Vibrational tunneling spectra of molecules via instanton theory

Marko Cvitaš

University of Zagreb

Mihael Eraković

Ruđer Bošković Institute

hrzz Croatian Science Foundation

Europska unija Zajedno do fondova EU

EUROPSKI STRUKTURNI I INVESTICIJSKI FONDOVI

Operativni program KONKURENTNOST I KOHEZIJA

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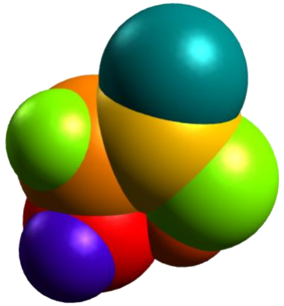
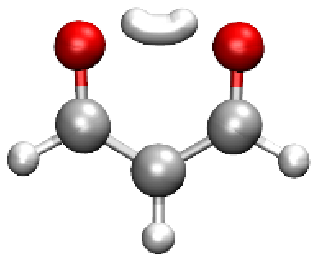
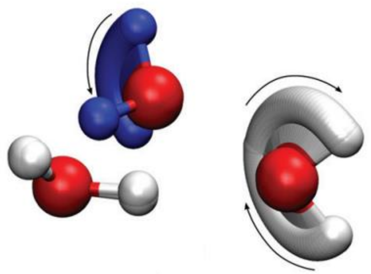


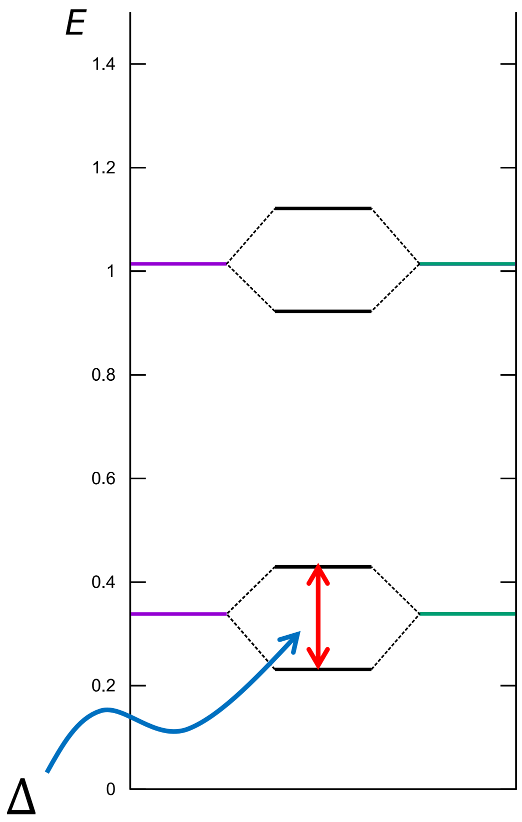
Outline

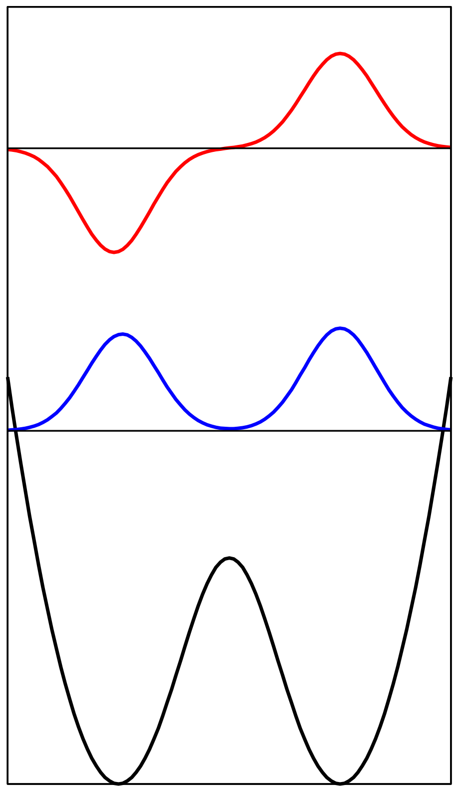
- Tunneling splittings & vibrational spectra
- Instanton theory of tunneling splittings
  - RPI, JFI, modified WKB
  - ground state, excited states
- Results: - malonaldehyde



