UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

Accurate and Efficient Pre-exponential Factor Approximations for the Semiclassical Initial Value Representation Propagator

Giovanni Di Liberto and Michele Ceotto

Lausanne, 8th June 2016

Overview

- A brief remind about the nature of the semiclassical prefactor.
- The problems of the semiclassical prefactor.
- Overview of the existing approximations.
- Derivation of a new class of prefactor approximations.
- Numerical test on chaotic potentials.
- Numerical test of real cases, i.e. molecules.

The origin of the semiclassical prefactor

Feynman path-integral $\left\langle \boldsymbol{q}_t \middle| e^{-\frac{i}{\hbar}\hat{H}t} \middle| \boldsymbol{q}_0 \right\rangle = \int_{q_0}^{q_t} D[\boldsymbol{q}(t)] e^{\frac{i}{\hbar} S_t(\boldsymbol{q}_t, \boldsymbol{q}_0)}$

$$\left\langle \boldsymbol{q}_t \middle| e^{-\frac{i}{\hbar}\hat{H}t} \middle| \boldsymbol{q}_0 \right\rangle \sim \int_{q_0}^{q_t} D[\boldsymbol{q}(t)] e^{\frac{i}{\hbar}\left[S_t^{cl}(\boldsymbol{q}_t, \boldsymbol{q}_0) + \frac{1}{2}\frac{\delta^2 S_t^{cl}(\boldsymbol{q}_t, \boldsymbol{q}_0)}{\delta \boldsymbol{q}_t^{\,2}} \delta \boldsymbol{q}_t^{\,2} \right]}$$

G. Di Liberto

[1] W. H. Miller, J. Chem. Phys. **53**, 3578 (1970).
[2] R.P. Feynman and A.R. Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill Companies,1965).
[3] M. V. Berry and K. E. Mount, Rep. Prog. Phys. 35, 315 (1972).

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The origin of the semiclassical prefactor

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$$\left\langle \boldsymbol{q}_t \middle| e^{-\frac{i}{\hbar}\hat{H}t} \middle| \boldsymbol{q}_0 \right\rangle \sim \int_{q_0}^{q_t} D[\boldsymbol{q}(t)] e^{\frac{i}{\hbar}\left[S_t^{cl}(\boldsymbol{q}_t,\boldsymbol{q}_0)+\frac{1}{2}\frac{\delta^2 S_t^{cl}(\boldsymbol{q}_t,\boldsymbol{q}_0)}{\delta \boldsymbol{q}_t^{\,2}}\delta \boldsymbol{q}_t^{\,2}\right]}$$

van-Vleck $$\left\langle \boldsymbol{q}_t \middle| e^{-\frac{i}{\hbar}\hat{H}t} \middle| \boldsymbol{q}_0 \right\rangle \sim \sum_{Cl\ paths} \sqrt{\frac{1}{(2\pi i\hbar)^N}\left|\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0}\right|^{-1}}\, e^{\frac{i}{\hbar}S_t^{cl}(\boldsymbol{q}_t,\boldsymbol{q}_0)-i\nu\frac{\pi}{2}}$$

IVR $$\left\langle \chi \middle| e^{-\frac{i}{\hbar}\hat{H}t} \middle| \chi \right\rangle \sim \iint d\boldsymbol{q}_0 d\boldsymbol{p}_0 \sqrt{(2\pi i\hbar)^N \left|\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0}\right|}\, \chi^*(\boldsymbol{q}_t)\chi(\boldsymbol{q}_0) e^{\frac{i}{\hbar}S_t^{cl}(\boldsymbol{q}_t,\boldsymbol{q}_0)-i\nu\frac{\pi}{2}}$$

Contains the quantum fluctuations around the classical trajectories.
At caustic points the determinant is zero.

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Semiclassical Initial Value Representation Dynamics

$$I(\mathbf{E}) = \langle\chi|\delta(\hat{H} - E)|\chi\rangle \Longrightarrow I(\mathbf{E}) = \frac{Re}{\pi}\int_0^\infty dt \left\langle\chi\middle|e^{-\frac{i}{\hbar}\hat{H}t}\middle|\chi\right\rangle e^{iEt}$$

SC-IVR[4,5]

$$e^{-\frac{i}{\hbar}\hat{H}t} = \left(\frac{1}{2\pi\hbar}\right)^F \iint dp_0 dq_0 C_t(p_0, q_0)\, e^{\frac{i}{\hbar}S_t(p_0,q_0)} |p_t q_t\rangle\langle p_0 q_0|$$

G. Di Liberto

[4] K.G. Kay, Annu. Rev. Phys. Chem. **56**, 255 (2005).
[5] W.H. Miller, Proc. Natl. Acad. Sci. U.S.A. 6660, **102** (2005).
[6] M. Ceotto et *al.*, J. Chem. Phys. **135**, 214108 (2011). M. Ceotto *et al.*,J. Chem. Phys. **130**, 234113 (2009)
[7] A. Kaledin and W.H. Miller, J. Chem. Phys. 118, 7174 (2003), J. Chem. Phys. **119**, 3078 (2003).

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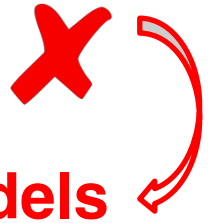
SC-IVR[4,5]

$$e^{-\frac{i}{\hbar}\hat{H}t} = \left(\frac{1}{2\pi\hbar}\right)^F \iint dp_0 dq_0 C_t(p_0,q_0)\, e^{\frac{i}{\hbar}S_t(p_0,q_0)} |p_t q_t\rangle\langle p_0 q_0|$$

Time Averaging – Separable Approximation[6,7]

$$I(E) = \left(\frac{1}{2\pi\hbar}\right)^F \iint dp_0 dq_0 \frac{1}{2\pi T}\left|\int_0^T dt e^{\frac{i}{\hbar}[S_t(p_0,q_0)+Et+\varphi_t]}\langle\chi|p_t q_t\rangle\right|^2$$

- Monodromy matrix dependent.
- Troubles for chaotic trajectories.



Development of new models

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[4] K.G. Kay, Annu. Rev. Phys. Chem. **56**, 255 (2005).
[5] W.H. Miller, Proc. Natl. Acad. Sci. U.S.A. 6660, **102** (2005).
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Numerical instability of the prefactor

$$C_t = \sqrt{det\left[\frac{1}{2}\left(\mathbf{M}_{qq} + \mathbf{M}_{pp} + \frac{i}{\hbar\gamma}\mathbf{M}_{pq} + \frac{\hbar\gamma}{i}\mathbf{M}_{qp}\right)\right]}$$

$$\mathbf{M} = \begin{pmatrix} \frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{p}_0} & \frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{q}_0} \\ \frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0} & \frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{q}_0} \end{pmatrix} = \begin{pmatrix} \mathbf{M}_{pp} & \mathbf{M}_{pq} \\ \mathbf{M}_{qp} & \mathbf{M}_{qq} \end{pmatrix}$$

$$\dot{\mathbf{M}} = \begin{pmatrix} \mathbf{0} & -\mathbf{K}_t \\ \frac{\mathbf{1}}{\boldsymbol{m}} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{M}_{pp} & \mathbf{M}_{pq} \\ \mathbf{M}_{qp} & \mathbf{M}_{qq} \end{pmatrix}$$

[8] H. Wang *et al.*, J. Chem. Phys. **115**, 6317 (2001).
[9] Y. Zhuang, M. R. Siebert, W.L. Hase, K.G. Kay, M. Ceotto, J. Chem. Theory and Comput, **9**, 54 (2013).

