

Semiclassical Dynamics: A Viable Route to Molecular Spectroscopy

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Reliable molecular spectroscopy simulations require an accurate quantum description of nuclear motion. Since purely quantum mechanical approaches are not affordable when dealing with high dimensional systems, an alternative path must be followed. Semiclassical methods have been demonstrated to provide a viable route to obtain quantum features starting from classical trajectories. Based on the time-averaged version of Miller's semiclassical initial value representation, we have developed new semiclassical techniques able to yield accurate vibrational spectra upon classical evolution of just a handful of trajectories. Our techniques can be interfaced to ab initio on-the-fly dynamics and can tackle problems involving hundreds of degrees of freedom by means of a divide-and-conquer strategy. We present some relevant applications that cover a large dimensionality range, going from ammonia (with tunneling splitting detection), to glycine (with a potential energy surface characterized by multiple shallow wells) and C₆₀ fullerene (a system made of 174 degrees of freedom).

$\vec{F} = m\vec{a}$
Easy but Unfit



$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$

Exact but Hard

Semiclassical Dynamics

Classical Trajectories Propagation



Feynman Quantum Path Integration



Quantum Mechanical Spectral Density

$$I(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt e^{iEt/\hbar} \langle \Psi | e^{-i\hat{H}t/\hbar} | \Psi \rangle = \sum_{i=1}^N |c_i|^2 \delta(E - E_i) \quad |\Psi\rangle = \sum_{i=1}^N c_i |E_i\rangle$$

Herman-Kluk (HK) Semiclassical Propagator

$$\left(e^{-i\hat{H}t/\hbar} \right)_{HK} = \frac{1}{(2\pi\hbar)^{N_{\text{vib}}}} \int \int d\mathbf{p}_0 d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t, \mathbf{q}_t\rangle \langle \mathbf{p}_0, \mathbf{q}_0|$$

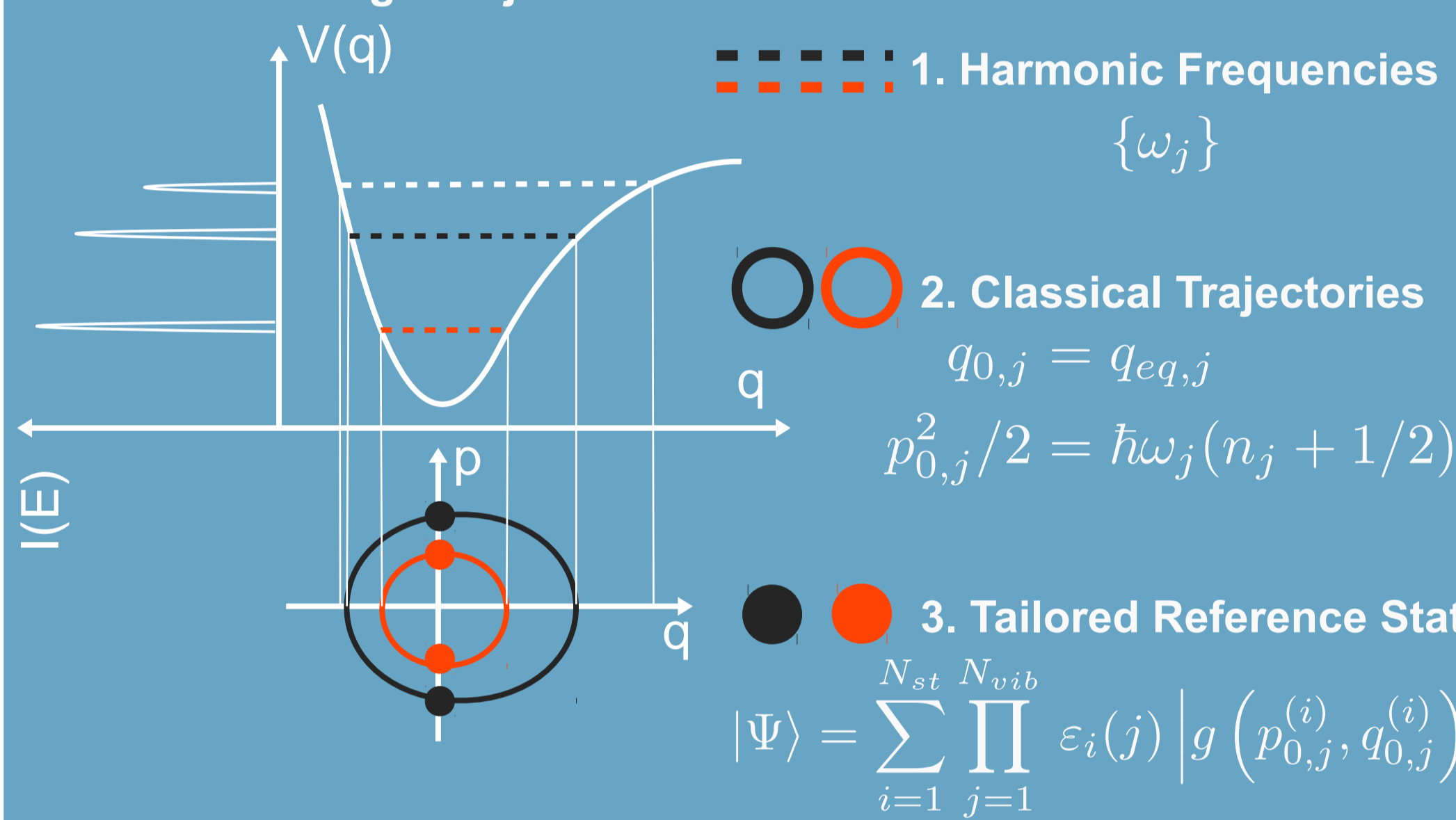
$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\frac{1}{2} \left(\frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} + \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} - i\hbar \Gamma \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} + \frac{i}{\hbar} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \right)} \quad S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' \left[\frac{\mathbf{p}(t')^2}{2} + V(\mathbf{q}(t')) \right] \quad (\mathbf{x}|\mathbf{p}, \mathbf{q}\rangle = \prod_{j=1}^{N_{\text{vib}}} \left(\frac{1}{\pi} \right)^{1/4} \exp \left[-\frac{i}{2} (x_j - q_j)^2 + i p_j (x_j - q_j) \right])$$

