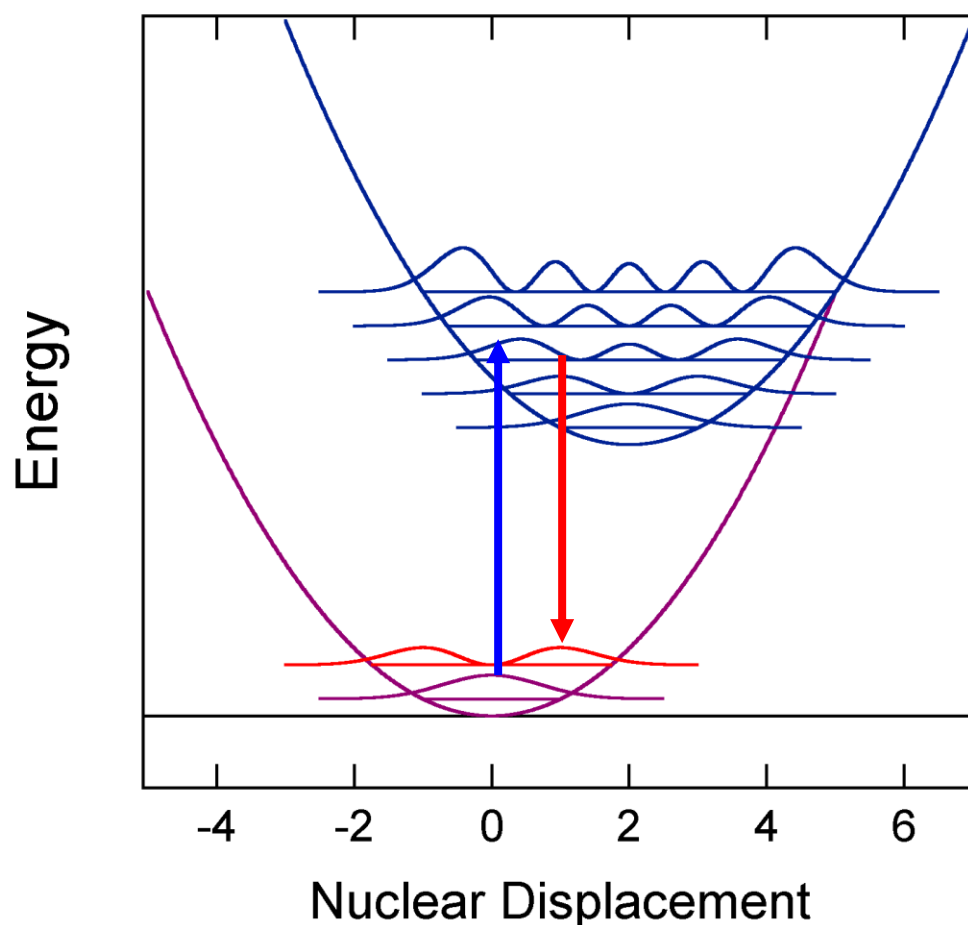


Raman Spectroscopy

- The wavepacket picture
- Kramers-Heisenberg-Dirac transition polarizability
- Time-correlator formalism