  - water pentamer
  - water trimer







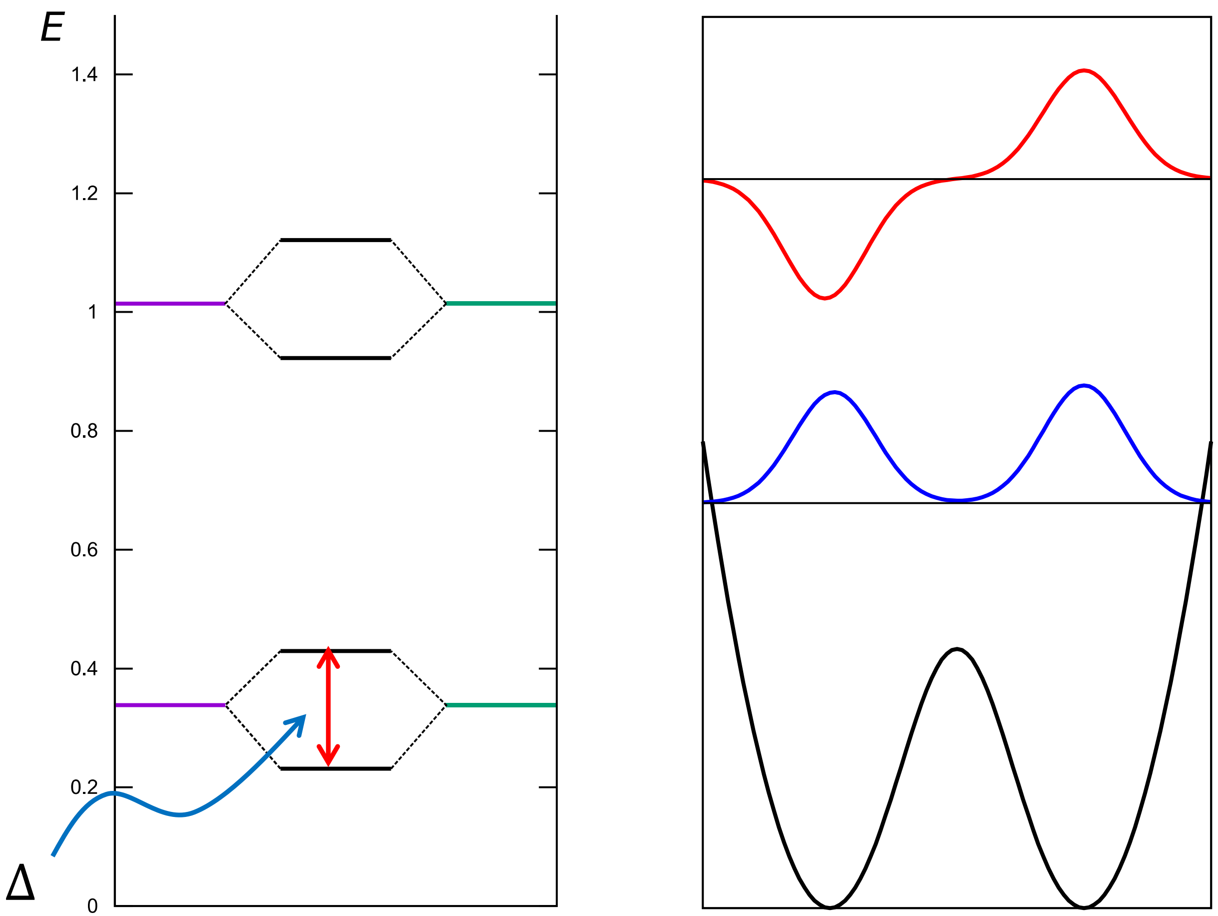
Tunneling splittings & vibrational spectra

Symmetric double well:

- Localized well states interact via tunneling to produce a delocalized wavefunctions.
- 2 × 2 matrix model: $\mathbf{H} = \begin{pmatrix} 0 & h \\ h & 0 \end{pmatrix}$
- Eigenvalues : ±*h.*
- Eigenfunctions : $\psi_+ = \frac{1}{\sqrt{2}}\phi^{(\mathrm{L})} + \frac{1}{\sqrt{2}}\phi^{(\mathrm{R})}$

$$\psi_- = \frac{1}{\sqrt{2}}\phi^{(\mathrm{L})} - \frac{1}{\sqrt{2}}\phi^{(\mathrm{R})}$$

- Tunneling splitting: $\Delta = -2h$



Tunneling splittings & vibrational spectra

Slightly asymmetric double well:

- 2 × 2 matrix model: $\mathbf{H} = \begin{pmatrix} 0 & h \\ h & d \end{pmatrix}$