Time-Averaged Semiclassical Initial Value Representation (TA-SCIVR)

$$I(E) = FT(\langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle) = \frac{1}{(2\pi\hbar)^{N_{\text{vib}}+1} T} \int d\mathbf{p}_0 d\mathbf{q}_0 \int_0^T dt \langle \chi | \mathbf{p}_t, \mathbf{q}_t \rangle e^{i[S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi_t(\mathbf{p}_0, \mathbf{q}_0)]/\hbar} \quad \phi_t = \text{phase}(C_t)$$

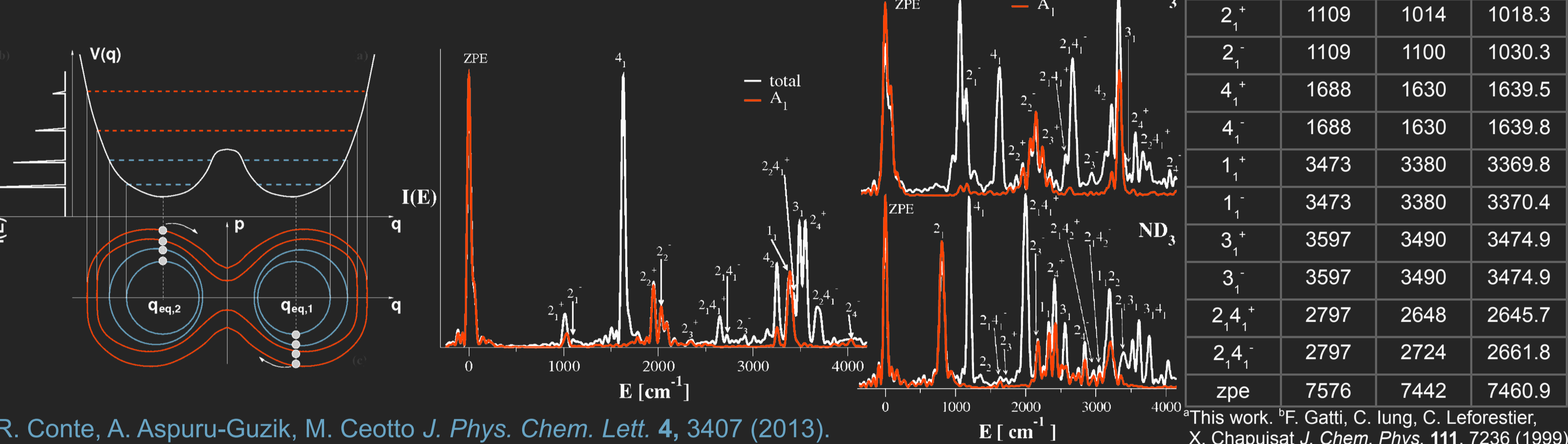
The Multiple Coherent Time Averaged Semi-Classical Initial Value Representation (MC-TA-SCIVR)