Resonance Raman is a two photon process

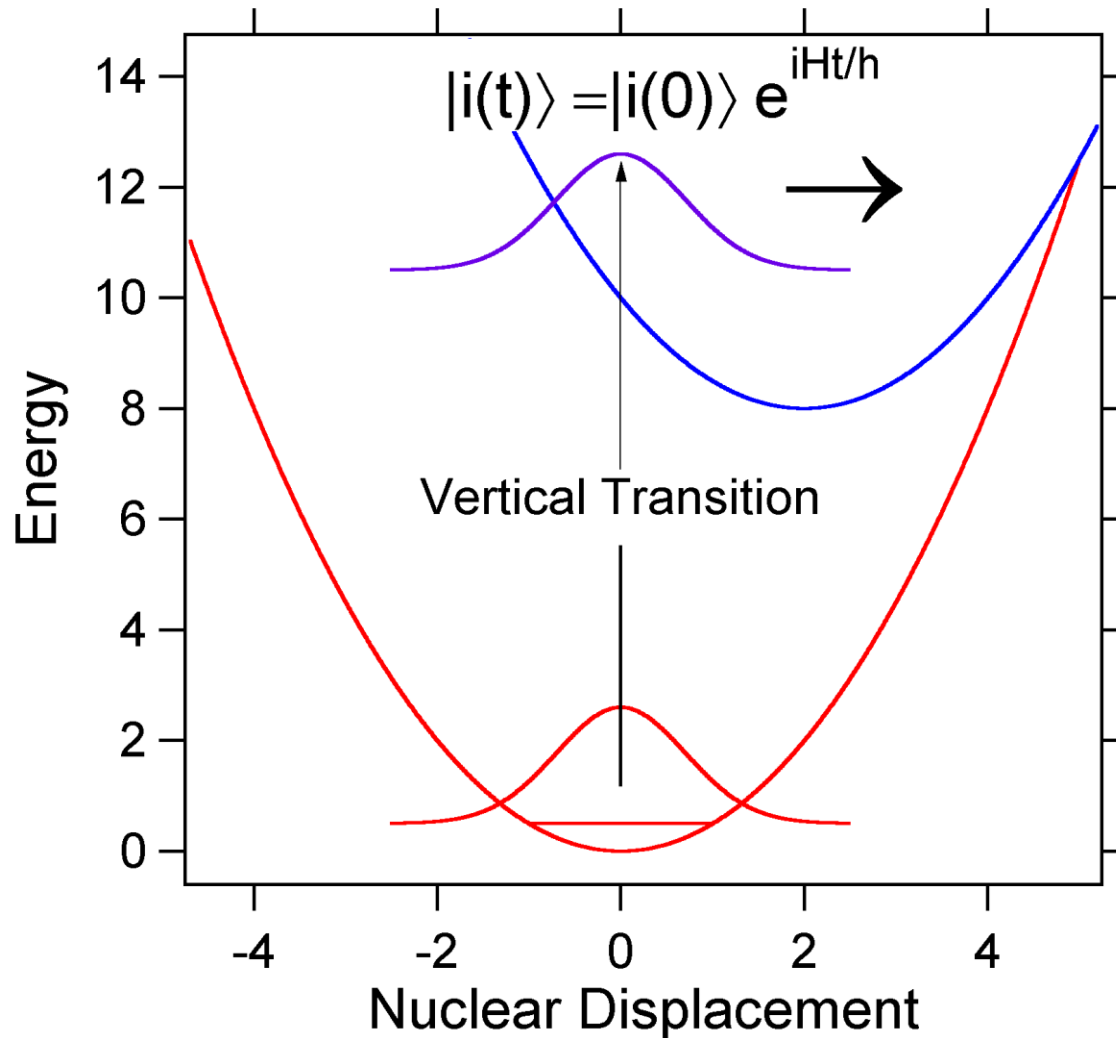


Incident photon
from a laser.

Scattered photon
has an energy shift.

The difference is
because the molecule
is left in an excited
vibrational state.

The wavepacket picture



The wavepacket represents the nuclear position in the ground state projected onto the excited state PES. Because of the nuclear displacement in the excited state the packet moves.

Kramers-Heisenberg-Dirac

Raman scattering depends on the molecular polarizability. The electric field drives the system into excited state $|n\rangle$ and then from $|n\rangle$ it returns to the final state $|f\rangle$.

$$(\alpha_{\rho\sigma})_i = \frac{1}{\hbar} \sum_n \left(\frac{\langle i|\mu_\rho|n\rangle\langle n|\mu_\sigma|i\rangle}{\omega - \omega_{ni}} - \frac{\langle i|\mu_\rho|n\rangle\langle n|\mu_\sigma|i\rangle}{\omega + \omega_{ni}} \right)$$

Two electric field interactions are required. In the above expression ρ and σ are any two Cartesian coordinates x , y , or z . The resonant term is: $\omega_{nf} = \omega_{eg} - n\omega_{\text{vib}}$.

$$(\alpha_{\rho\sigma})_0 = \frac{2}{\hbar} \left\{ \sum_n \left(\frac{\omega_{n0} \langle 0|\mu_\sigma|n\rangle\langle n|\mu_\rho|0\rangle}{\omega^2 - \omega_{n0}^2} \right) \right\}$$

Resonant KHD

If the incident frequency ω_0 is in resonance with an electronic transition of the molecule the anti-resonant term (with $\omega_0 + \omega_{eg}$ in the denominator) can be neglected and only the resonant term contributes to Raman scattering. If we keep terms up to linear in Q , we may express the transition polarizability as a sum of two terms

$$\left(\alpha_{\rho\sigma}\right)_{VV'} = A_{VV'} + B_{VV'}$$

These terms are called the Albrecht A and B terms. The first of these terms arises from the Condon approximation. The Condon approximation states that there is no nuclear coordinate dependence to the wave function. The second term arises from vibronic coupling. This term depends on the derivative of the transition moment with respect to nuclear coordinate.

The Albrecht A-term

For resonant Raman scattering within the Condon approximation the following expression applies

$$A_{\nu\nu'} = \frac{1}{\hbar} (\mu_{ge}^0)_\rho (\mu_{ge}^0)_\sigma \sum_{ev} \left(\frac{\langle \nu' | \nu \rangle \langle \nu | \nu' \rangle}{\omega_{ev,gv} - \omega_0 - i\Gamma_{ev}} \right)$$

In this expression the energy of an incident photon is equal to that of the energy difference between a ground state vibrational energy level gv' and an excited state level ev . The term $i\Gamma_{ev}$ is a phenomenological damping term. This term arises from dephasing and lifetime broadening in the excited state levels. One can envision the contribution of Γ as an energy width to each of the excited state energy levels. Note that this is a sum-over-states expression and requires explicit calculation of all possible excited state contributions to the transition polarizability.

Vibronic coupling: the B term

The transition polarizability is

$$\left(\alpha_{\rho\sigma}\right)_{0v'} = \frac{1}{\hbar} \sum_e \left(\frac{\left(\mu_{ge}^0\right)_\rho \left(\frac{\partial \mu_{ge}^0}{\partial Q}\right)_\sigma \langle 0|Q|v'\rangle}{\omega_0 + \omega_{eg}} - \frac{\left(\mu_{ge}^0\right)_\sigma \left(\frac{\partial \mu_{ge}^0}{\partial Q}\right)_\rho \langle 0|Q|v'\rangle}{\omega_0 - \omega_{eg}} \right)$$

The selection rules arise from the requirement that $\langle 0|Q|v''\rangle$ does not vanish. Specifically $v'' = 1$ as we know from infrared spectroscopy. Thus, the 0-0' is not observed for vibronic coupling and (in theory) is not observed for non-resonant Raman scattering.

We note that totally-symmetric modes are observed in non-resonant Raman scattering. Does this mean that they are allowed only by the Herzberg-Teller coupling mechanism?