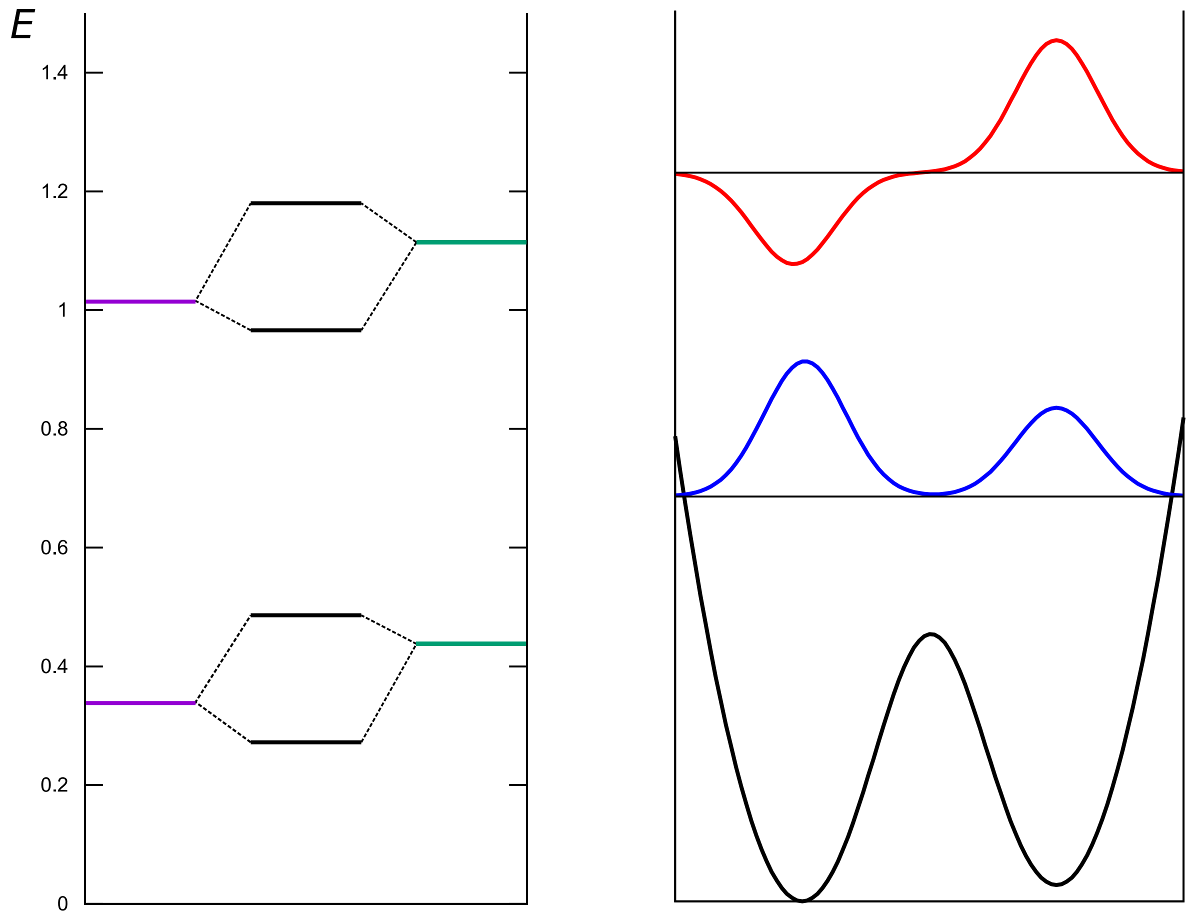
- Tunneling splitting: $\Delta = \sqrt{d^2 + 4h^2}$

- Eigenfunctions:

$$\psi_+ = \cos(\varphi)\,\phi^{(\mathrm{L})} + \sin(\varphi)\phi^{(\mathrm{R})}$$

$$\psi_- = \sin(\varphi)\,\phi^{(\mathrm{L})} - \cos(\varphi)\,\phi^{(\mathrm{R})}$$

