UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

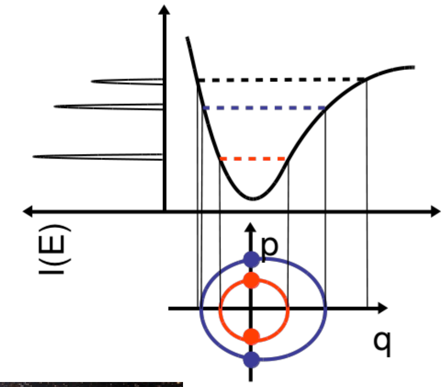
Investigating Molecular Quantum Vibrational Frequencies with Semiclassical Dynamics: Theory and Application to Systems of Astrochemical Interest

Riccardo Conte, Fabio Gabas, Giovanni Di Liberto, Michele Ceotto

ASTRO-Winter Modeling
Bologna, February 16th, 2018

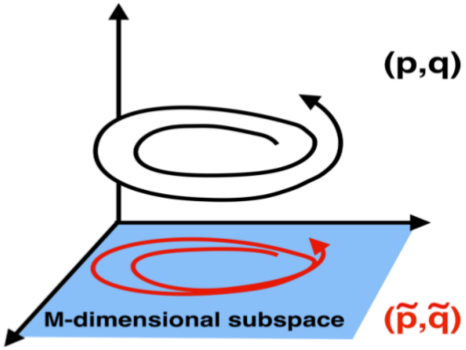
Outline of the Talk

Calculation of Molecular Quantum Frequencies of Vibration with Semiclassical Dynamics

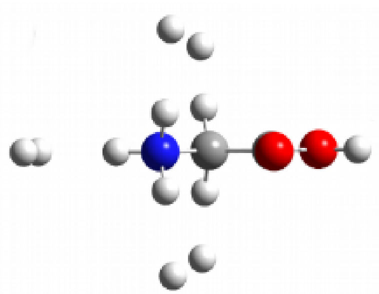


Application to Glycine: Basic Constituent of Proteins. Searched for in the ISM.

Semiclassical Dynamics in Higher Dimensionality



GlycineH$^+$ – nH$_2$ and Protonated Glycine Dimer: The Importance of Anharmonicity in Vibrational Frequency Estimates



Semiclassical Dynamics for Vibrational Frequency Calculations

Vibrational spectral density as Fourier-transform of the survival amplitude of an arbitrary reference state $|\Psi\rangle = \sum_j c_j |E_j\rangle$

$$I(E) = \Re\left[\frac{1}{\pi\hbar}\int_0^\infty dt\, e^{iEt}\langle\Psi|e^{-i\hat{H}t/\hbar}|\Psi\rangle\right] = \sum_j |c_j|^2\,\delta(E-E_j)$$

W.H. Miller *J. Chem. Phys.* **53**, 3578 (1970); *Adv. Chem. Phys.* **25**, 69 (1974); *J. Phys. Chem. A* **105**, 2942 (2001).
E. J. Heller *J. Chem. Phys.* **67**, 3339 (1977); *J. Chem. Phys.* **75**, 2923 (1981); *Acc. Chem. Res.* **39**, 127 (2006).
K.G. Kay *J. Chem. Phys.* **100**, 4432 (1994); *J. Chem. Phys.* **100**, 4377 (1994); *Annu. Rev. Phys. Chem.* **56**, 255 (2005).
R. Walton, and D. E. Manolopoulos *Mol. Phys.* **87**, 961 (1996); S.S. Zhang, and E. Pollak *J. Chem. Phys.* **121**, 3384 (2004).
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Herman-Kluk (HK) propagator

Semiclassical Initial Value Representation (SCIVR)

$$\langle\Psi|e^{-i\hat{H}t/\hbar}|\Psi\rangle_{HK} = \frac{1}{(2\pi\hbar)^F}\int\int \mathbf{dp_0 dq_0}\, C_t(\mathbf{p_0},\mathbf{q_0})e^{iS_t(\mathbf{p_0},\mathbf{q_0})/\hbar}$$
$$\langle\Psi|g(\mathbf{p_t},\mathbf{q_t})\rangle\langle g(\mathbf{p_0},\mathbf{q_0})|\Psi\rangle$$

W.H. Miller *J. Chem. Phys.* **53**, 3578 (1970); *Adv. Chem. Phys.* **25**, 69 (1974); *J. Phys. Chem. A* **105**, 2942 (2001).
E. J. Heller *J. Chem. Phys.* **67**, 3339 (1977); *J. Chem. Phys.* **75**, 2923 (1981); *Acc. Chem. Res.* **39**, 127 (2006).
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Time Averaged SCIVR Working Formula

$$I(E) = \frac{(2\pi\hbar)^{-F}}{2\pi\hbar T}\int\int d\mathbf{p_0}d\mathbf{q_0} \left|\int_0^T dt\langle\Psi|g(\mathbf{p_t},\mathbf{q_t})\rangle e^{(i/\hbar)(S_t(\mathbf{p_0},\mathbf{q_0})+Et+\phi_t(\mathbf{p_0},\mathbf{q_0}))}\right|^2$$

A. L. Kaledin, and W. H. Miller *J. Chem. Phys.* **118**, 7174 (2003); *J. Chem. Phys.* **119**, 3078 (2003).

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Required Advances

1) Accurate Results based on Few Classical Trajectories

2) Sensible Spectroscopic Signal for High Dimensional Systems

Time Averaged SCIVR Working Formula

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Further Reducing the Computational Effort

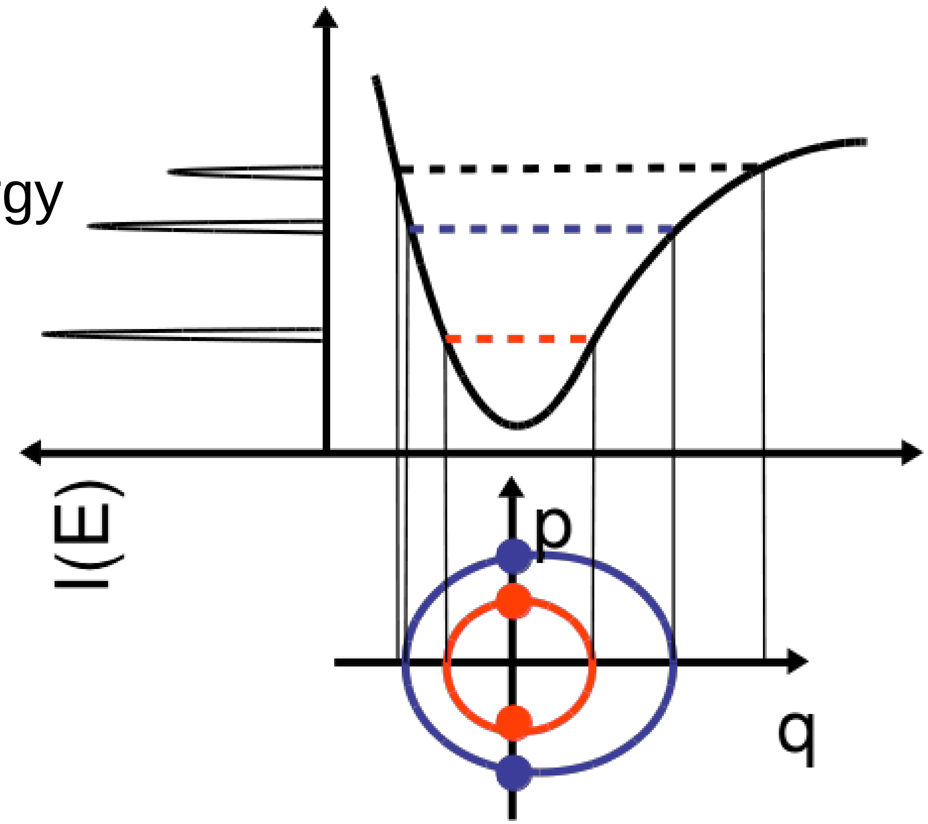
De Leon and Heller:
Accurate Semiclassical Eigenvalues and Eigefunctions with A Single Trajectory with Correct Energy

1) Classical Trajectories with Tailored Energy

q_{eq} at Equilibrium Geometry
Harmonic Sampling for p_{eq}

2) Tailored Choice of Reference State

$$|\Psi\rangle = \sum_{i=1}^{N_{st}} \prod_{j=i}^{F} \varepsilon_i(j) |p_{eq,j}^{(i)}, q_{eq,j}^{(i)}\rangle$$