Non-resonant KHD

We can define a polarizability derivative such that the transition polarizability is

$$(\alpha_{\rho\sigma})_{v'v''} = \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_i} \right) \langle v | Q_i | v' \rangle = \alpha'_{\rho\sigma} \langle v | Q_i | v' \rangle$$

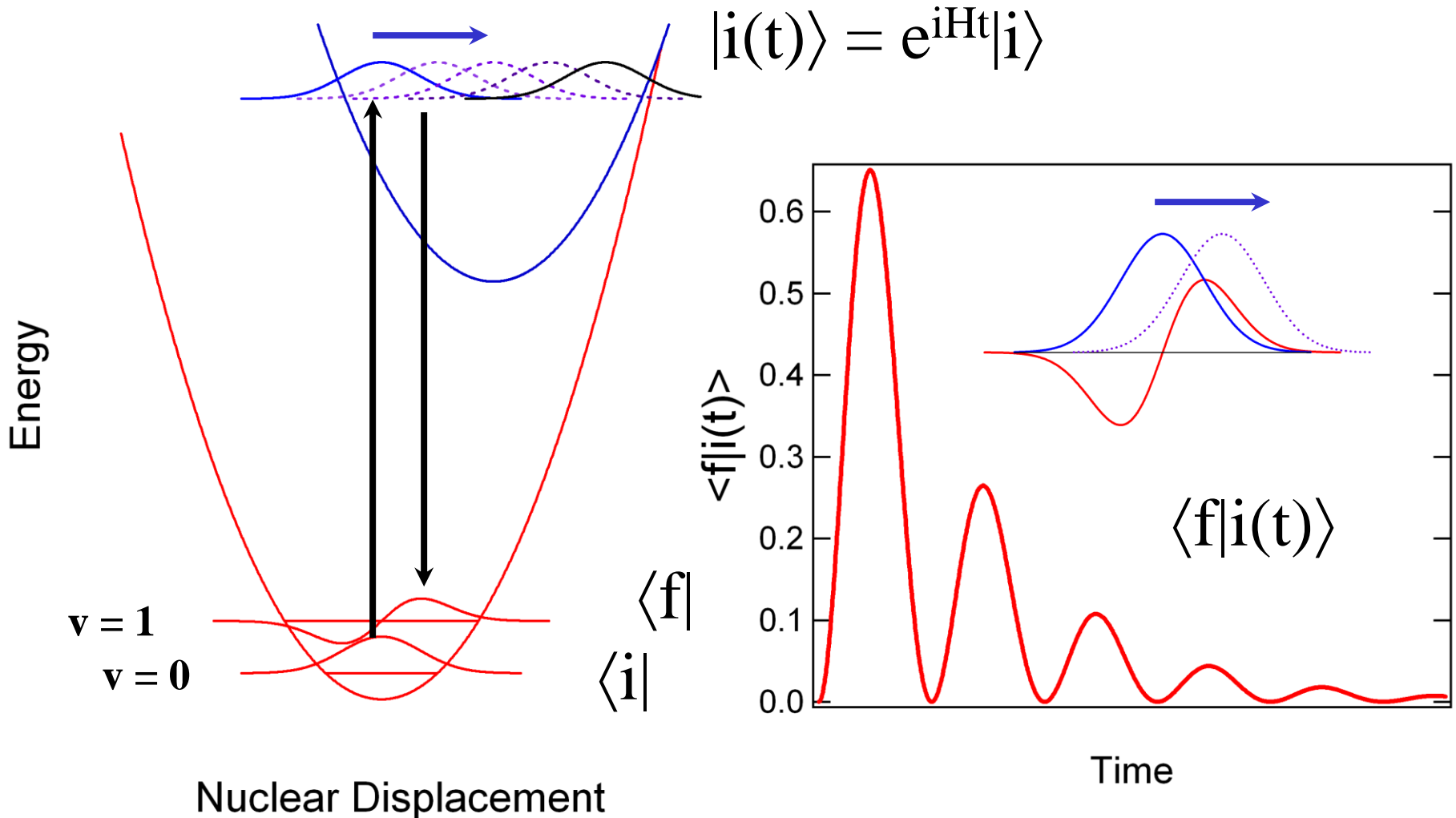
where α'_{rs} is the polarizability derivative also called the derived polarizability. The terms α'_{rs} and $(\partial \alpha_{rs} / \partial Q_i)$ are equivalent. For a harmonic oscillator $\langle v | Q | v' \rangle$ vanishes except when $v' = v \pm 1$. Thus, the selection rule of $\Delta v = \pm 1$ applies to non-resonant Raman scattering as well as infrared spectroscopy (within the harmonic approximation).

