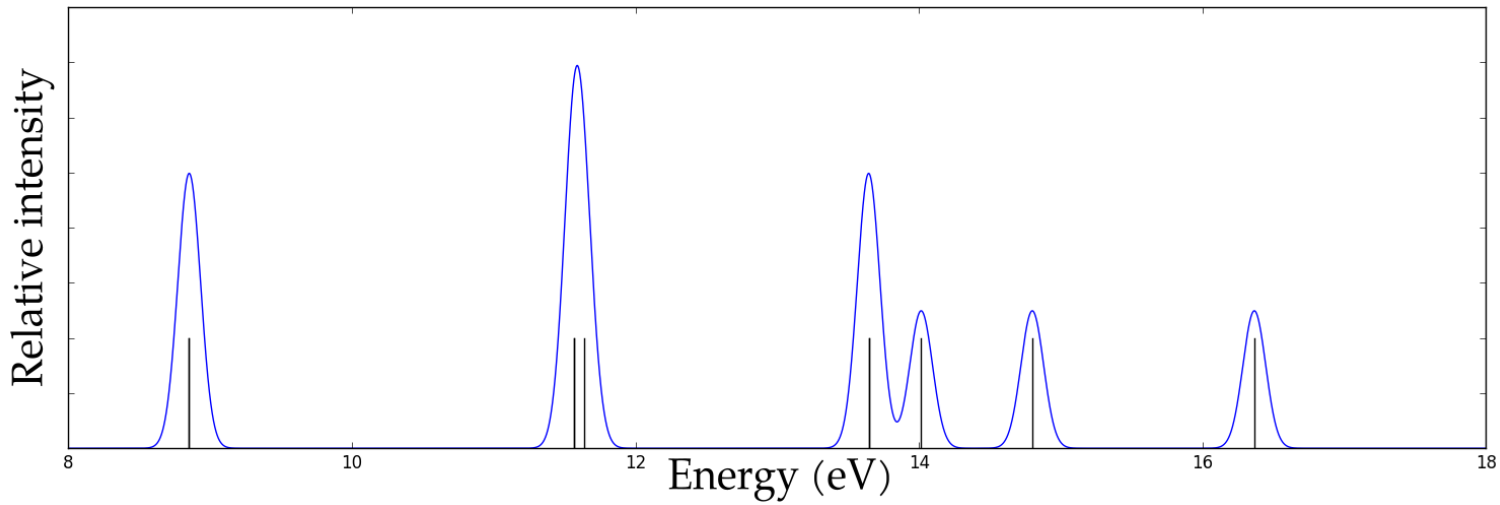
Vibrational effects on molecular spectra

Arttu Hyvönen

August 9, 2019

Starting point and goal

Benzene ionization spectrum $\mathrm{G_0W_0@PBE}$



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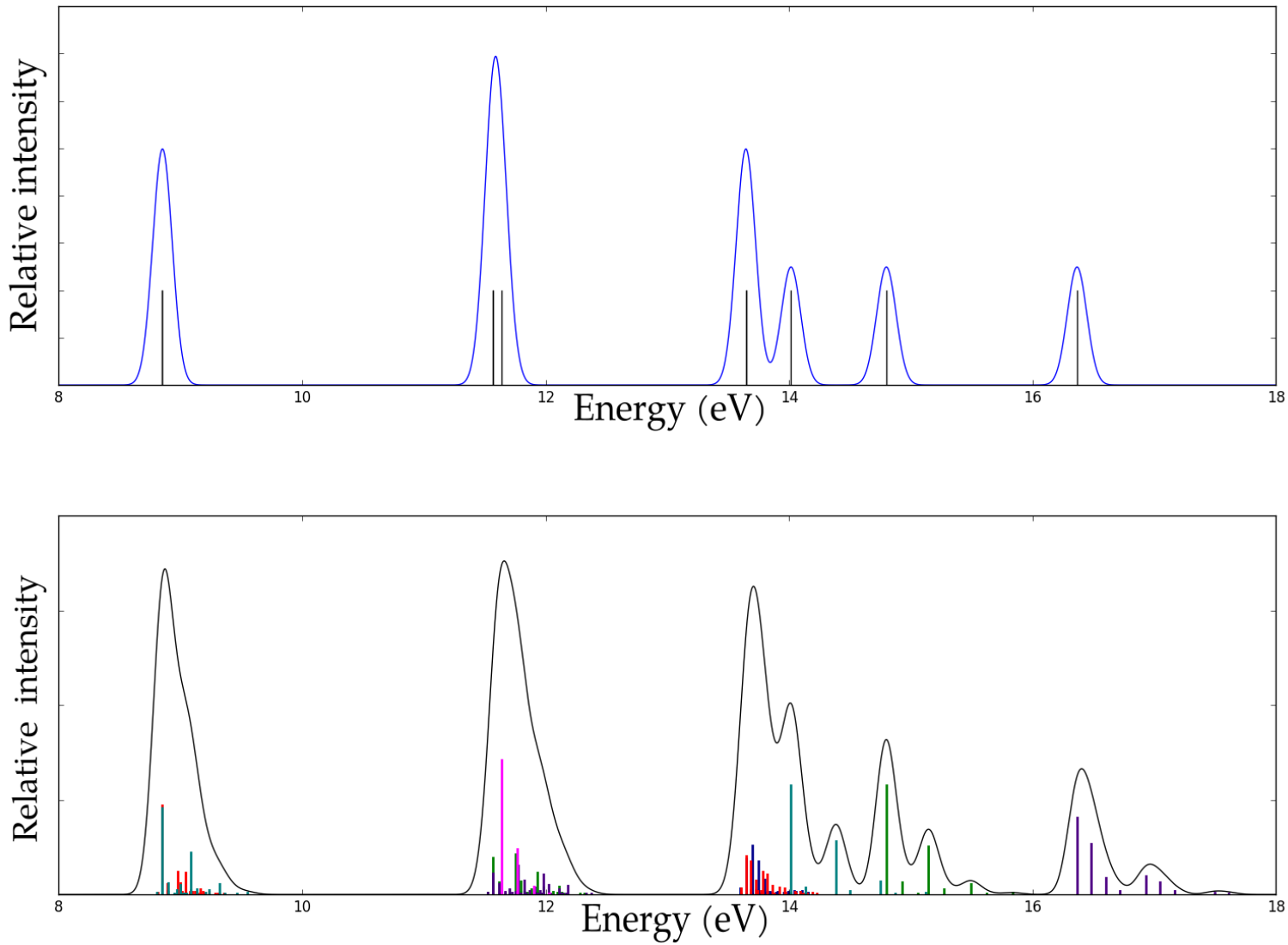
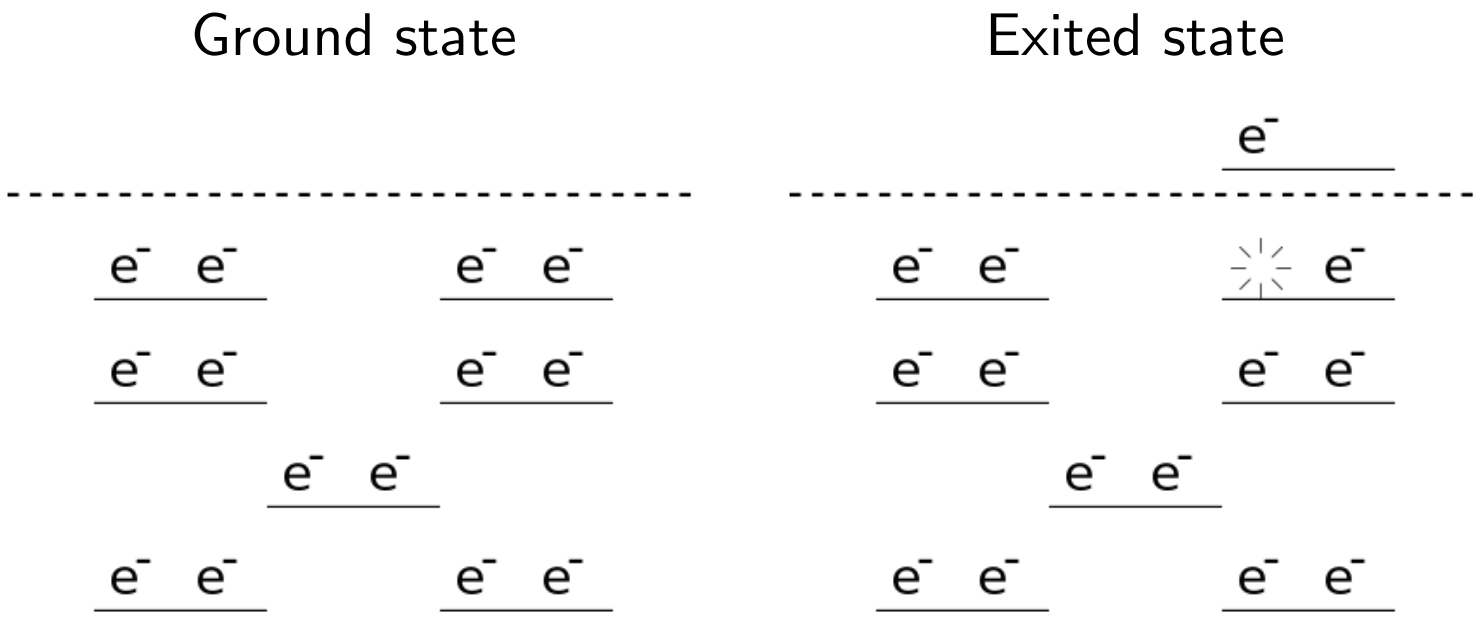
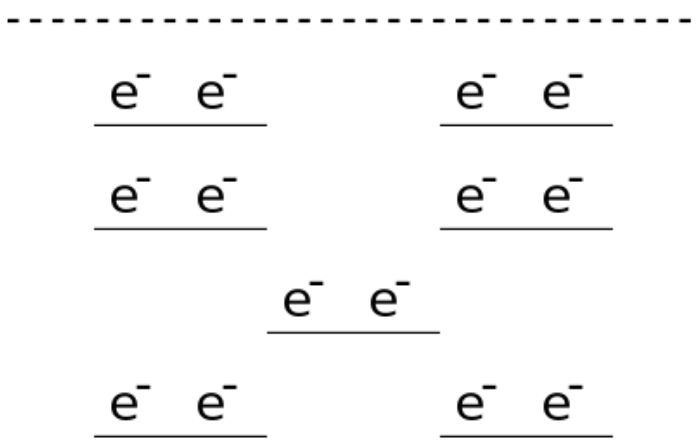


Electronic transition

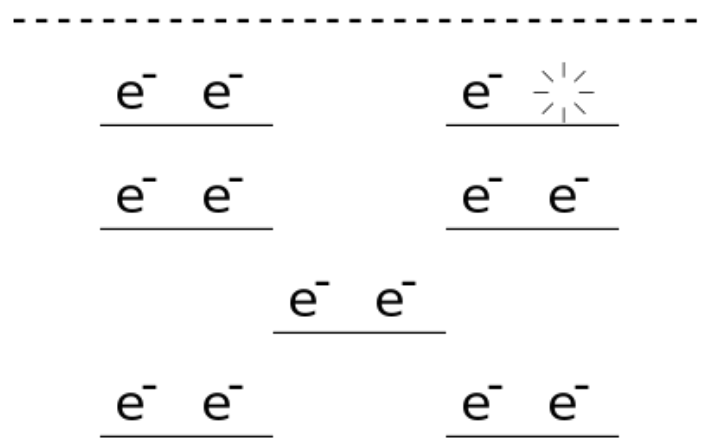


Electronic transition

Ground state



Exited state



Quantum harmonic oscillator

$$\hat{H} = \frac{\hbar}{2\mu}\frac{\partial^2}{\partial x^2} + \underbrace{\tfrac{1}{2}k\hat{x}^2}_{\text{Harmonic potential}}$$

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle$$

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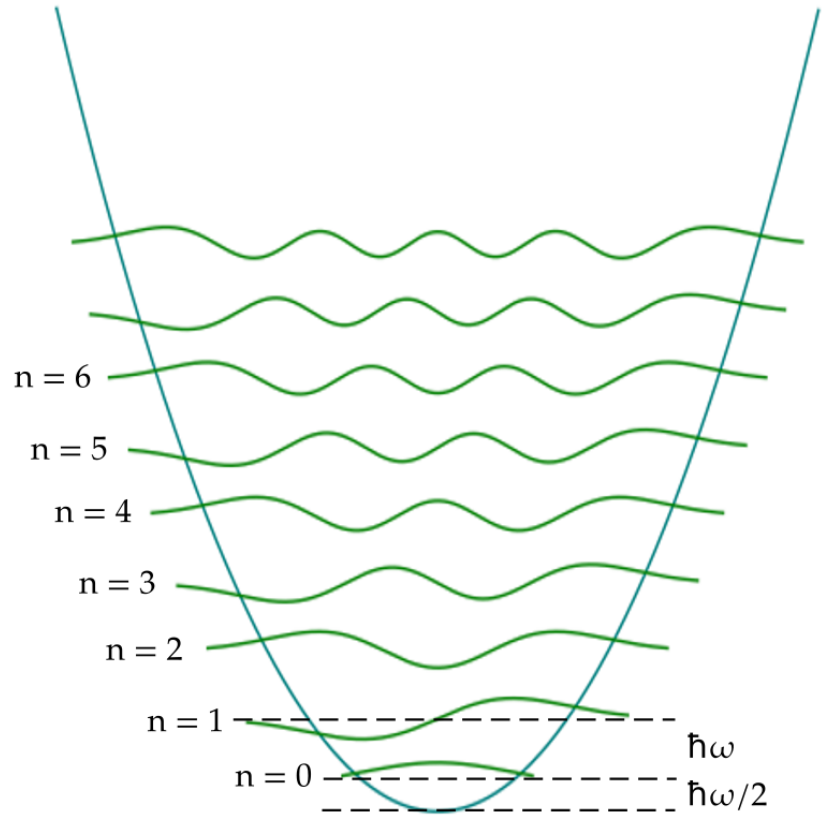