Classical "Eigentrajectories"



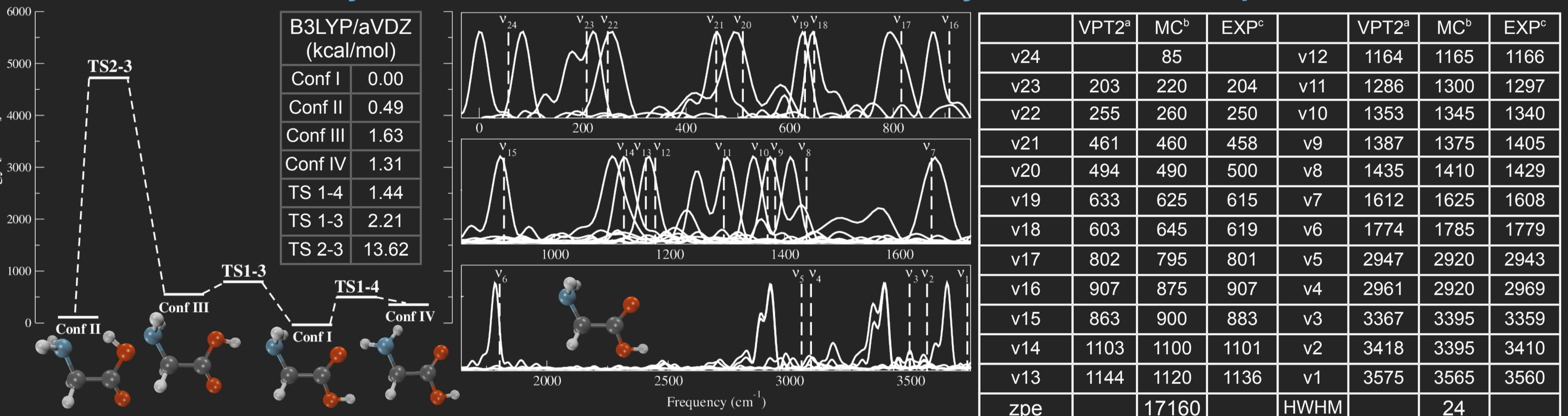
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Reproducing Deep Tunneling Splittings, Resonances, and Quantum Frequencies in Vibrational Spectra from a Handful of Direct ab initio Semiclassical Trajectories