The time correlator method

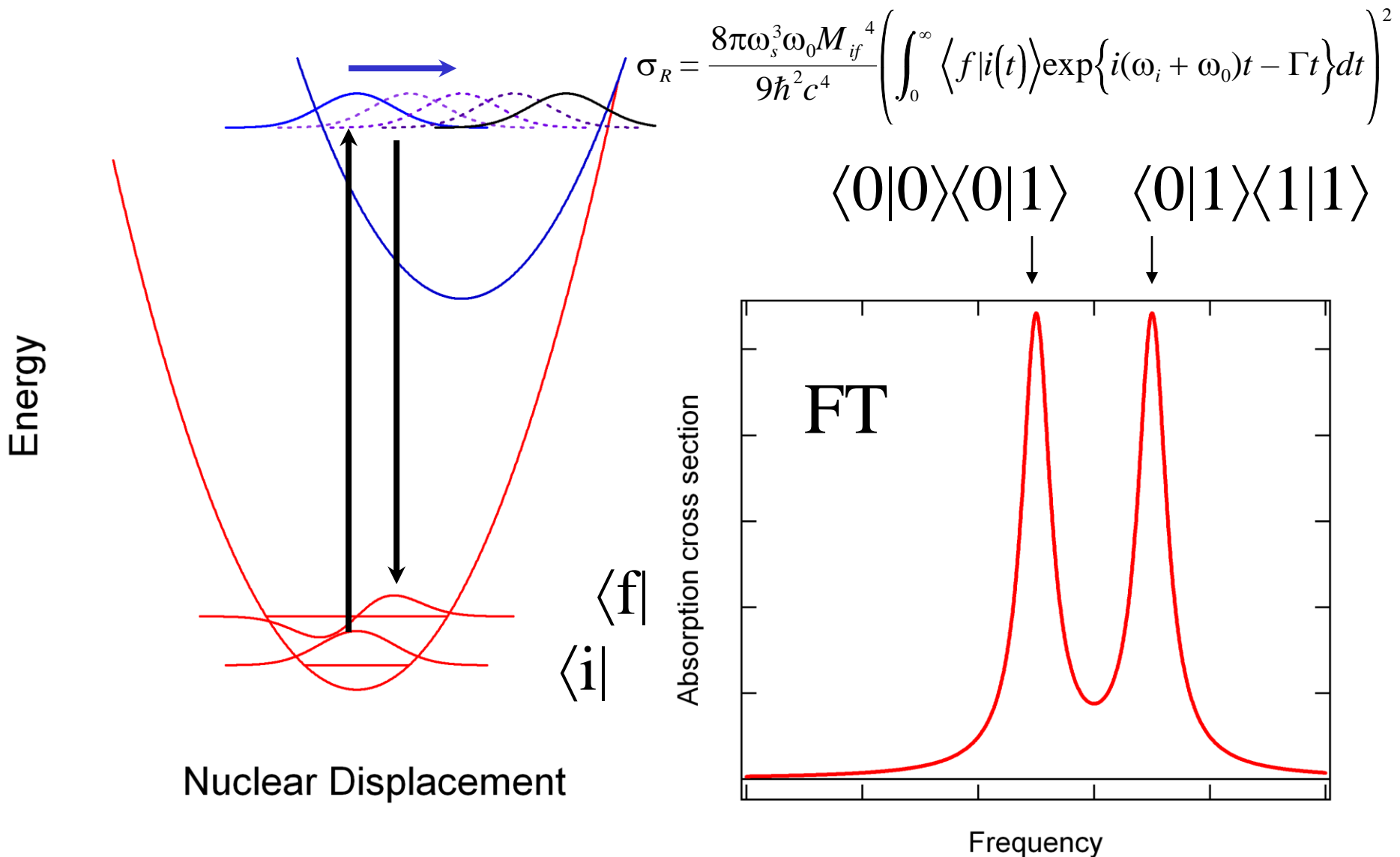
The preceding slides presented a method for calculating Raman cross sections based on a “sum over states” approach. This means that we count all of the possible paths from the initial vibrational state $|0\rangle$ to the final state $|1\rangle$ through excited state vibrational levels, v' . The advantage of the sum-over-states approach is that we can discuss both Franck-Condon allowed and Herzberg-Teller or Vibronic mechanisms for Raman. These correspond to the Albrecht A and B terms, respectively.

The Franck-Condon method applies only to totally symmetric modes. For these modes we can use a different approach known as the time correlator or wave packet approach to calculation of Raman cross sections.

Wavepacket dynamics: Raman



FT of $\langle f|i(t) \rangle$ yields the REP



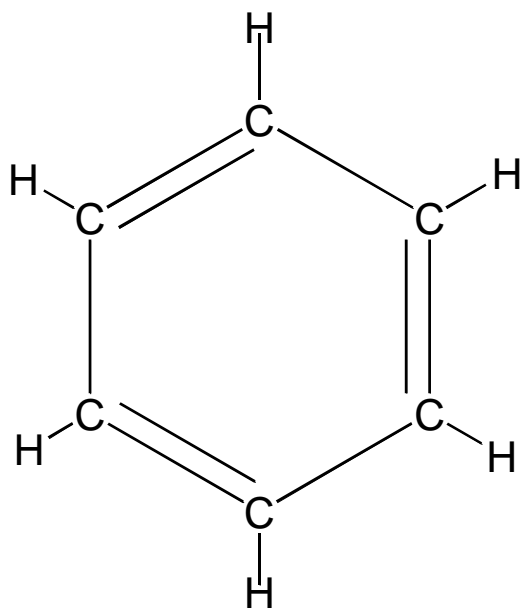
Calculation of excited state displacement

The time correlator approach is based on the fact that the excited state is shifted in geometry with respect to the ground state. We can calculate the excited displacements using quantum chemical methods. Among these the most widely used today are density functional theory methods.

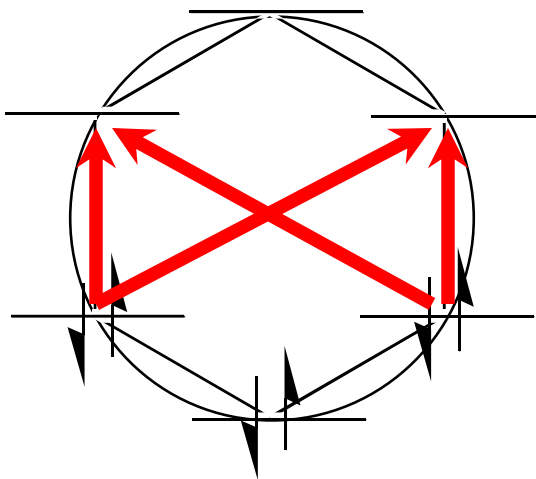
Calculating Resonant Raman Cross Sections

- Perform an optical absorption calculation
- Identify relevant states (e.g. four orbital model)
- Perform a vibrational frequency calculation
- Project along eigenvectors for each normal mode
- Plot potential energy surfaces and determine displacements
- Use dimensionless deltas in time correlator to calculate σ_R

We can construct molecular orbitals of benzene using the six electrons in p orbitals