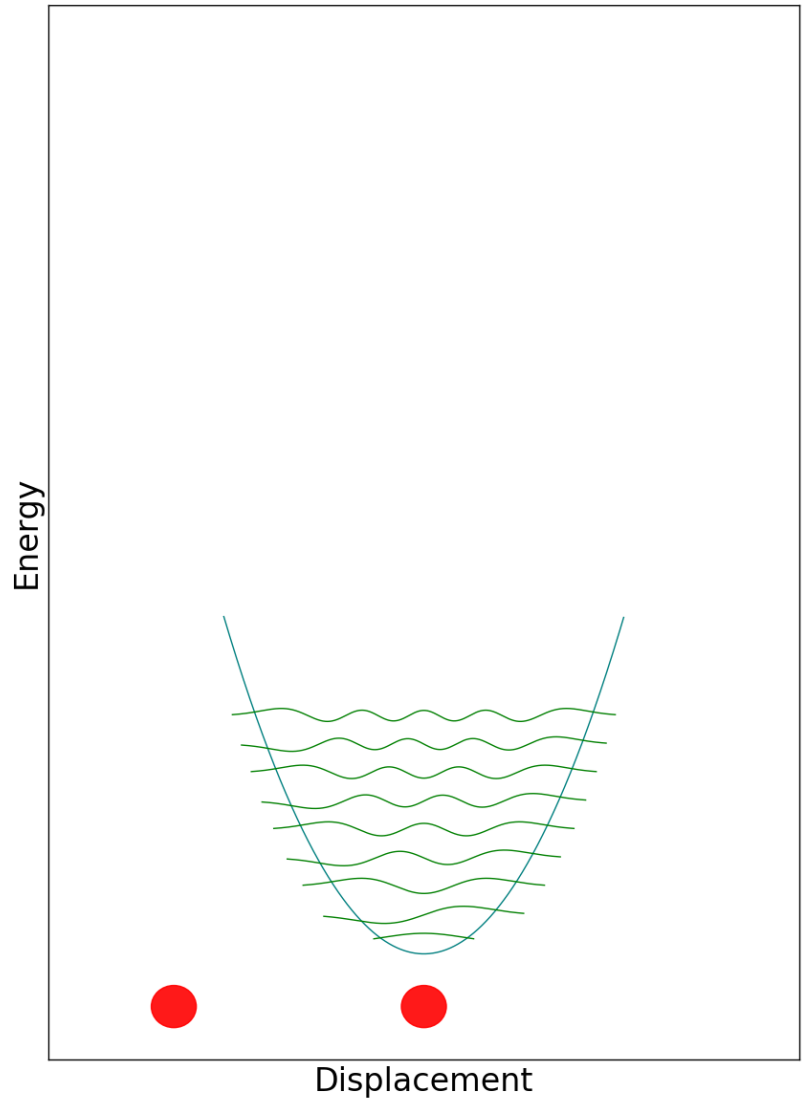
After solving

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{\mu\omega x^2}{2\hbar}} H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}x\right)$$

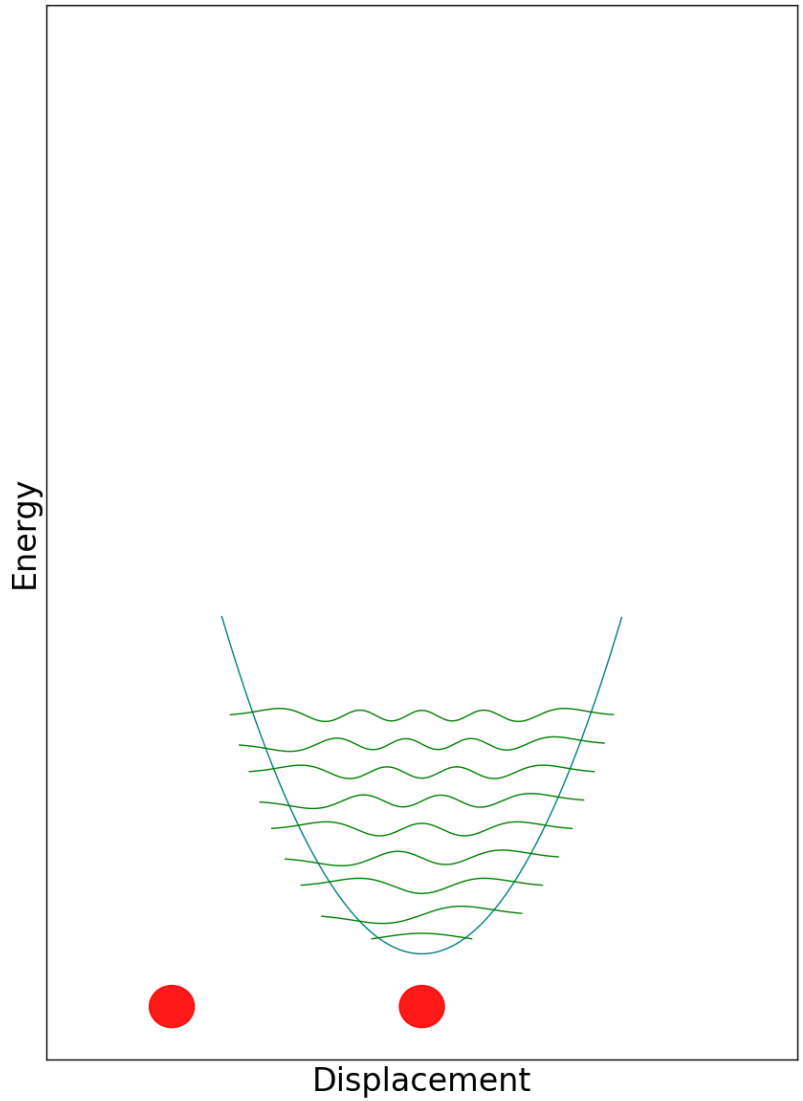
Diatomic molecules

Equilibrium distance d



Diatomic molecules

Equilibrium distance d
Frequency ω
Force constant k
Reduced mass μ



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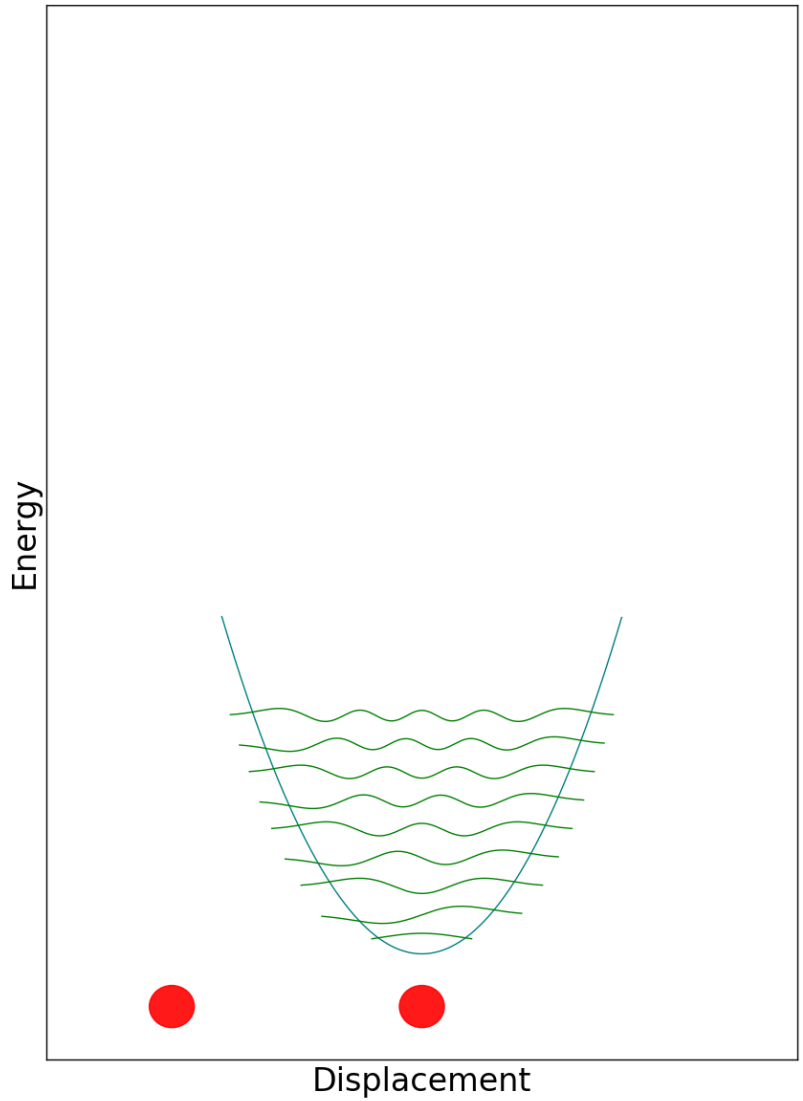
Energy $E_n = \hbar\omega(n + \frac{1}{2})$



Diatomic molecules

Equilibrium distance d
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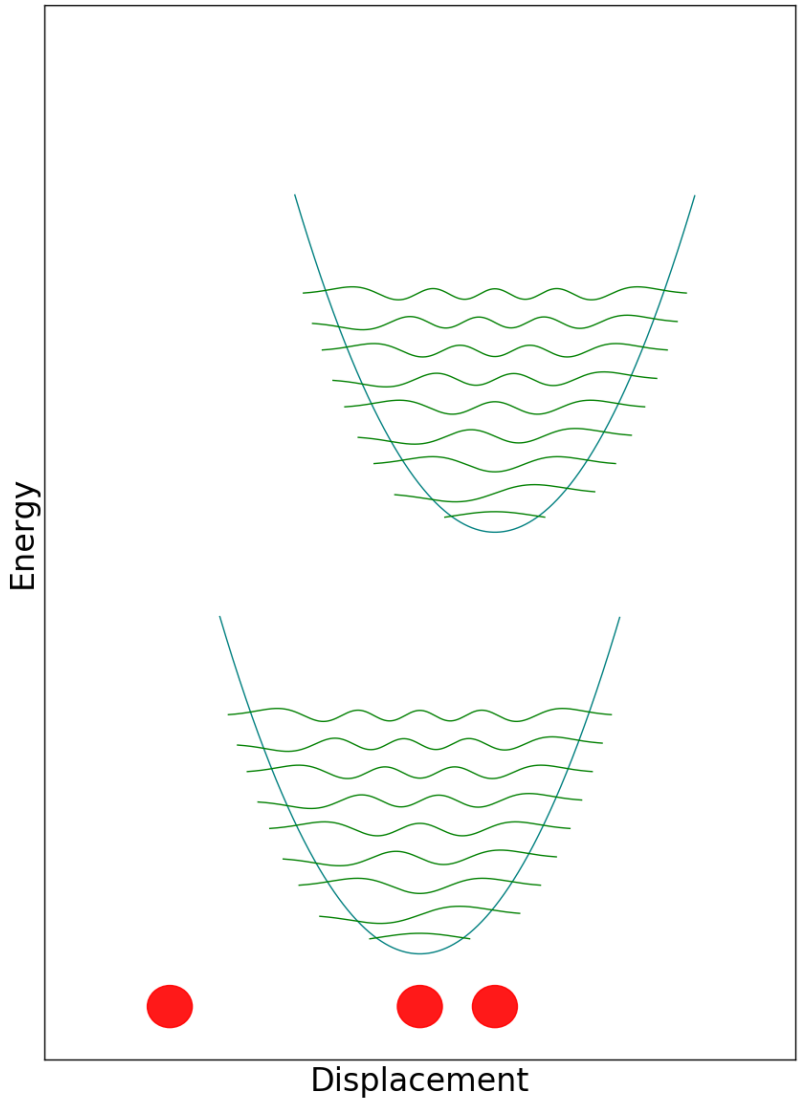
Energy $E_n = \hbar\omega(n + \frac{1}{2})$
Equilibrium distance d'
Energy $E_{n'} = \hbar\omega(n' + \frac{1}{2})$