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$$\dot{\mathbf{M}} = \begin{pmatrix} \mathbf{0} & -\mathbf{K}_t \\ \frac{\mathbf{1}}{\boldsymbol{m}} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{M}_{pp} & \mathbf{M}_{pq} \\ \mathbf{M}_{qp} & \mathbf{M}_{qq} \end{pmatrix}$$

$$\mathbf{M}^t \boldsymbol{J} \mathbf{M} = \boldsymbol{J} \quad |\mathbf{M}| = \mathbf{1} \; \forall t$$

$$\boldsymbol{J} = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{pmatrix}$$

$$det(\mathbf{M}^t\mathbf{M}) = 1$$

⇓

$$det(\mathbf{M}^t\mathbf{M}) \neq 1$$

⇓

C_t numerically unstable

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Approximations to the Prefactor

Adiabatic[10,11]

$$\boldsymbol{Q}_t = \frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{q}_0} + \frac{\hbar\boldsymbol{\gamma}}{i}\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0} \qquad \boldsymbol{P}_t = \dot{\boldsymbol{Q}}_t = \frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{q}_0} + \frac{\hbar\boldsymbol{\gamma}}{i}\frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{p}_0} \qquad C_t = \sqrt{det\left[\frac{1}{2}\left(\boldsymbol{Q}_t + \frac{i}{\hbar\gamma}\boldsymbol{P}_t\right)\right]}$$

$$\mathbf{U}^{\dagger}\mathbf{K}_t\mathbf{U} = \boldsymbol{\omega}_t \qquad \begin{cases}\mathbf{U}^{\dagger}\mathbf{Q}_t\mathbf{U} = \widetilde{\mathbf{Q}}_t \\ \mathbf{U}^{\dagger}\mathbf{P}_t\mathbf{U} = \widetilde{\mathbf{P}}_t\end{cases} \qquad C_t = \sqrt{\prod_{i=1}^{F}\left[\frac{1}{2}\left(\tilde{Q}(i,i) + \frac{i}{\hbar\gamma}\tilde{P}(i,i)\right)\right]}$$

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[10] V. Guallar *et al.*, J. Chem. Phys. **110**, 9922 (1999).
[11] V. Guallar *et al.*, J. Chem. Phys. **113**, 9510 (2000).
[12] J. Thatchen *et al.*, J. Chem. Phys. **134**, 134104 (2011).

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Approximations to the Prefactor

Adiabatic[10,11]

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$$\mathbf{U}^{\dagger}\mathbf{K}_t\mathbf{U} = \boldsymbol{\omega}_t \qquad \begin{cases}\mathbf{U}^{\dagger}\mathbf{Q}_t\mathbf{U} = \widetilde{\mathbf{Q}}_t \\ \mathbf{U}^{\dagger}\mathbf{P}_t\mathbf{U} = \widetilde{\mathbf{P}}_t\end{cases} \qquad C_t = \sqrt{\prod_{i=1}^{F}\left[\frac{1}{2}\left(\tilde{Q}(i,i) + \frac{i}{\hbar\gamma}\tilde{P}(i,i)\right)\right]}$$

Poor Person's[12] (PPs)

$$\left\langle \boldsymbol{p_{eq}q_{eq}}\middle| e^{-\frac{i}{\hbar}\hat{H}t}\middle|\boldsymbol{p_{eq}q_{eq}}\right\rangle = \left(\frac{\mathbf{1}}{\boldsymbol{2\pi\hbar}}\right)^{\boldsymbol{F}} \boldsymbol{C_t(p_{eq}, q_{eq})} \iint \boldsymbol{dp_0 dq_0}\, \boldsymbol{e^{\frac{i}{\hbar}S_t(p_0,q_0)}} \langle \boldsymbol{p_{eq}q_{eq}}|\boldsymbol{p_t q_t}\rangle\langle \boldsymbol{p_0 q_0}|\boldsymbol{p_{eq}q_{eq}}\rangle$$

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Prefactor in the Log-Derivative formulation[13]

$$C_t = \sqrt{det\left[\frac{1}{2}\left(\boldsymbol{Q}_t + \frac{i}{\hbar\gamma}\boldsymbol{P}_t\right)\right]}$$

$$\begin{cases} \boldsymbol{P}_t = \dot{\boldsymbol{Q}}_t \\ \ddot{\boldsymbol{Q}}_t = -\mathbf{K}_t\boldsymbol{Q}_t \end{cases}$$

$$\boldsymbol{R}_t = \frac{\dot{\boldsymbol{Q}}_t}{\boldsymbol{Q}_t}$$

$$C_t = \sqrt{det\left[\frac{1}{2}\left(\boldsymbol{I} + \frac{i}{\hbar\boldsymbol{\gamma}}\boldsymbol{R}_t\right)\right]}\, e^{\frac{1}{2}\int_o^t d\tau Tr(\boldsymbol{R}_\tau)}$$

How to compute $\mathbf{R}_t$?

$$\dot{\mathbf{R}}_t = -\left(\frac{\dot{\mathbf{Q}}_t}{\mathbf{Q}_t}\right)^2 - \frac{\ddot{\mathbf{Q}}_t}{\mathbf{Q}_t} = -\mathbf{R}_t^{\,2} - \mathbf{K}_t$$

[13] R. Gelabert *et al.*, J. Phys. Chem. A **104**, 10321 (2000).

Approximate solutions of the Riccati equation

Harmonic

$$\dot{\boldsymbol{R}}_t = -\boldsymbol{R}_t{}^2 - \hbar^2\boldsymbol{\gamma}^2$$

$$\boldsymbol{R}_t = -\hbar\boldsymbol{\gamma}\frac{i + tan(\hbar\boldsymbol{\gamma}t)}{1 - itan(\hbar\boldsymbol{\gamma}t)} = -i\hbar\boldsymbol{\gamma}$$

$$\boldsymbol{\gamma} = \boldsymbol{\omega}$$

$$C_t = e^{-\frac{1}{2}\hbar t\sum_{i=1}^{N}\gamma_i} = e^{-\frac{1}{2}\hbar t\sum_{i=1}^{N}\omega_i}$$

Harmonic Zero Point Energy contribution

Approximate solutions of the Riccati equation

Harmonic

$$\dot{R}_t = -R_t{}^2 - \hbar^2\gamma^2$$

$$R_t = -\hbar\gamma\frac{i + tan(\hbar\gamma t)}{1 - itan(\hbar\gamma t)} = -i\hbar\gamma$$

$$\gamma = \omega$$

$$C_t = e^{-\frac{1}{2}\hbar t\sum_{i=1}^{N}\gamma_i} = e^{-\frac{1}{2}\hbar t\sum_{i=1}^{N}\omega_i}$$

Harmonic Zero Point Energy contribution

Johnson

$$\dot{R}_t \sim 0 \Longrightarrow \begin{cases} R_t{}^2 = -K_t \\ R_0 = -i\hbar\gamma \end{cases} \Longrightarrow R_t = -i\sqrt{K_t}$$

$$C_t = \sqrt{det\left[\frac{1}{2}\left(I + \frac{K_t}{\hbar\gamma}\right)\right]}\, e^{-\frac{1}{2}\int_o^t d\tau Tr(K_\tau)} \sim e^{-\frac{i}{2}\int_o^t d\tau \sum_{i=1}^{N}\omega_\tau}$$

Miller's prefactor approximation

$$\begin{cases} \boldsymbol{R}_t \sim -i\hbar\boldsymbol{\gamma} + \boldsymbol{\varepsilon} \\ \dot{\boldsymbol{\varepsilon}}_t \sim 0 \end{cases}$$

$$0 = \hbar^2\boldsymbol{\gamma}^2 + 2i\hbar\boldsymbol{\gamma}\boldsymbol{\varepsilon} - \cancel{\boldsymbol{\varepsilon}^2} - \boldsymbol{K}_t$$

$$\boldsymbol{R}_t = -\frac{i}{2}\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)$$

Purely imaginary solution

$$C_t = \sqrt{det\left[\frac{1}{2}\left(\boldsymbol{I} + \frac{i}{\hbar\boldsymbol{\gamma}}\boldsymbol{R}_t\right)\right]}\, e^{\frac{1}{2}\int_o^t d\tau Tr(\boldsymbol{R}_\tau)}$$

No divergence in the exponential part

[13] R. Gelabert *et al.*, J. Phys. Chem. A **104**, 10321 (2000).

