Absorption Lineshape for the Displaced Harmonic Oscillator Model

Finite temperature calculations

Lets work in units of $k := 1$ $\quad hbar := 1$

Define the frequency of the electronic transition: $\Omega_0 := 10$ $\quad \omega_{eg} := \Omega_0$

and the vibrational frequency: $\omega_0 := 1$

The unitless displacement of the two harmonic wells is: $D := 0.5$

Define thermal occupation factor $\quad n(T) := \left(\exp\left(\frac{hbar \cdot \omega_0}{k \cdot T}\right) - 1\right)^{-1}$

$\delta(g) := \mathrm{if}(g = 0, 1, 0)$

Set up frequency grid: $\quad i := 0 .. 100$ $\quad \omega_i := -5 + \Omega_0 + 0.1 \cdot i$

Absorption lineshape:

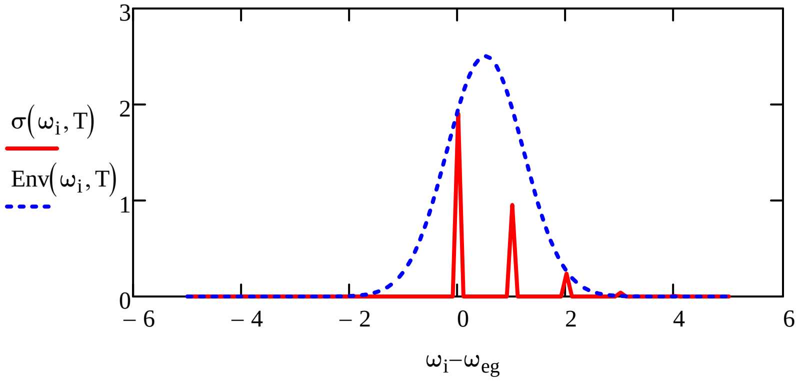
$$\sigma(\omega, T) := \pi \cdot e^{-D \cdot (2 \cdot n(T) + 1)} \cdot \sum_{J=0}^{10} \sum_{K=0}^{10} \left[\frac{D^{J+K}}{J! \cdot K!} \cdot (n(T) + 1)^J \cdot n(T)^K \cdot \left[\delta\left[\omega - \omega_{eg} - (J - K) \cdot \omega_0\right]\right]\right]$$

Envelope of vibronic progression:

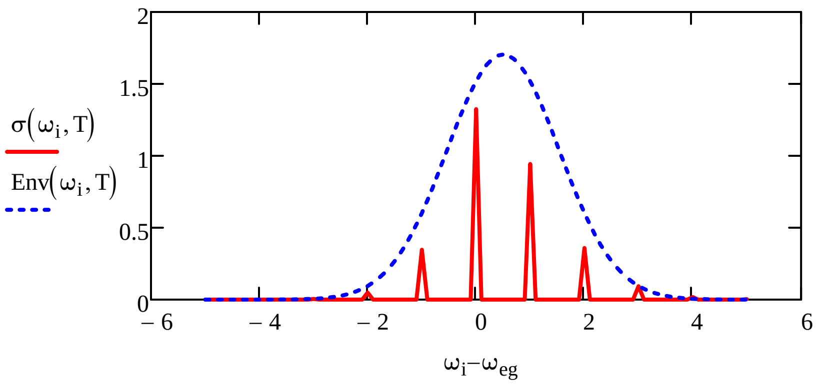
$$Env(\omega, T) := \sqrt{\frac{\pi}{\left[D \cdot \omega_0^2 \cdot (2 \cdot n(T) + 1)\right]}} \cdot \exp\left[\frac{-\left(\omega - \omega_{eg} - D \cdot \omega_0\right)^2}{2 \cdot D \cdot \omega_0^2 \cdot (2 \cdot n(T) + 1)}\right]$$

Plot lineshapes for low, mid and high temperatures. Temperature is defined relative to nuclear frequency (T/ω)

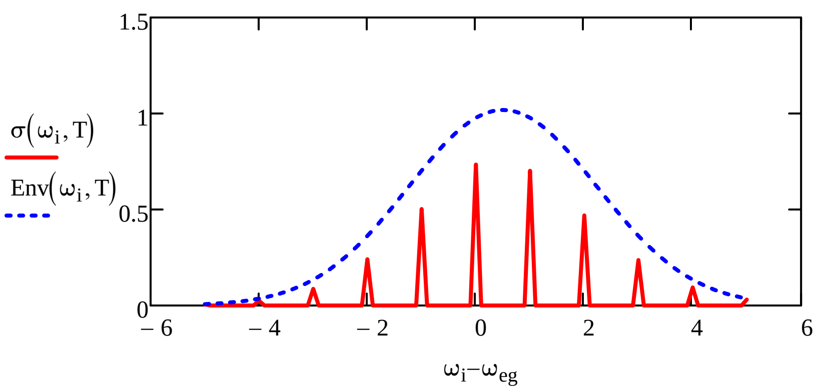
(a) $T := 0.01$ $\frac{\omega_0}{T} = \infty$



(b) $T := 1$ $\frac{\omega_0}{T} = 1$



(c) $T := 3$ $\frac{\omega_0}{T} = 0.333$



$D = 0.5 \qquad \omega_0 = 1$