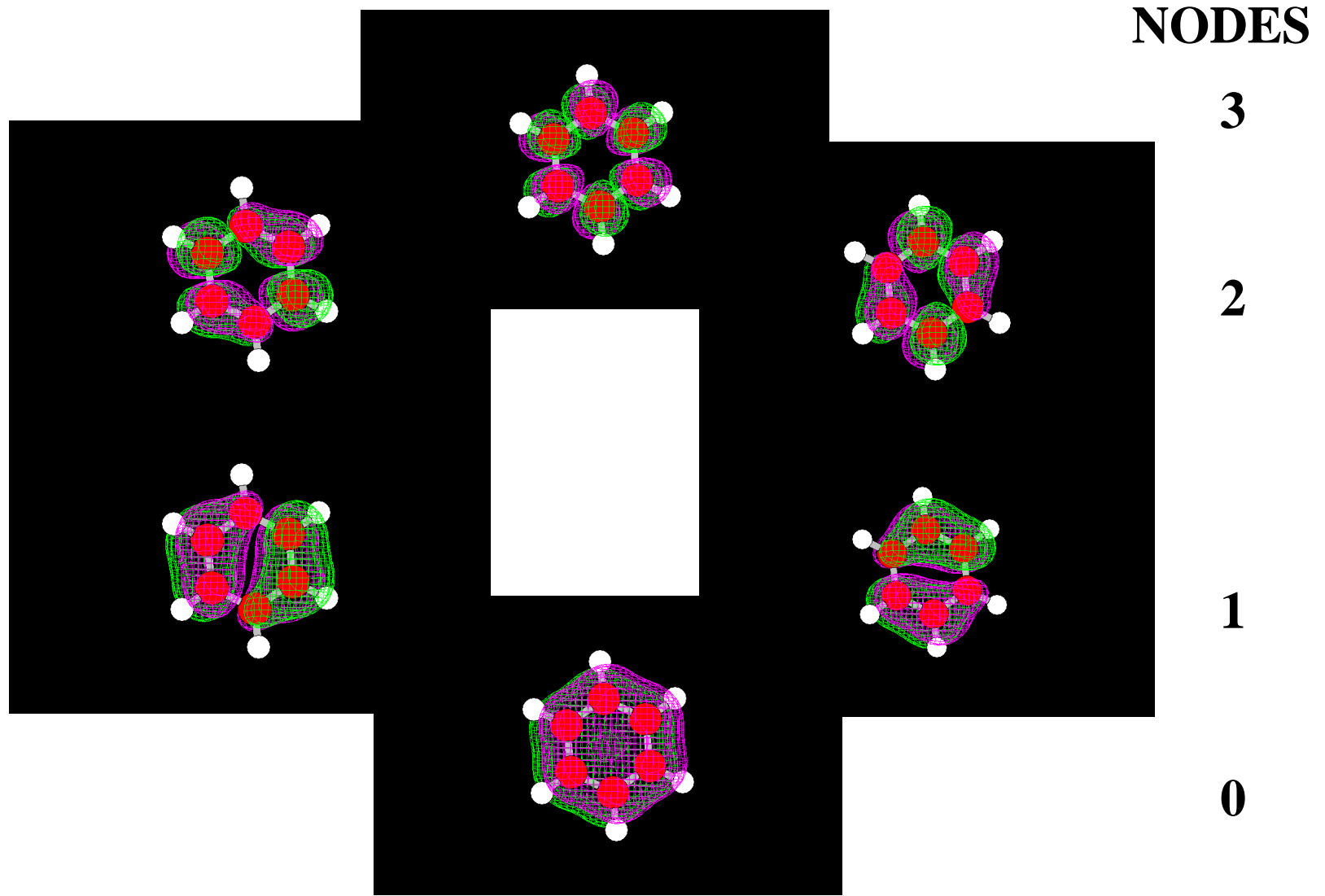


Benzene Structure

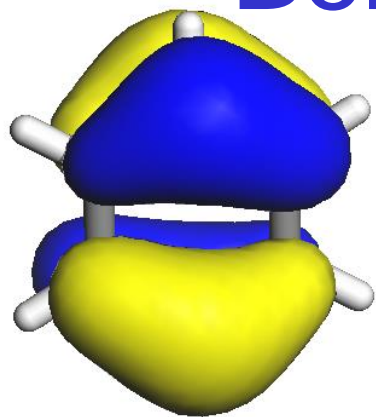


Electronic Energy Levels

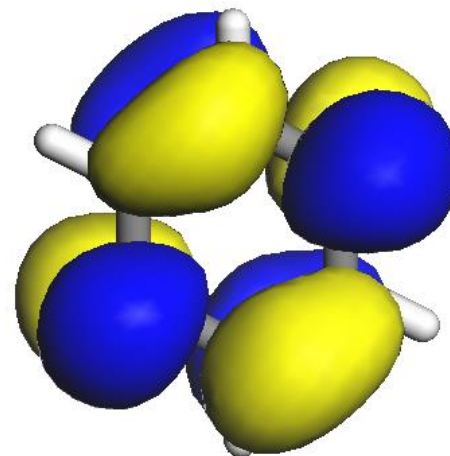
An electronic wavefunction corresponds to each energy level



