A system-bath model to investigate the interaction of a molecule with its environment

Loïse Attal[1], Cyril Falvo[1,2], Florent Calvo[2] and Pascal Parneix[1]

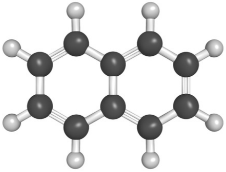
[1]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France

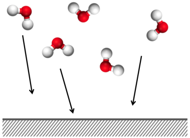
[2]Université Grenoble Alpes, CNRS, LiPhy, Grenoble, France

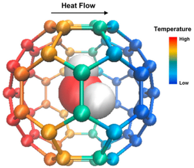
07 July 2023

Vibrational dynamics of high dimensional systems

- Vibrational dynamics of large isolated molecules (>10 atoms) *e.g.* molecules of astrophysical interest in the gas phase
- Dynamics of small molecules interacting with an environment → molecules at surfaces, in clusters or in matrices...







Y. Gao, B. Xu, J. Phys. Chem. C 2015, 119

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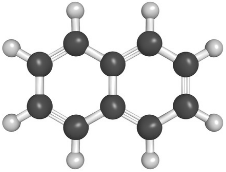
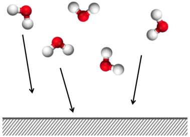
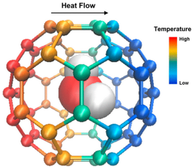


- High dimensional systems: very difficult to consider the full dimensional problem and to solve the quantum dynamics

⇒ Curse of dimensionality





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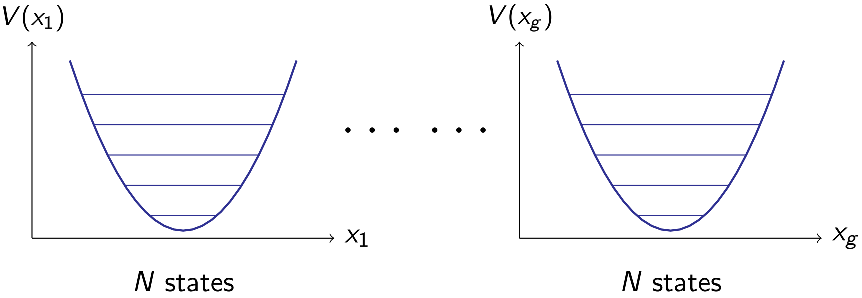
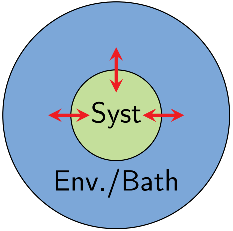
The curse of dimensionality

- For g degrees of freedom $\rightarrow N^g \propto e^g$ states needed
- Brute force strategy limited to $g = 6$ *i.e.* molecules with 4 atoms
- Numerous methods: vibrational configuration interaction, vib. coupled cluster, vib. (time-dependent) self-consistent field, (ML-)MCTDH...



System-bath methods

- For larger systems → identify important degrees of freedom
- (Sub-)System: rigorous treatment, quantum dynamics
- Bath (environment): more approximations → harmonic approximation, classical dynamics, use of effective potentials...



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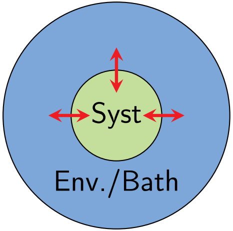

- Baths are usually seen as infinite → always at equilibrium, unperturbed by the system, no information on the state of the bath

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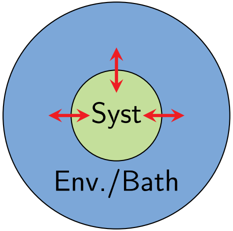
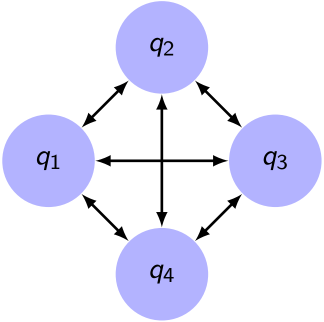


