Quantum Molecular Dynamics Homework 8 Spring, 2000

1. In the text, the resonance Raman polarizability matrix element was expressed as:
$$\alpha_{fi}(\tilde{\omega}_I) = \int_0^\infty C_{fi}(t) e^{i\tilde{\omega}_I t} dt \tag{1.1}$$
where
$$C_{fi}(t) =< \phi_f | \phi_i(t) > . \tag{1.2}$$
Show that if $\phi_i(0) = (\frac{\alpha}{\pi})^{1/4} e^{-\frac{\alpha}{2}x^2}$ is a coherent state, displaced from the excited state equilibrium by $-x_0$, and $\phi_f = \frac{1}{(2^n n!)^{1/2}} H_n(\alpha^{1/2}x) e^{-\alpha x^2/2}$, is the nth harmonic oscillator eigenstate the time-dependent overlap is given by
$$C_{fi}(t) = \exp[-\Delta^2/2(1-e^{-i\omega t}) - i\omega t/2] \times (1-e^{-i\omega t})^n \frac{(-1)^n \Delta^n}{(2^n n!)^{1/2}} e^{-i\omega_0 t}, \tag{1.3}$$
where $\alpha \equiv \frac{m\omega}{\hbar}$ and $\Delta \equiv \alpha x_0$ is the dimensionless displacement. [Hint: Use the generating function relation,
$$\sum_{n=0}^{\infty} H_n(x) \frac{z^n}{n!} = e^{2xz - z^2}]. \tag{1.4}$$
(see D. J. Tannor and E. J. Heller, J. Chem. Phys. 77, 202 (1982).) Compare the analytical result with numerical calculations using MATLAB.

2. (i) Expand the expression for $C_{fi}(t)$ in exercise 1. up to short times. Note that the formulas in the exercises below that follow from this short time expansion are expected to be accurate for moderate to large detunings of ω_I from the absorption maximum, as well as for dissociative excited states.
Defining the function
$$F_n(\omega) = | \int_0^\infty e^{i\omega t - t^2/2} t^n dt|^2 \tag{2.1}$$
show that the Raman intensity for scattering into a fundamental vibration is given by:
$$|\alpha_{10}(\omega_I)|^2 = \frac{1}{\sigma^2} F_1(\frac{\tilde{\omega}_I - E}{\sigma}) \tag{2.2}$$
and that the Raman intensity for scattering into an overtone vibration is given by:
$$|\alpha_{20}(\omega_I)|^2 = \frac{V_x^4}{8\omega_0^2 \sigma^6} F_2(\frac{\tilde{\omega}_I - E}{\sigma}) \tag{2.3}$$
where $\sigma^2 = \frac{V_x^2}{2\omega_0}$.
(ii) Use the formula from part (i) to show that the ratio of Raman intensities into two different fundamentals goes as:
$$\frac{I_{10}^k}{I_{10}^{k'}} = \frac{\omega_{0k'}}{\omega_{0k}} (\frac{V_k}{V_{k'}})^2. \tag{2.4}$$

(iii) Show that the ratio of the Raman intensity into the overtone relative to the fundamental is:

$$\frac{I_{20}^k}{I_{10}^k} = \frac{V_k^2}{4\omega_{0k}\sigma^2}\frac{F_2(\frac{\tilde{\omega}_I - E}{\sigma})}{F_1(\frac{\tilde{\omega}_I - E}{\sigma})} \tag{2.5}$$

Calculate the ratio $F_2(\omega)/F_1(\omega)$ numerically. Discuss the detuning dependence of the different overtones relative to the fundamental, and draw a connection with the time-energy uncertainty principle. (see E. J. Heller, R. L. Sundberg and D. J. Tannor, J. Phys. Chem. 86, 1822 (1982) for this and the following exercises).
(iv) Compare the analytical result in parts (i), (ii), and (iii) with the numerical harmonic oscillator results from MATLAB without any short time assumption. Show that they agree in the pre- and post-resonant frequency regions.

3. Show that in the case of multiple displaced modes one must replace σ in the above formulas by:

$$\sigma^2 = \sum_k \frac{V_k^2}{2\omega_{0k}}. \tag{3.1}$$

Next, show that in the short time limit the absorption spectrum is given by:

$$\epsilon(\omega_I) = \kappa\omega_I \exp[-\frac{(\tilde{\omega}_I - E)^2}{2\sigma^2}] \tag{3.2}$$

Discuss how the absorption spectrum, eq. 3.2 with eq. 3.1, together with the preresonance Raman intensities, eq. 2.4, can be combined to infer the absolute value of the slope in each coordinate on the excited state surface.

4. Now consider the case that $\phi_0(0)$ is a Gaussian centered on a parabolic barrier, so there is wavepacket spreading but no displacement of the center. Take the state ϕ_f again as the nth harmonic oscillator eigenstate. Use the general form for a spreading Gaussian together with the generating function for the Hermite polynomials to calculate $C_{fi}(t)$. Show that $C_{fi}(t) = 0$ if n is odd. Compare your results with numerical calculations using MATLAB.

5. Expand the expression for $C_{fi}(t)$ in exercise 4. up to short times. Show that

$$|\alpha_{20}(\omega_I)|^2 = \frac{(\omega_0^2 - V_x x)^2}{8\omega_0^2\sigma^4} F_1(\frac{\tilde{\omega}_I - E}{\sigma}) \tag{5.1}$$

From your numerical study of the ratio $F_2(\omega)/F_1(\omega)$ in exercise 2., comment on the detuning dependence of the intensity of overtones arising from wavepacket spreading vs. those arising from wavepacket displacement. Compare the analytical result in the pre- and post-resonant frequency region with the numerical harmonic oscillator results from MATLAB without any short time assumption.