Diatomic molecules

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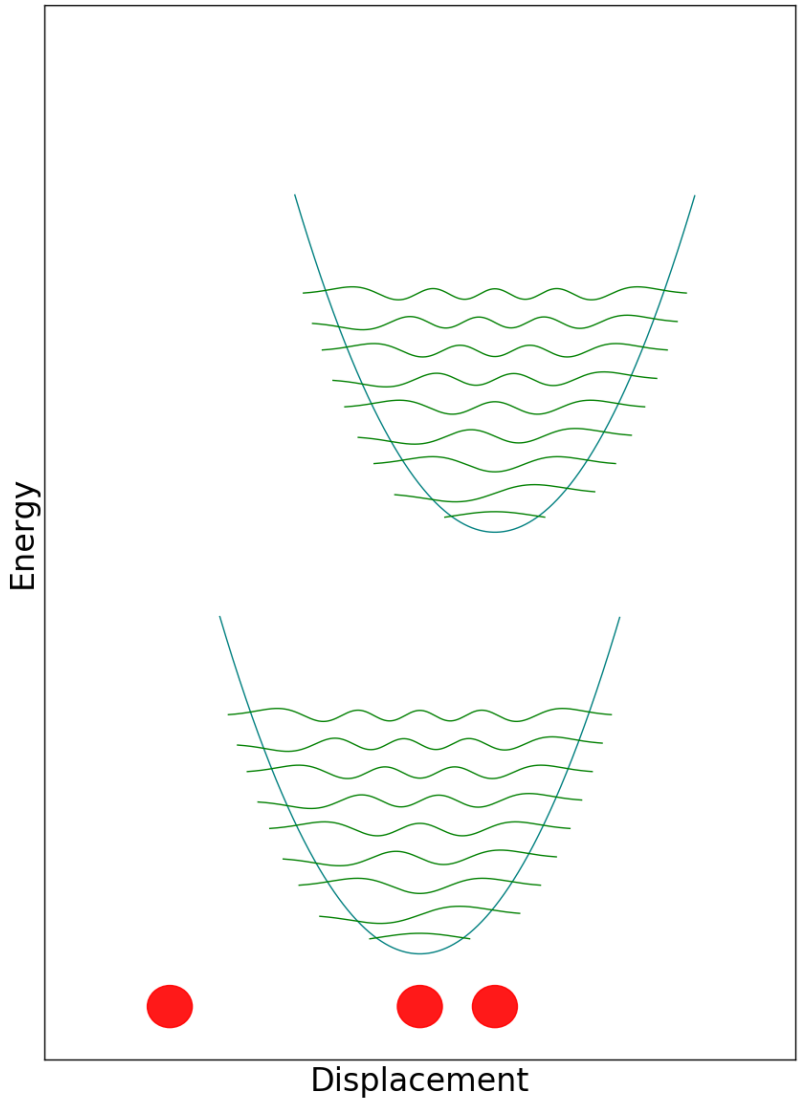
Energy $E_n = \hbar\omega(n + \frac{1}{2})$
Equilibrium distance d'
Energy $E_{n'} = \hbar\omega(n' + \frac{1}{2})$
Displacement $\delta = d' - d$



Diatomic molecules

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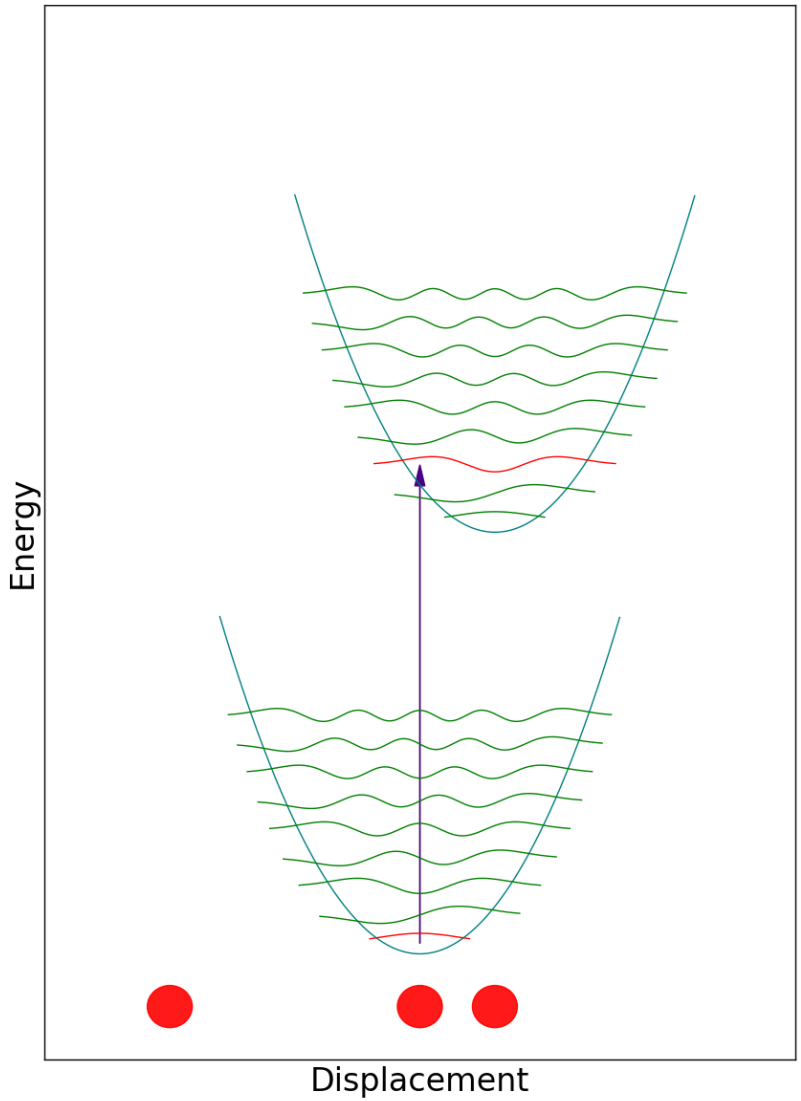
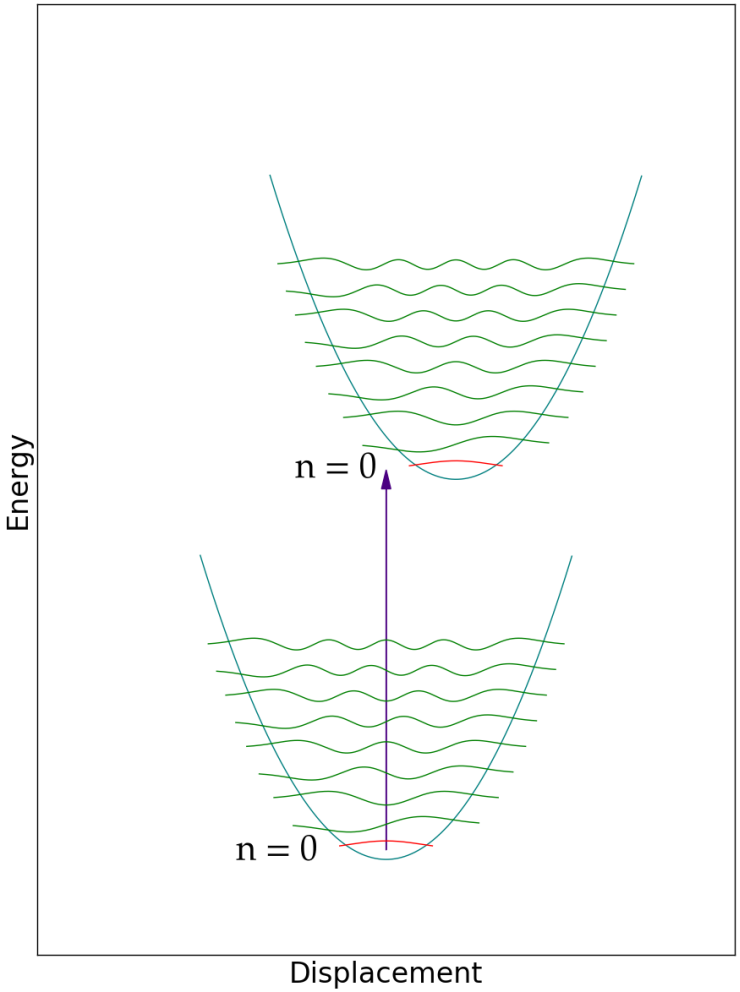
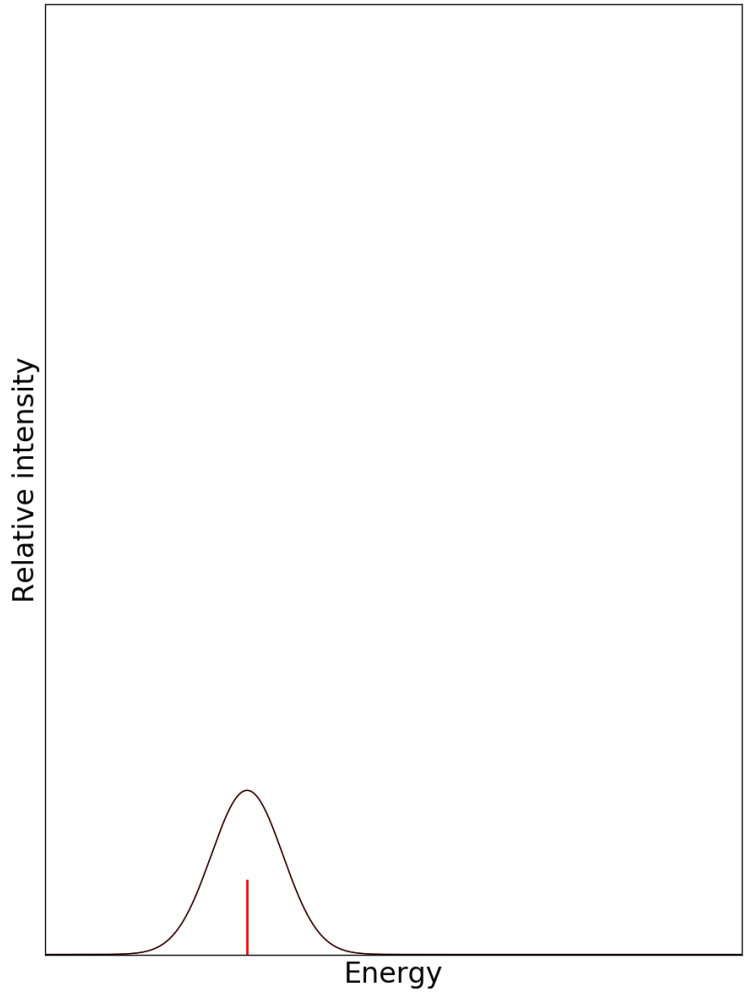


$$\begin{aligned} \mathrm{I}_{relative} &= |\langle \psi^*_{final} | \psi_{initial} \rangle|^2 \\ &= \mathrm{FCI}(n, n')^2 \end{aligned}$$