R. Conte, A. Aspuru-Guzik, M. Ceotto *J. Phys. Chem. Lett.* 4, 3407 (2013).

On-the-fly ab initio Semiclassical Calculation of Glycine Vibrational Spectrum



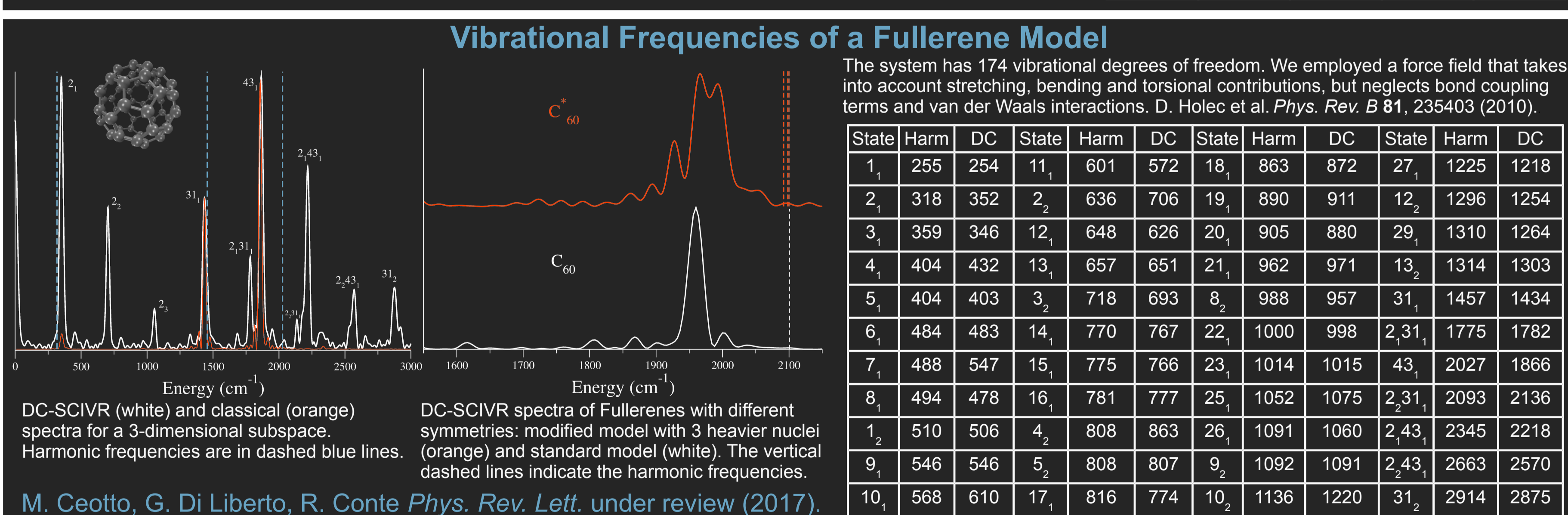
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^a V. Barone et al. *J. Chem. Theory Comput.* 9, 1533 (2013). ^b This work. ^c S. G. Stepanian *J. Phys. Chem. A* 102, 1041 (1998).

Glycine and GlycineH⁺ Vibrational Frequencies via on-the-fly DC-SCIVR

	DC ^a		MC ^b	DC ^a		MC ^b
v24	80	85	v12	1160	1165	
v23	200	220	v11	1290	1300	
v22	250	260	v10	1350	1345	
v21	450	460	v9	1380	1375	
v20	490	490	v8	1400	1410	
v19	620	625	v7	1660	1625	
v18	660	645	v6	1780	1785	
v17	800	795	v5	2900	2920	
v16	880	875	v4	2900	2920	
v15	900	900	v3	3380	3395	
v14	1100	1100	v2	3360	3395	
v13	1120	1120	v1	3640	3565	
zpe	17086	17160	HWHM	33	24	

	DC ^a		DC ^a	EXP ^b
v27	90	v13	1260	
v26	230	v12	1400	
v25	280	v11	1390	
v24	470	v10	1460	
v23	590	v9	1570	
v22	630	v8	1580	
v21	640	v7	1800	
v20	820	v6	2890	
v19	910	v5	2950	
v18	950	v4	3060	
v17	1070	v3	3270	3311
v16	1090	v2	3360	3355
v15	1150	v1	3600	3546
v14	1270	zpe	19880	



M. Ceotto, G. Di Liberto, R. Conte *Phys. Rev. Lett.* under review (2017).

Divide-and-Conquer Semiclassical Initial Value Representation (DC-SCIVR)

Vectors and matrices that appear in the semiclassical expression for the spectral density can be projected into subspaces by means of a singular value decomposition procedure.

$$\langle \tilde{x} | \tilde{p}, \tilde{q}_t \rangle = \left(\frac{\det(\tilde{\Gamma})}{\pi^M} \right)^{\frac{1}{4}} e^{-\frac{1}{2} (\tilde{x} - \tilde{q}_t)^T \tilde{\Gamma} (\tilde{x} - \tilde{q}_t) + \frac{i}{\hbar} \tilde{p}^T (\tilde{x} - \tilde{q}_t)}$$

For instance $\tilde{\Gamma} = U U^T U U^T$ provides the projected Gaussian width matrix. U is the singular-value decomposition matrix.