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Our recursive approach

$$\dot{\varepsilon}_t \sim 0 \qquad \dot{K}_t \sim 0 \qquad R_t^{(2)} = -\frac{i}{2}\left(\hbar\gamma + \frac{K_t}{\hbar\gamma}\right) + \varepsilon = R_t^{(1)} + \varepsilon \qquad \varepsilon^2 \sim 0$$

$$0 = \frac{1}{4}\left(\hbar^2\gamma^2 + \frac{K_t^{\,2}}{\hbar^2\gamma^2} + 2K_t\right) + i\varepsilon\left(\hbar\gamma + \frac{K_t}{\hbar\gamma}\right) - K_t = \frac{1}{4}\left(\hbar\gamma - \frac{K_t}{\hbar\gamma}\right)^2 + i\varepsilon\left(\hbar\gamma + \frac{K_t}{\hbar\gamma}\right)$$

$$R_t^{(2)} = -\frac{i}{2}\left(\hbar\gamma + \frac{K_t}{\hbar\gamma}\right) + \frac{i\left(\hbar\gamma - \frac{K_t}{\hbar\gamma}\right)^2}{4\left(\hbar\gamma + \frac{K_t}{\hbar\gamma}\right)}$$

$$R_t^{(2)} = R_t^{(1)} + \frac{\left(\hbar\gamma - \frac{K_t}{\hbar\gamma}\right)^2}{2^3 R_t^{(1)}}$$

- **Purely imaginary solution.**
- **As $R_t^{(1)}$, the exponential part of the prefactor is oscillating.**

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Our recursive approach

$$\boldsymbol{R}_t^{(3)} = -\frac{i}{2}\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right) + \frac{i\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^2}{4\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)} + \boldsymbol{\varepsilon} = \boldsymbol{R}_t^{(2)} + \boldsymbol{\varepsilon}$$

$$\boldsymbol{R}_t^{(3)} = \boldsymbol{R}_t^{(2)} + \frac{i}{8}\frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^4}{\left[2\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^3 - \left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^2\right]} = \boldsymbol{R}_t^{(2)} - \frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^4}{2^7\boldsymbol{R}_t^{(1)^2}\boldsymbol{R}_t^{(2)}}$$

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$$\boldsymbol{R_t}^{(3)} = -\frac{i}{2}\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right) + \frac{i\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^2}{4\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)} + \boldsymbol{\varepsilon} = \boldsymbol{R_t}^{(2)} + \boldsymbol{\varepsilon}$$

$$\boldsymbol{R_t}^{(3)} = \boldsymbol{R_t}^{(2)} + \frac{i}{8}\frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^4}{\left[2\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^3 - \left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^2\right]} = \boldsymbol{R_t}^{(2)} - \frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^4}{2^7\boldsymbol{R_t}^{(1)^2}\boldsymbol{R_t}^{(2)}}$$

$$\boldsymbol{R_t}^{(4)} = \boldsymbol{R_t}^{(3)} + \boldsymbol{\varepsilon}$$

$$\boldsymbol{R_t}^{(4)} = \boldsymbol{R_t}^{(3)} + \frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K_t}}{\hbar\boldsymbol{\gamma}}\right)^8}{2^{15}\boldsymbol{R_t}^{(1)^4}\boldsymbol{R_t}^{(2)^2}\boldsymbol{R_t}^{(3)}}$$

Recursive expression of $\boldsymbol{R_t}^{(n)}$ from $\boldsymbol{R_t}^{(n-1)}$?

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Recursive formula

n=2

$$\boldsymbol{R}_t^{(2)} = \boldsymbol{R}_t^{(1)} + \frac{\left(\hbar\gamma - \frac{K_t}{\hbar\gamma}\right)^2}{2^3 \boldsymbol{R}_t^{(1)}}$$

n=3

$$\boldsymbol{R}_t^{(3)} = \boldsymbol{R}_t^{(2)} - \frac{\left(\hbar\gamma - \frac{\boldsymbol{K}_t}{\hbar\gamma}\right)^4}{2^7 \boldsymbol{R}_t^{(1)^2} \boldsymbol{R}_t^{(2)}}$$

n=4

$$\boldsymbol{R}_t^{(4)} = \boldsymbol{R}_t^{(3)} + \frac{\left(\hbar\gamma - \frac{\boldsymbol{K}_t}{\hbar\gamma}\right)^8}{2^{15} \boldsymbol{R}_t^{(1)^4} \boldsymbol{R}_t^{(2)^2} \boldsymbol{R}_t^{(3)}}$$

$$\boldsymbol{R}_t^{(n)} = \boldsymbol{R}_t^{(n-1)} + \frac{(-)^n \left(\hbar\gamma - \frac{\boldsymbol{K}_t}{\hbar\gamma}\right)^{2^{(n-1)}}}{2^{(2^n-1)} \prod_{j=0}^{n-2} \boldsymbol{R}_t^{(n-1-j)^{2^j}}}$$

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Approximations summary

Log-Derivative formulation

$$C_t = \sqrt{det\left[\frac{1}{2}\left(\boldsymbol{I} + \frac{i}{\hbar\boldsymbol{\gamma}}\boldsymbol{R}_t\right)\right]}\, e^{\frac{1}{2}\int_o^t d\tau Tr(\boldsymbol{R}_\tau)}$$

$$\boldsymbol{R}_t^{\boldsymbol{HO}} = -i\hbar\boldsymbol{\gamma}$$

$$\boldsymbol{R}_t^{(\boldsymbol{1})} = -\frac{i}{2}\left(\hbar\boldsymbol{\gamma} + \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)$$

$$\boldsymbol{R}_t^{(\boldsymbol{2})} = \boldsymbol{R}_t^{(\boldsymbol{1})} + \frac{\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^2}{2^3\boldsymbol{R}_t^{(\boldsymbol{1})}}$$

$$\boldsymbol{R}_t^{(\boldsymbol{n})} = \boldsymbol{R}_t^{(\boldsymbol{n-1})} + \frac{(-)^n\left(\hbar\boldsymbol{\gamma} - \frac{\boldsymbol{K}_t}{\hbar\boldsymbol{\gamma}}\right)^{2^{(n-1)}}}{2^{(2^n-1)}\prod_{j=0}^{n-2}\boldsymbol{R}_t^{(\boldsymbol{n-1-j})^{2^j}}}$$

$$C_t^{ad} = \sqrt{\prod_{i=1}^{N}\left[\frac{1}{2}\left(Q(i,i) + \frac{i}{\hbar\gamma}P(i,i)\right)\right]}$$