- Baths are usually seen as infinite → always at equilibrium, unperturbed by the system, no information on the state of the bath
- Finite baths (clusters, part of the molecule) → influenced by the system, out of equilibrium dynamics, complex energy exchanges and possible recurrences

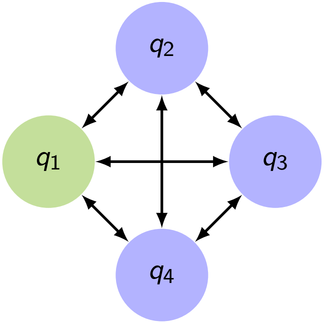
A new system-bath model - Main ideas

- We develop a new system-bath approach to treat a one dimensional system coupled to a finite harmonic bath (∼10-1000 modes)
- Example: 4 degrees of freedom (vibrational normal modes)



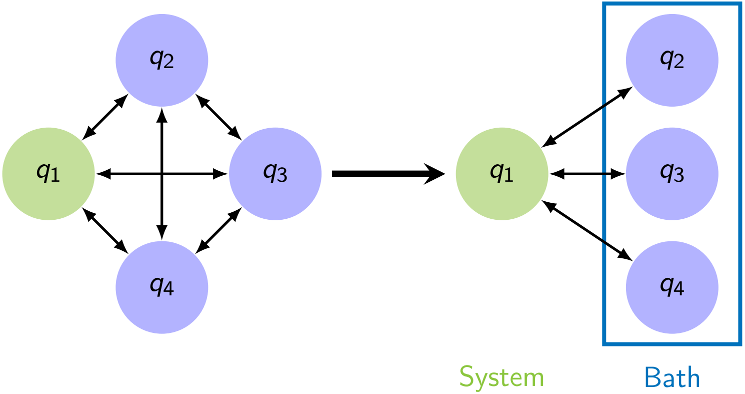
A new system-bath model - Main ideas

- (S) $= \{q_1\}$
- (B) $= \{q_2, q_3, q_4\}$



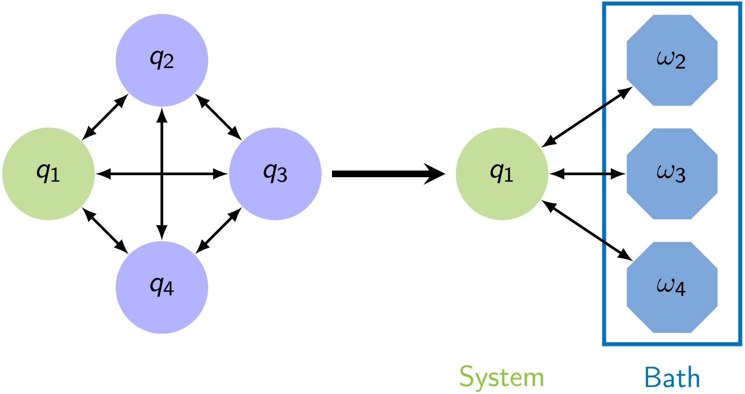
A new system-bath model - Main ideas

- (S) = $\{q_1\}$
- (B) = $\{q_2, q_3, q_4\}$ $\rightarrow$ decoupled



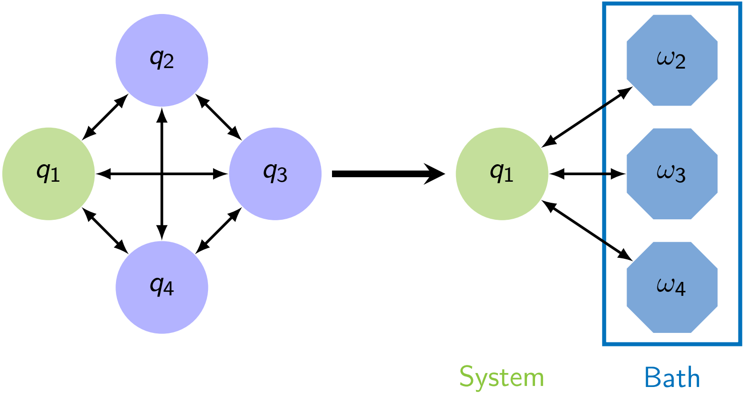
A new system-bath model - Main ideas

- (S) $= \{q_1\}$
- (B) $= \{q_2, q_3, q_4\} \to$ decoupled $\to$ harmonic