$$\tilde{S} = \int_0^T \tilde{T}(\tilde{p}_M) - \tilde{V}(\tilde{q}_M) dt'$$

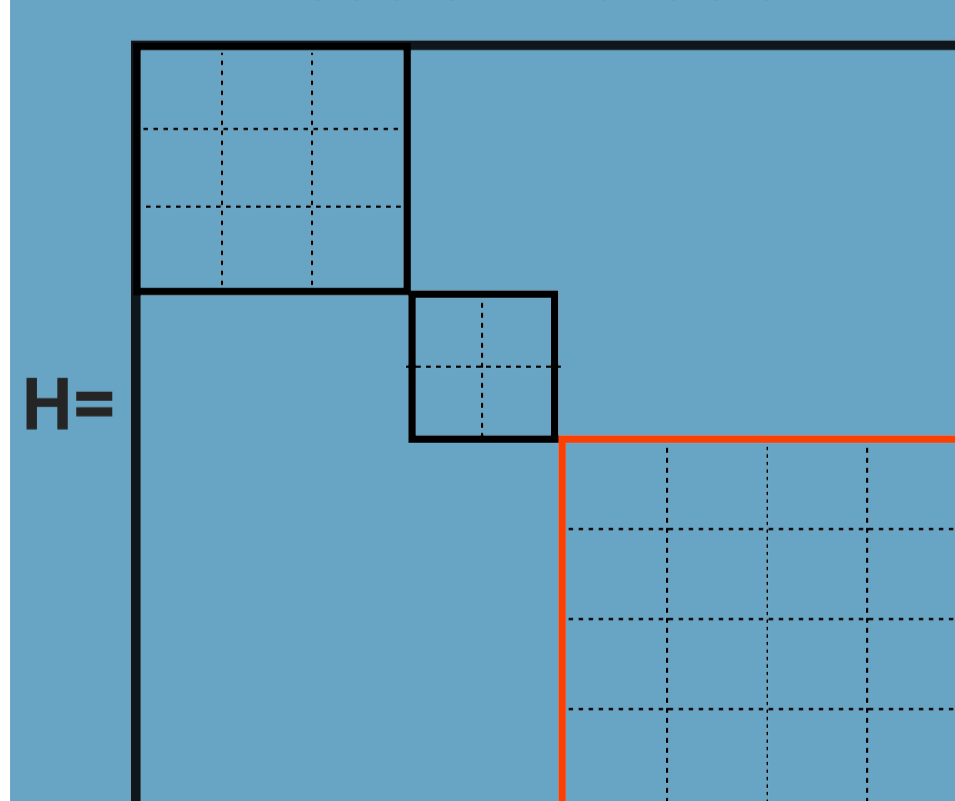
$$\tilde{V}(\tilde{q}_M) \equiv V(\tilde{q}_M; \mathbf{q}_{N_{\text{vib}}-M}) = V(\tilde{q}_M; \mathbf{q}_{N_{\text{vib}}-M}^{eq}) + \lambda(t)$$

The external field $\lambda(t)$ accounts for the non separability of the potential. It is chosen in a way that the projected potential is exact in the separable limit.