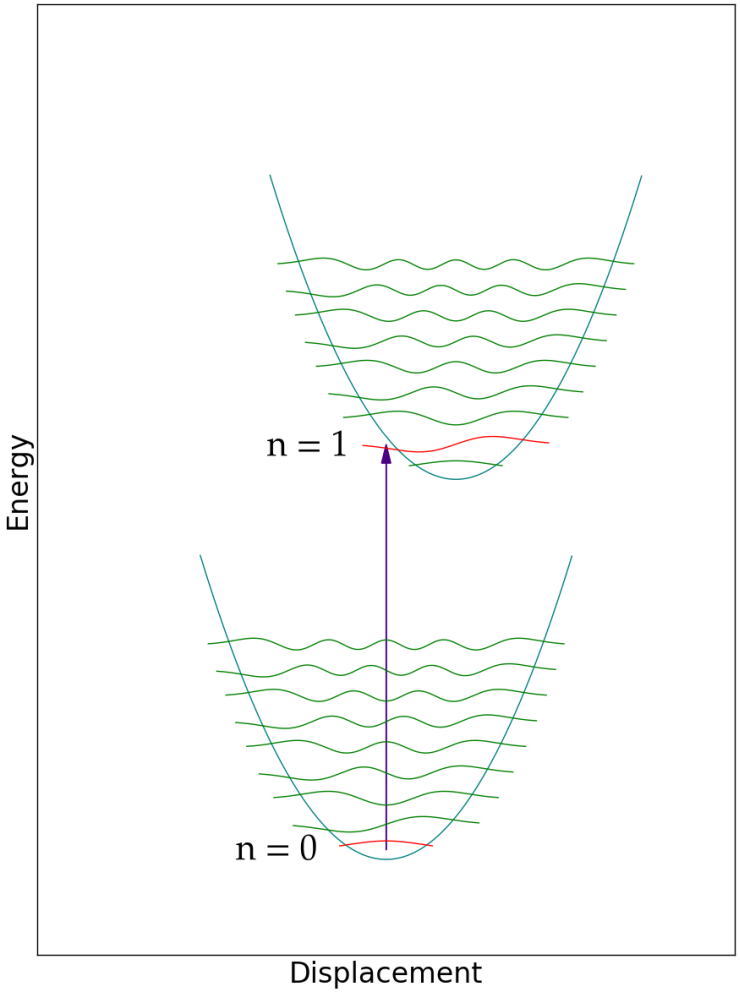
$$n \rightarrow n'$$

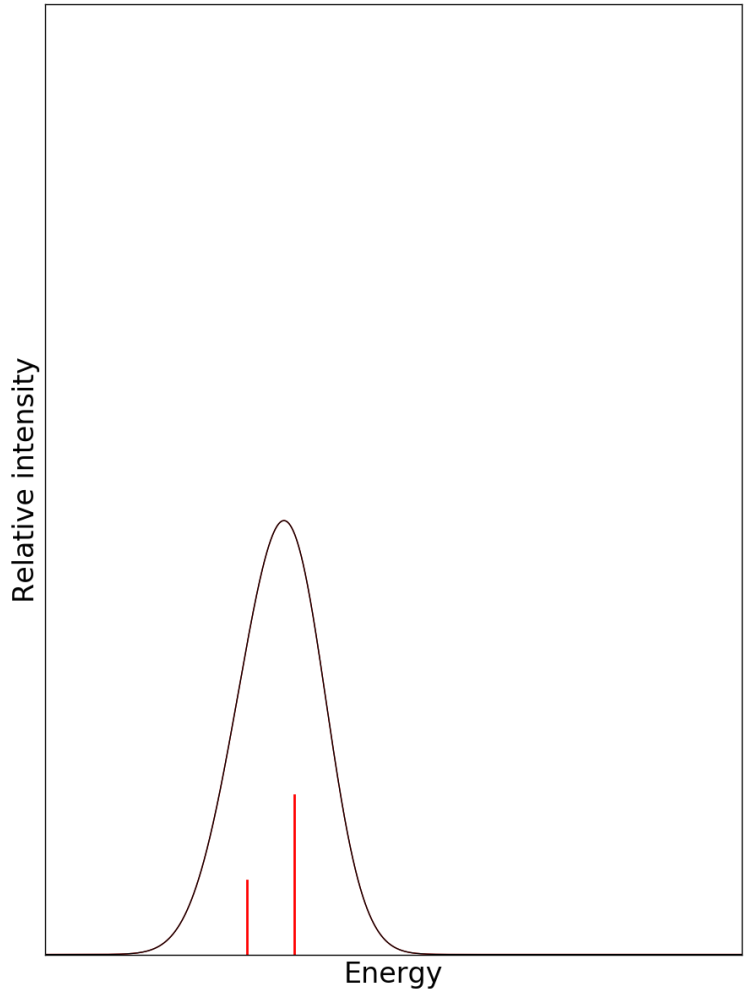
Transitions for diatomic molecule



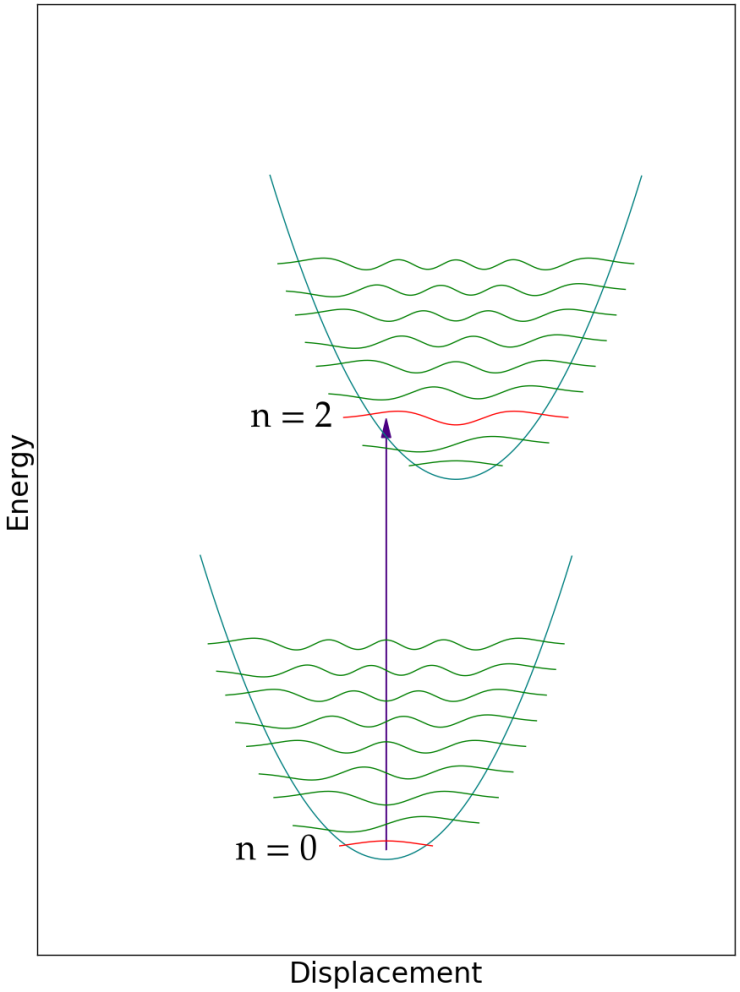


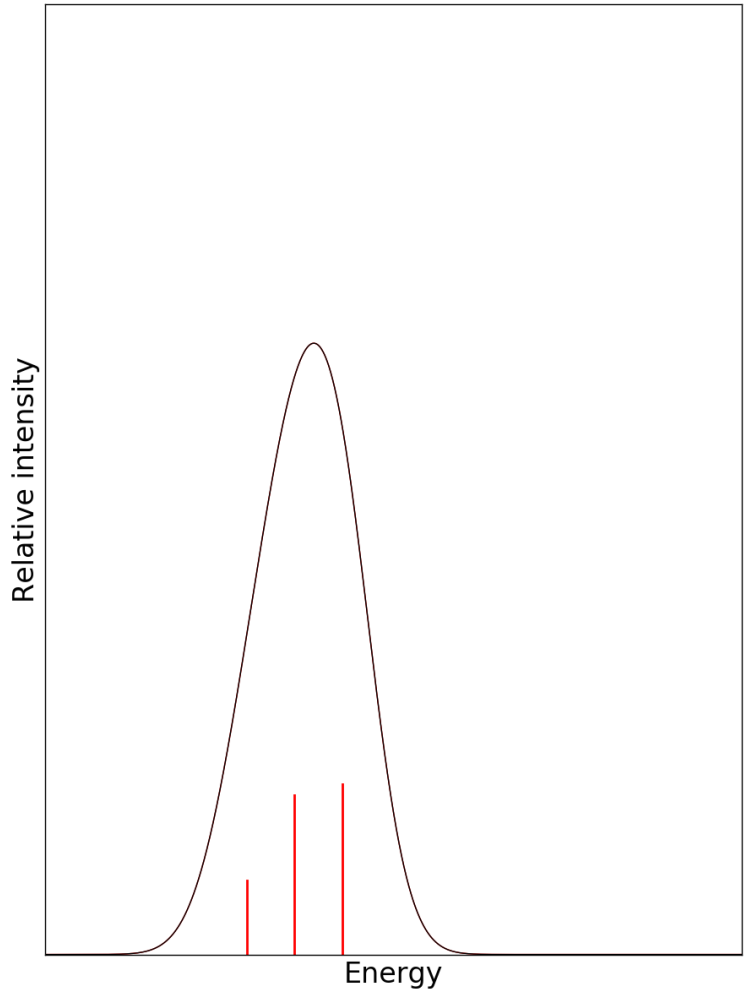
Transitions for diatomic molecule





Transitions for diatomic molecule





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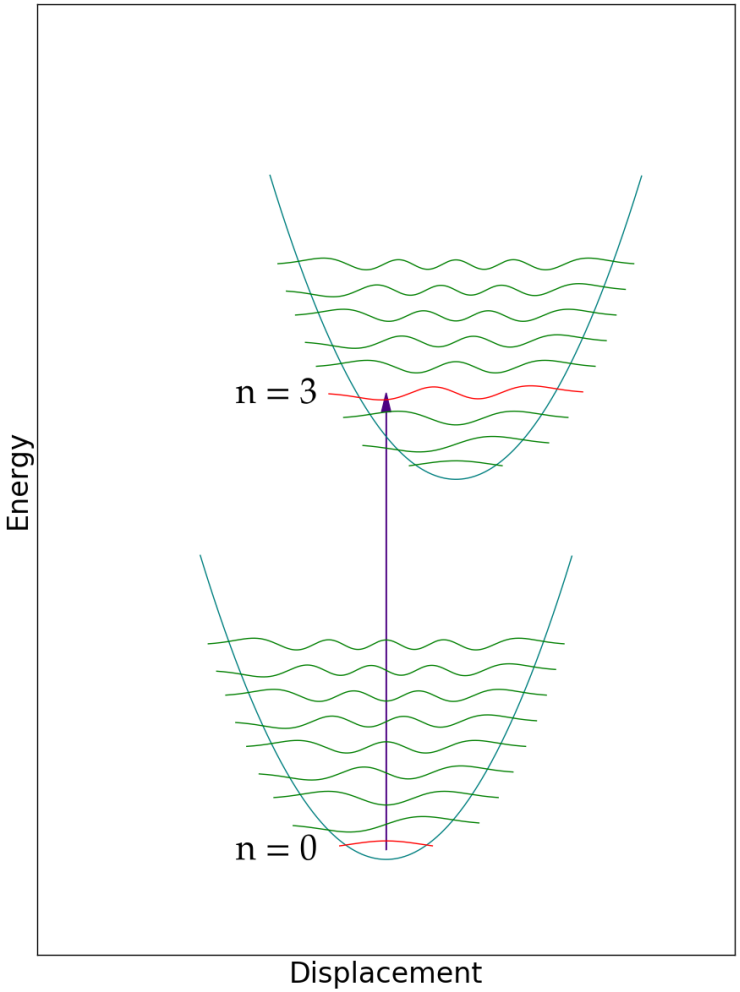

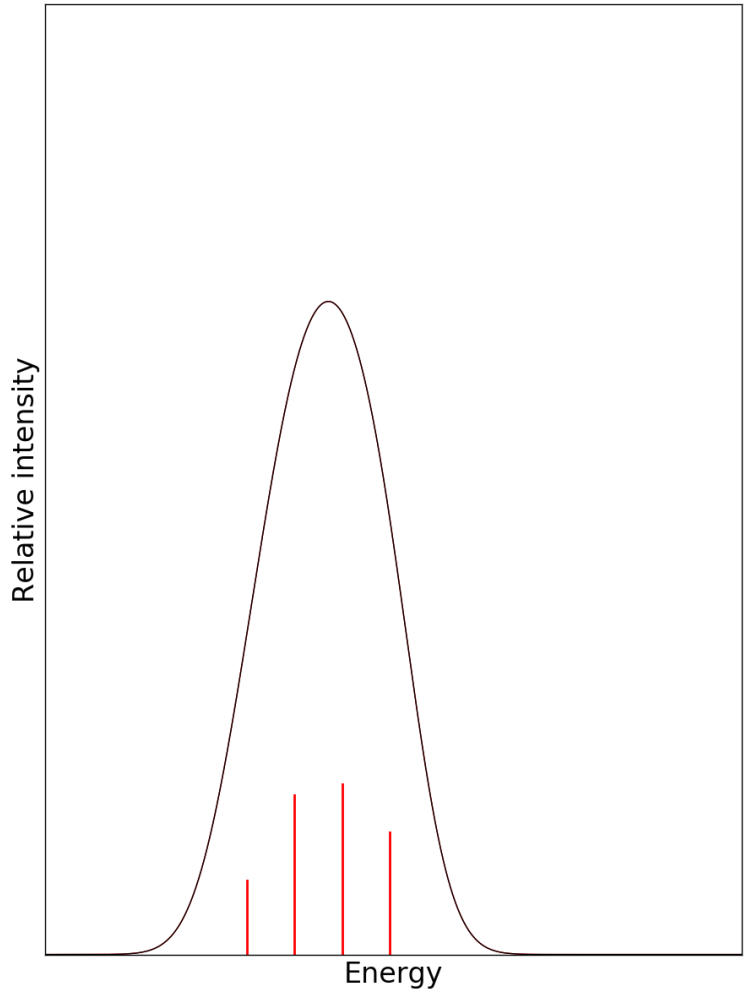

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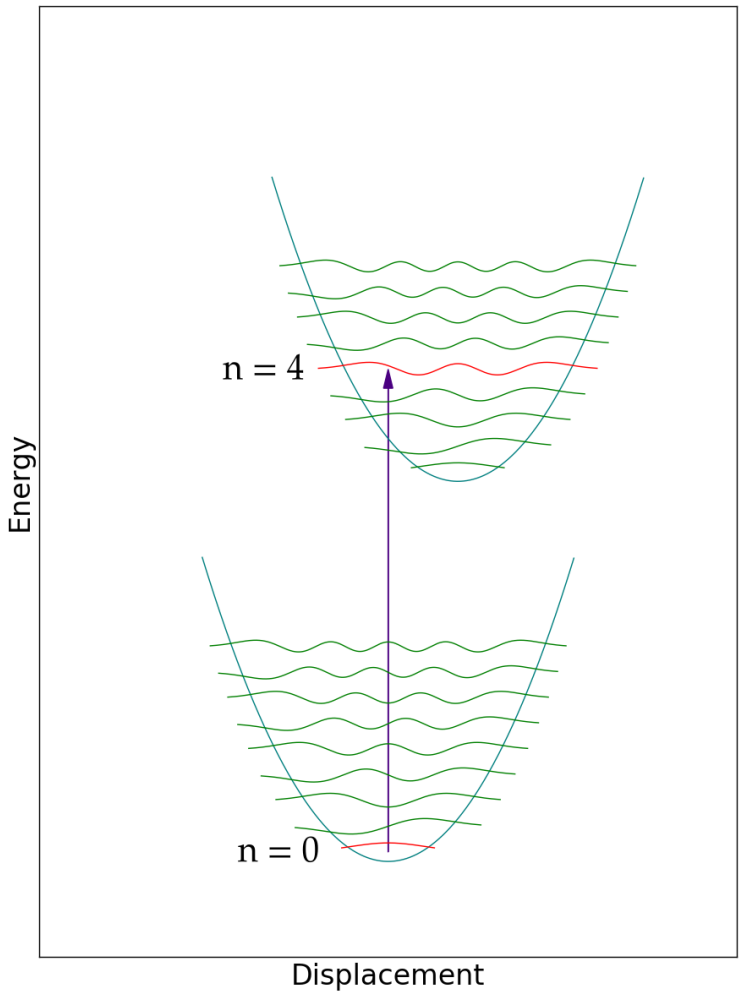