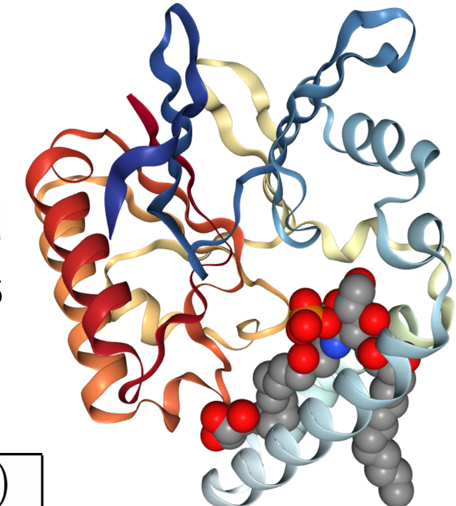
Multiple Coherent SCIVR

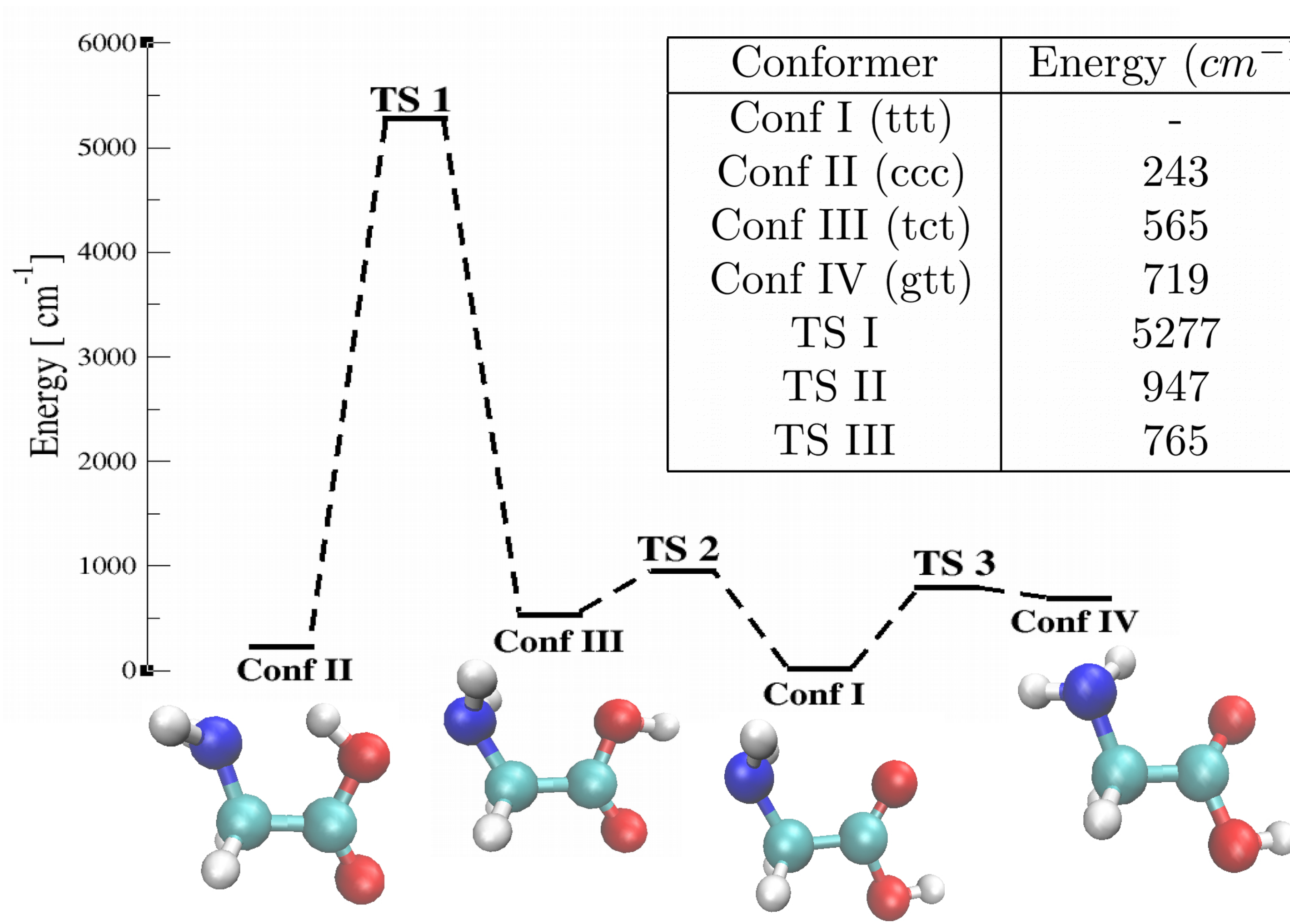
N. De Leon and E. J. Heller *J. Chem. Phys.* **78**, 4005 (1983).
M. Ceotto, S. Atahan, S. Shim, G. F. Tantardini, and A. Aspuru-Guzik *Phys. Chem. Chem. Phys.* **11**, 3861 (2009).
M. Ceotto, S. Atahan, G. F. Tantardini, and A. Aspuru-Guzik *J. Chem. Phys.* **130**, 234113 (2009).
M. Ceotto, D. Dell'Angelo, and G.F. Tantardini *J. Chem. Phys.* **133**, 054701 (2010).
M. Ceotto, S. Valleau, G.F. Tantardini, and A. Aspuru-Guzik *J. Chem. Phys.* **134**, 234103 (2011).
R. Conte, A. Aspuru-Guzik, and M. Ceotto *J. Phys. Chem. Lett.* **4**, 3407 (2013).
Y. Zhuang, M. R. Siebert, W.L. Hase, K.G. Kay, and M. Ceotto *J. Chem. Theory Comput.* **9**, 54 (2013).
D. Tamascelli, F.S. Dambrosio, R. Conte, and M. Ceotto *J. Chem. Phys.* **140**, 174109 (2014).

“On-the-fly” Application to Glycine

Presence in interstellar medium

Used in bio-nanodevices and basic constituent of proteins

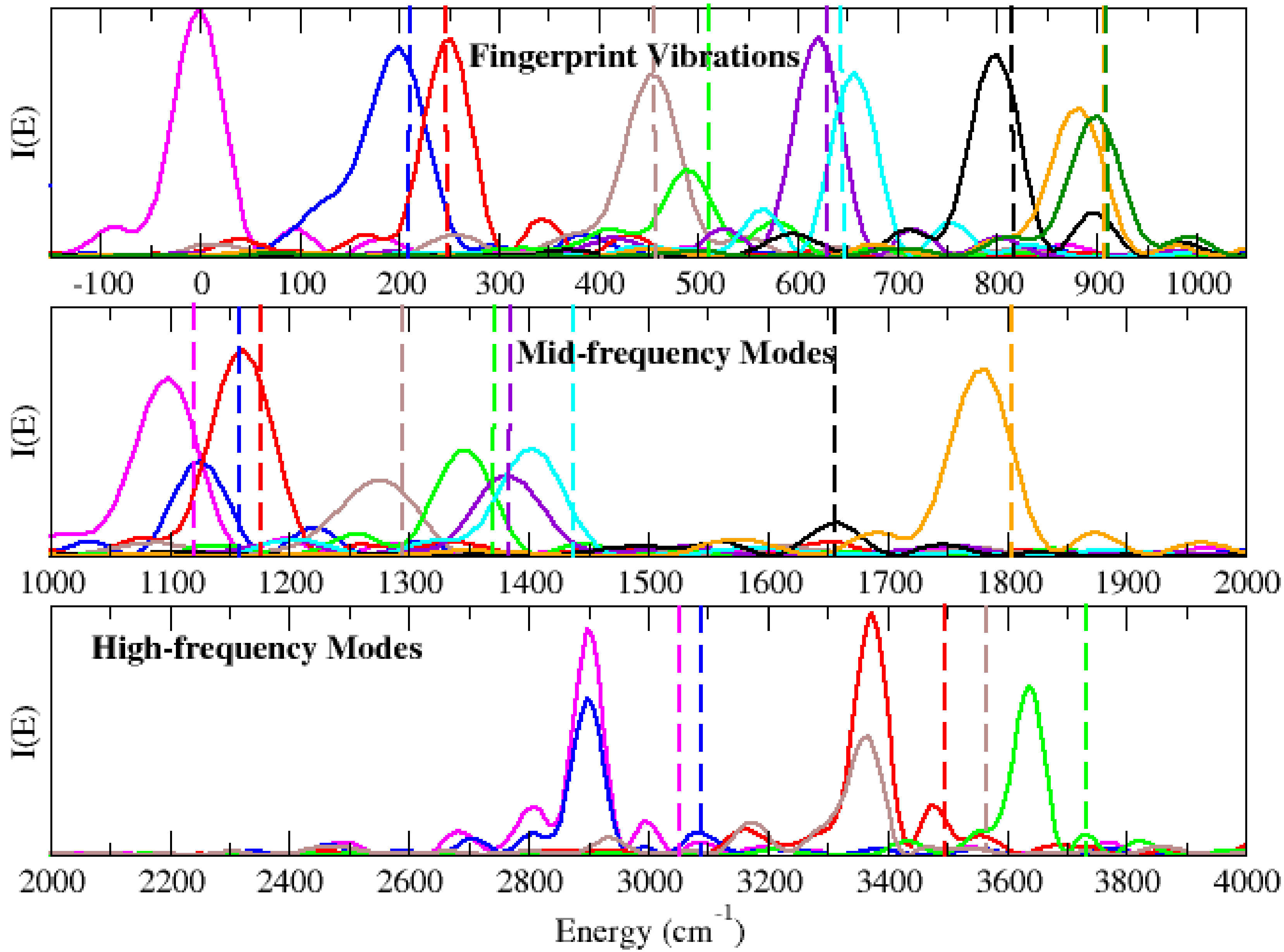




Conformer	Energy (cm^{-1})
Conf I (ttt)	-
Conf II (ccc)	243
Conf III (tct)	565
Conf IV (gtt)	719
TS I	5277
TS II	947
TS III	765

“On-the-fly” Application to Glycine

$$|\Psi\rangle = \prod_{j=1}^{24} \left(|p_{eq,j}, q_{eq,j}\rangle + \varepsilon(j) | -p_{eq,j}, q_{eq,j}\rangle \right)$$



“On-the-fly” Application to Glycine

Low frequency

	2	3	4	5	6	7	8	9	10
Harmonic	208	249	458	510	629	647	816	908	911
MC-SCIVR[a]	180	275	470	485	625	600	795	845	900
VPT2[b]	203	255	461	494	633	603	802	907	863
Exp[c]	204	250	458	500	615	619	801	907	883

Mid frequency

	11	12	13	14	15	16	17	18	19
Harmonic	1120	1158	1175	1294	1371	1384	1438	1656	1804
MC-SCIVR[a]	1090	1120	1165	1300	1330	1375	1410	1625	1785
VPT2[b]	1103	1144	1164	1286	1353	1387	1435	1612	1774
Exp[c]	1101	1136	1166	1297	1340	1405	1429	1608	1779

zpe = 17160 cm^{-1} MAE ~ 20 cm^{-1}

High frequency

	20	21	22	23	24
Harmonic	3051	3089	3495	3568	3735
MC-SCIVR[a]	2885	2920	3395	3390	3565
VPT2[b]	2947	2961	3367	3418	3575
Exp[c]	2943	2969	3359	3410	3585

[a] F. Gabas, R. Conte, and M. Ceotto *J. Chem. Theory Comput.* **13**, 2378 (2017).
[b] V. Barone, M. Biczysko, J. Bloino, and C. Puzzarini *J. Chem. Theory Comput.* **9**, 1533 (2013).
[c] S. G. Stepanian et al. *J. Phys. Chem. A* **102**, 1041 (1998).