$$\tan(\varphi/2) = -\frac{h}{d}$$

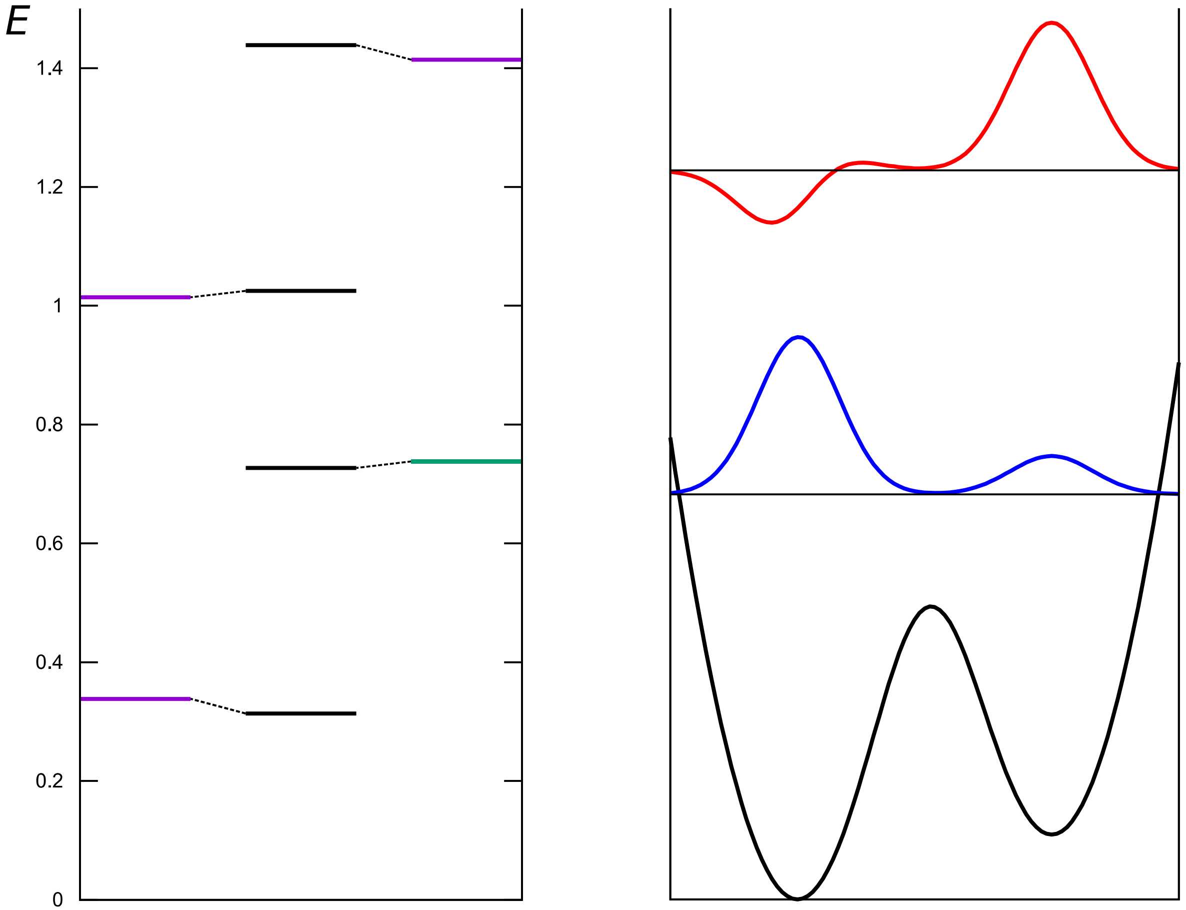


Tunneling splittings & vibrational spectra

Double well with large asymmetry:

- Localized vibrational wavefunctions.

