\omega_r g_r^2$$

we obtain the "displaced harmonic oscillator" model (DHO)

$$H_g = \sum_r \hbar\omega_r b_r^+ b_r \tag{19.8}$$

$$H_e = \sum_r \hbar\omega_r b_r^{e\dagger} b_r^e$$

$$= H_g + \sum_r g_r \hbar\omega_r (b_r^\dagger + b_r) + \sum_r g_r^2 \hbar\omega_r \tag{19.9}$$

where the superscript g is omitted from now and the last term is the reorganization energy

$$E_R = \sum_r g_r^2 \hbar \omega_r. \tag{19.10}$$

The correlation function (18.50)

$$F(t) = \left\langle e^{-\frac{it}{\hbar} H_g} e^{\frac{it}{\hbar} H_e} \right\rangle_g = Q^{-1} \text{tr} \left(e^{-H_g/k_B T} e^{-\frac{it}{\hbar} H_g} e^{\frac{it}{\hbar} H_e} \right) \tag{19.11}$$

with

$$Q = \text{tr}(e^{-H_g/k_B T}) \tag{19.12}$$

factorizes in the parallel mode approximation

$$F(t) = \prod_r F_r(t) \tag{19.13}$$

$$\begin{aligned} F_r(t) &= Q_r^{-1} \text{tr} \left(e^{-\hbar \omega_r b_r^\dagger b_r / k_B T} e^{-it\omega_r b_r^\dagger b_r} e^{it\omega_r (b_r^\dagger + g_r)(b_r + g_r)} \right) \\ &= \left\langle e^{-it\omega_r b_r^\dagger b_r} e^{it\omega_r (b_r^\dagger + g_r)(b_r + g_r)} \right\rangle. \end{aligned} \tag{19.14}$$

As shown in the appendix this can be evaluated as

$$\begin{aligned} F_r(t) &= \exp\left(g_r^2 \left[(e^{i\omega_r t} - 1)(\overline{n_r} + 1) + (e^{-i\omega_r t} - 1)\overline{n_r} \right] \right) \\ &= \exp\left(g_r^2 (2\overline{n_r} + 1)(\cos \omega_r t - 1) + i g_r^2 \sin \omega_r t \right) \end{aligned} \tag{19.15}$$

with the average phonon numbers

$$\overline{n_r} = \frac{1}{e^{\hbar \omega_r / k_B T} - 1}. \tag{19.16}$$
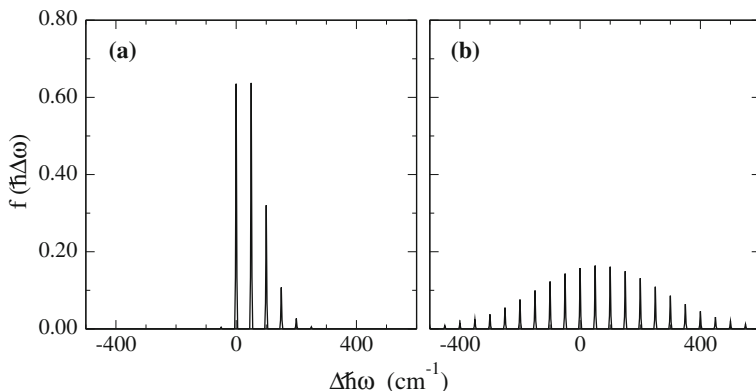
Expression (19.14) contains phonon absorption (positive frequencies) and emission processes (negative frequencies). We discuss two important limiting cases.

19.2   High Frequency Modes

In the limit $\hbar \omega_r \gg k_B T$ the average phonon number

$$\overline{n_r} = \frac{1}{e^{\hbar \omega / k_B T} - 1} \tag{19.17}$$

is small and the correlation function becomes

Fig. 19.2 Progression of a low frequency mode. The Fourier transform of (19.15) is shown for typical values of $\hbar\omega = 50\,\text{cm}^{-1}$, 1, $E_r = 50\,\text{cm}^{-1}$ and (**a**) $kT = 10\,\text{cm}^{-1}$ (**b**) $kT = 200\,\text{cm}^{-1}$. A small damping was introduced to obtain finite linewidths

$$F_r(t) \rightarrow \exp\left(g_r^2(\mathrm{e}^{\mathrm{i}\omega t} - 1)\right). \tag{19.18}$$