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DFT/B3LYP/aVDZ level of theory

Semiclassical Approximation

Multiwell / Multireference Effect

[a] F. Gabas, R. Conte, and M. Ceotto *J. Chem. Theory Comput.* **13**, 2378 (2017).
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Semiclassical Dynamics in High Dimensionality

$$I(E) = \frac{1}{(2\pi\hbar)^F} \frac{Re}{\pi\hbar T} \sum_{i=1}^{n_{states}} \left| \int_0^T dt \left\langle \sum_{i=1}^{n_{states}} \mathbf{p^i}_{eq}, \mathbf{q^i}_{eq} | \mathbf{p}_t, \mathbf{q}_t \right\rangle e^{i\left(S_t\left(\mathbf{p}^i_{eq}, \mathbf{q}^i_{eq}\right) + Et + \phi(t)\right)/\hbar} \right|^2$$

$$\left\langle \mathbf{p}_{eq}\mathbf{q}_{eq} \middle| \mathbf{p}_t \boldsymbol{q}_t \right\rangle = \left\langle p^1_{eq}, q^1_{eq} \middle| p^1_t, q^1_t \right\rangle \ldots \left\langle p^F_{eq}, q^F_{eq} \middle| p^F_t, q^F_t \right\rangle$$

M. Ceotto, G. Di Liberto, and R. Conte *Phys. Rev. Lett.* **119**, 010401 (2017).

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$$I\left(E\right) = \frac{1}{\left(2\pi\hbar\right)^F}\frac{Re}{\pi\hbar T}\sum_{i=1}^{n_{states}}\left|\int_0^T dt\left\langle \sum_{i=1}^{n_{states}} \mathbf{p^i}_{eq},\mathbf{q^i}_{eq}|\mathbf{p}_t,\mathbf{q}_t\right\rangle e^{i\left(S_t\left(\mathbf{p}^i_{eq},\mathbf{q}^i_{eq}\right)+Et+\phi(t)\right)/\hbar}\right|^2$$

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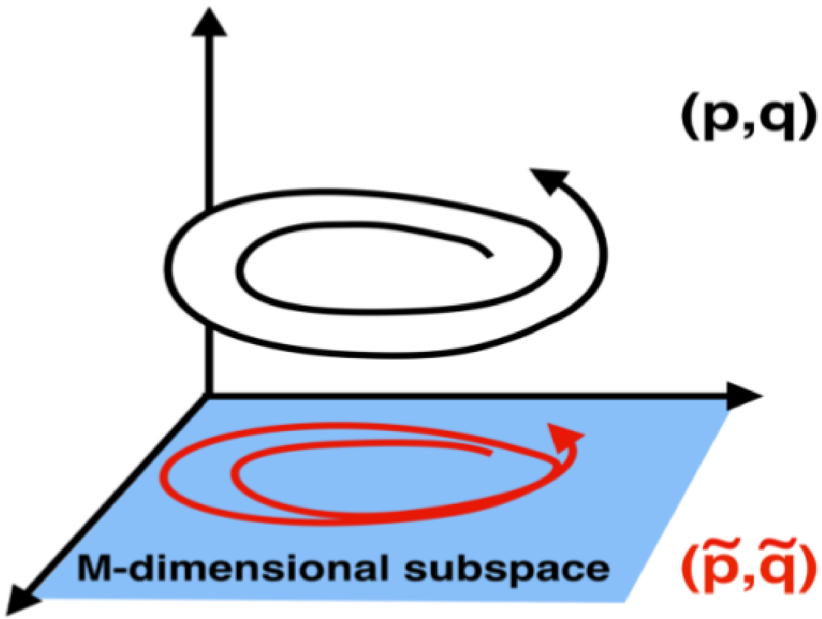

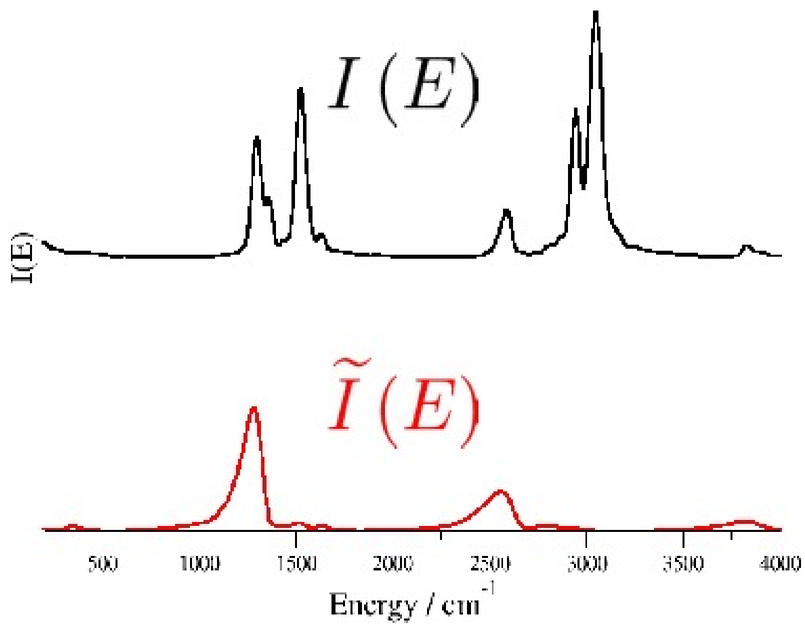

$$\tilde{I}\left(E\right) = \left(\frac{1}{2\pi\hbar}\right)^M \int\int d\tilde{\mathbf{p}}_0 d\tilde{\mathbf{q}}_0 \frac{1}{2\pi\hbar T}\left|\int_0^T e^{\frac{i}{\hbar}\left[\tilde{S}_t(\tilde{\mathbf{p}}_0,\tilde{\mathbf{q}}_0)+Et+\tilde{\phi}_t\right]}\left\langle\tilde{\chi}\,|\tilde{\mathbf{p}}_t,\tilde{\mathbf{q}}_t\right\rangle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

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Subspace Partition

The Hessian Method

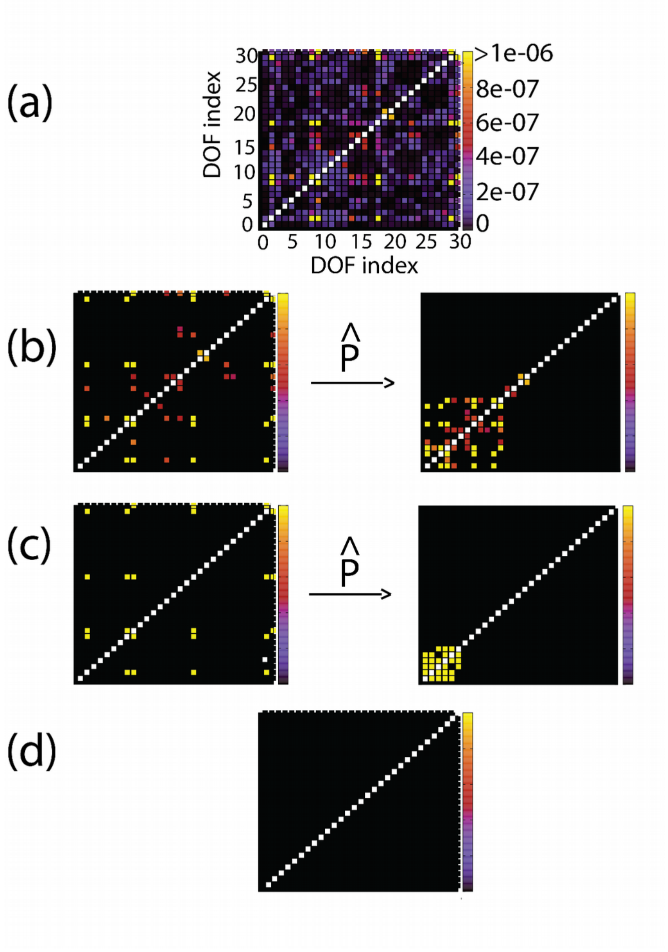
1. Evaluation of the averaged Hessian elements

$$\widetilde{H}_{ij} = \frac{1}{N_{steps}} \sum_{k=1}^{N_{steps}} H_{ij}$$

2. Set-up of the coarse grain threshold

$$\left| \widetilde{H}_{ij} \right| \geq \varepsilon$$

3. Arrange the Hessian in sub-blocks



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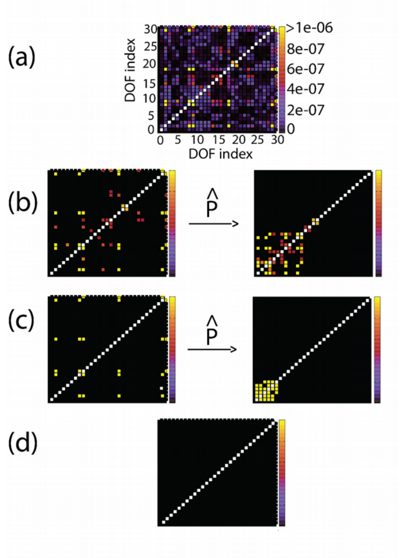
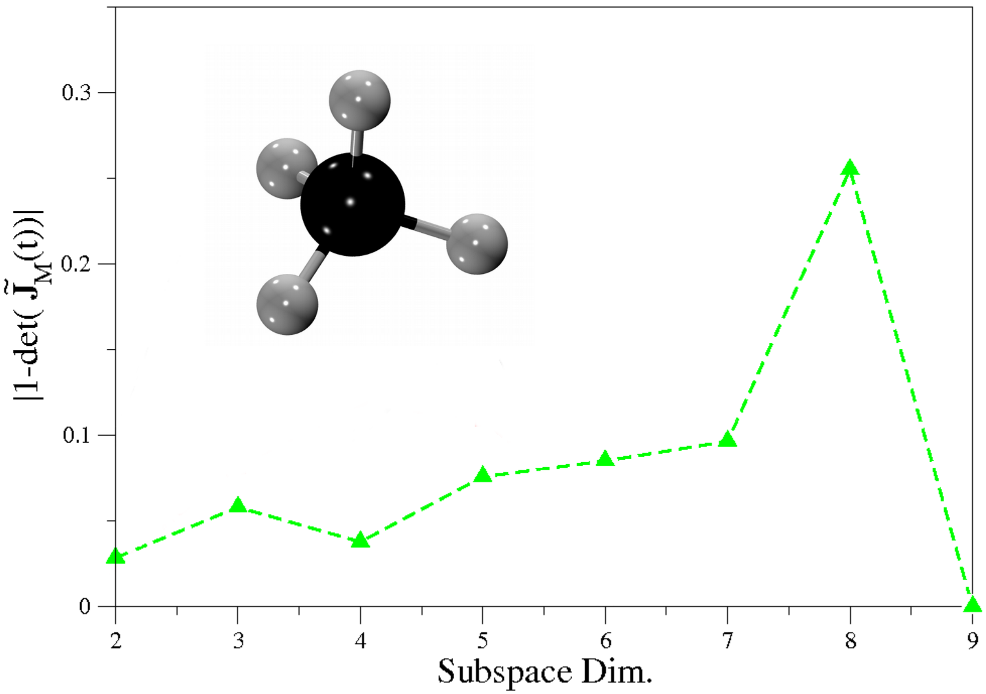