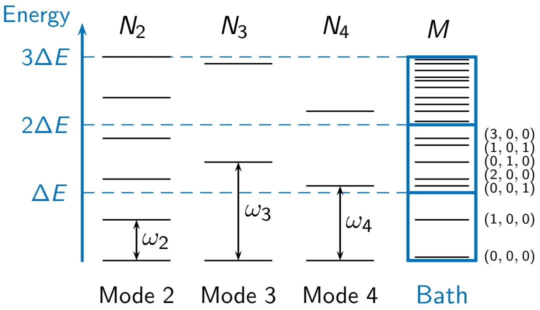


A new system-bath model - Main ideas

- (S) $= \{q_1\}$: anharmonic & radiant
- (B) $= \{q_2, q_3, q_4\} \rightarrow$ decoupled $\rightarrow$ harmonic $\rightarrow$ dark states



Effective energy states for the bath



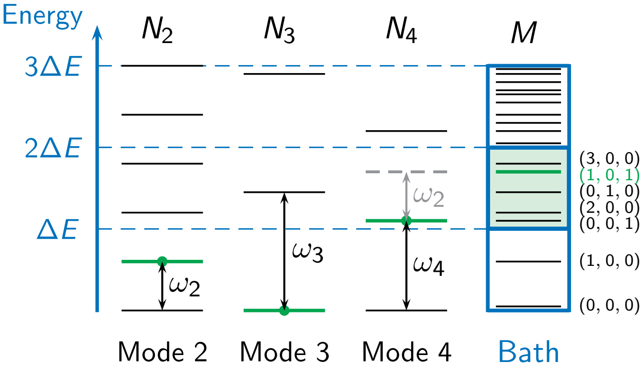
- Quantified bath energy: $E_{\text{bath}} \to m\Delta E$
- Effective states $|m\rangle$ such that $(n_2, n_3, n_4) \in |m\rangle$ if

$$m\Delta E \leq n_2\hbar\omega_2 + n_3\hbar\omega_3 + n_4\hbar\omega_4 < (m+1)\Delta E$$

Effective energy states for the bath

$$\Delta E \leq 1 \times \hbar\omega_2 + 0 \times \hbar\omega_3 + 1 \times \hbar\omega_4 < 2\,\Delta E$$

$$\Rightarrow (1, 0, 1) \in |m = 1\rangle$$



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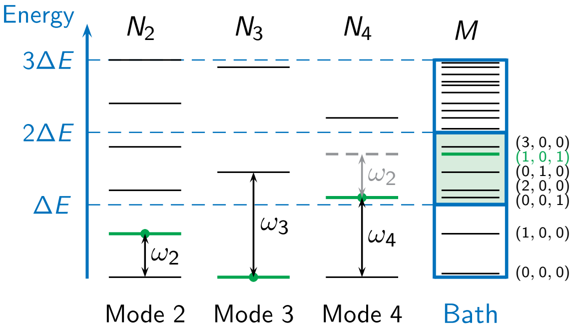

→ Effective states $|m\rangle$ with an energy $m\Delta E$ and a density of states $\rho(m)$

→ $N_2 \times N_3 \times N_4 = 54$ harmonic states → $M = 3$ effective states $|m\rangle$