Expansion of $F_r(t)$ as a power series of g_r^2 gives

$$F_r(t) = \sum_j \frac{g_r^{2j}}{j!} \mathrm{e}^{-g_r^2} \mathrm{e}^{\mathrm{i}(j\omega_r)t} \tag{19.19}$$

which corresponds to a progression of transitions $0 \rightarrow j\,\omega_r$ with Franck–Condon factors (Fig. 19.2)

$$FC(0, j) = \frac{g_r^{2j}}{j!} \mathrm{e}^{-g_r^2}. \tag{19.20}$$

19.3 Low Frequency Modes

In the high temperature limit ($\hbar\omega_r \ll k_BT$) the time-correlation function of one oscillator (19.15) has peaks at $t = 0, \pm\frac{2\pi}{\omega_r}, \ldots$ which become very sharp for large $\bar{n}_r \approx k_BT/\hbar\omega_r$[3] (Fig. 19.3). The product correlation function of many oscillators is non vanishing only around $t = 0$, i.e. the correlation function decays rapidly and can be approximated by the Taylor series (in this context also known as short time approximation)
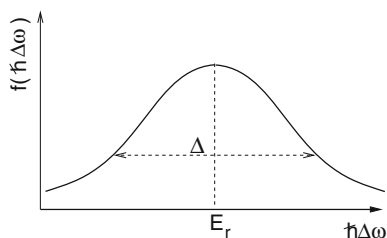
$$F(t) \approx \exp\left\{-t^2 \sum_r (\bar{n}_r + \tfrac{1}{2})g_r^2\omega_r^2 + it \sum_r g_r^2\omega_r\right\} \approx \exp\left\{-t^2 \frac{E_R k_B T}{\hbar^2} + \frac{it}{\hbar}E_R\right\}. \tag{19.21}$$

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[3] Also for very strong vibronic coupling g_r.
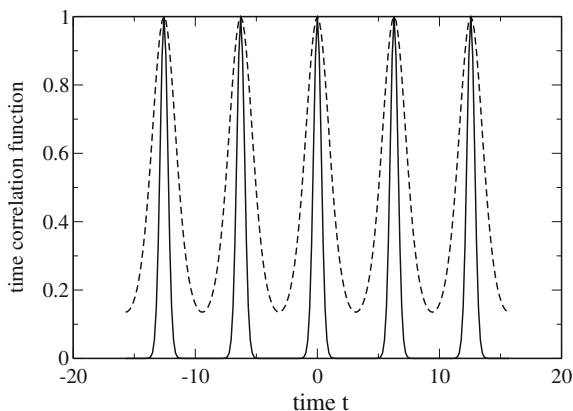
Fig. 19.3 Time-correlation function. $|F_r(t)| = \exp\left\{g_r^2(2\bar{n}_r + 1)(\cos(t) - 1)\right\}$ is shown for $g_r^2(2\bar{n}_r + 1) = 1$(*broken curve*) and $g_r^2(2\bar{n}_r + 1) = 10$(*full curve*)

Fig. 19.4 Gaussian envelope

The lineshape is approximately given by a Gaussian (Fig. 19.4)

$$FCD(\hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{-i\omega_0 t} \exp\left\{-t^2 \frac{E_R k_B T}{\hbar^2} + \frac{it}{\hbar} E_R\right\} \tag{19.22}$$

$$= \frac{1}{2\pi\hbar} \sqrt{\frac{\pi\hbar^2}{E_R k_B T}} \exp\left\{-\frac{(\hbar\omega - E_R)^2}{4 E_R k_B T}\right\}$$

$$= \sqrt{\frac{1}{4\pi E_R k_B T}} \exp\left\{-\frac{(\hbar\omega - E_R)^2}{4 E_R k_B T}\right\}$$

with the reorganization energy

$$E_r = \sum_r g_r^2 \hbar\omega_r \tag{19.23}$$

and the variance

$$\Delta^2 = 2 E_R k_B T. \tag{19.24}$$