The Jacobian Method

$$\mathbf{J}(t) = \begin{pmatrix} \partial \mathbf{q}_t / \partial \mathbf{q}_0 & \partial \mathbf{q}_t / \partial \mathbf{p}_0 \\ \partial \mathbf{p}_t / \partial \mathbf{q}_0 & \partial \mathbf{p}_t / \partial \mathbf{p}_0 \end{pmatrix}$$

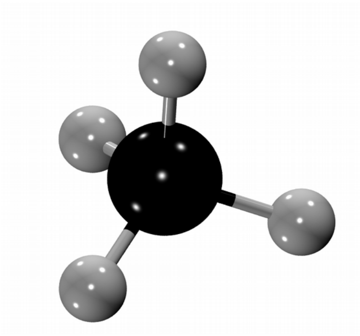
Separable Systems $\prod_{i=1}^{N_{sub}} det(\tilde{J}_i(t)) = 1$

Non-Separable Systems $\prod_{i=1}^{N_{sub}} det(\tilde{J}_i(t)) \neq 1$

G. Di Liberto, R. Conte, and M. Ceotto *J. Chem. Phys.* **148**, 014307 (2018).

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

Mode	Exact	TA SCIVR	DC SCIVR (Jacobi)	DC SCIVR (Hessian)	Harmonic
1_1	1313	1300	1296	1300	1345
2_1	1535	1529	1530	1532	1570
$1_1 2_1$	2836	2825	2830	2834	2915
3_1	2949	2948	2960	2964	3036
2_2	3067	3048	3060	3050	3140
4_1	3053	3048	3056	3044	3157
MAE		9	9	10	61



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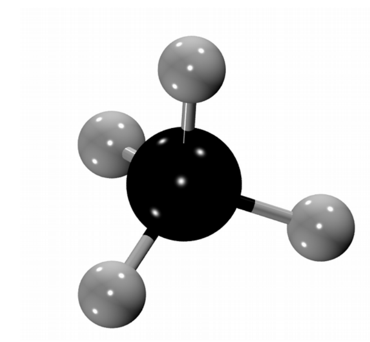
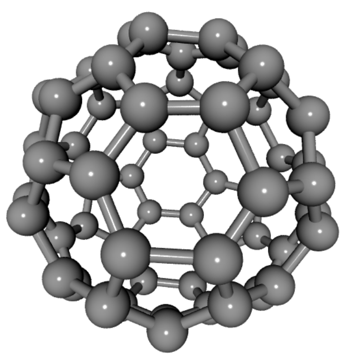
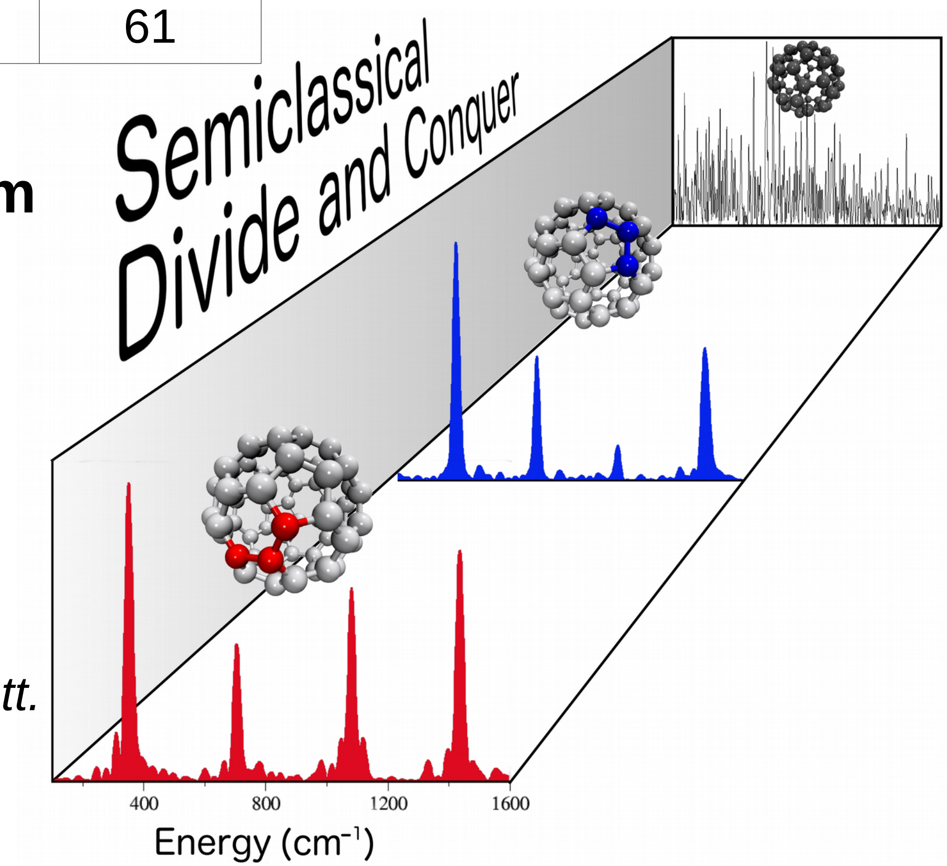


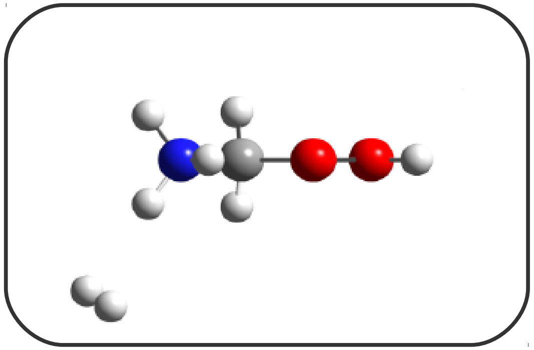
C_{60} Fullerene – 174 Degrees of Freedom