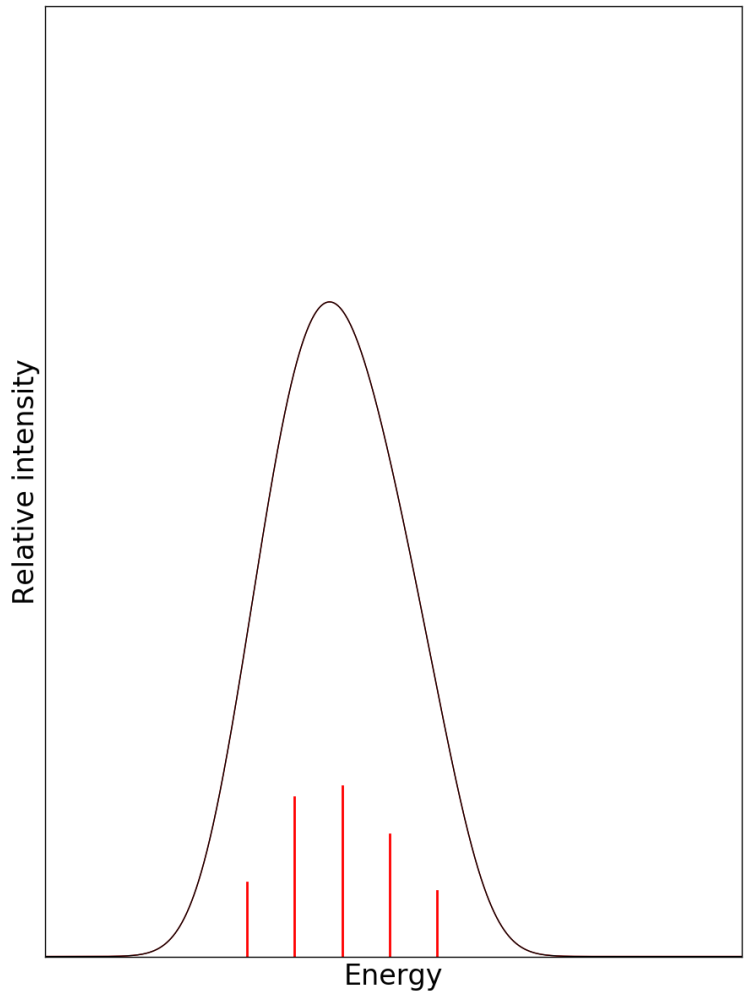

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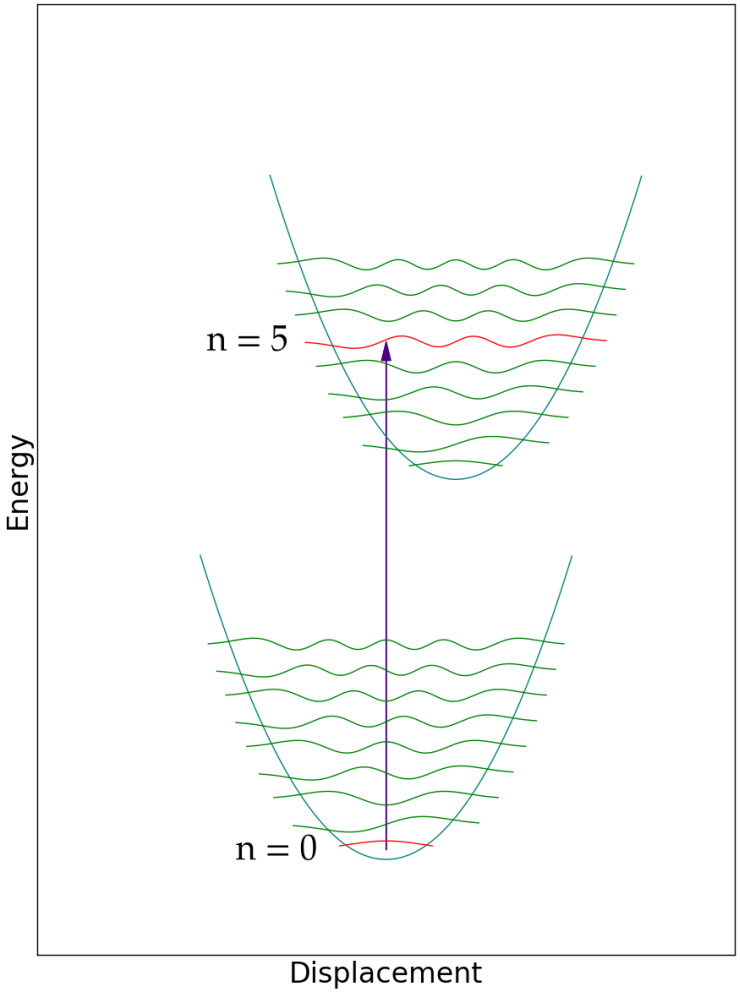

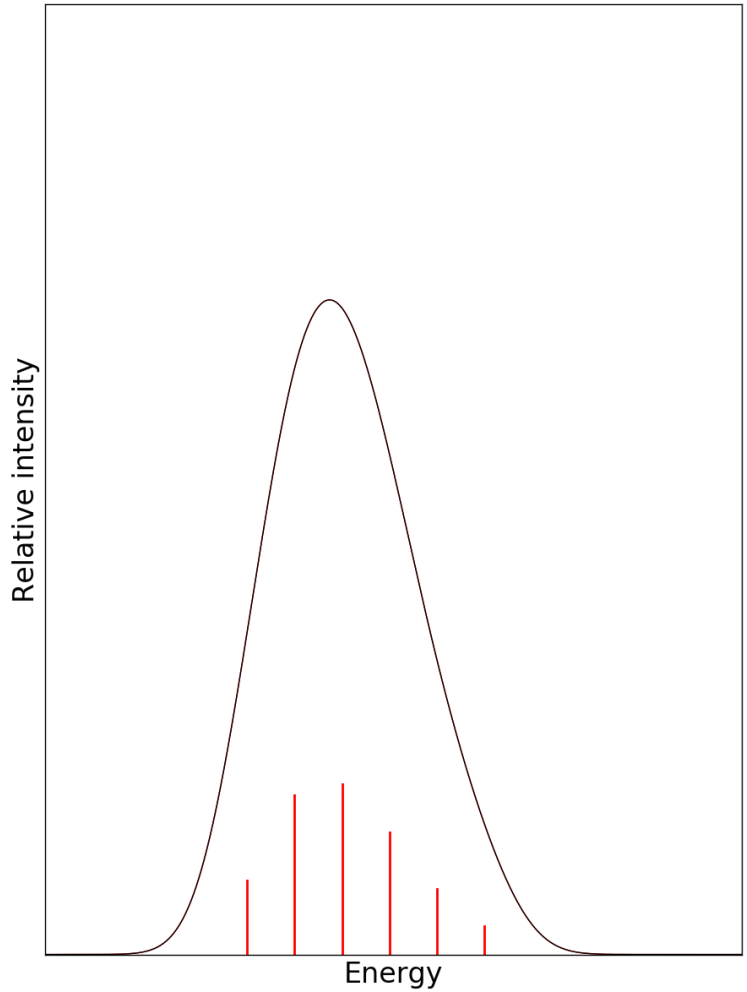

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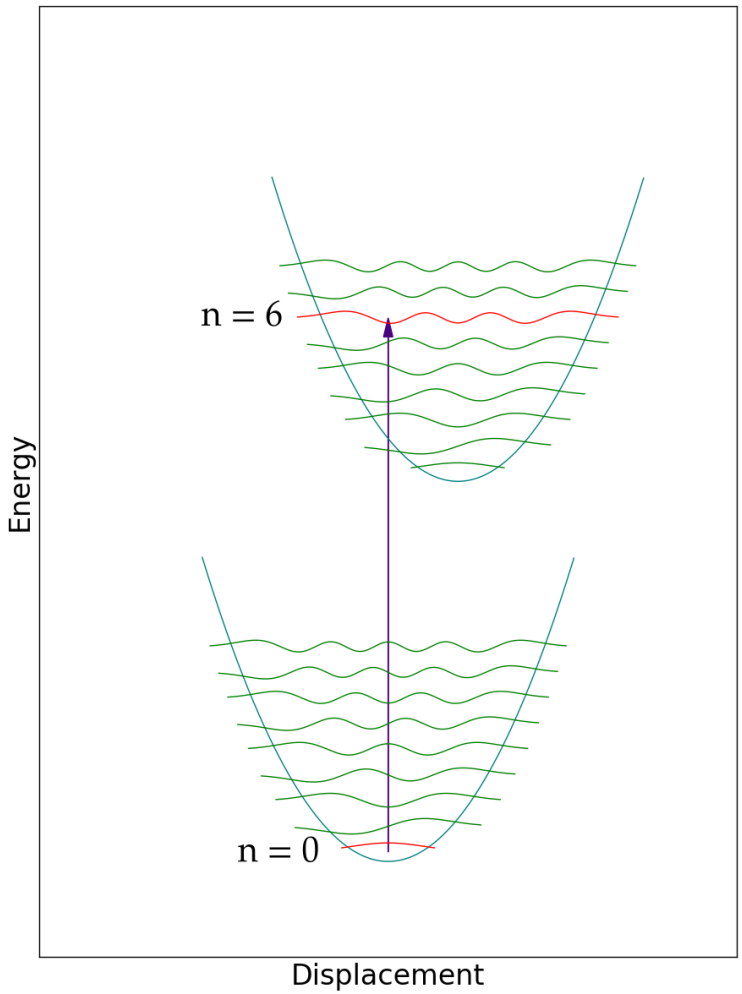

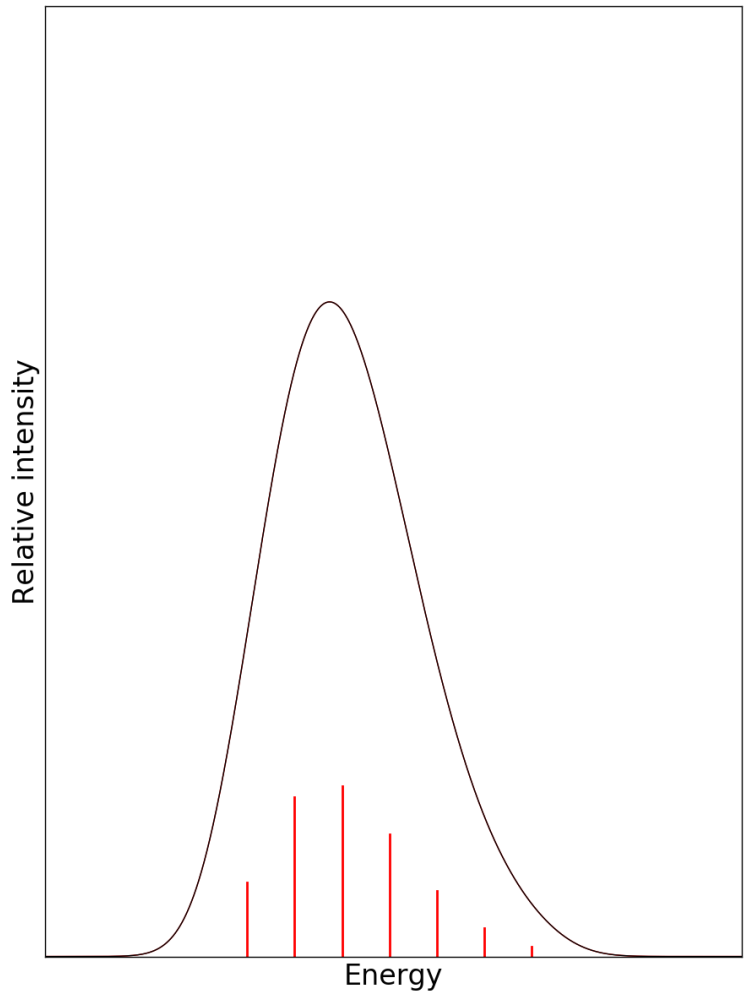

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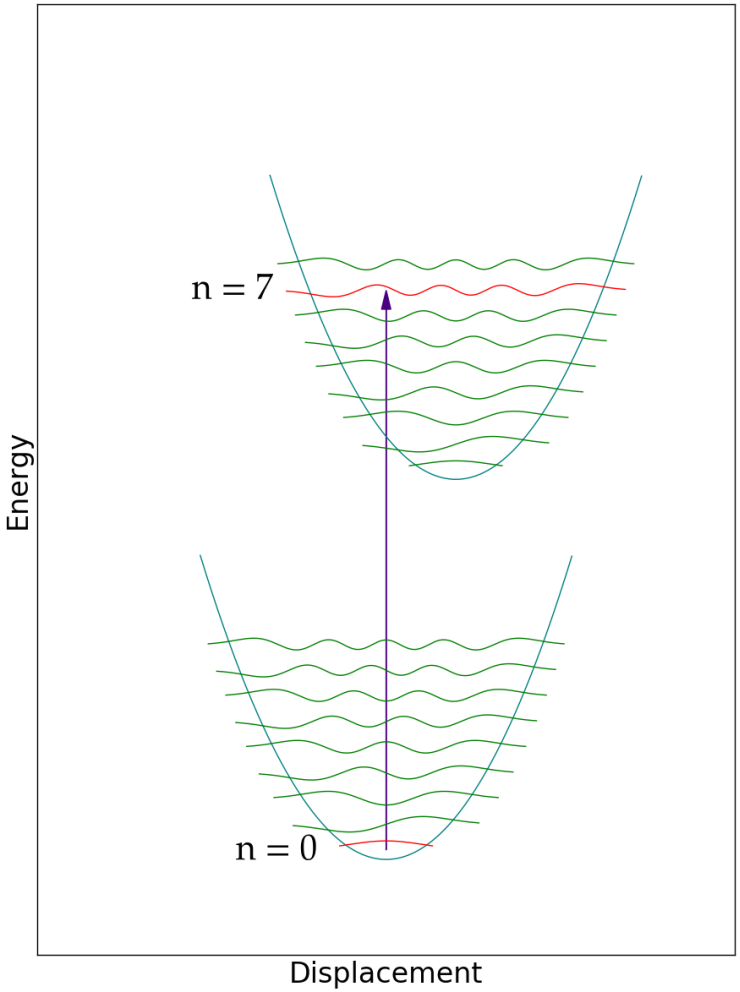