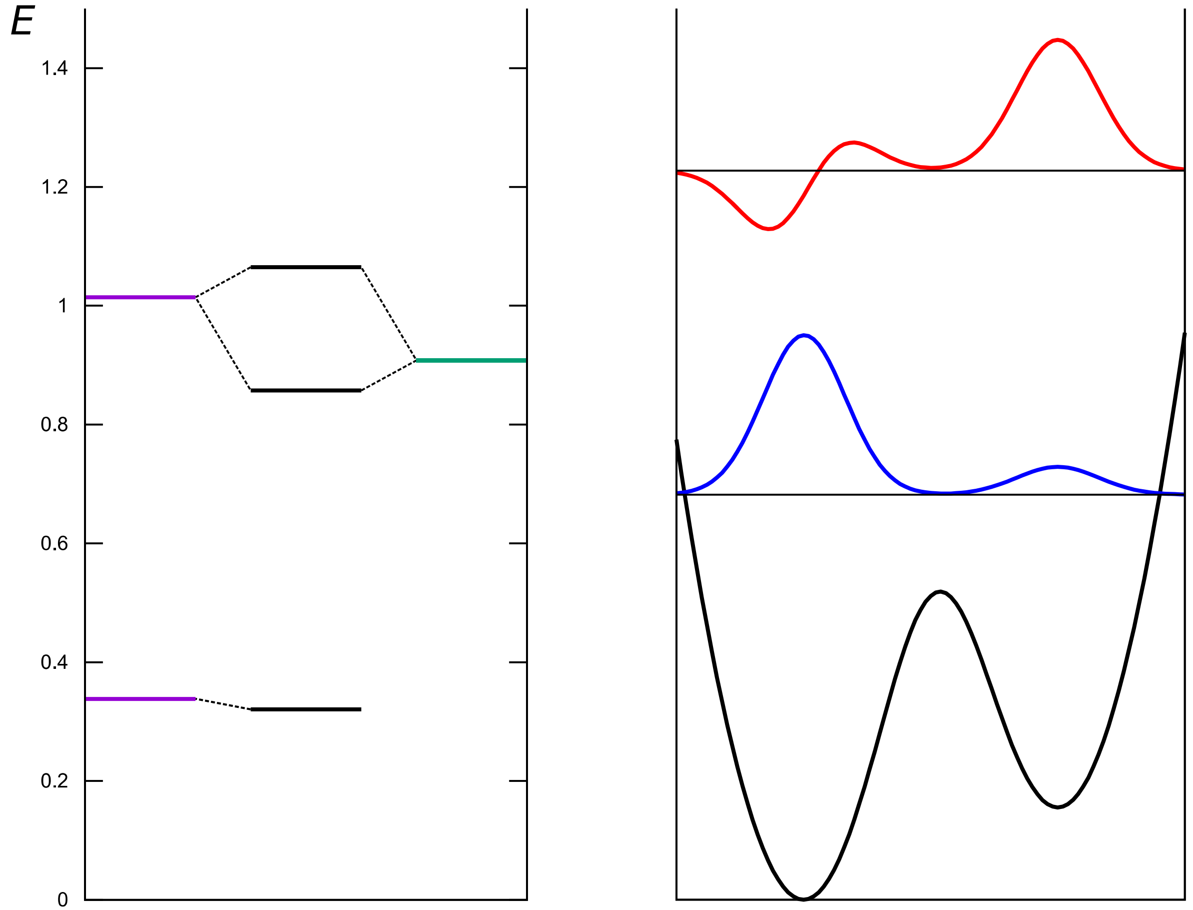
$$\psi_+ \approx \phi^{(\mathrm{L})}$$
$$\psi_- \approx \phi^{(\mathrm{R})}$$
$$\varphi \approx 0$$



Tunneling splittings & vibrational spectra

Double well with large asymmetry:

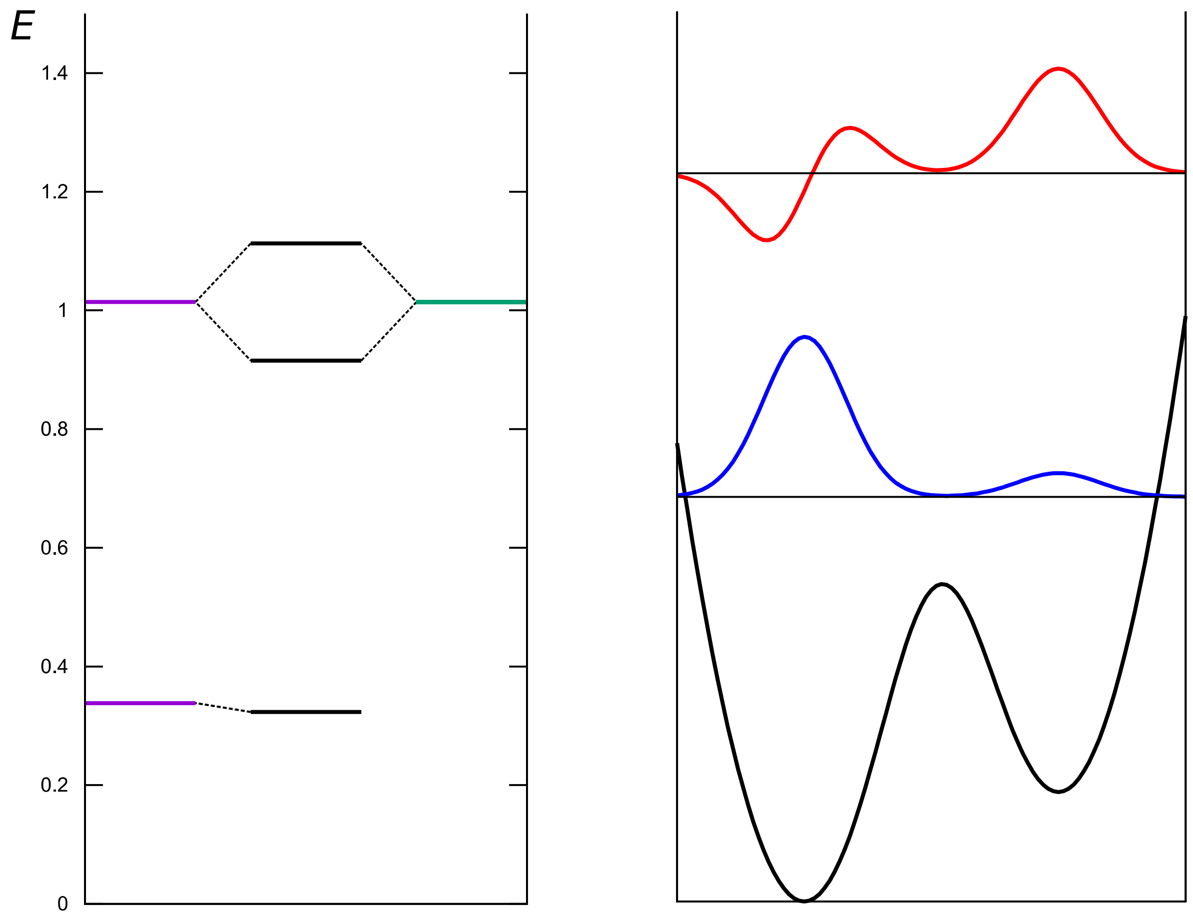
- Interaction of non-equivalent vibrational states of different minima.