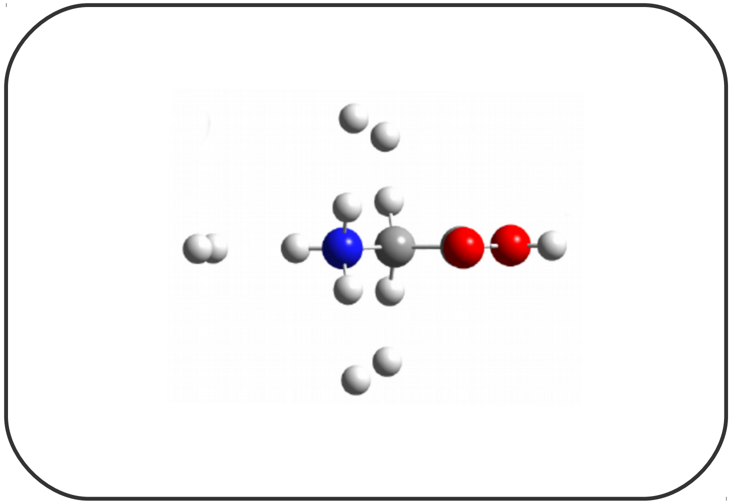


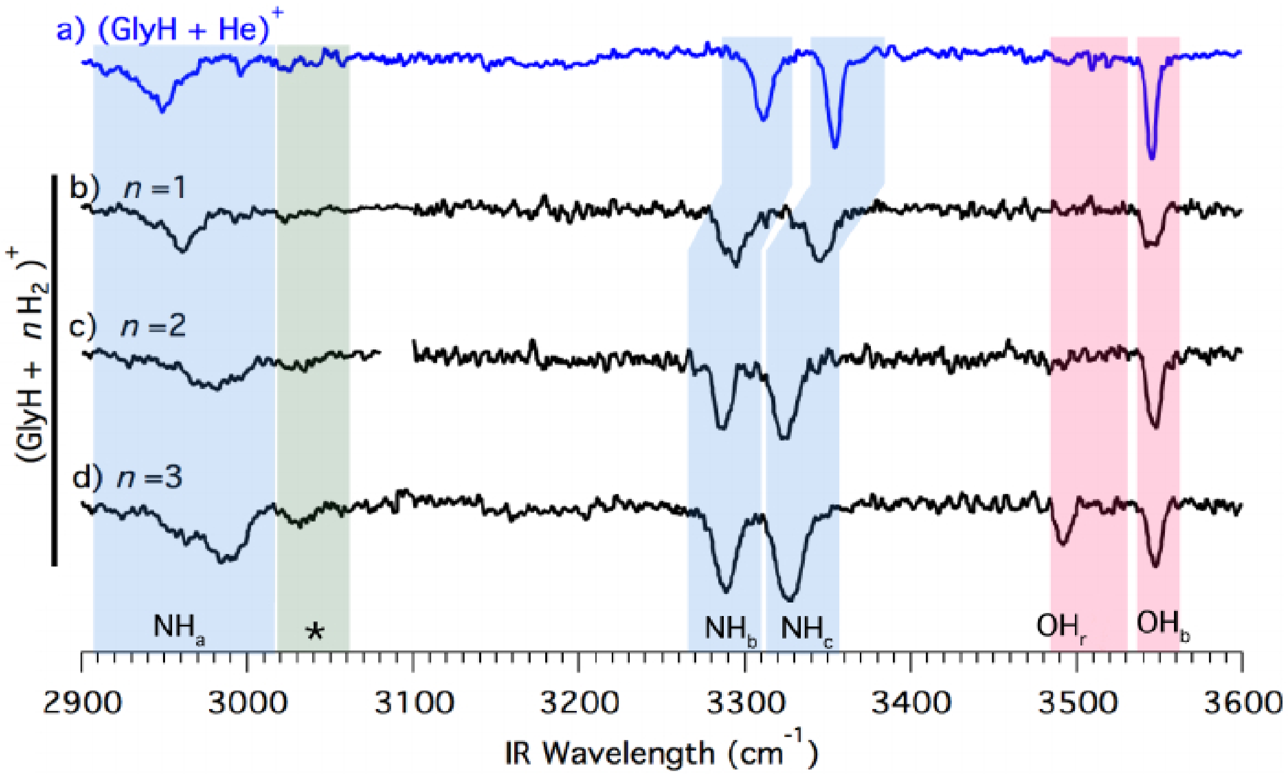


M. Ceotto, G. Di Liberto, and R. Conte *Phys. Rev. Lett.* **119**, 010401 (2017).

H_2 - tagging of Protonated Glycine







A. Masson, E. R. Williams, T. R. Rizzo, *J. Chem. Phys.* **143**, 104313, (2015).

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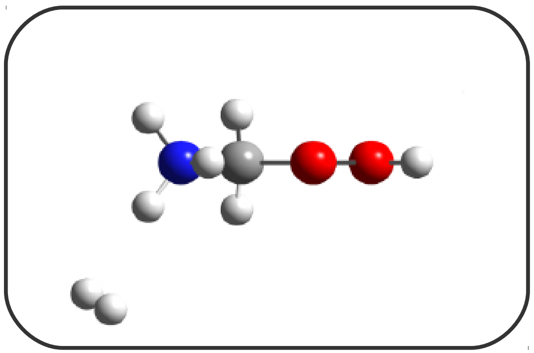

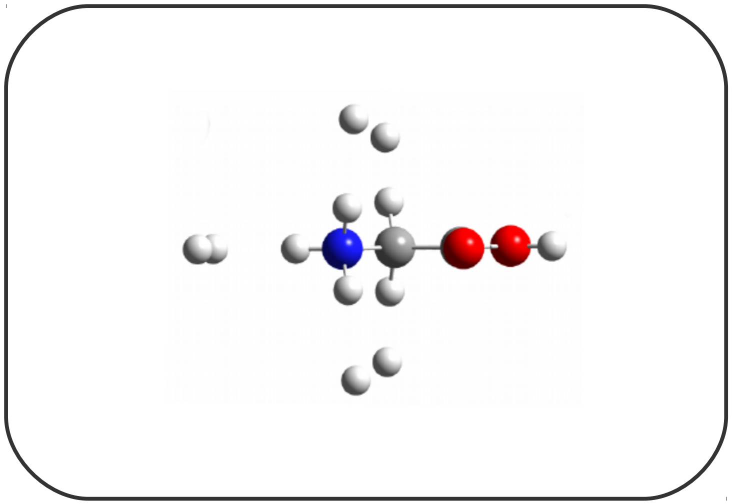

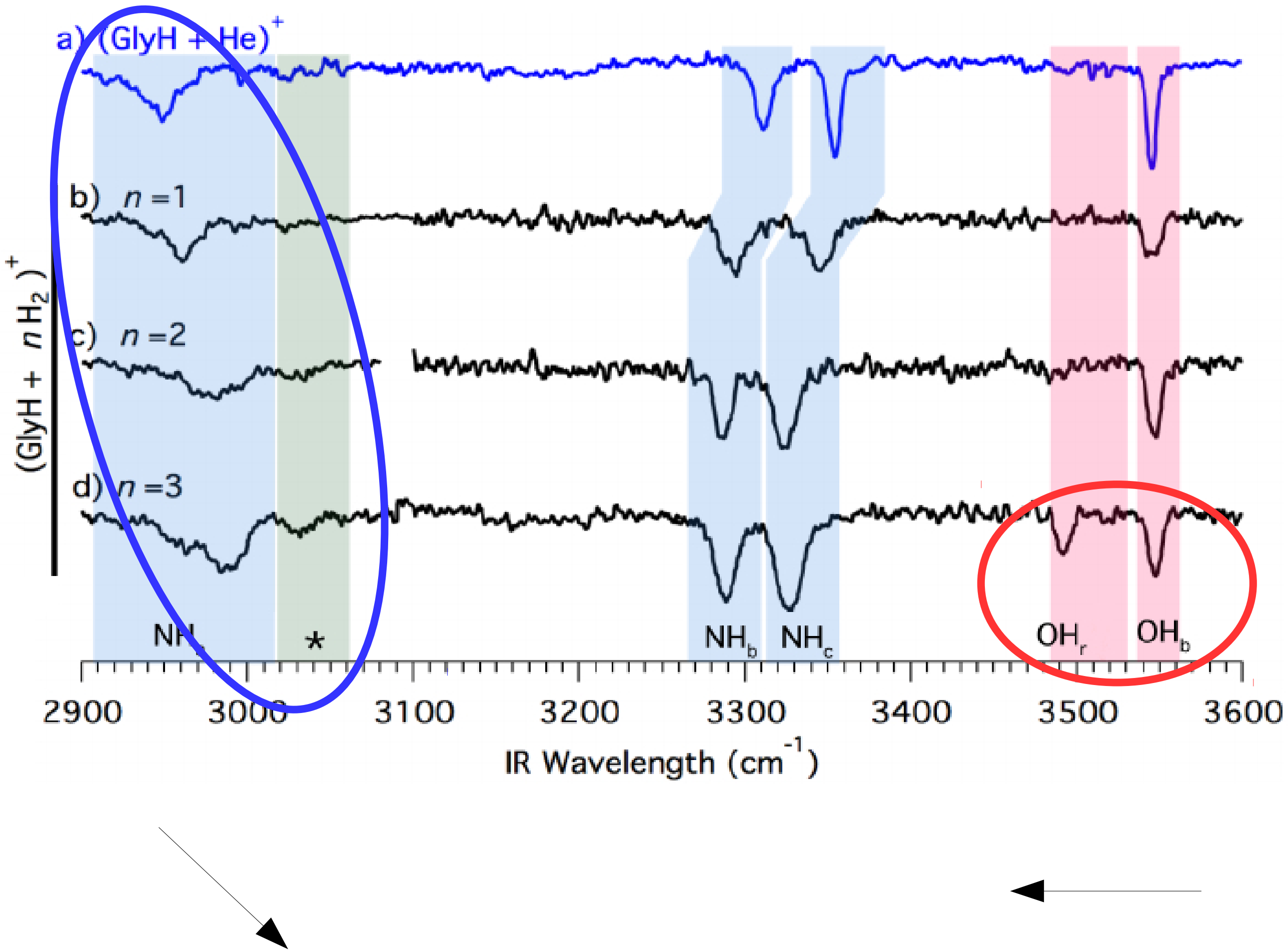

NH
Blue shift

OH
Red shift

A. Masson, E. R. Williams, T. R. Rizzo, *J. Chem. Phys.* **143**, 104313, (2015).

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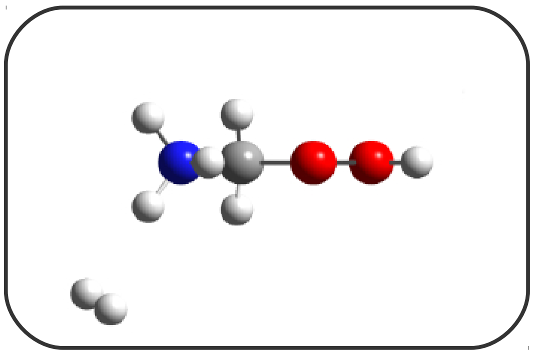