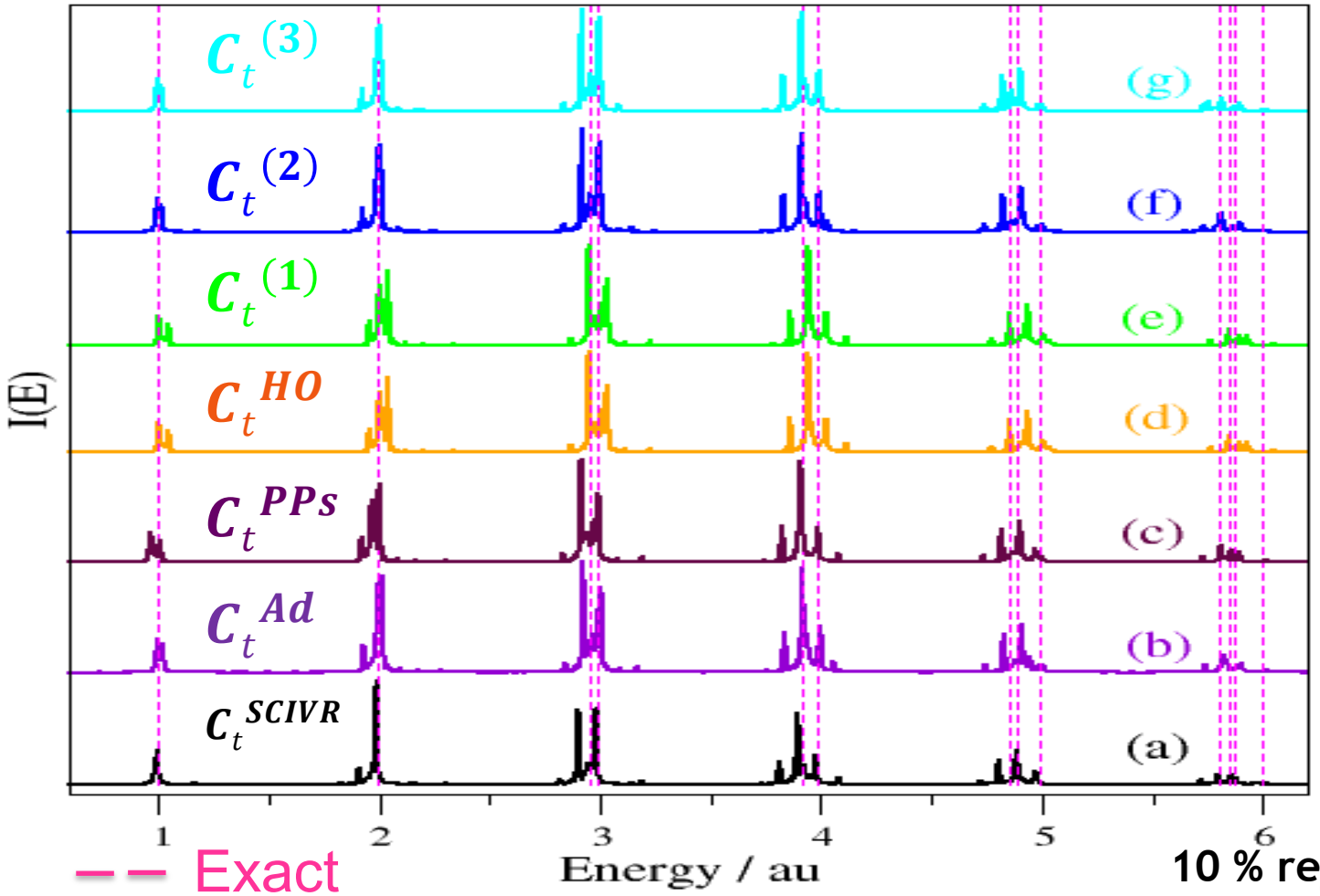
$$C_{\boldsymbol{t}}^{PPs}(\boldsymbol{p}_0, \boldsymbol{q}_0) = C_{\boldsymbol{t}}(\boldsymbol{p}_{eq}, \boldsymbol{q}_{eq})\ \ \forall(\boldsymbol{p}_0, \boldsymbol{q}_0)$$

$$C_t^{Johnson} \sim e^{-\frac{i}{2}\int_o^t d\tau \sum_{i=1}^{N}\boldsymbol{\omega}_\tau}$$

Numerical test: Henon-Heiles potential

$$V(x,y) = \frac{1}{2}(x^2 + y^2) + \lambda x^2 y - \frac{\lambda}{3} y^3$$

$\lambda = 0.11803$



	Traj.	MAE / au
$C_t^{(3)}$	5000	0.015
$C_t^{(2)}$	5000	0.014
$C_t^{(1)}$	5000	0.032
C_t^{HO}	5000	0.033
C_t^{PPs}	5000	0.016
C_t^{Ad}	5000	0.017
C_t^{SCIVR}	5000	0.011

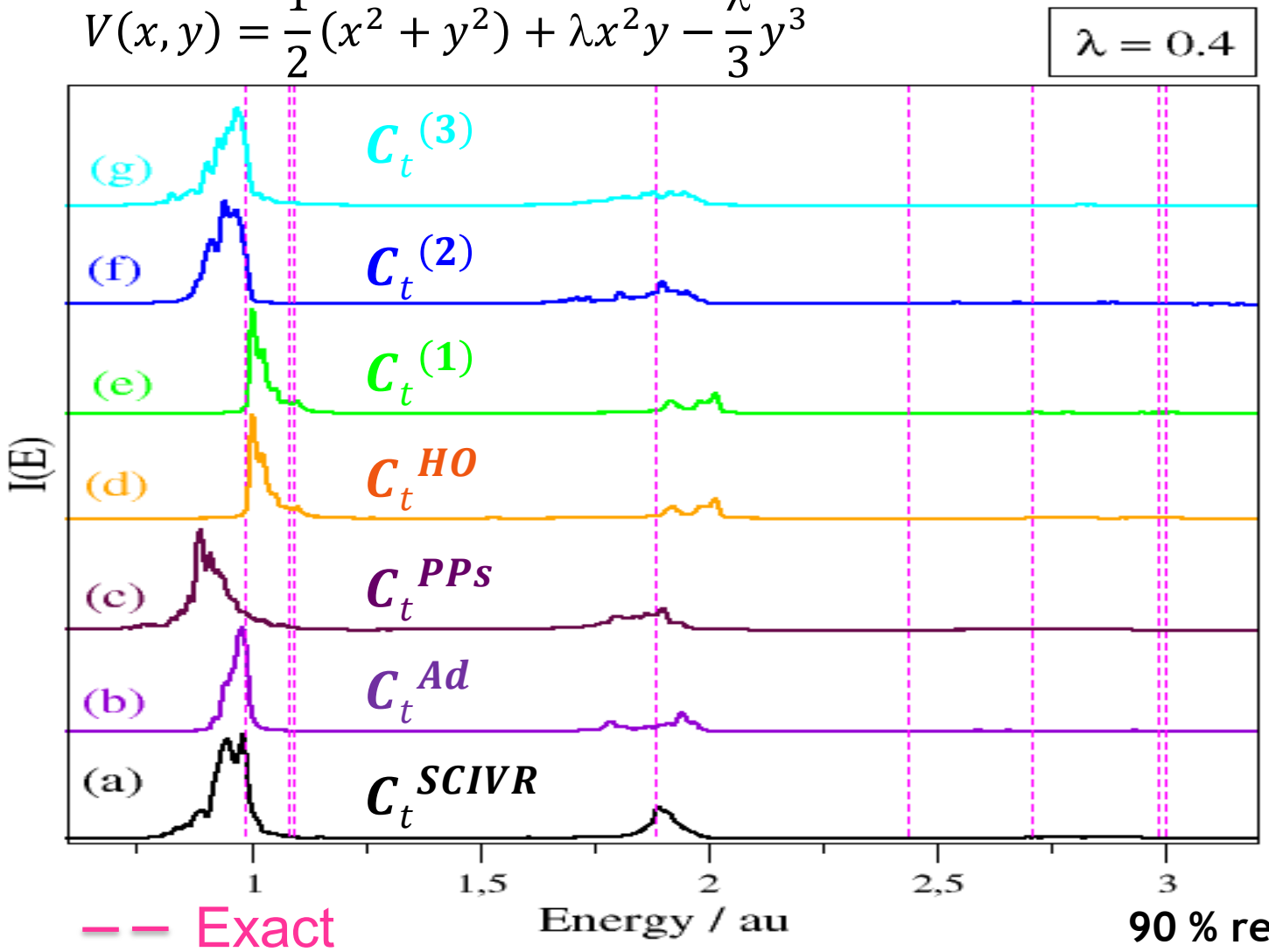
– – Exact

10 % rejected Trajectories

[8] H. Wang *et al.*, J. Chem. Phys. **115**, 6317 (2001).
[14] M.L. Brewer, J. Chem. Phys. **111**, 6168 (1999).