System-Bath basis and effective Hamiltonian

- System: $\hat{q}_1$ described by N anharmonic states $|v\rangle$
- Bath: $\hat{q}_2, \ldots, \hat{q}_g$ (decoupled & harmonic) described by M effective energy states $|m\rangle$

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- Effective Hamiltonian in the basis $|v, m\rangle = |v\rangle \otimes |m\rangle$

$$\hat{H}_{\mathrm{eff}} = \sum_v \sum_m (E_v + m\Delta E) |v, m\rangle \langle v, m| + \sum_{v,v'} \sum_{m,m'} \langle v| \hat{V}_S(\hat{q}_1) |v'\rangle \langle m| \hat{V}_B(\hat{q}_2, \ldots, \hat{q}_g) |m'\rangle |v, m\rangle \langle v', m'|$$

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→ Dimension reduction: $N^g \to N \times M$

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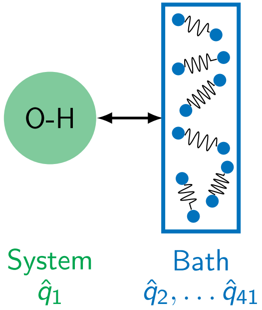
→ Dimension reduction: $N^g \to N \times M$

→ Simulating a bath with $E \in [E_0, E_0 + \Delta E]$ requires only one trajectory instead of sampling over numerous micro-states $(n_2, \ldots, n_g) \Rightarrow$ quantum dynamics at $T \neq 0$K more accessible

Relaxation of a diatomic molecule on a surface

- Dynamics at 0K of a 41D model system → comparison to MCTDH calculations[1]
- System: one O-H stretching mode
- Bath: a "surface" of $g - 1 = 40$ harmonic oscillators with frequencies $\omega_k = \omega_0 + k \times \Delta\omega$



[1] F. Bouakline, *et al.*, J. Phys. Chem. A 2012, 116, 46, 11118–11127

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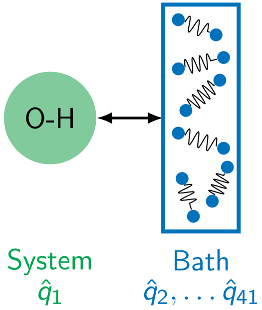
- System: one O-H stretching mode
- Bath: a "surface" of $g - 1 = 40$ harmonic oscillators with frequencies $\omega_k = \omega_0 + k \times \Delta\omega$
- One bath mode is in resonance with the O-H frequency
- System-Bath coupling:

$$\hat{H}_{\mathrm{SB}} = -\frac{1 - e^{-\alpha \hat{q}_1}}{\alpha} \times \sum_{k=2}^{g} c_k \hat{q}_k$$



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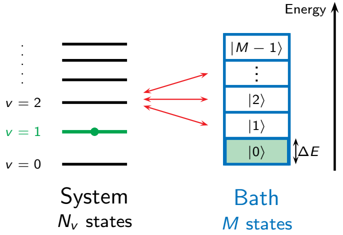
Dynamics of the first vibrational excited state



- Initial state: $v_0 = 1$, $m_0 = 0$ $(E_0 = 0)$
- Follow evolution of (S) and (B) populations