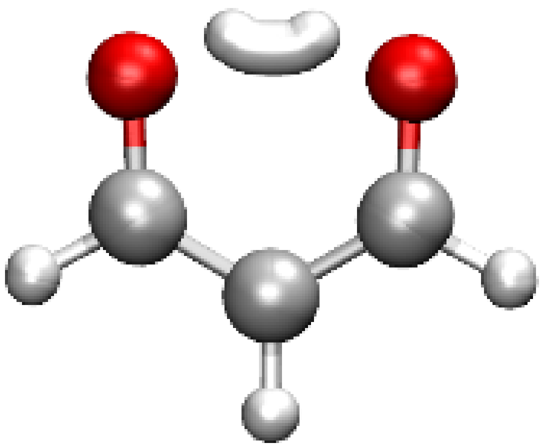
Tunneling splittings & vibrational spectra

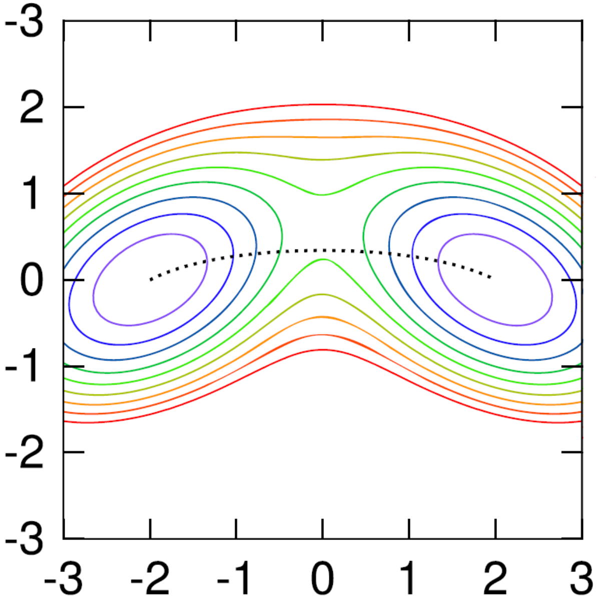
Double well with large asymmetry:

- Non-equivalent vibrational states of different minima in resonance.