Numerical test: Henon-Heiles potential

$$V(x,y) = \frac{1}{2}(x^2 + y^2) + \lambda x^2 y - \frac{\lambda}{3} y^3$$

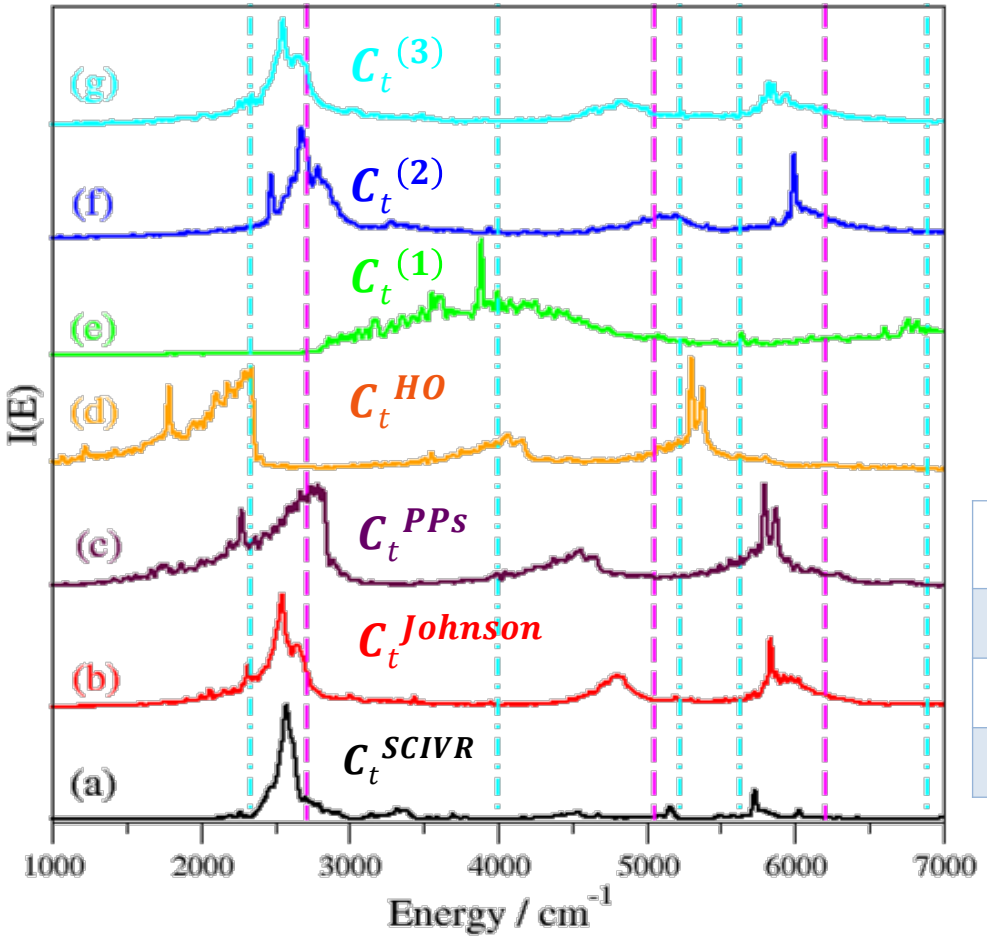


Traj.	MAE / au
5000	0.079
5000	0.073
5000	0.056
5000	0.055
5000	0.092
5000	0.072
50000	0.077

90 % rejected Trajectories

Numerical test: quartic potential

$$V(x,y) = D\left\{\left[1-e^{-\alpha_x(x-x_{eq})}\right]^2 + \left[1-e^{-\alpha_y(y-y_{eq})}\right]^2\right\} + \frac{\lambda}{2}\left((x-x_{eq})^4 + (y-y_{eq})^4\right) + \frac{0.02\lambda}{4}(x-x_{eq})^2(y-y_{eq})^2$$



> 90 % rejected Trajectories $\lambda = 10^{-6}$

High chaotic regime

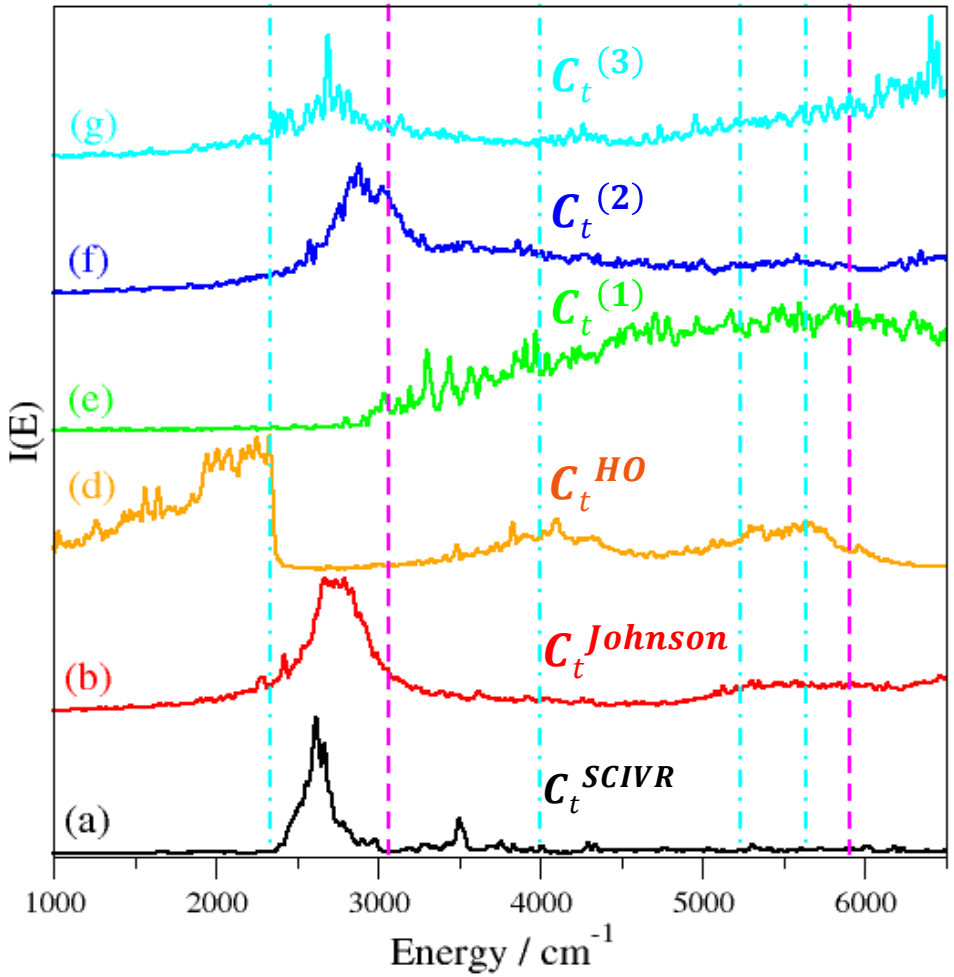
Traj.	80000	5000	5000	5000	5000
DVR	SCIVR	Johnson	PPs	$R_t^{(2)}$	$R_t^{(3)}$
2715.986	2577	2546	2781	2676	2553
5048.746	5160	4840	4556	5151	4825
6208.047	6030	5839	5794	6000	5842

—— Exact

—·— Uncoupled

Numerical test: quartic potential

$$V(x,y) = D\left\{\left[1-e^{-\alpha_x(x-x_{eq})}\right]^2 + \left[1-e^{-\alpha_y(y-y_{eq})}\right]^2\right\} + \frac{\lambda}{2}\left((x-x_{eq})^4 + (y-y_{eq})^4\right) + \frac{0.02\lambda}{4}(x-x_{eq})^2(y-y_{eq})^2$$