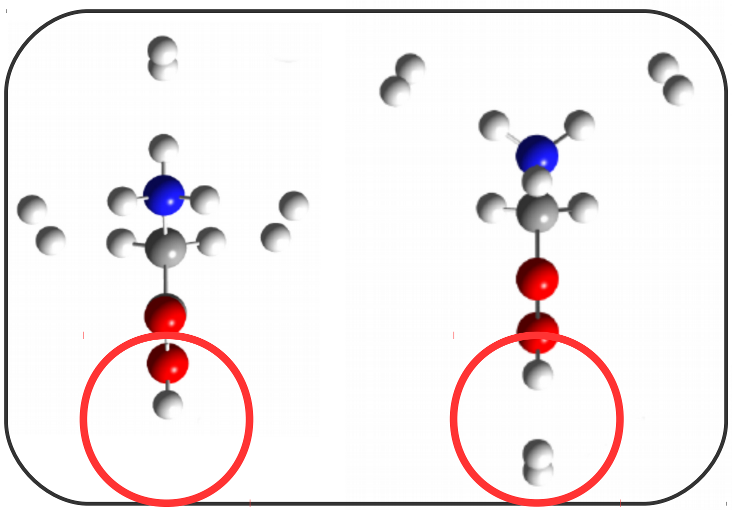

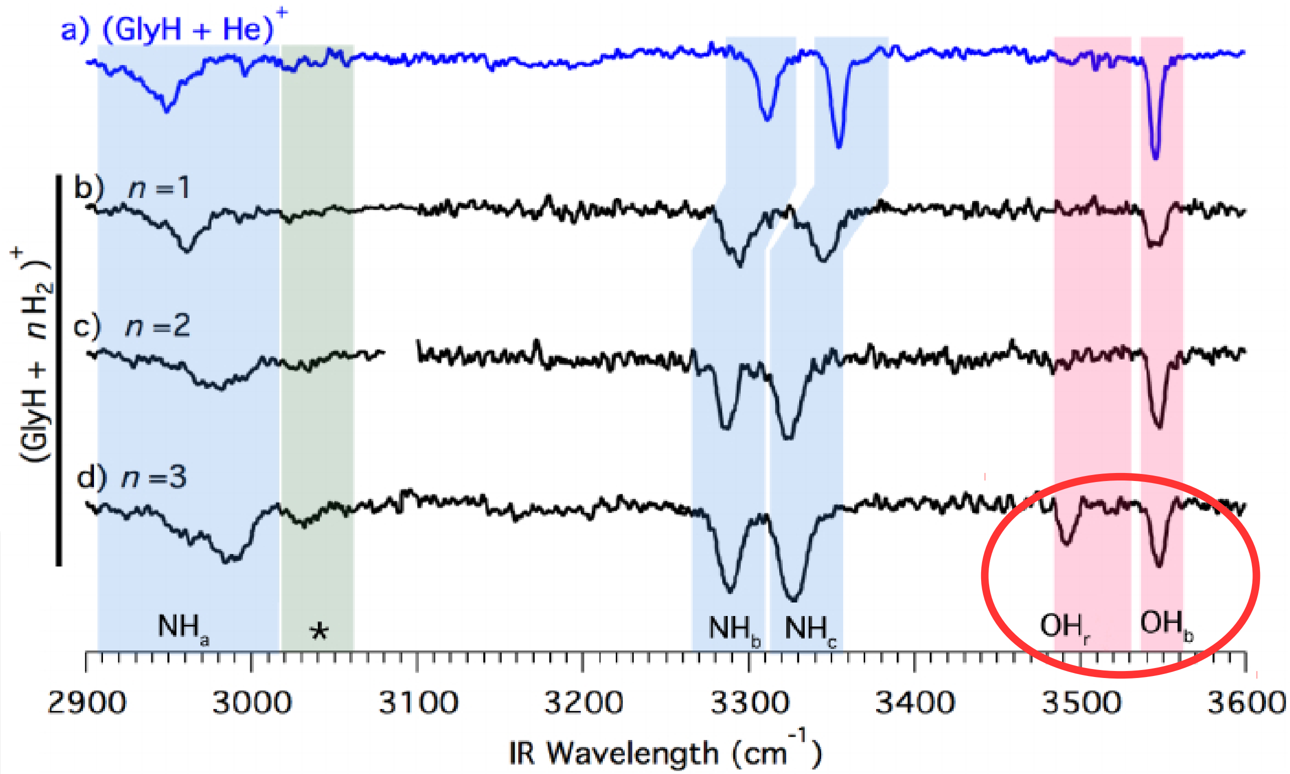

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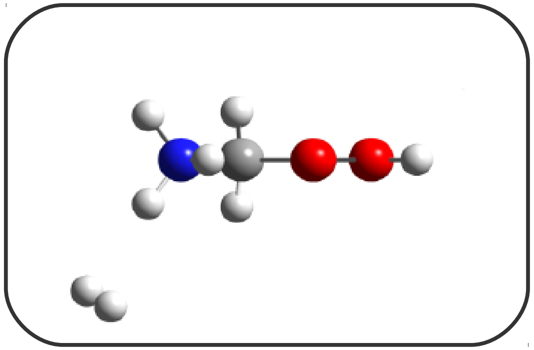
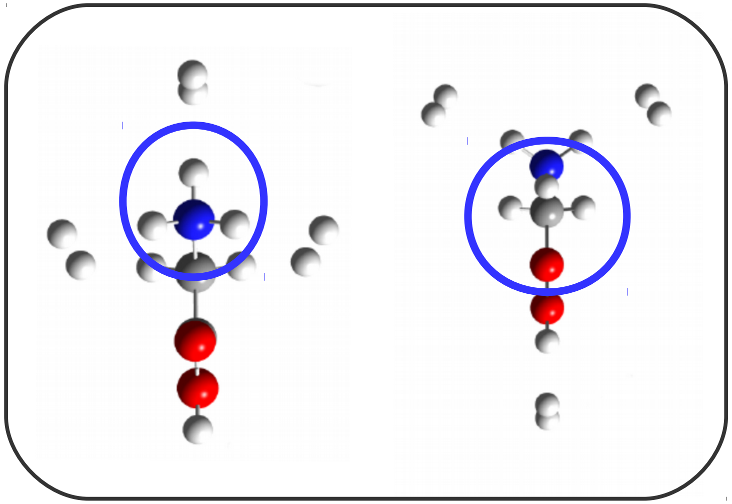
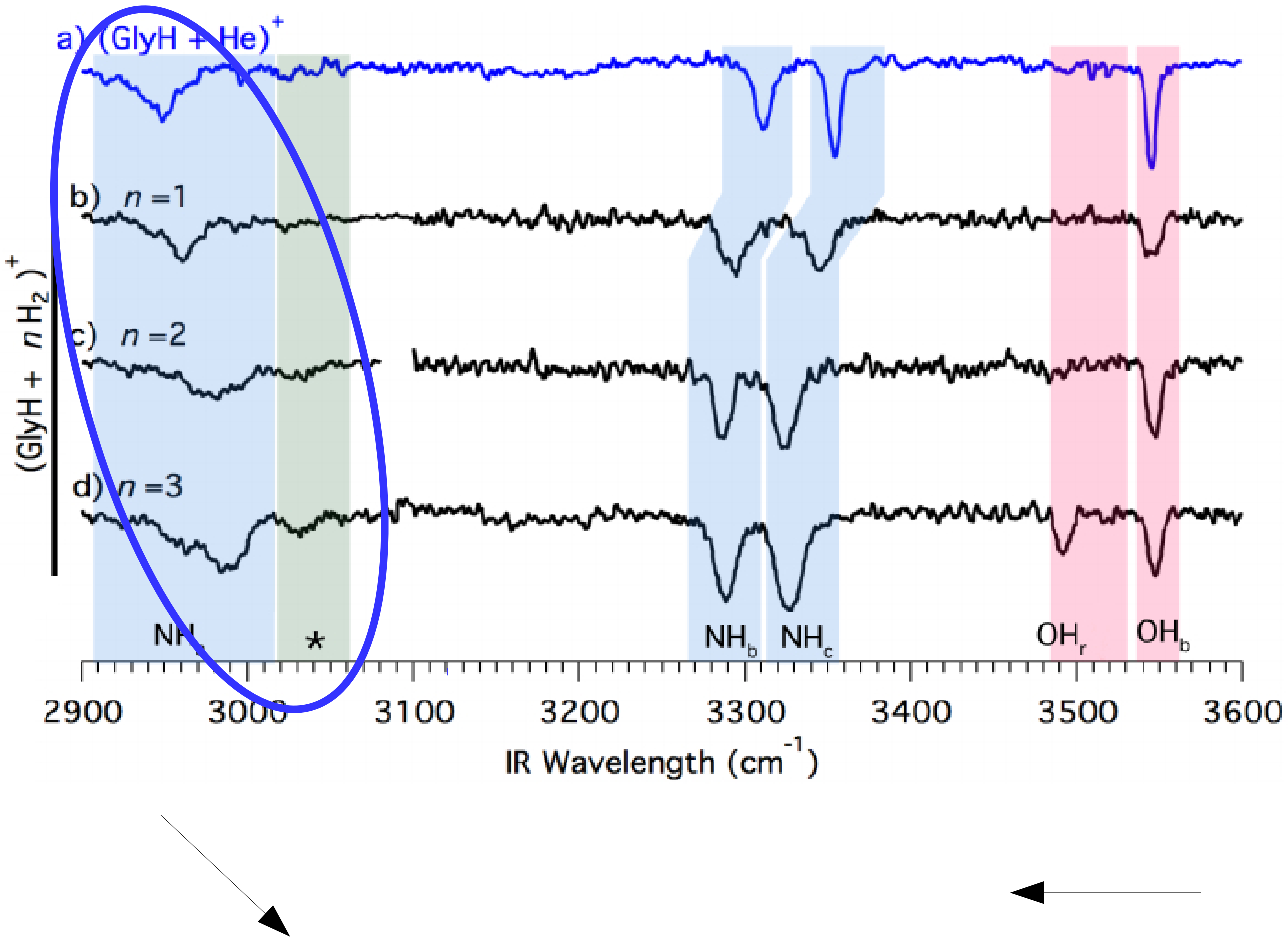
H_2 - tagging of Protonated Glycine