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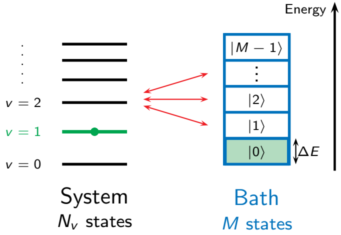
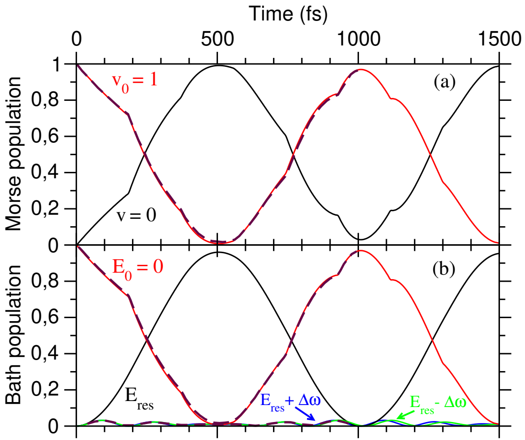
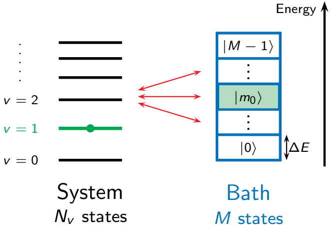




- Initial state: $v_0 = 1,\ m_0 = 0\ (E_0 = 0)$
- Follow evolution of (S) and (B) populations
- Excellent agreement with MCTDH results[1] (dashed lines)
- Parameters: $N = 5,\ M = 6\,000,\ \Delta E = 2\,\mathrm{cm}^{-1}$

[1] F. Bouakline, *et al.*, J. Phys. Chem. A 2012, 116, 46, 11118–11127

Adding energy into the bath - $E_0 > 0$



- Initial state: $v_0 = 1,\ m_0 > 0$
  $\Rightarrow E_0 = m_0 \Delta E > 0$
- Opens new channels towards higher excited states ($v > 1$)

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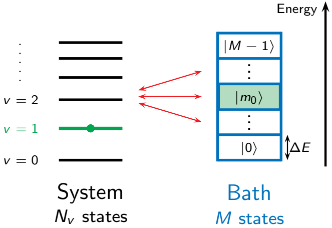

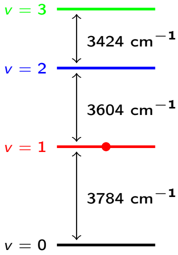

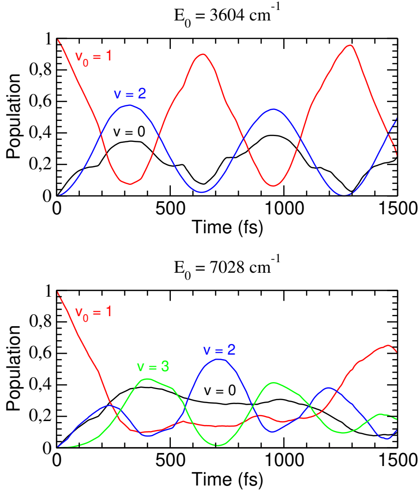

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  $\Rightarrow E_0 = m_0 \Delta E > 0$
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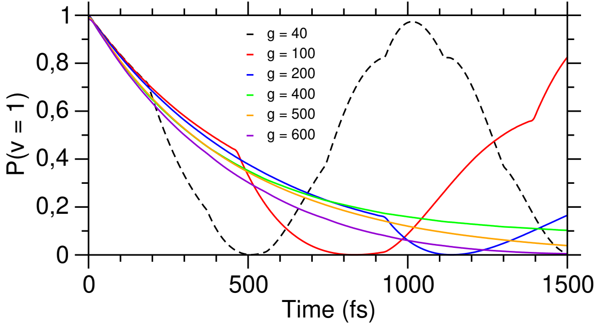
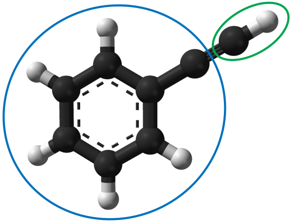
Effect of the bath size

- Increase the number of bath modes : $g = 40 \rightarrow 600$
- Reduce the gap between the frequencies: if $g \rightarrow n \times g$ then $\Delta\omega \rightarrow \Delta\omega / n$
- Keep the same resonance conditions for all trajectories



Towards vibrational dynamics of complex molecules

- Study of (deuterated) phenylacetylene
- System: acetylenic C-H/C-D mode
- Bath: the 35 other vibrational modes



- IR absorption spectra with temperature effects
- IR emission spectra (density matrix approach)
- Intramolecular vibrational energy redistribution (IVR)

⇒ Comparison with experimental time- and wavelength-resolved emission spectra[1]

[1] O. Lacinbala, *et al.*, J. Phys. Chem. A 2022, 126, 30, 4891–4901

Thank you for your attention!