> 98 % rejected Trajectories $\lambda = 2.5 \cdot 10^{-6}$

Extreme chaotic regime[15]

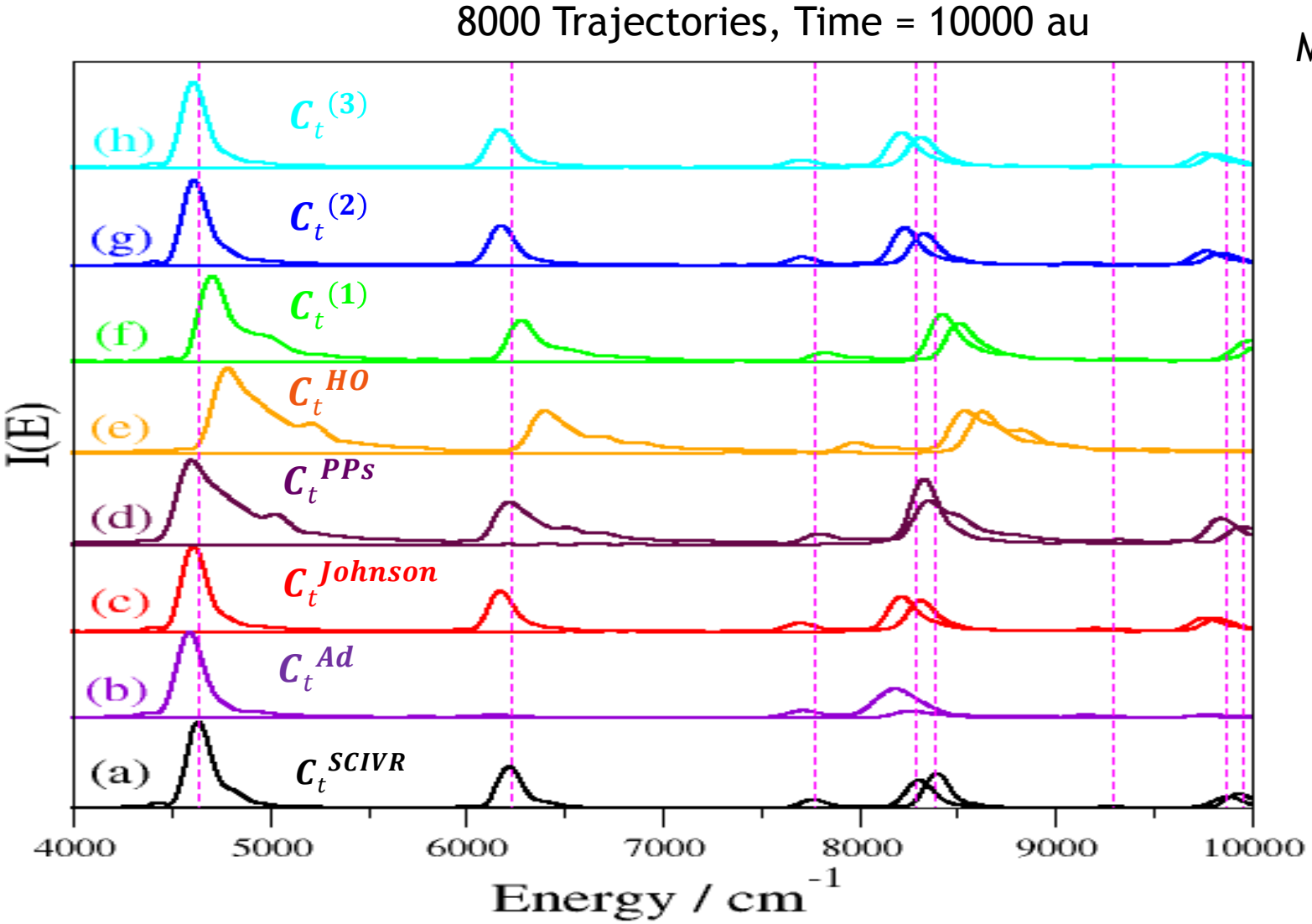
Traj.	250000	5000	5000	5000	5000
DVR	SCIVR	Johnson	$R_t^{(2)}$	$R_t^{(3)}$
3062	2620	2746	2885	2693

Exact

Uncoupled

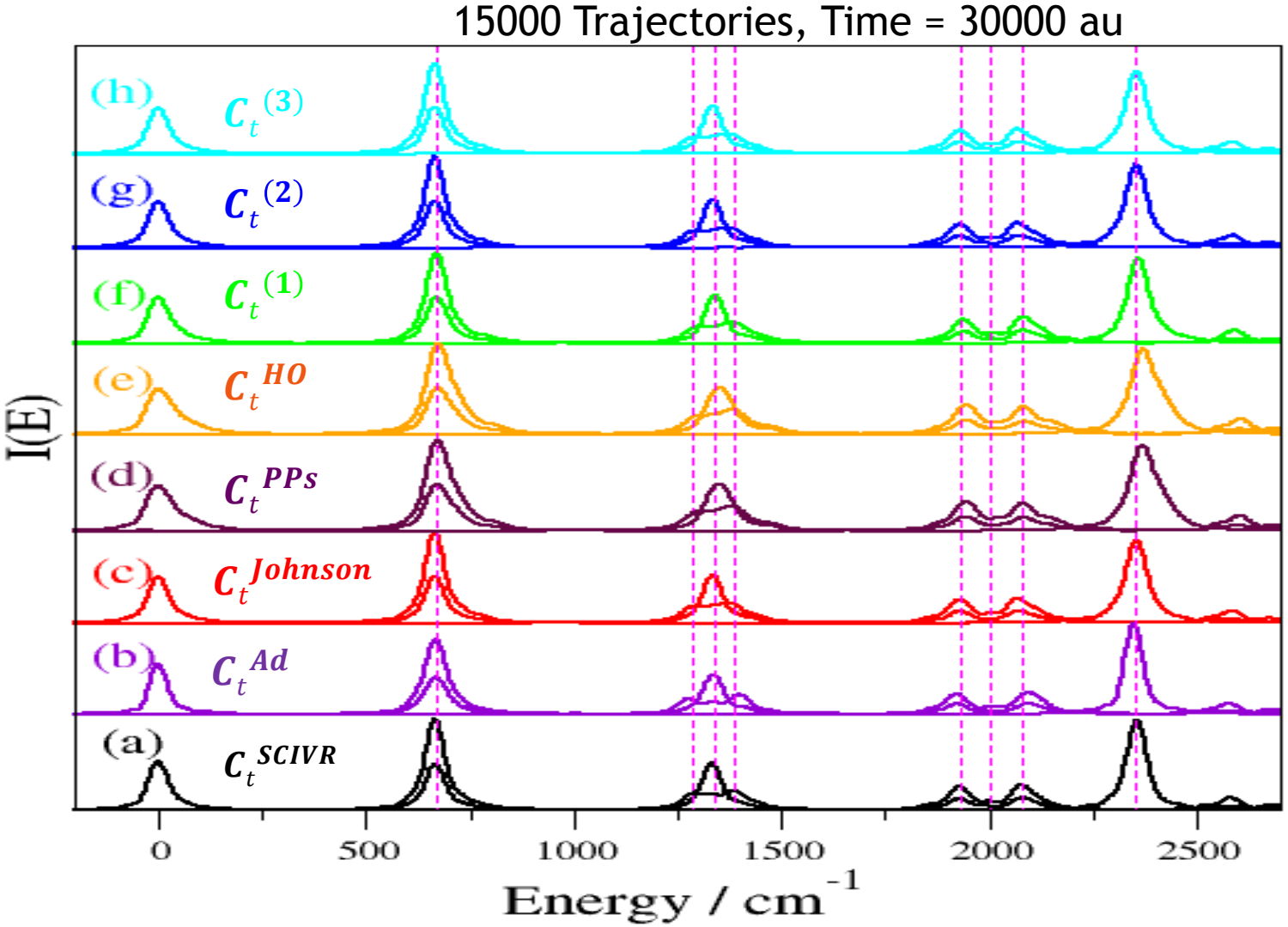
[15] K.G. Kay, J. Chem. Phys. **101**, 2250 (1994).