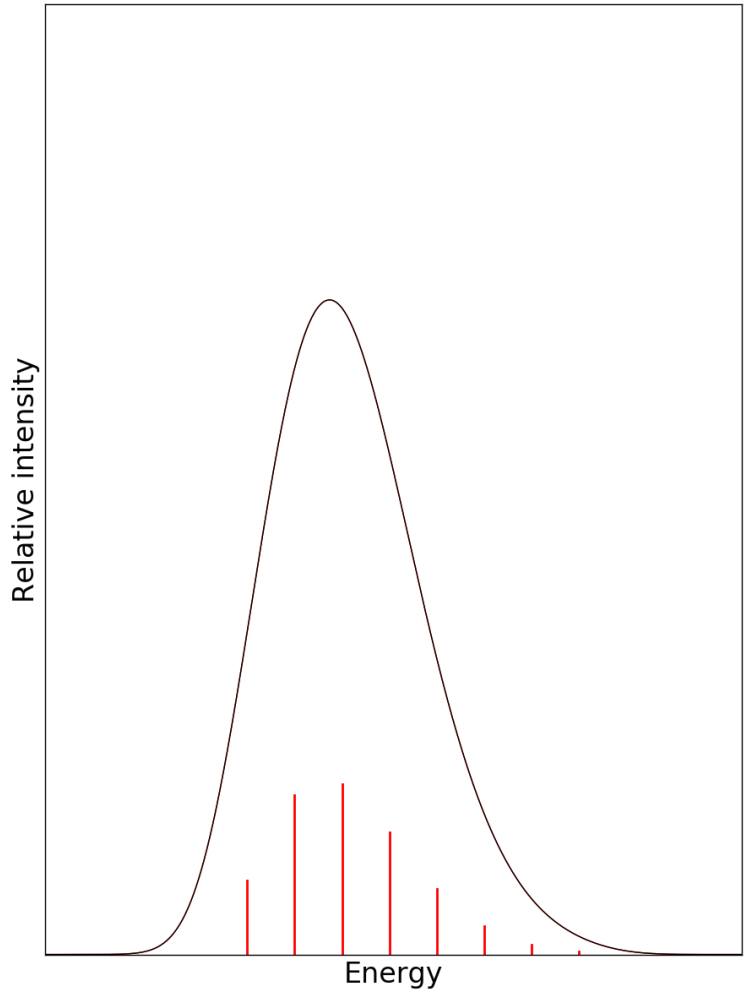

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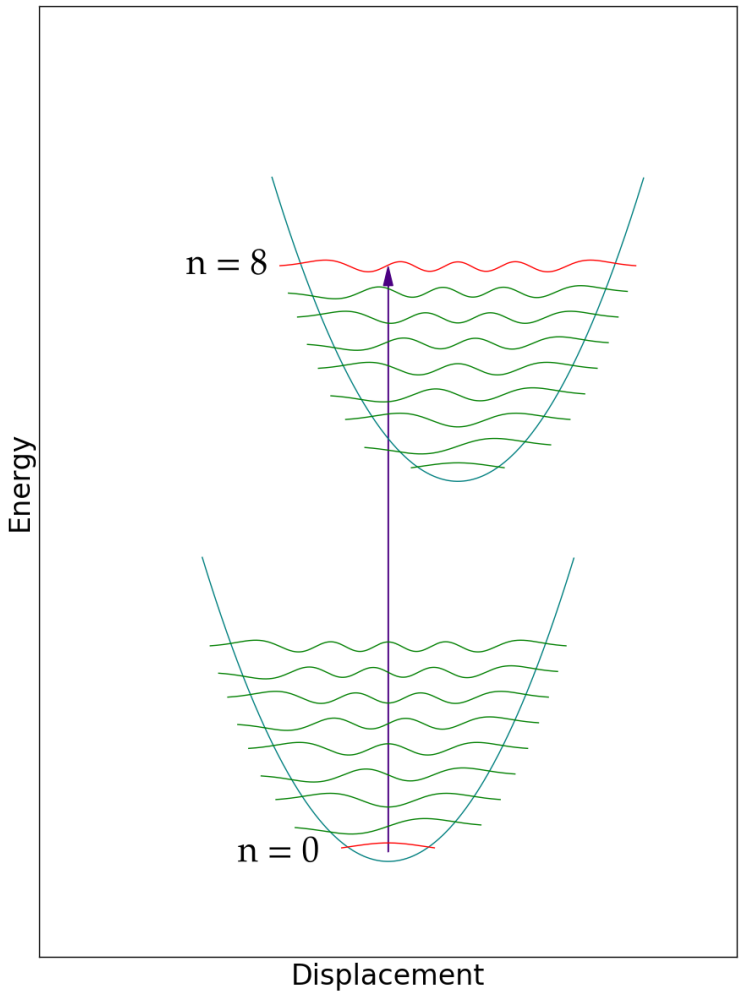

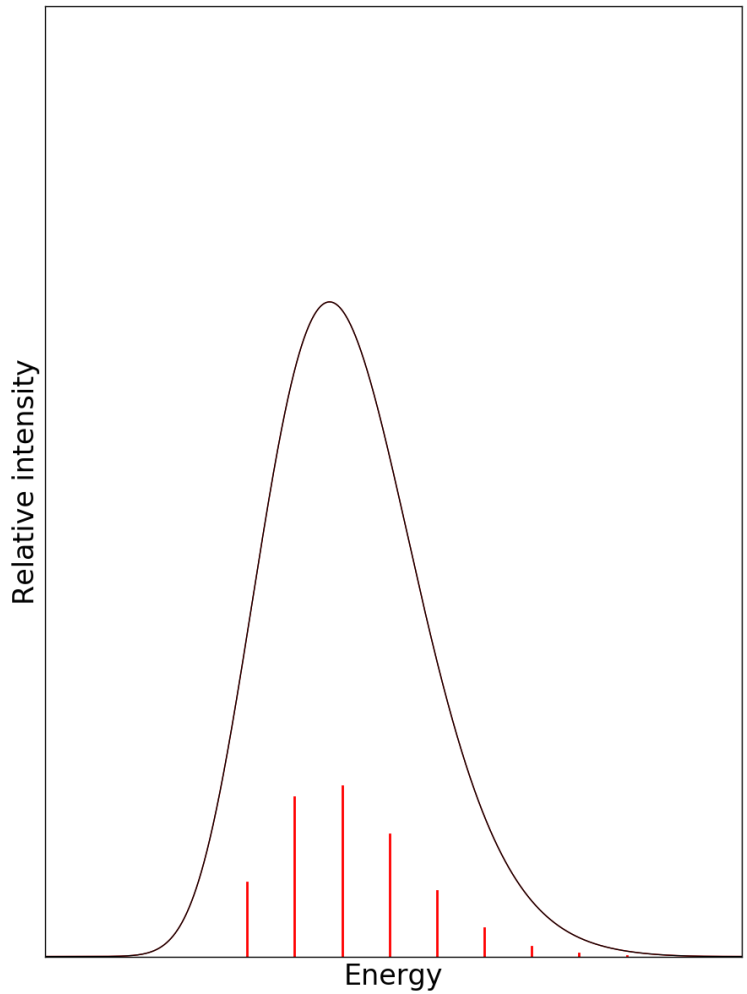

Generalization to N atoms

3N vibrational modes

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$$d \rightarrow (d_1, d_2, ...d_{3N}), n \rightarrow (n_1, n_2, ...n_{3N}),$$
$$\mu \rightarrow (\mu_1, \mu_2, ...\mu_{3N}), f \rightarrow (f_1, f_2, ...f_{3N})$$

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Irrelevant modes are dropped out
$\to 2 \leq p \leq 10$ relevant modes

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$\to 2 \leq p \leq 10$ relevant modes

$$\mathrm{I}(n, n') = \prod_{i=1}^{p} \overbrace{\mathrm{FCI}(n_i, n_i')^2}^{\text{Overlap integral}} \underbrace{\exp\left(\frac{-\hbar n_i f_i}{k_B T}\right)}_{\text{Temperature term}}$$

Calculating the integral

Analytic solution when using harmonic potential

$$\mathrm{FCI}(n_i, n_i')^2 = e^{-S_i} S_i^{n_i'-n_I} \frac{n_i!}{n_i'!} \left[L_{n_i}^{n_i'-n_i}(S_i) \right]^2$$

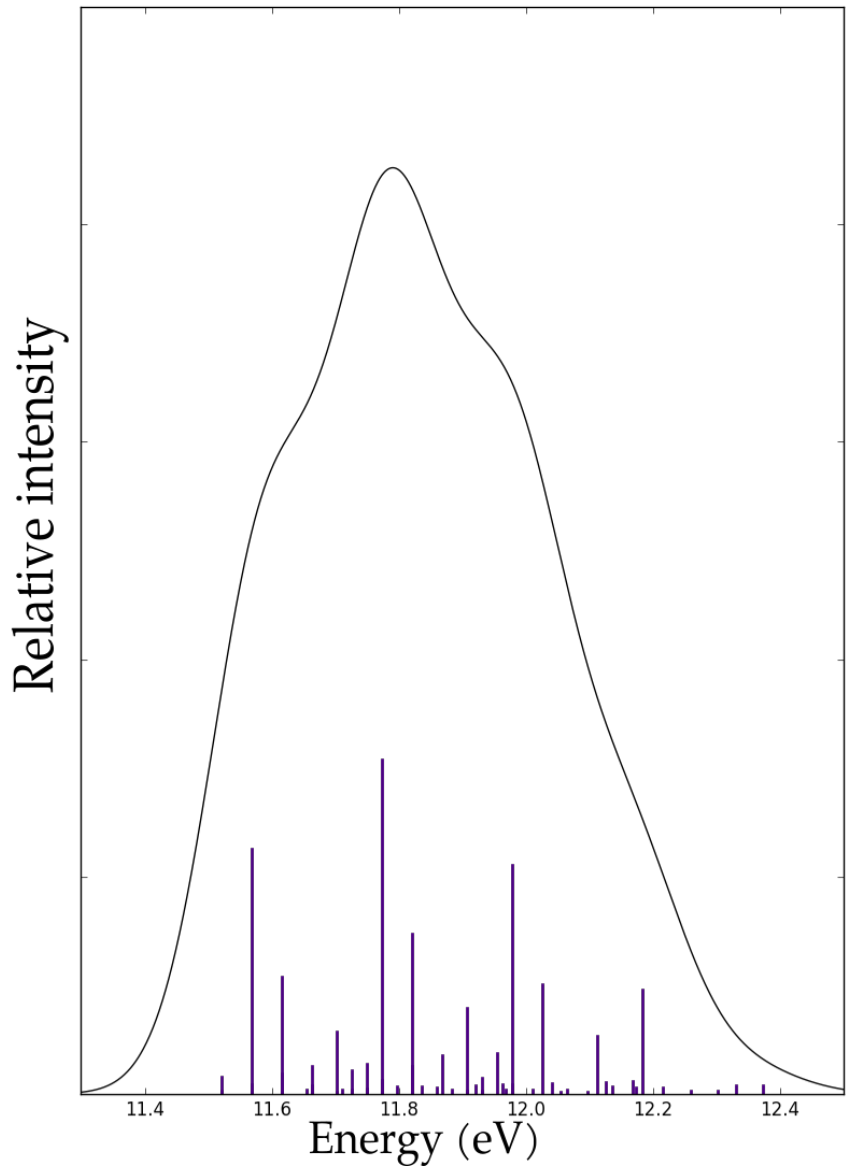
$$S_i = \frac{\delta_i^2 \mu_i f_i}{2\hbar}$$

If $S_i < S_{min}$ then mode i is dropped out

Values for δ, μ and f from AIMS

Transitions for Benzene

More vibrational modes
$\rightarrow$ more peaks



Transitions for Benzene

More vibrational modes
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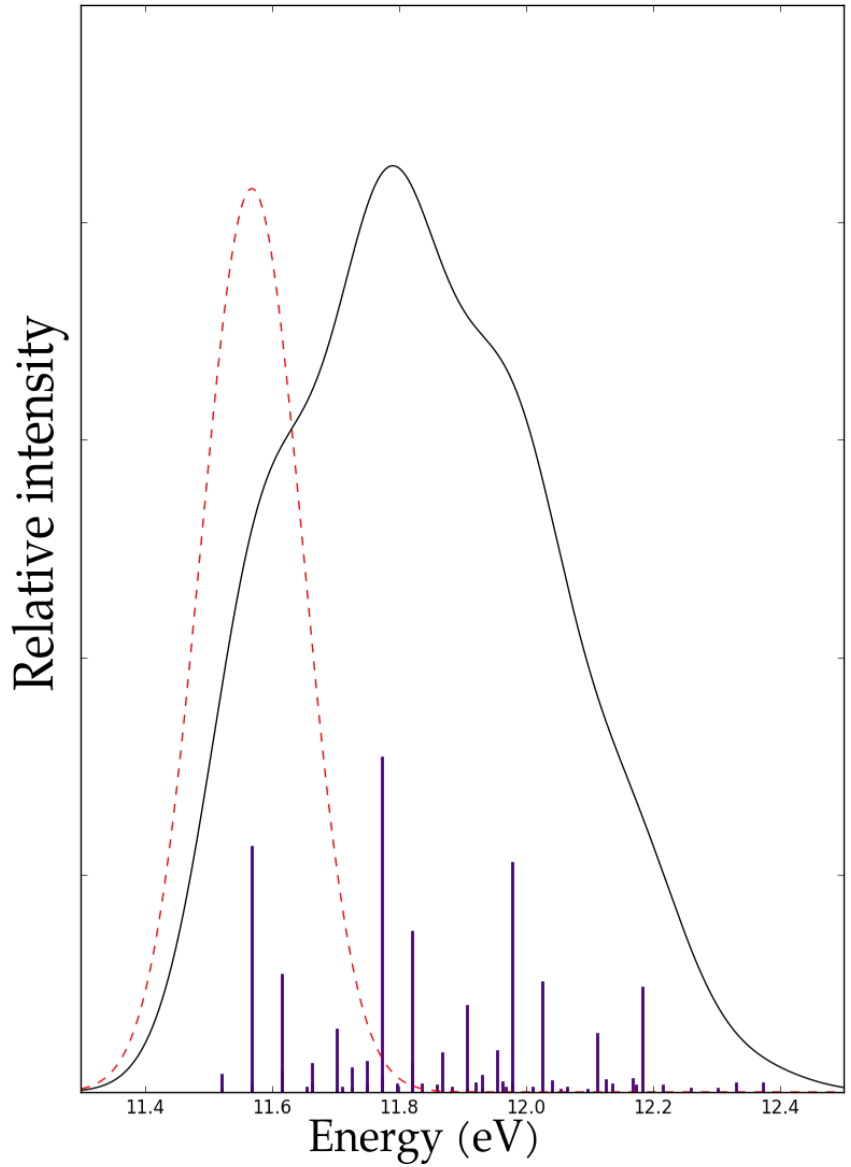
Clear difference to the peak without vibrations