Bath Hamiltonian and effective states

Bath Hamiltonian:

$$\hat{H}_{\mathrm{B}} = \sum_{\mathrm{n}} E(\mathrm{n}) |\mathrm{n}\rangle \langle\mathrm{n}| = \sum_{m} \sum_{\mathrm{n}\in m} E(\mathrm{n}) |\mathrm{n}\rangle \langle\mathrm{n}| \approx \sum_{m} m\Delta E \sum_{\mathrm{n}\in m} |\mathrm{n}\rangle \langle\mathrm{n}| \quad (1)$$

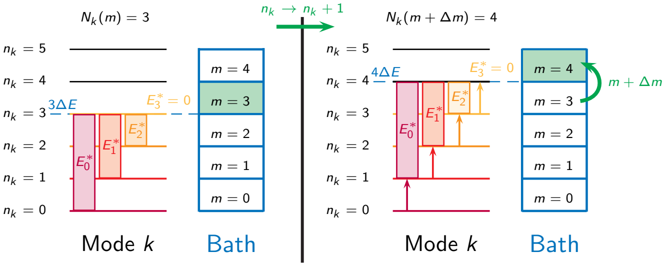
Micro-states seen as a representation of the effective state $|m\rangle$:

$$|\mathrm{n}\rangle \mapsto \frac{1}{\sqrt{\rho(m)\Delta E}} |m\rangle \quad (2)$$

Effective bath Hamiltonian:

$$\sum_{\mathrm{n}\in m} |\mathrm{n}\rangle \langle\mathrm{n}| \mapsto \sum_{\mathrm{n}\in m} \frac{1}{\rho(m)\Delta E} |m\rangle \langle m| = |m\rangle \langle m| \Rightarrow \hat{H}_{\mathrm{B}} = \sum_{m=0}^{M-1} m\Delta E \, |m\rangle \langle m| \quad (3)$$

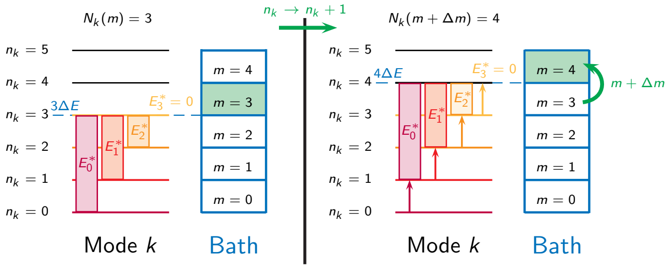
System-Bath coupling



For a given bath mode k, starting from a given bin m:

- Choose a n_k available in m with probability $\mathbb{P}(m, n_k)$
- Transition $n_k \to n_k \pm 1$ with coupling strength $\langle n_k \pm 1| \hat{q}_k |n_k\rangle$
- It defines the coupled bins $m' = m \pm \Delta m_k$
- Sum $\langle n_k \pm 1| \hat{q}_k |n_k\rangle \times \mathbb{P}(m, n_k)$ over all possible n_k

System-Bath coupling



Sum over all bins m and over all bath modes k:

$$\sum_{k=1}^{g} c_k \sum_{m=0}^{M'-1} \sum_{n_k=0}^{N_k(m)} \sqrt{\frac{\hbar(n_k+1)}{2\omega_k}}\, \mathbb{P}(m, n_k)\ |v, m\rangle \langle v', m + \Delta m_k|$$