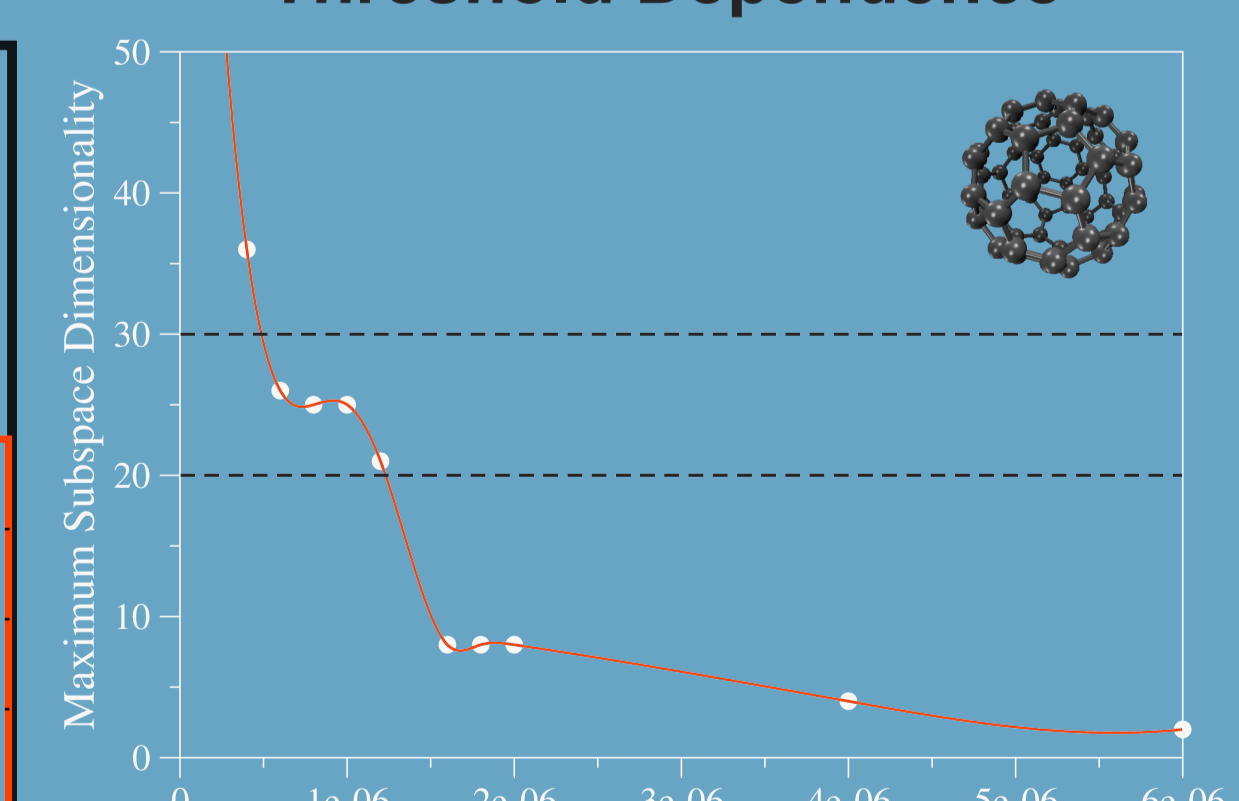
$$\lambda(t) = V(\tilde{q}_M; \mathbf{q}_{N_{\text{vib}}-M}) - [V(\tilde{q}_M; \mathbf{q}_{N_{\text{vib}}-M}^{eq}) + V(\tilde{q}_M; \mathbf{q}_{N_{\text{vib}}-M})]$$

$$\tilde{I}(E) = \left(\frac{1}{2\pi\hbar} \right)^M \int \int d\tilde{p}_0 d\tilde{q}_0 \frac{1}{2\pi\hbar T} \int_0^T dt e^{i[S_t(\tilde{p}_0, \tilde{q}_0) + Et + \phi_t]} \langle \chi | \tilde{p}_t, \tilde{q}_t \rangle^2$$