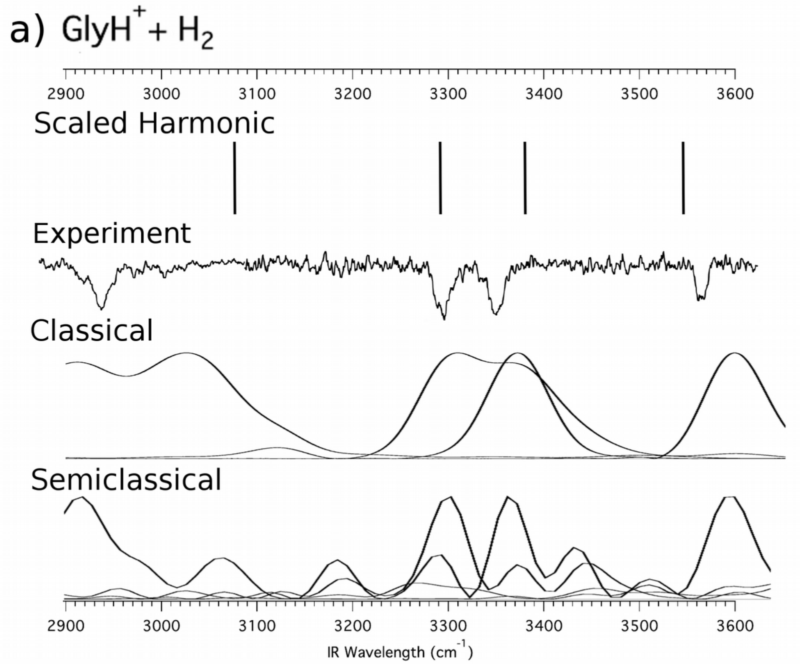


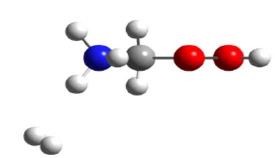
NH
Blue shift

OH
Red shift

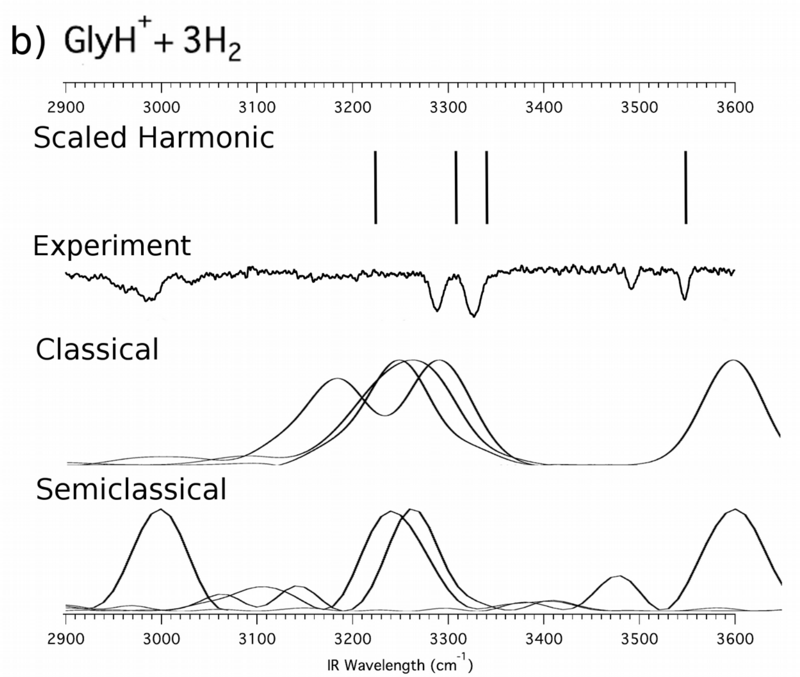
A. Masson, E. R. Williams, T. R. Rizzo, *J. Chem. Phys.* **143**, 104313, (2015).

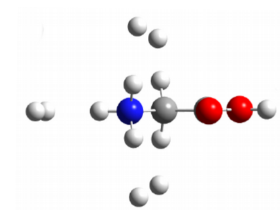
H_2 - tagging of Protonated Glycine



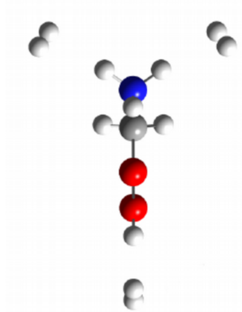


	NH_a	NH_b	NH_c	OH
Exp	2960	3294	3344	3546
DC SCIVR	2920	3280	3370	3610
Harm (0.96)	3077	3298	3380	3546



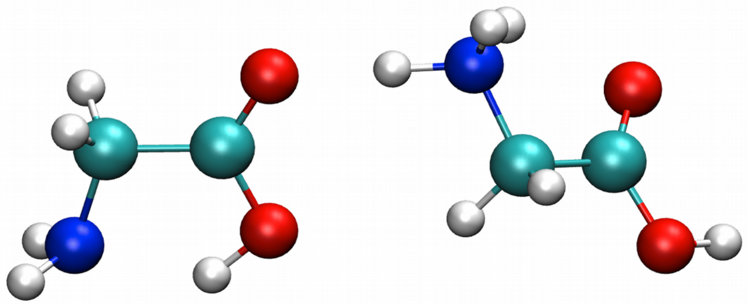


	NH_a	NH_b	NH_c	OH
Exp	3030	3288	3325	3546
DC SCIVR	3000	3240	3270	3600
Harm (0.96)	3223	3304	3340	3546



	OH
Exp	3491
DC SCIVR	3470
Harm (0.945)	3491

Protonated Glycine Dimer

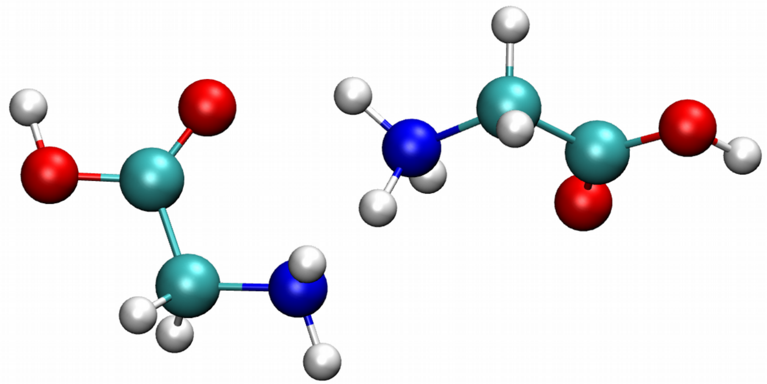


C_s I

Wu and Mc Mahon:

1000-2000 cm^{-1} region. Scaled Harmonic (0.985) points to C_s I as the dominant conformer.

R. Wu and T. Mc Mahon *J. Am. Chem. Soc.* **129**, 4864 (2007).



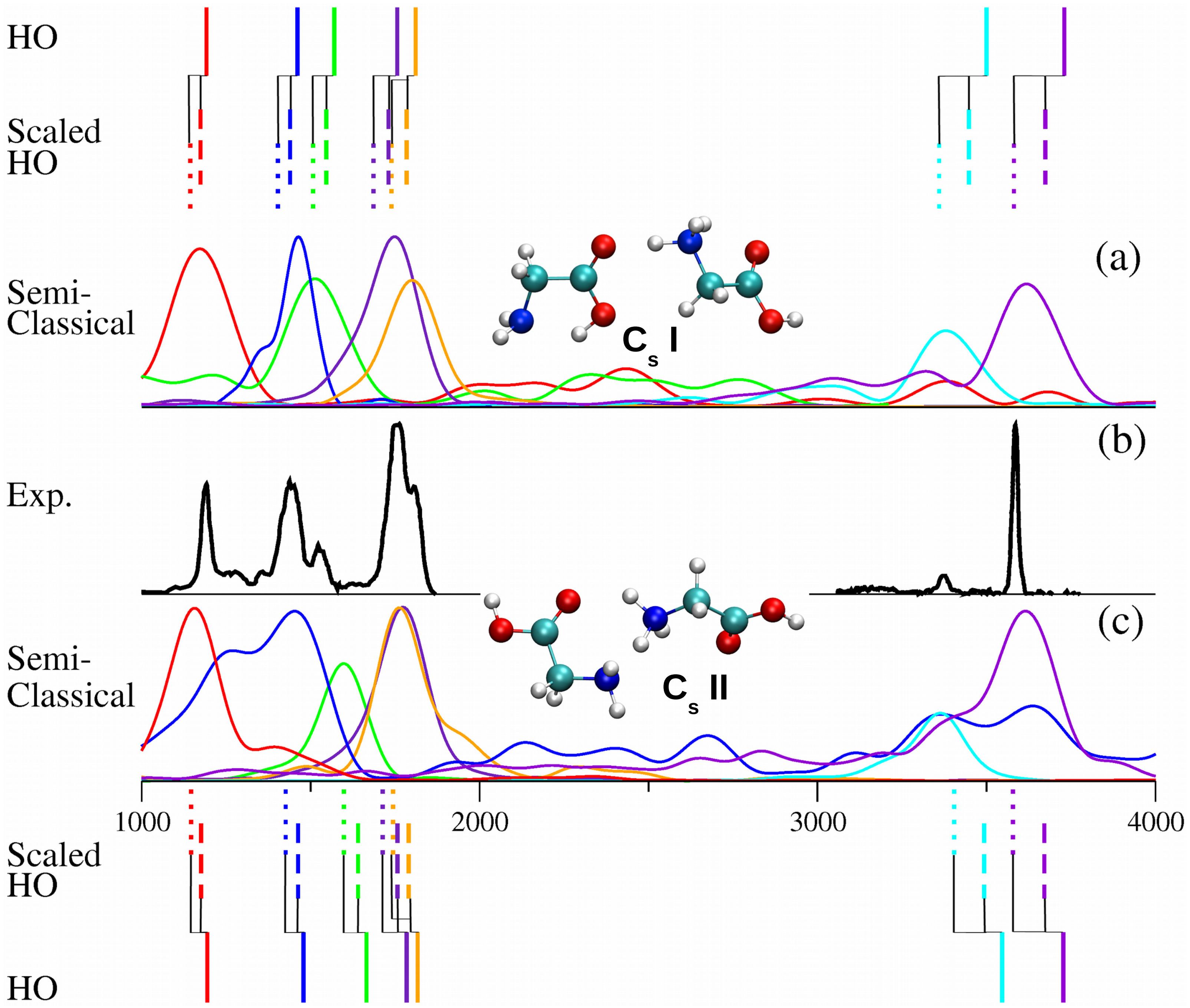
C_s II

Mc Lafferty:

High Frequency region (> 3000 cm^{-1}). Scaled Harmonic (0.97) points to C_s II.

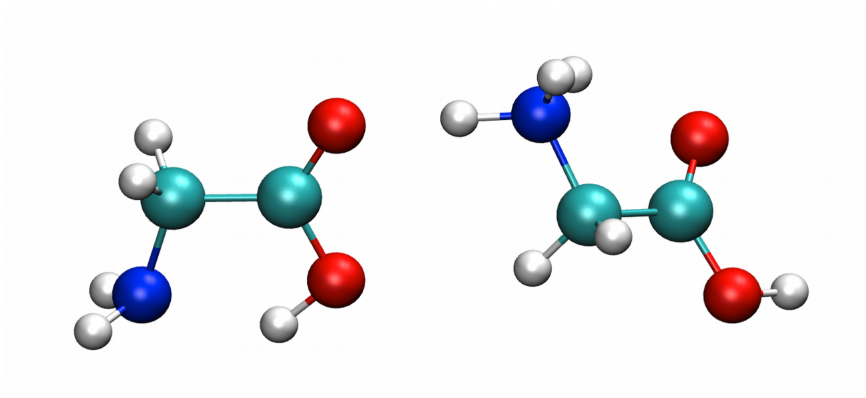
F. Mc Lafferty et al. *J. Am. Chem. Soc.* **127**, 4076 (2005).