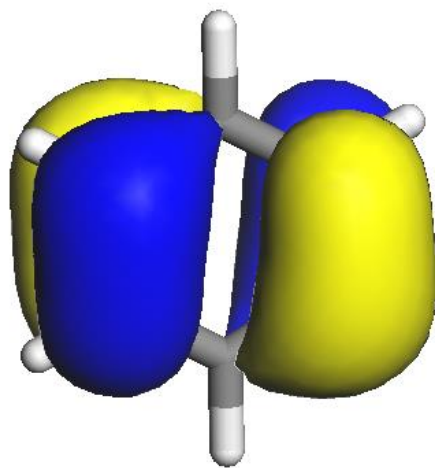
Benzene transitions



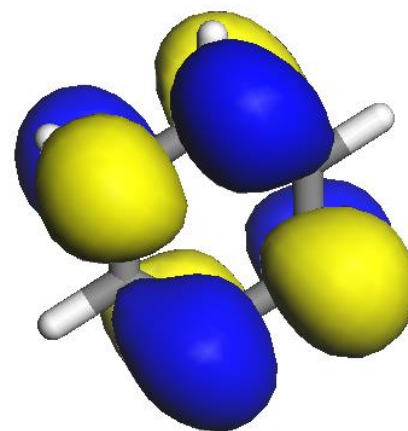
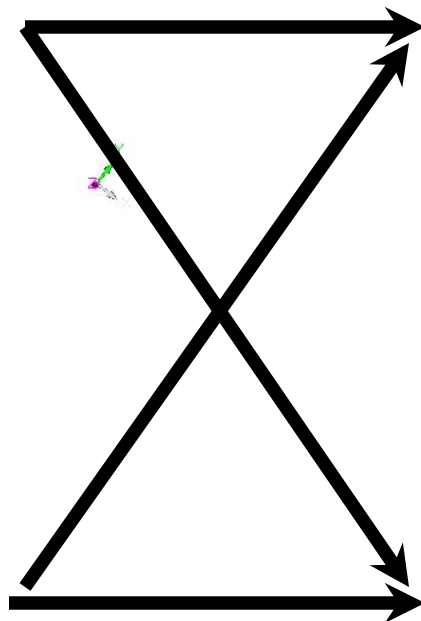
20



22



21



23

Optical absorption using DMol3

--- Transition Dipoles $\langle i(\text{occ}) | x, y, z | a(\text{virt}) \rangle$; Alpha Orbitals---

[50 Transitions with high Intensity] [Atomic Units]

Transition			$\langle i x a \rangle$	$\langle i y a \rangle$	$\langle i z a \rangle$	Ea-Ei	Intensity	Ea-Ei (cm ⁻¹)
21a	->	22a	0.0000	1.4229	0.0000	0.1925 (a)	2.02	42249.5
21a	->	23a	1.4226	0.0000	0.0000	0.1925 (a)	2.02	42253.6
20a	->	22a	1.4228	0.0000	0.0000	0.1926 (a)	2.02	42271.0
20a	->	23a	0.0000	1.4230	0.0000	0.1926 (a)	2.02	42275.0
19a	->	25a	0.0000	0.7098	0.0000	0.4067 (a)	0.50	89267.5
18a	->	25a	0.7078	0.0000	0.0000	0.4067 (a)	0.50	89270.3
19a	->	26a	0.7065	0.0000	0.0000	0.4074 (a)	0.50	89420.1
18a	->	26a	0.0000	0.7024	0.0000	0.4074 (a)	0.49	89422.9

Relevant states for four orbital model.

All are predicted to have roughly the same intensity and energy by DMol3. This is flat wrong!

Observed weak band 260 nm and intense band 168 nm.

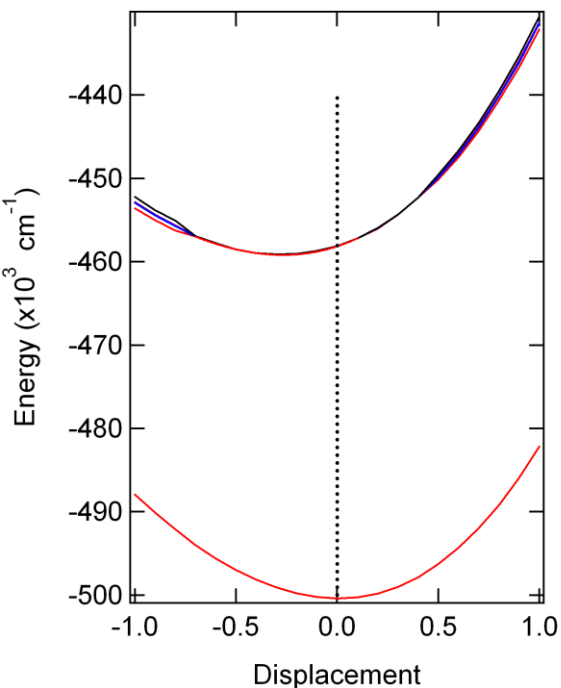
TD-DFT calculation

ABSORPTION SPECTRUM

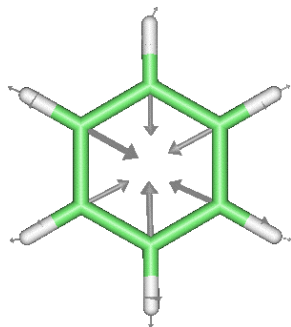
State	Energy (cm-1)	fosc	T2 (D**2)	TX (D)	TY (D)	TZ (D)
1	43315.4	0.0000001917	0.000000	-0.000016	0.000119	-0.000000
2	50254.5	0.0000047538	0.000004	-0.000408	-0.000436	-0.000001
3	58106.6	0.0000000001	0.000000	0.000002	0.000000	0.000001
4	58415.1	0.557203304	0.41790	0.47285	-0.44082	-0.000000
5	58429.5	0.557697442	0.41827	0.44174	0.47237	0.000000
6	58890.3	0.0000344538	0.000026	0.000002	0.000000	-0.01607
7	58909.6	0.0000001236	0.000000	-0.000001	0.000001	-0.000096
8	59188.2	0.005716550	0.00429	0.000001	0.000002	-0.06548

Prediction is for only a strong band at 171 nm.
This is only 3 nm from the observed band!
The reason the weak band is not found is that
no vibronic coupling is included.