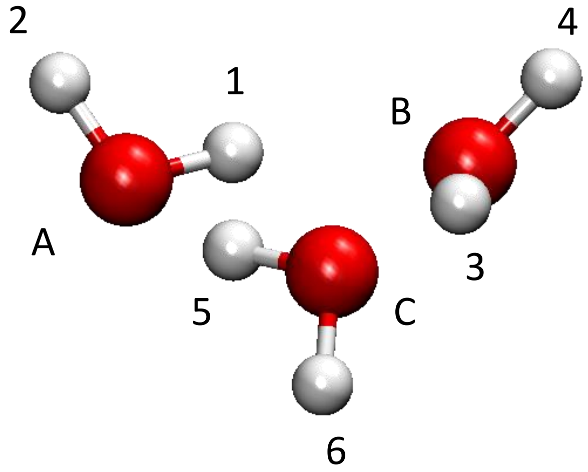
Tunneling splittings & vibrational spectra





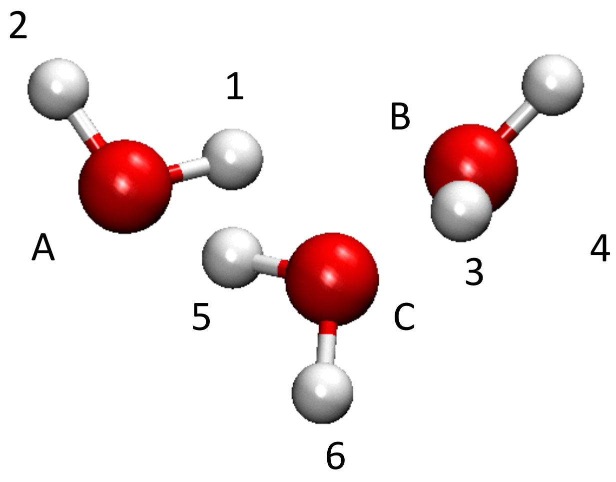
1. Symmetric systems

Tunneling splittings & vibrational spectra



1. Symmetric systems
2. Tunneling path asymmetry

Tunneling splittings & vibrational spectra



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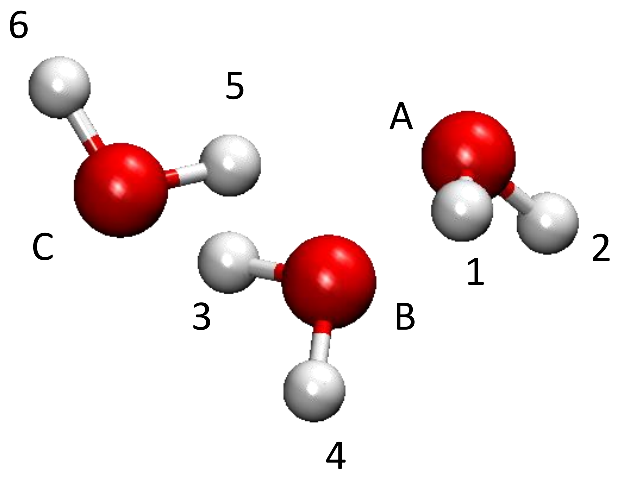
Tunneling splittings & vibrational spectra



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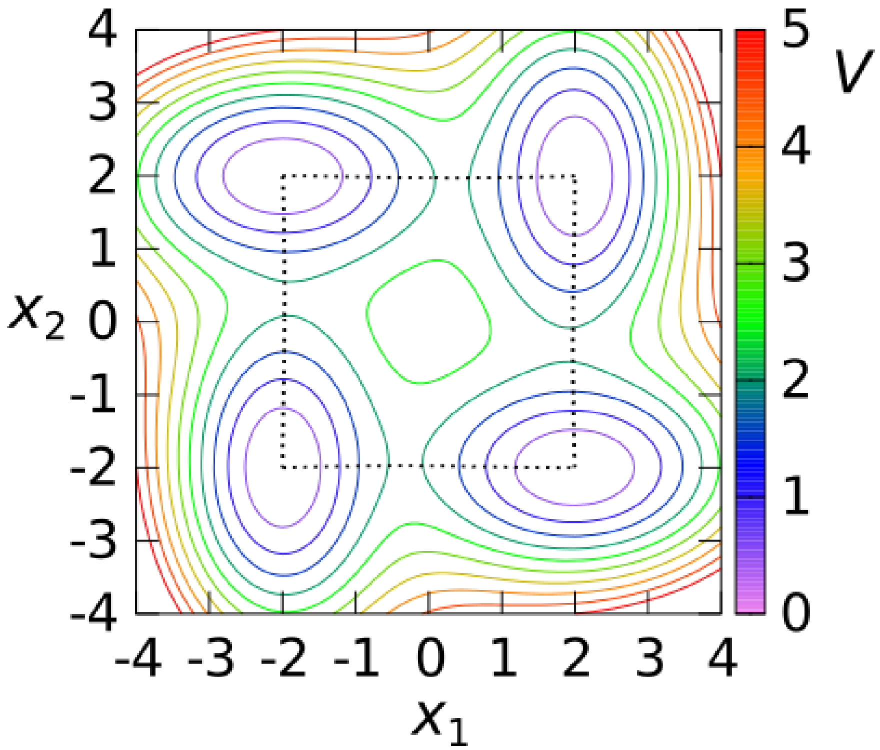
Tunneling splittings & vibrational spectra