Probabilities and energy splitting

We split the energy $m\Delta E$ between mode k and the spectator modes:

$$m\Delta E = n_k \hbar\omega_k + E^*_{n_k} \tag{4}$$

Same with $m'\Delta E$:

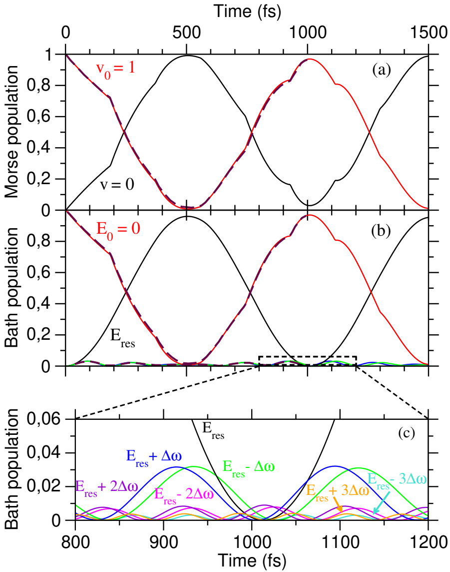
$$m'\Delta E = (n_k \pm 1)\hbar\omega_k + E^*_{n_k} \tag{5}$$

Using the fact that $E^*_{n_k}$ is unchanged, we have the transition:

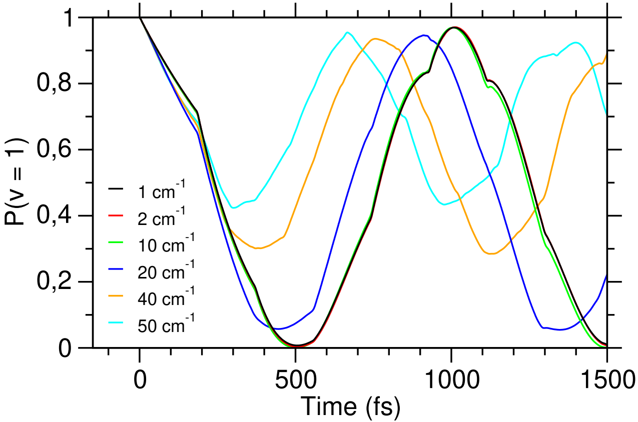
$$\Delta m_k = \left|\frac{\Delta n_k \hbar\omega_k}{\Delta E}\right| = \frac{\hbar\omega_k}{\Delta E} \tag{6}$$

Probability to choose n_k in bin m:

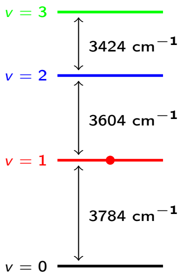
$$\mathbb{P}(m, n_k) \quad = \quad \frac{\rho^{(k)}(E^*_{n_k})}{\rho(m\Delta E)} = \frac{\rho^{(k)}(m\Delta E - n_k\hbar\omega_k)}{\rho(m\Delta E)} \tag{7}$$