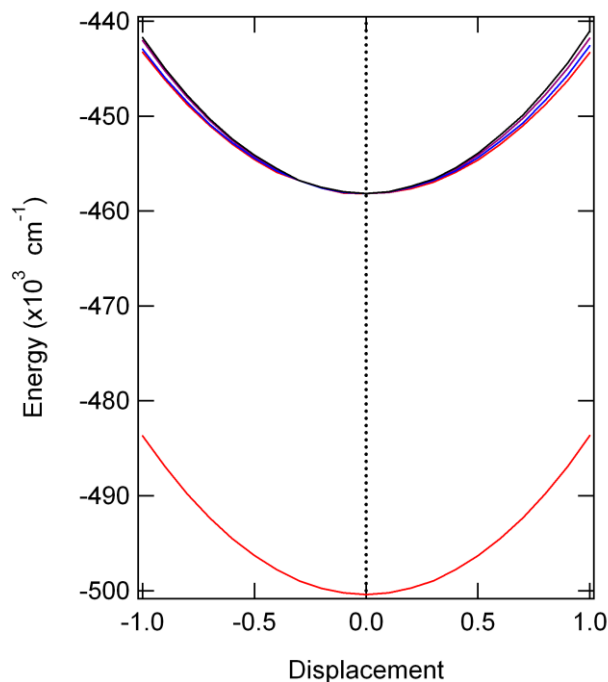
Potential energy surfaces



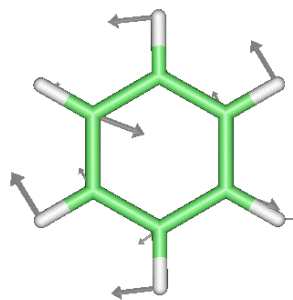
Shifted



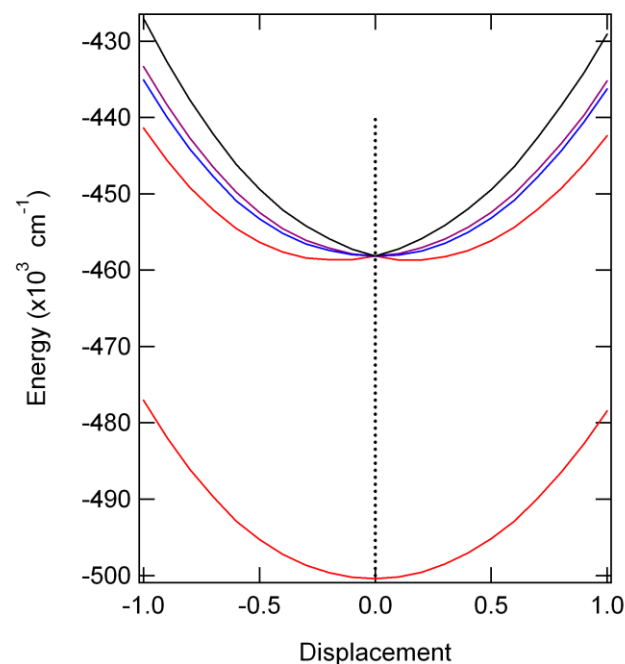
A_{1g} 1101 cm^{-1}



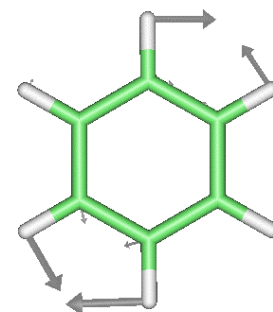
Unshifted



E_{1u} 1035 cm^{-1}



Vibronic



E_{2g} 1141 cm^{-1}

Corrections

- Anharmonicity

Solved currently using Numerov-Cooley algorithm

Example: Vibrational Stark Effect

- Configuration Interaction

Solved currently using ex situ TD-DFT calculations

Example: Solvatochromism

- Vibronic coupling

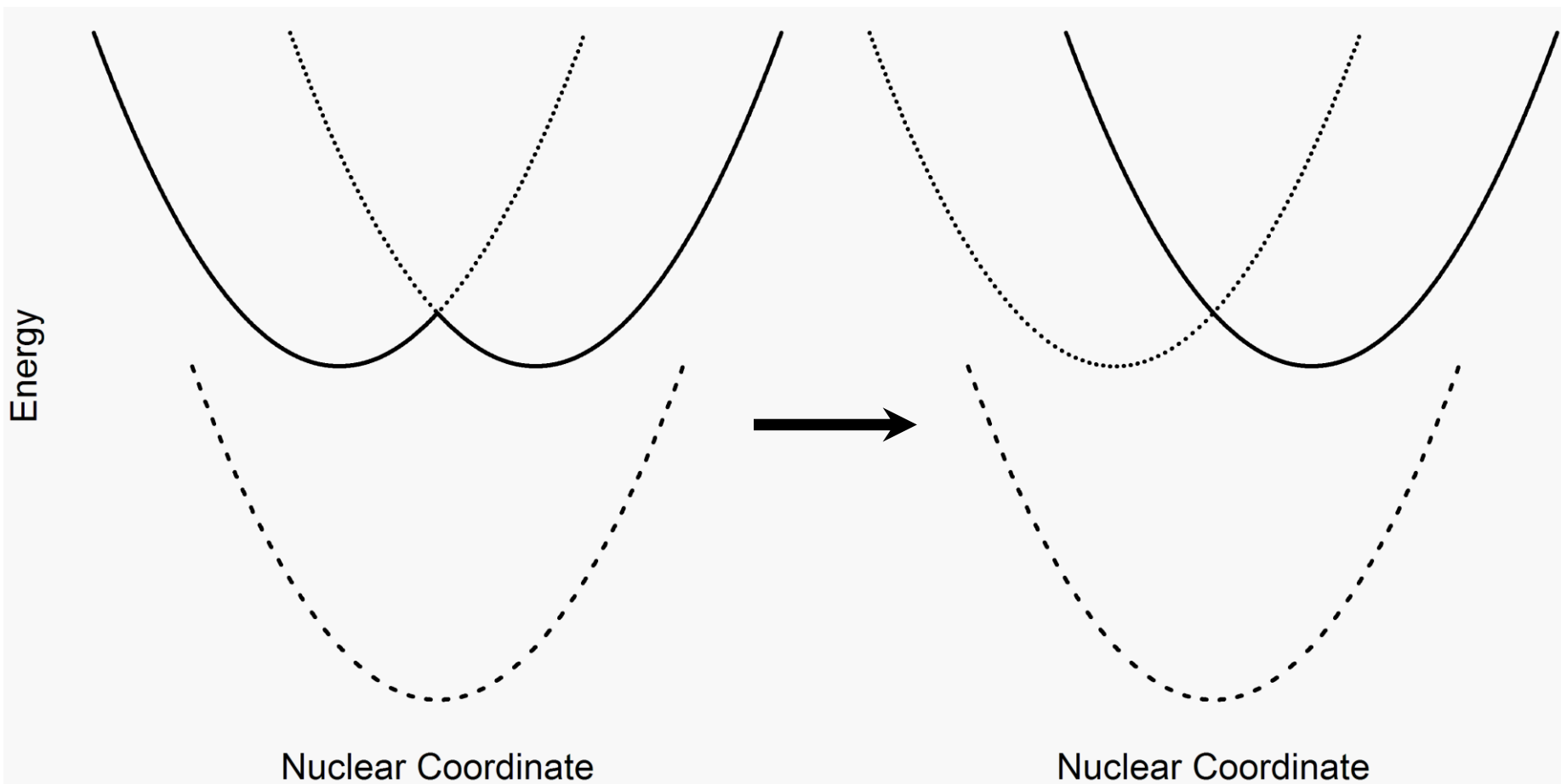
No general solution although one is possible