Numerical test: H_2O



[7] A. Kaledin and W.H. Miller, J. Chem. Phys. **118**, 7174 (2003); J. Chem. Phys. **119**, 3078 (2003).
[16] J.M. Bowman *et al.*, Chem. Phys. Lett. **150**, 269 (1988).
[17] D. Tamascelli, F.S. Dambrosio, R. Conte, M. Ceotto, J. Chem Phys., **140**, 174109 (2014).

Numerical test: CO_2



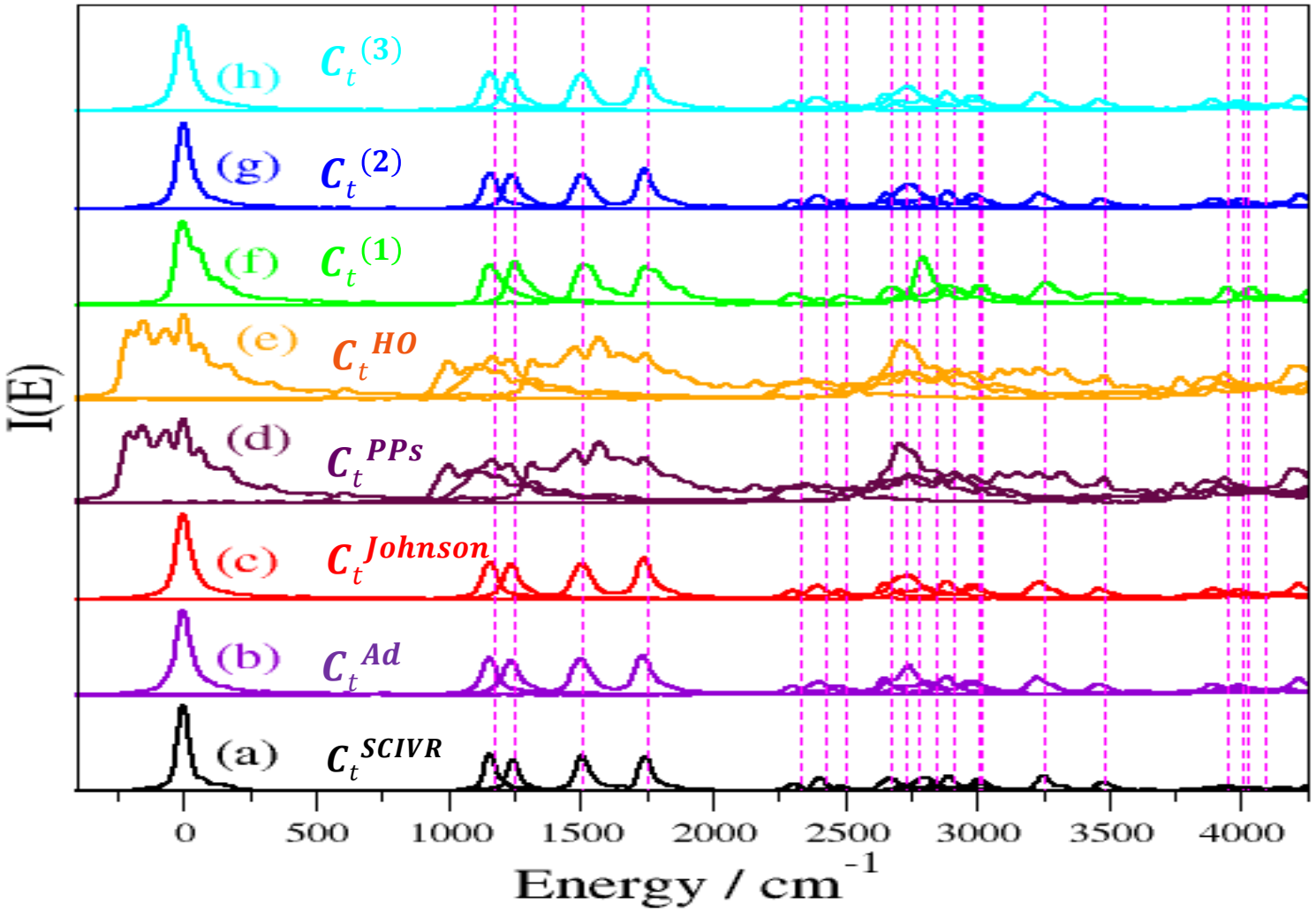
MAE[18,19] / cm^{-1}

(h) $C_t^{(3)}$	3.9
(g) $C_t^{(2)}$	3.2
(f) $C_t^{(1)}$	6.3
(e) C_t^{HO}	12.4
(d) C_t^{PPs}	11.4
(c) $C_t^{Johnson}$	3.8
(b) C_t^{Ad}	6.9
(a) C_t^{SCIVR}	3.0

[18] M. Ceotto *et al.*, Phys. Chem. Chem. Phys. **11**, 3861 (2009).
[19] J. Vazquez *et al.*, J. Chem. Theory Comput. **7**, 1428 (2011).