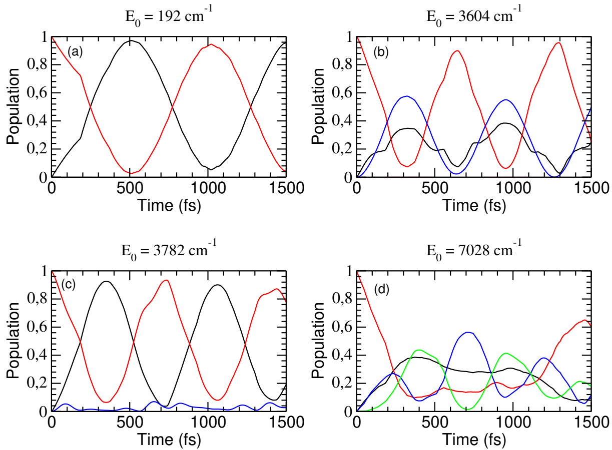

Time (fs)
0
500
1000
1500
Morse population
$v_0 = 1$
v = 0
(a)
Bath population
$E_0 = 0$
E_{res}
(b)
(c)
E_{res}
$E_{res} + \Delta\omega$
$E_{res} - \Delta\omega$
$E_{res} + 2\Delta\omega$
$E_{res} - 2\Delta\omega$
$E_{res} + 3\Delta\omega$
$E_{res} - 3\Delta\omega$
800
900
1000
1100
1200
Time (fs)

Convergence in ΔE

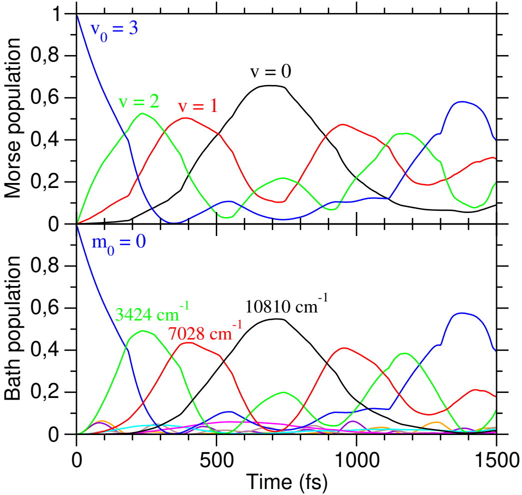


Adding energy into the bath

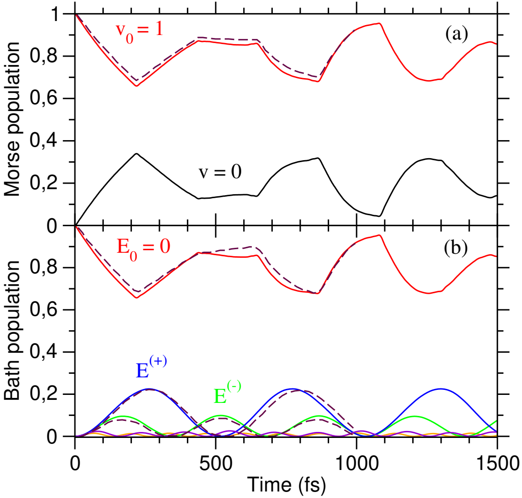




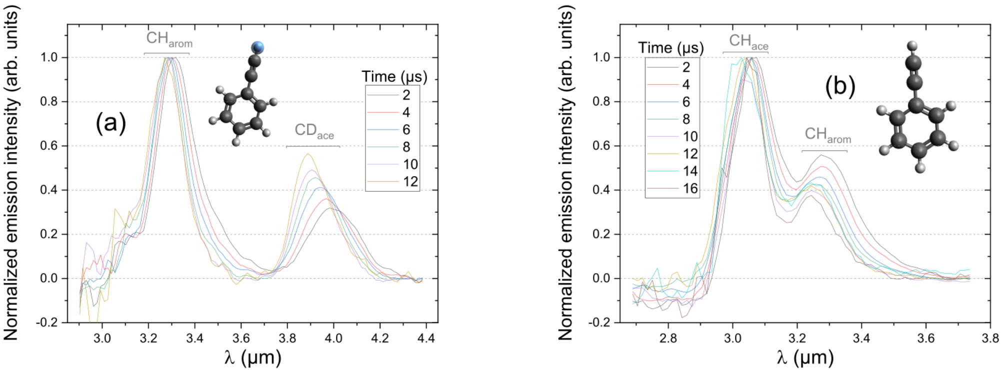
Higher excited states - $v_0 = 3$



Off resonant bath



Experimental IR emission spectra[1]



[1] O. Lacinbala, *et al.*, J. Phys. Chem. A 2022, 126, 30, 4891–4901