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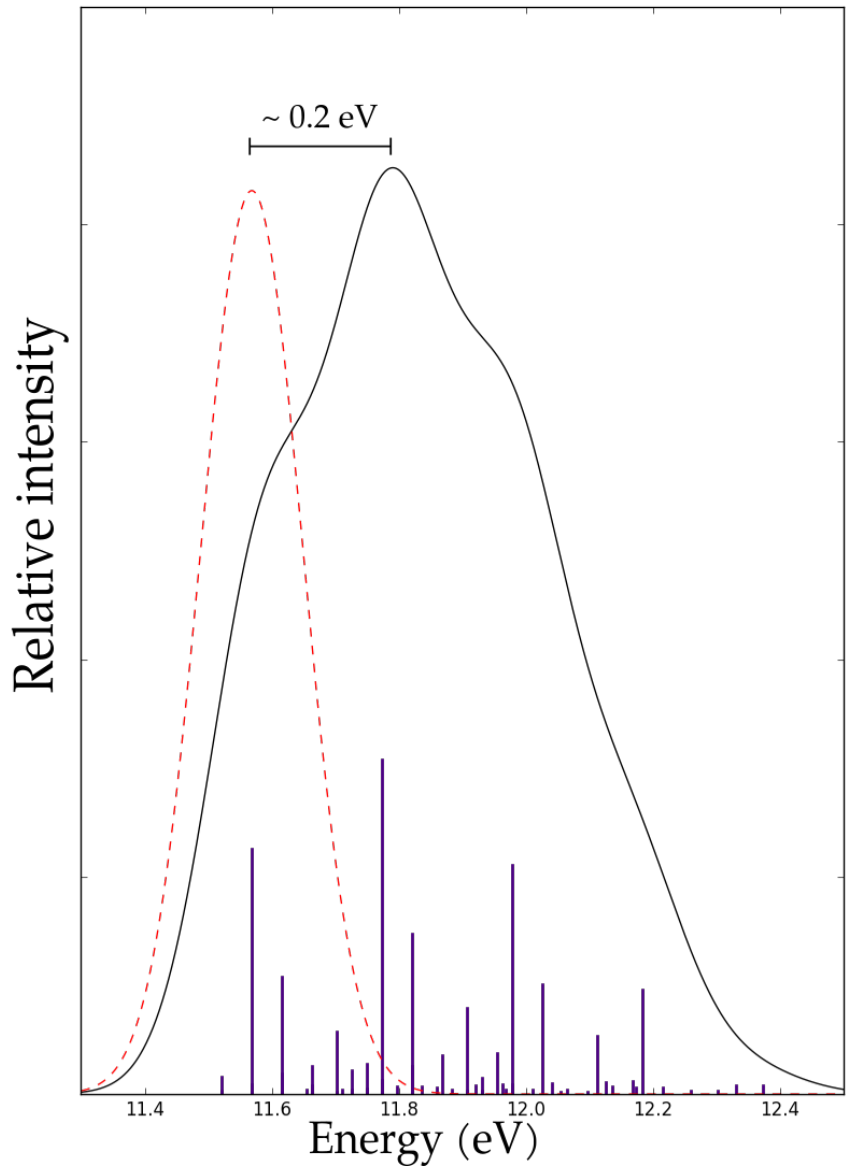
Clear difference to the peak without vibrations

Peaks shift from 0 to 0.5 eV



Transitions for Benzene

More vibrational modes
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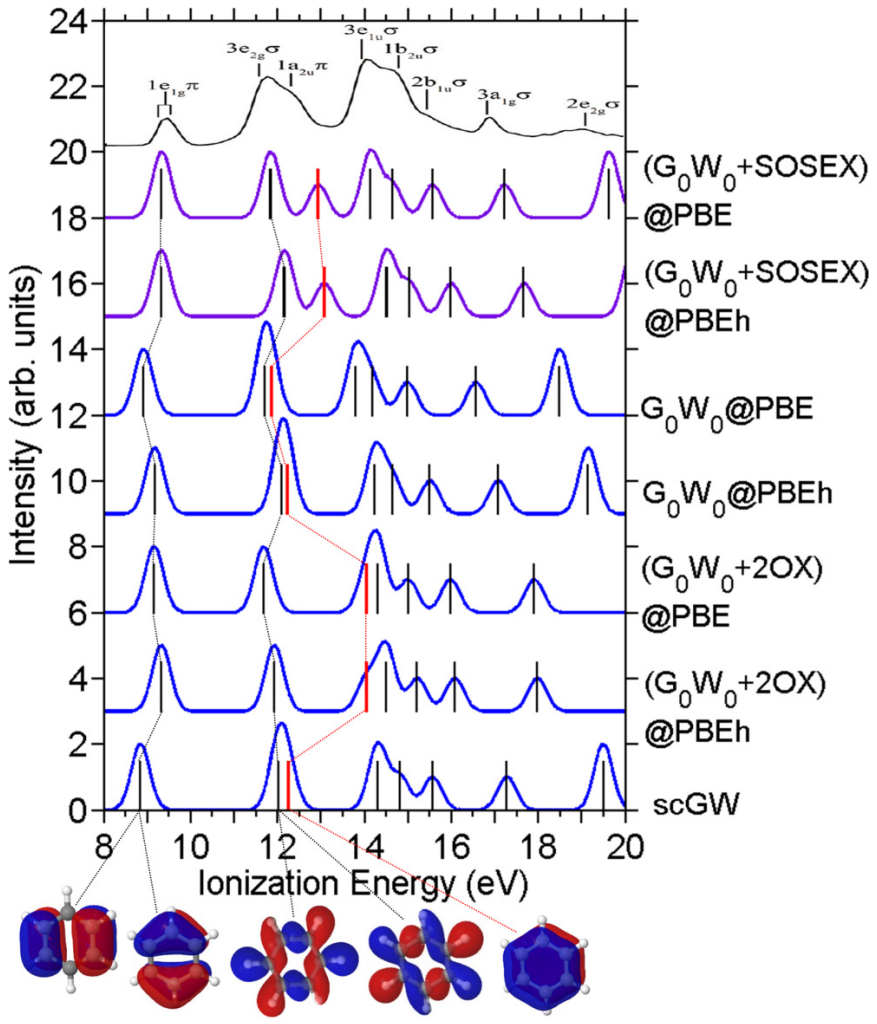
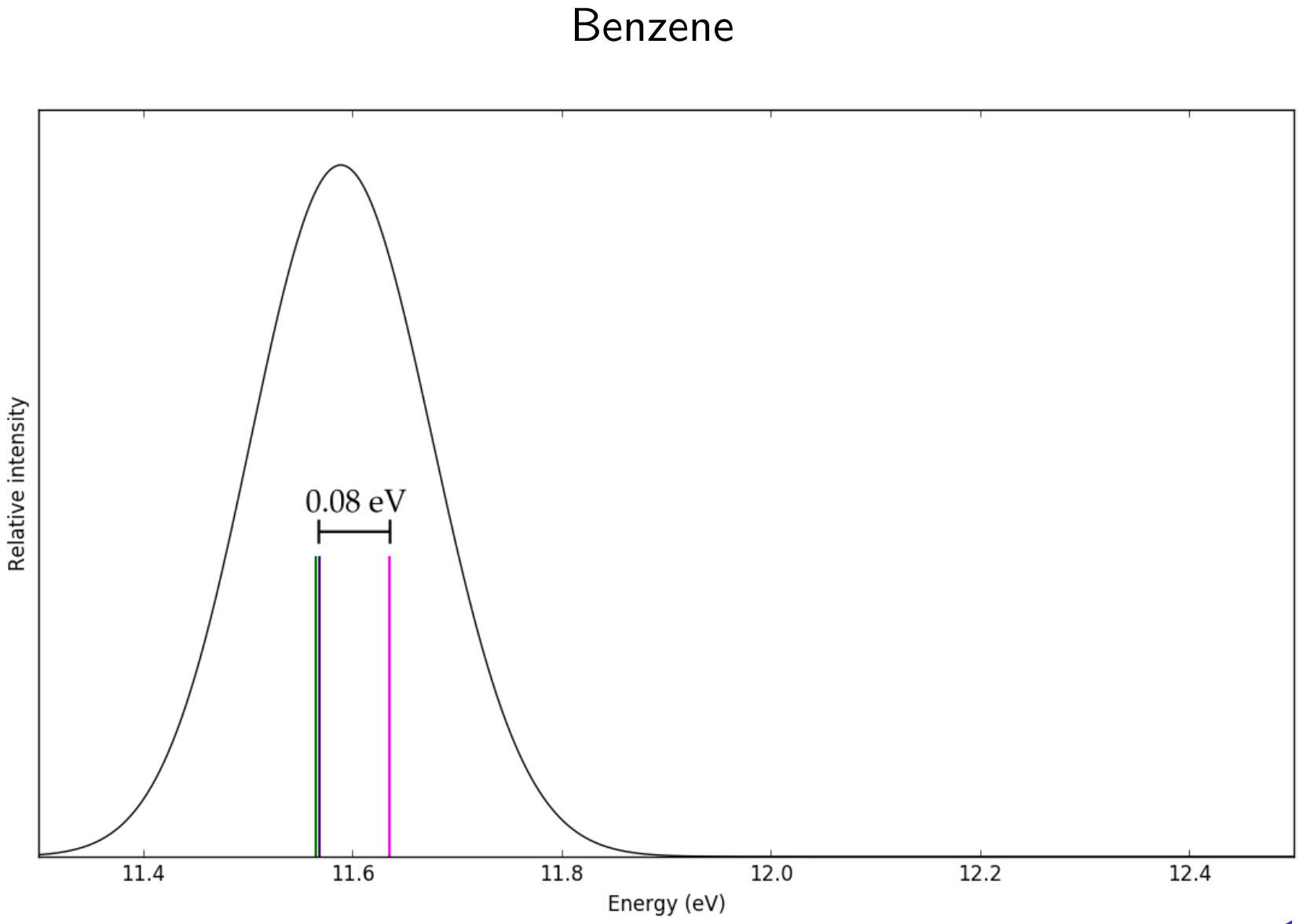
Clear difference to the peak without vibrations

Peaks shift from 0 to 0.5 eV

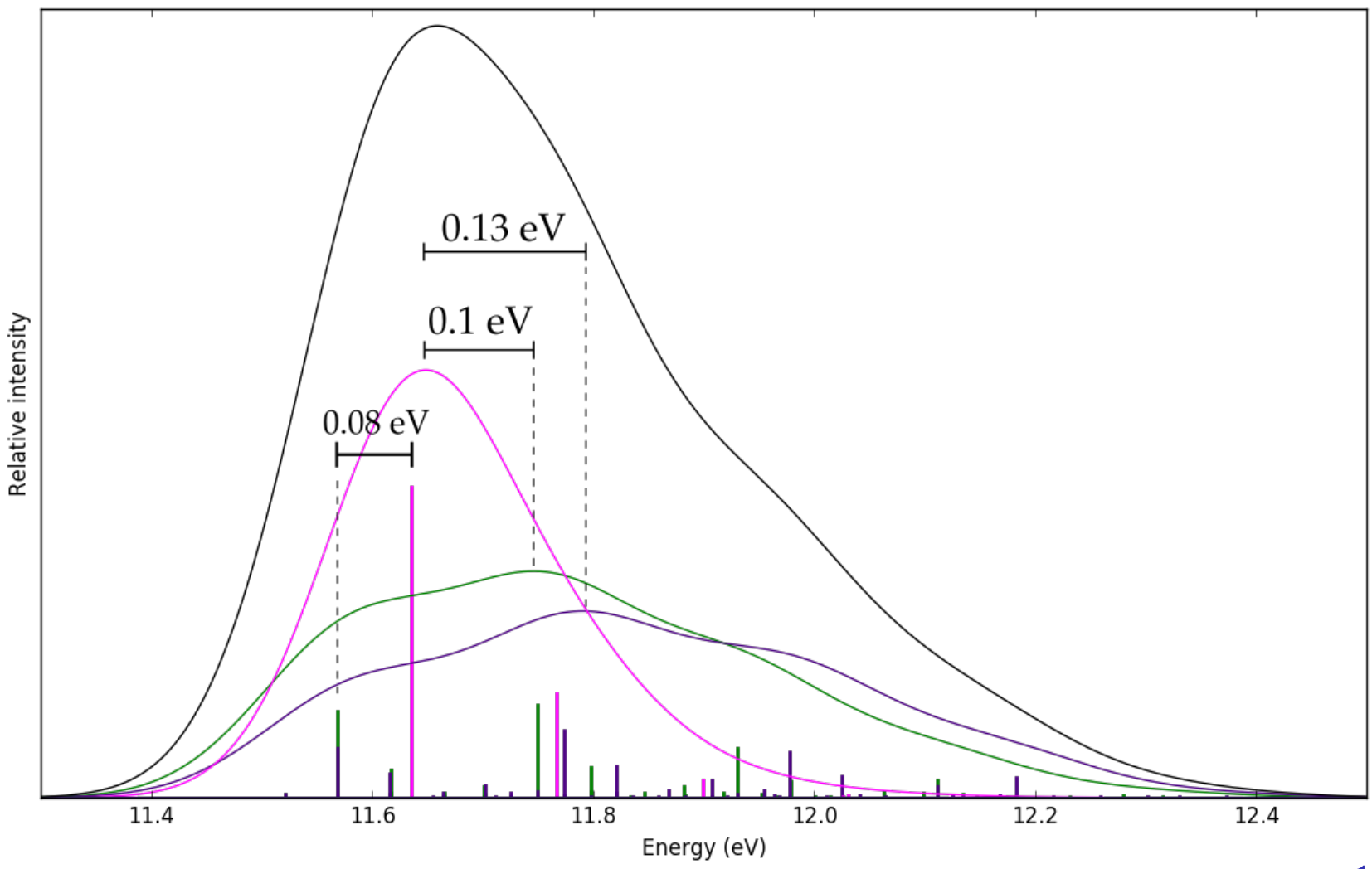
Same order of magnitude as difference between theories