Numerical test: H_2CO

8000 Trajectories, Time = 30000 au

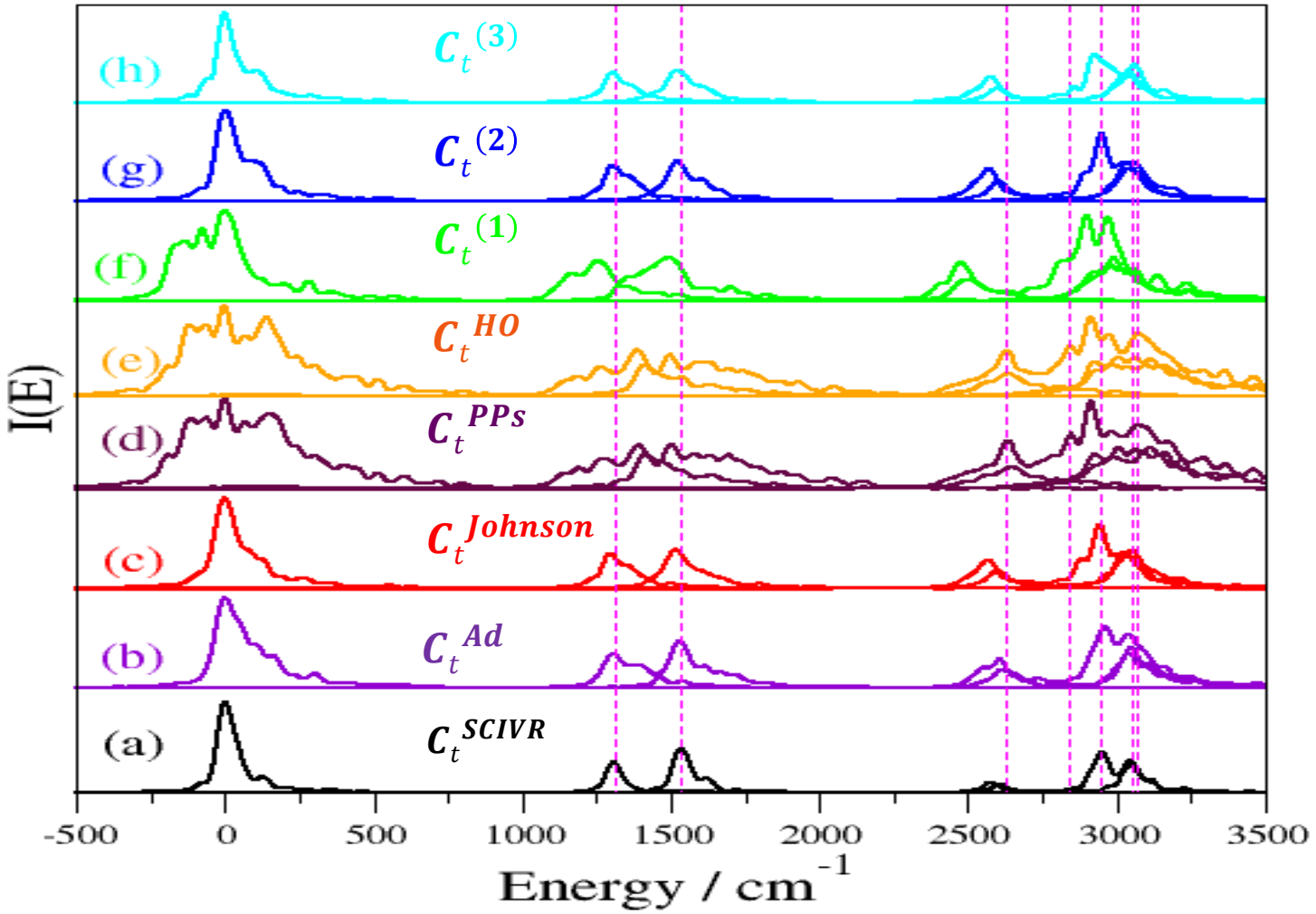


MAE[20] / cm^{-1}
30.2
23.2
12.3
91.9
91.1
25.2
31.9
11.3

[7] A. Kaledin and W.H. Miller, J. Chem. Phys. **118**, 7174 (2003); J. Chem. Phys. **119**, 3078 (2003).
[20] S. Carter *et al.*, Chem. Phys. Lett. **240**, 400 (1995).
[17] D. Tamascelli, F.S. Dambrosio, R. Conte, M. Ceotto, J. Chem Phys., **140**, 174109 (2014).

Numerical test: CH_4

14000 Trajectories, Time = 30000 au

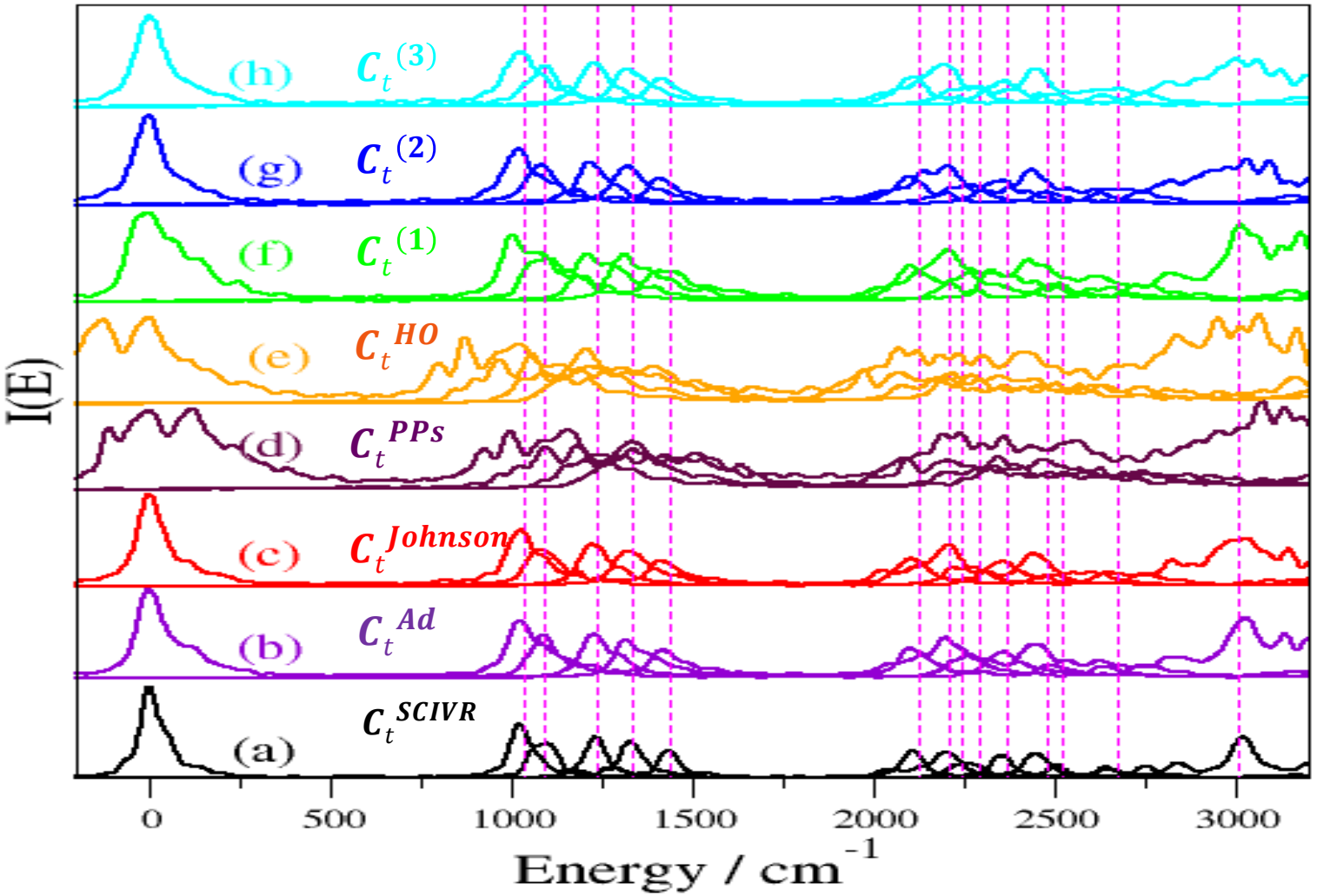


MAE[21] / cm^{-1}
15.6
13.0
68.1
34.9
39.8
18.6
7.8
7.8

[7] A. Kaledin and W.H. Miller, J. Chem. Phys. **118**, 7174 (2003); J. Chem. Phys. **119**, 3078 (2003).
[21] S. Carter *et al.*, J. Chem. Phys. **110**, 8417 (1999).

Numerical test: CH_2D_2

14000 Trajectories, Time = 30000 au



MAE[20] / cm^{-1}

$C_t^{(3)}$	17.5
$C_t^{(2)}$	23.4
$C_t^{(1)}$	22.9
C_t^{HO}	60.3
C_t^{PPs}	74.7
$C_t^{Johnson}$	18.3
C_t^{Ad}	18.5
C_t^{SCIVR}	19.1

[21] S. Carter *et al.*, J. Chem. Phys. **110**, 8417 (1999).
[17] D. Tamascelli, F.S. Dambrosio, R. Conte, M. Ceotto, J. Chem Phys., **140**, 174109 (2014).

Conclusions and Outlooks

1. The most reliable approximations are the Adiabatic, Johnson and our proposed ones.

2. The adiabatic and Johnson approximations can numerically diverge for chaotic potentials.

3. Deep investigations of some of the existent prefactor approximations.

4. Development a new class of approximate solutions of the Herman-Kluk prefactor in the Log-Derivative formulation.

5. No need to evaluate the amount of chaos, all trajectories contribute to the Monte Carlo integration.

- Enhance the accuracy of the developed approximations.
- Increase the stability of the prefactor for very complex systems.

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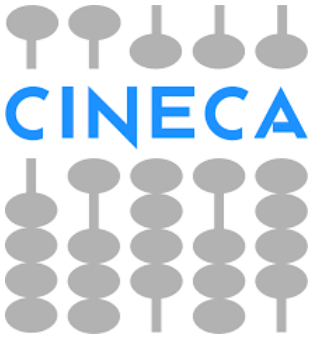

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Thank you for your kind attention

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