

Chem 542

Homework for Part 7: molecule-light interaction

1. Based on the Feynman diagram discussed in lecture, and the energy level diagram discussed for DFWM, draw two of the Feynman diagrams for this process, carefully labeling the left and right hand states of the density matrix.
2. From the correlation function derived in lecture, derive the correlation function in the form shown below by choosing a diagonal density matrix $\rho = \exp[-E_i/kT]/Q$. Then, using the general formulas for the absorption intensity in terms of $P^{(1)} = \chi^{(1)} E$ given in section 12 of the notes, show that the absorbed intensity I is proportional to $\int dt \exp[-i\omega t] C(t)$, where $C(t)$ is the dipole-dipole autocorrelation function

$$C(t) \sim \text{Tr} \{ e^{-\hat{H}_{mol}/kT} \hat{\mu}(t) \hat{\mu} \}.$$

This is the same formula we derived at the beginning of the course for one-photon perturbation theory, showing the relationship between the generalized nonlinear correlation functions of chapter 12 and the simple linear case discussed at the beginning of the course. The relationship provides a convenient relation of a linear absorption spectrum to the dynamics of molecular motion (e.g. rotational dephasing of dipoles in solution).

3. Consider the dipole autocorrelation function for a collection of vibrating diatomic molecules at some temperature T (assuming the harmonic oscillator approximation and neglecting rotational effects). The transition dipole term in $C(t)$ of importance in this case is

$$\langle v | \mu' \Delta r | v \pm 1 \rangle \langle v \pm 1 | \mu' \Delta r(t) | v \rangle, \text{ where } \mu' = \partial \mu / \partial r |_{r_e}, \Delta r = r - r_e,$$

and $\Delta r(t) = e^{+iHt/\hbar} \Delta r e^{-iHt/\hbar}$ is the Heisenberg position operator.

- a. Rather than performing the full quantum-mechanical trace over $\exp[-E_0/kT]/Q |\mu'|^2 \Delta r \Delta r(t)$ to get $C(t)$, consider a classical approximation in terms of action-angle variables, with the Schrödinger and Heisenberg operators replaced by classical variables $\Delta r(t=0)$ and $\Delta r(t)$, where

$$\Delta r(t) = \Delta r_{\max} \cos(\omega_0 t),$$

ω_0 being the vibrational frequency of the molecule. Compute $C(t)$ by replacing the trace by an integral over the classical action variable I (Remember, $E=vI$ classically, or $E = \hbar v(n+1/2)$ quantum-mechanically, or $I \approx \hbar n$.) You may approximate the partition function by

$$Q = \sum \exp[-E(n)/kT] \approx \int_0^{\infty} \exp[-E(n)/kT] dn \approx \frac{1}{\hbar} \int_0^{\infty} \exp[-E(I)/kT] dI$$

and make similar approximations in the trace integral to obtain $C(t)$. Keep in mind that Δr_{\max} , the maximum deviation from equilibrium, is a function of v (and hence I).

- b. Calculate the line shape $I(\omega)$ by Fourier transform of $C(t)$.