Peak shift

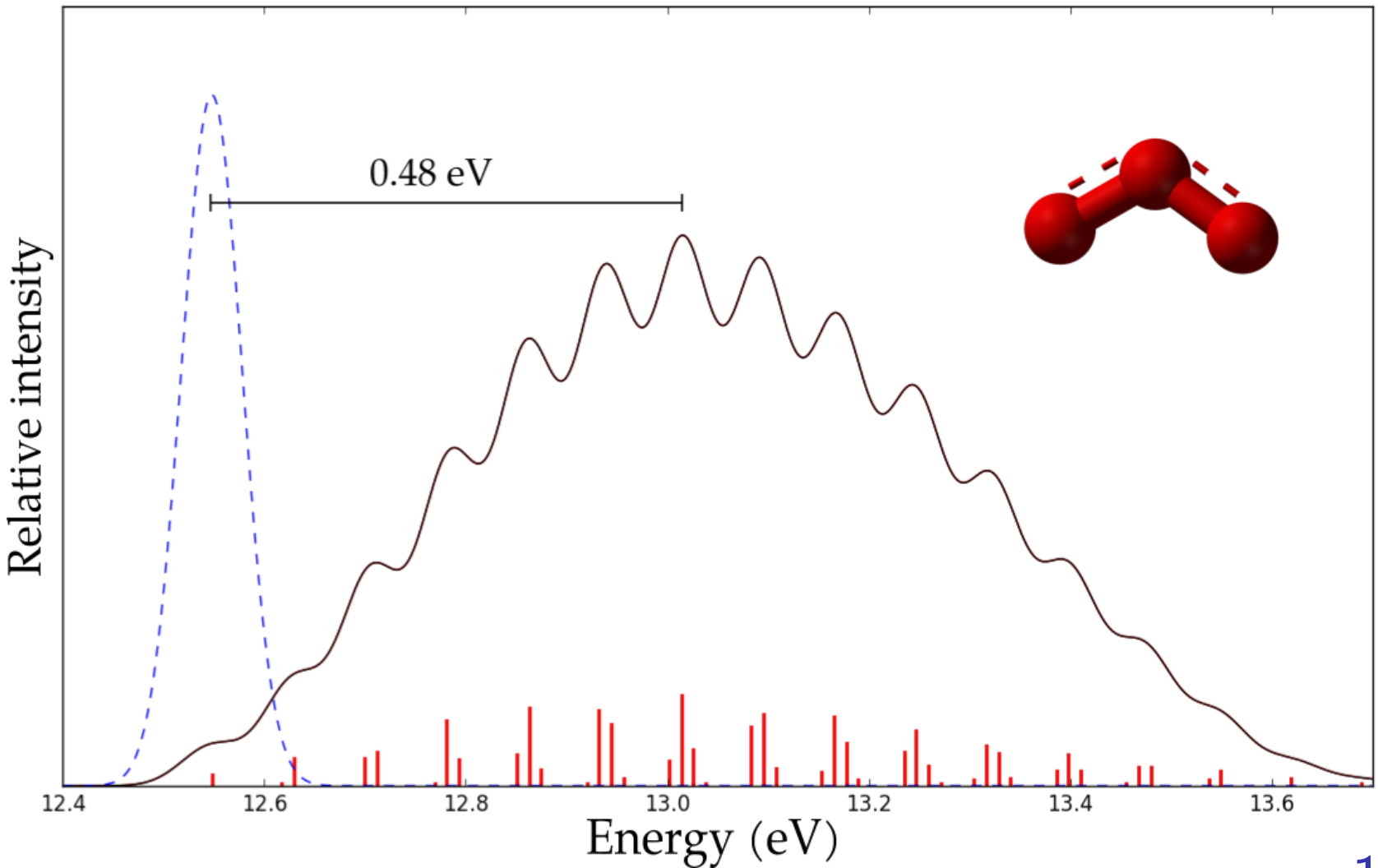

Benzene
Relative intensity
0.08 eV
11.4
11.6
11.8
12.0
12.2
12.4
Energy (eV)

Peak shift


Benzene
0.13 eV
0.1 eV
0.08 eV
Relative intensity
11.4
11.6
11.8
12.0
12.2
12.4
Energy (eV)

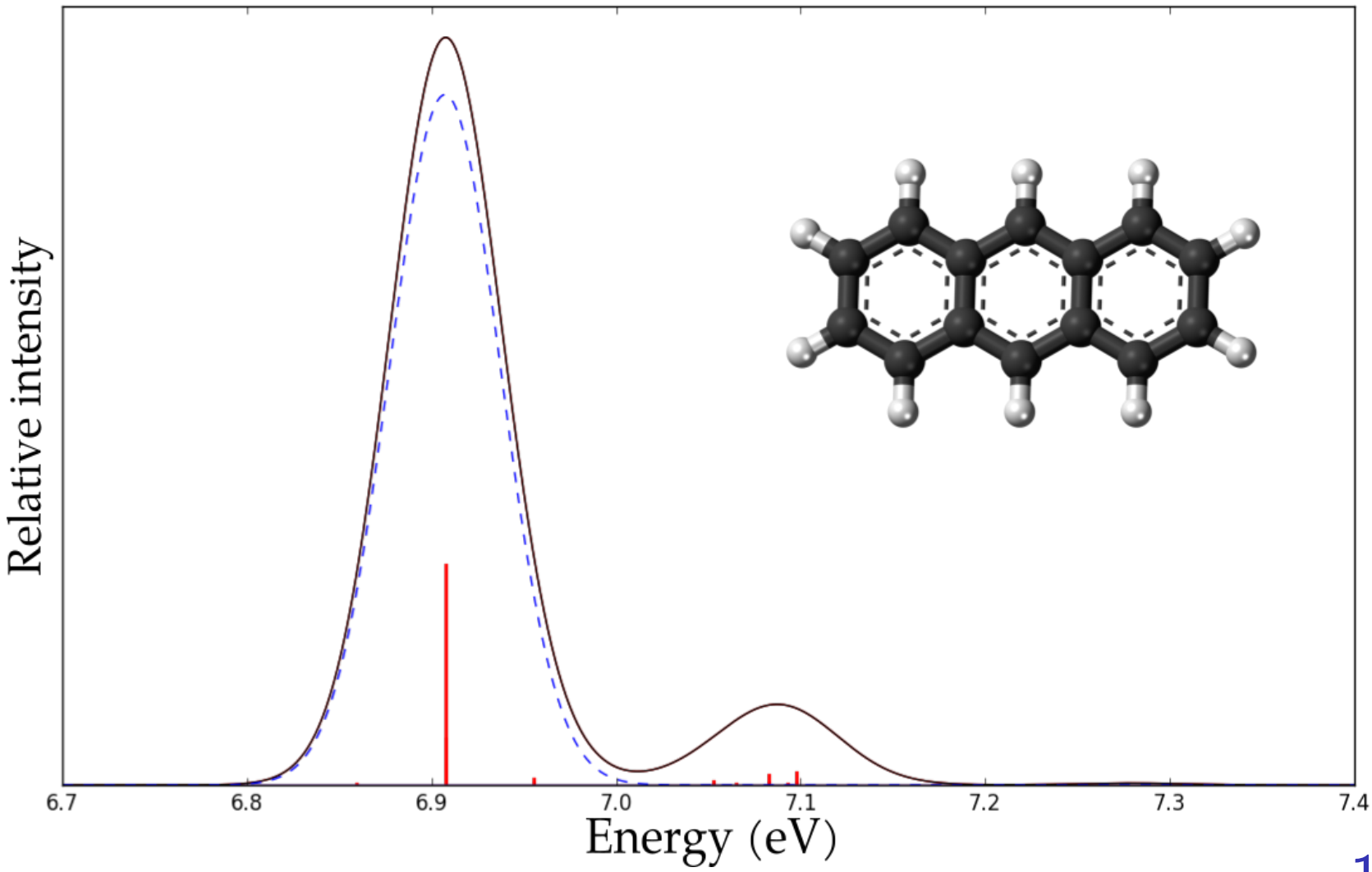
Peak shift

Ozone

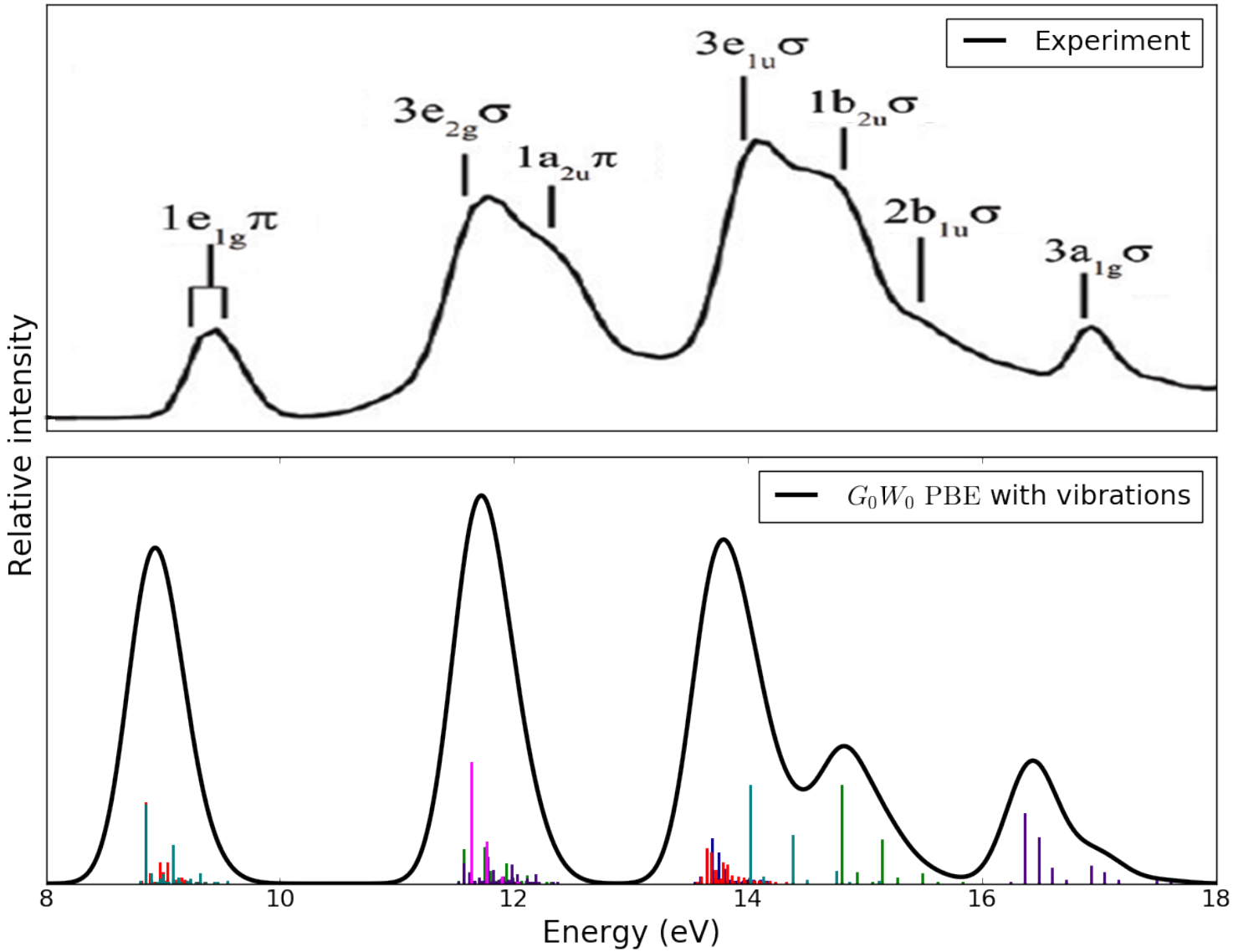


Peak shift

Anthracene



Benzene ionization spectra



Thank you!

Questions?