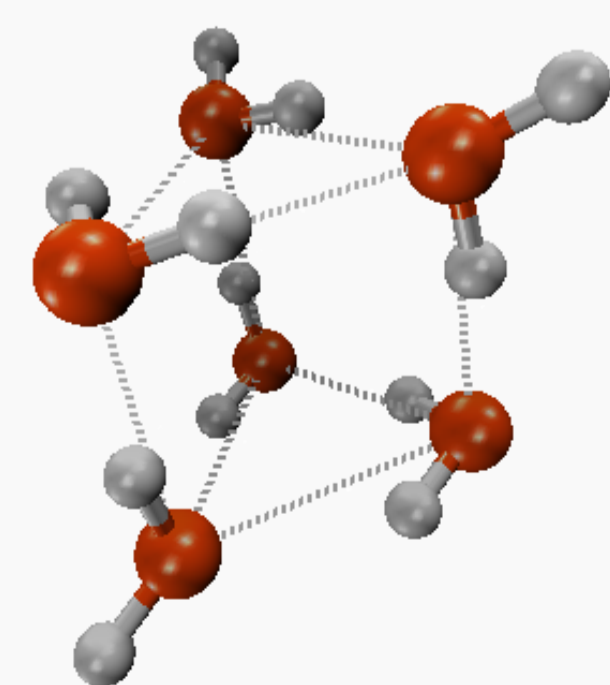
Hessian Partition



Threshold Dependence

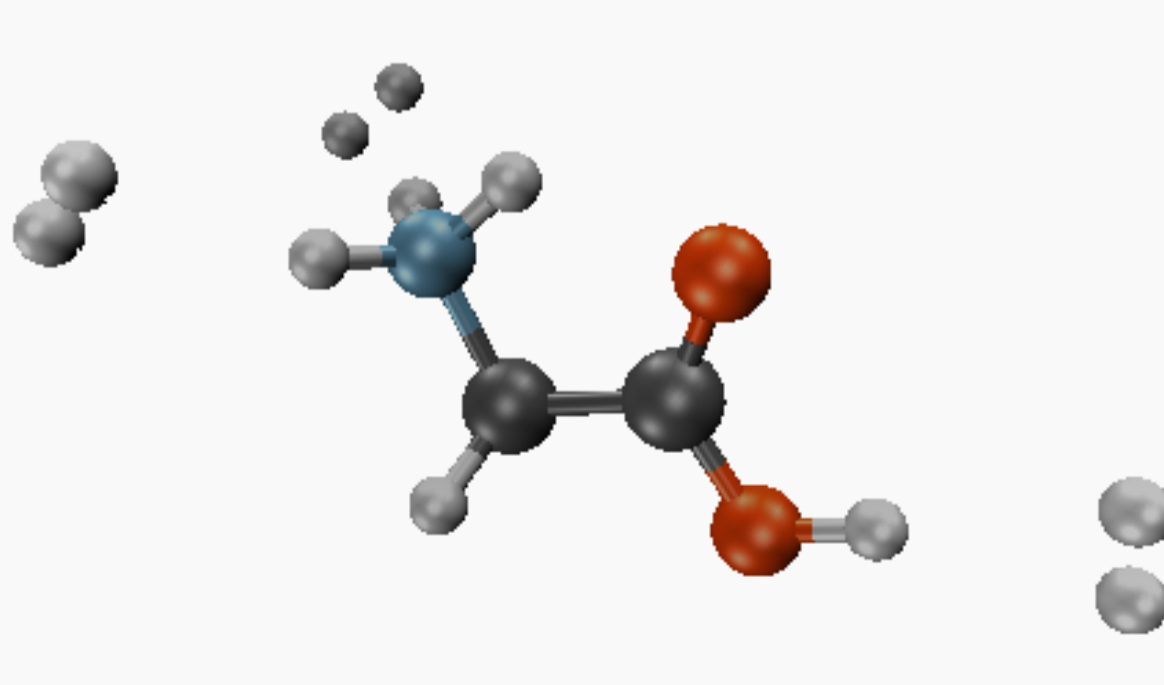


Vibrational Frequencies of Water Clusters



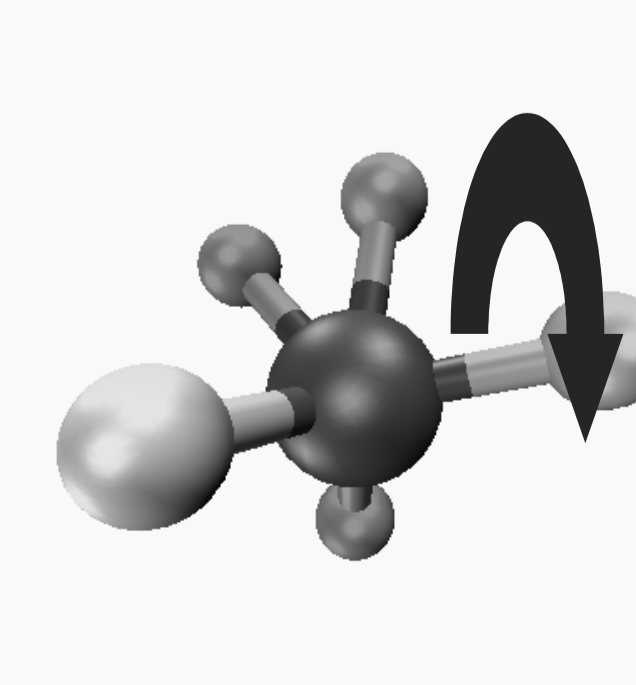
Semiclassical investigation of the effect of Inter-molecular hydrogen bonding on vibrational frequencies. Comparison to Bowman's MULTIMODE results.

H₂-tagged Protonated Glycine



Effect of local molecular-hydrogen tagging on high frequency O-H and N-H stretches. Comparison to experimental results by Thomas Rizzo.

Semiclassical Rotational Spectra



Rotational spectra of H₃⁺ and CH₃⁺. Advance of Heller's pioneering work on rigid rotors.

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