Currently use rediagonalization assumption

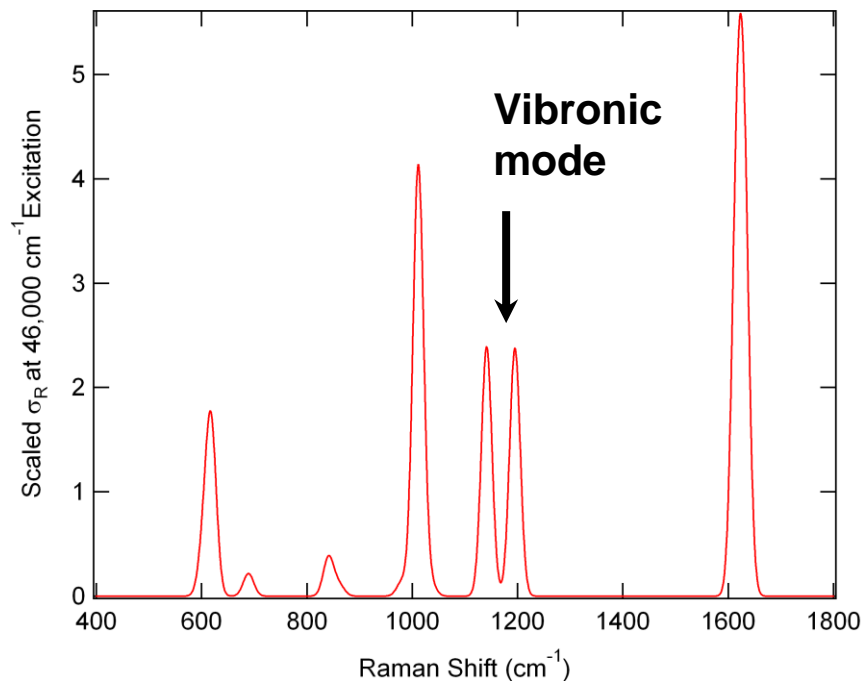
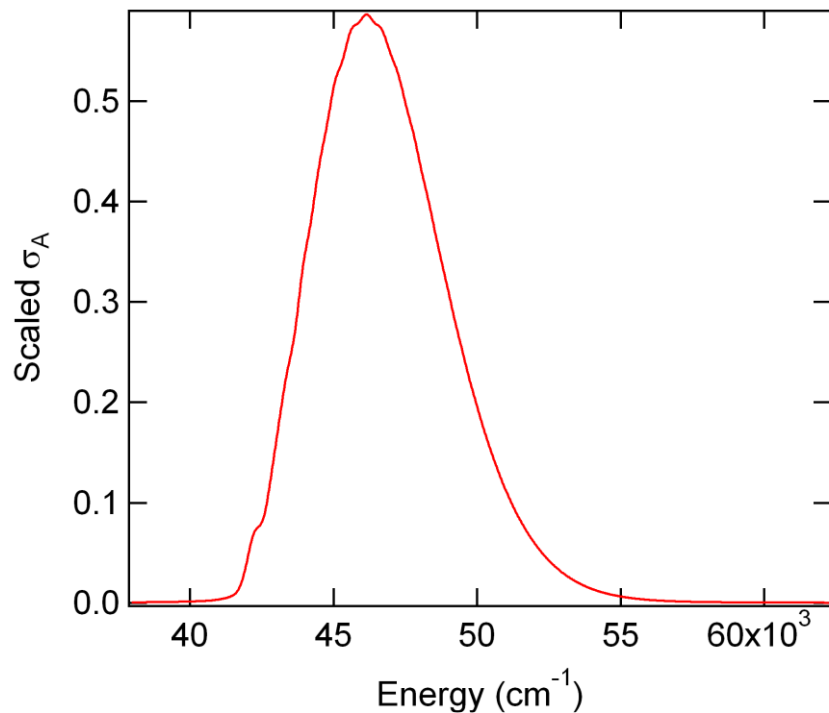
Radiagonalization hypothesis

Vibronic

Radiagonalized



Calculated Benzene Absorption and Raman Spectra



Line broadening is added artificially based on experimental spectral widths.