Protonated Glycine Dimer



Protonated Glycine Dimer

								MAE
Exp	1191	1439	1523	1757	1808	3372	3585	
DC SCIVR (Cs I)	1172	1450	1511	1756	1804	3375	3618	12
DC SCIVR (Cs II)	1155	1466	1598	1771	1761	3362	3615	35
Scaled HO (0.985)	1174	1439	1546	1730	1784	3448	3674	37
Scaled HO (0.96)	1144	1403	1507	1686	1739	3360	3581	37



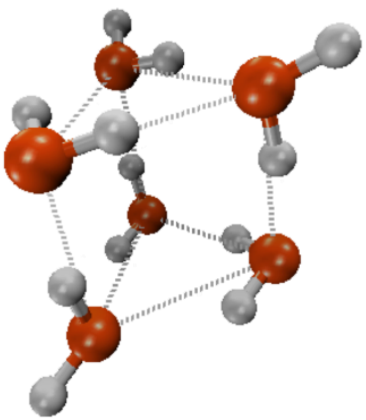
C_s I

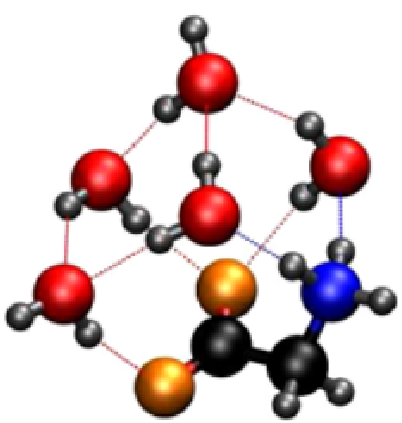
Summary and Perspectives

Semiclassical Dynamics is a Powerful Tool for Molecular Spectroscopy.
It may be adopted also for Large Molecular and Supra-Molecular Systems.

Semiclassical Dynamics correctly describes Quantum Anharmonicities.
Ability to interpret and explain Experimental Findings.

Vibrational Spectroscopy of Water Clusters





Protonated / Zwitterionic Glycine Solvated by Water

Acknowledgments

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CINECA

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Iscra C Project “VIBROGLY”

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European Commission

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Ceotto's Group

UNIVERSITÀ DEGLI STUDI
DI MILANO
DIPARTIMENTO DI CHIMICA

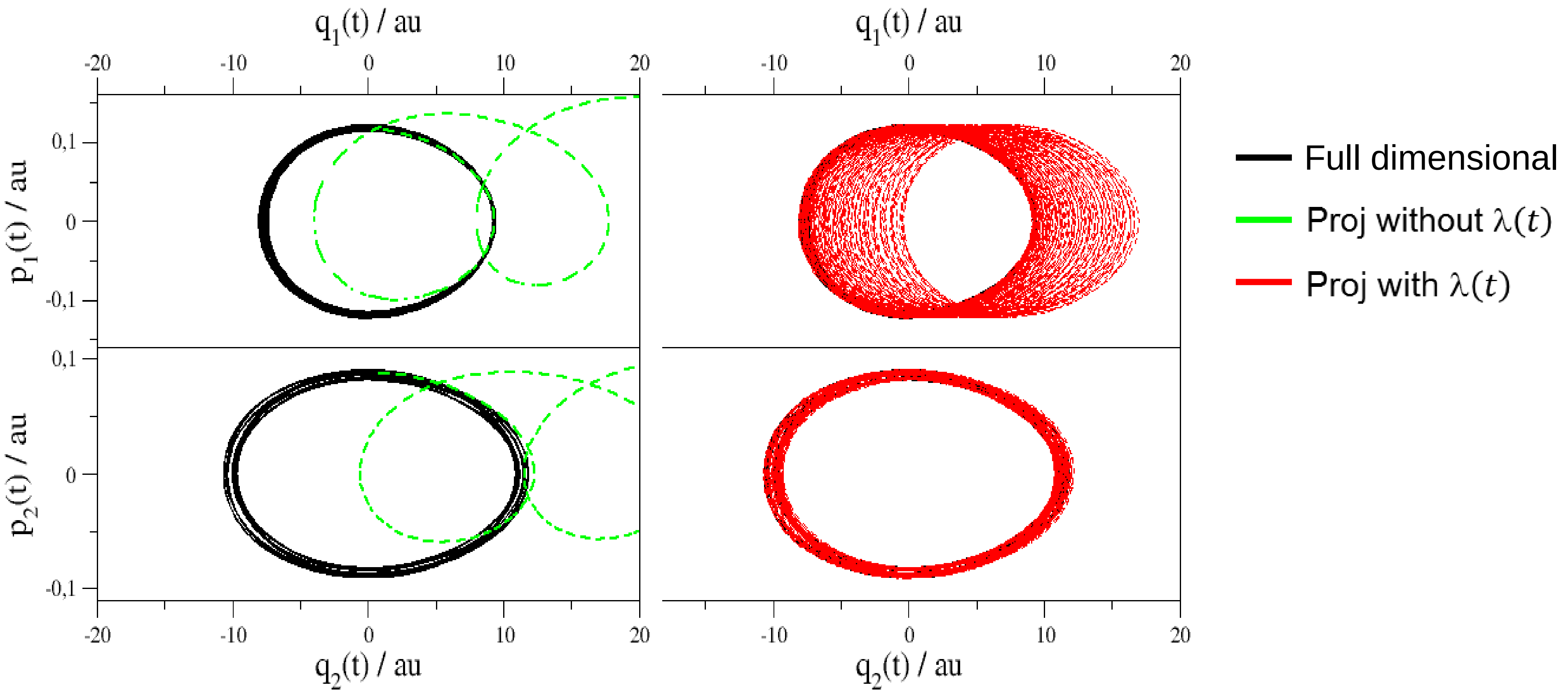
Thank You For Your Kind Attention

Semiclassical Dynamics in High Dimensionality

$$\tilde{V}\left(\tilde{\mathbf{q}}_s\right) \equiv \mathrm{V}\left(\tilde{\mathbf{q}}_s ; \mathbf{q}_{N_{vib}-M}\right)$$

$$\tilde{V}\left(\mathbf{q}_s\right) = V\left(\tilde{\mathbf{q}}_s ; \mathbf{q}^{eq}_{N_{vib}-M}\right)$$

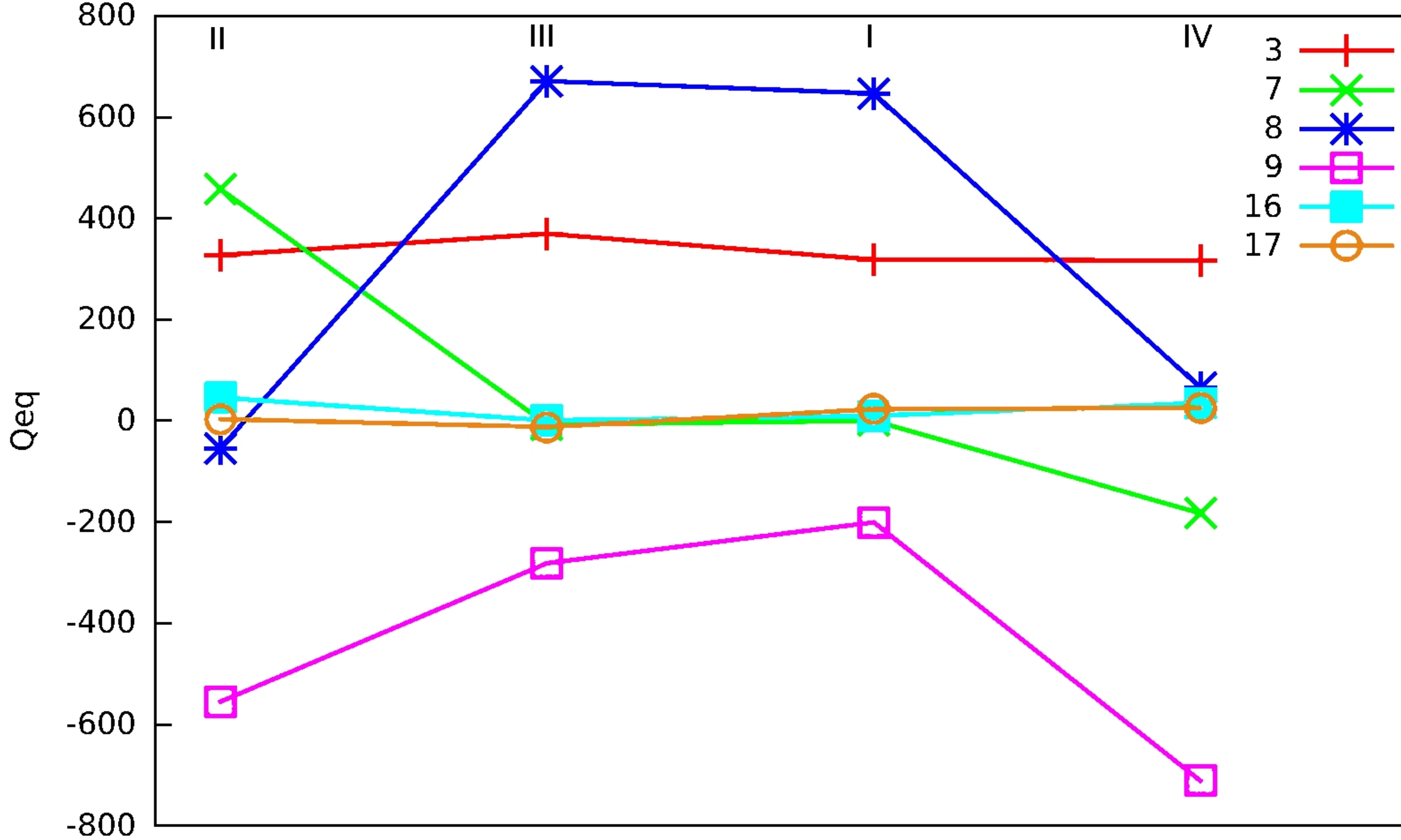
$$\tilde{V}\left(\mathbf{q}_s\right) = V\left(\tilde{\mathbf{q}}_s ; \mathbf{q}^{eq}_{N_{vib}-M}\right) + \lambda\left(t\right)$$



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

Conformer Inter-conversion

$$\mathcal{H}_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \qquad \mathcal{D}_H = \mathcal{U}^{-1}\mathcal{H}\mathcal{U} \qquad Q_{eq,i} = \sum_j \mathcal{U}_{ij}^T X_{eq,j}$$



Importance of Multiple Coherent Sampling