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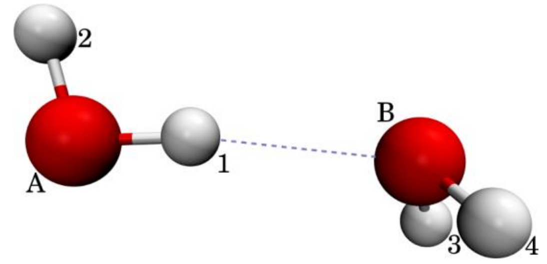
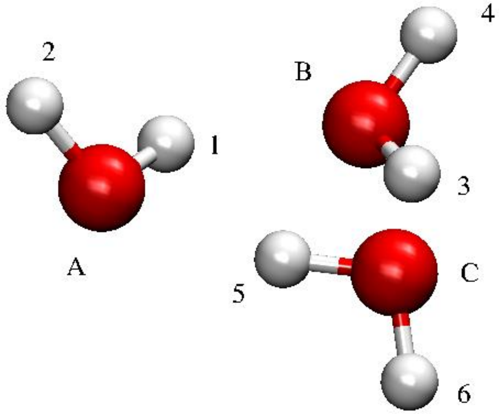
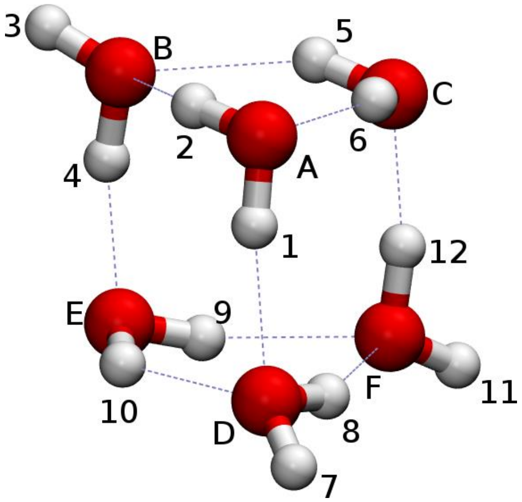
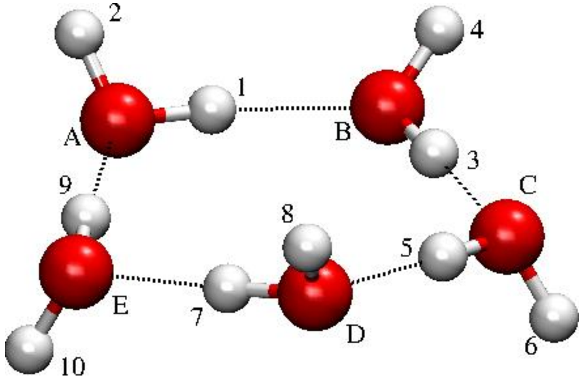
Tunneling splittings & vibrational spectra



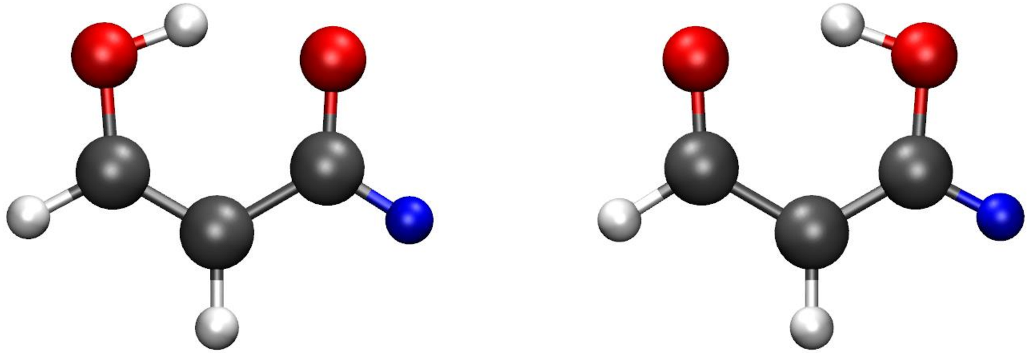


1. Symmetric systems
2. Tunneling path asymmetry



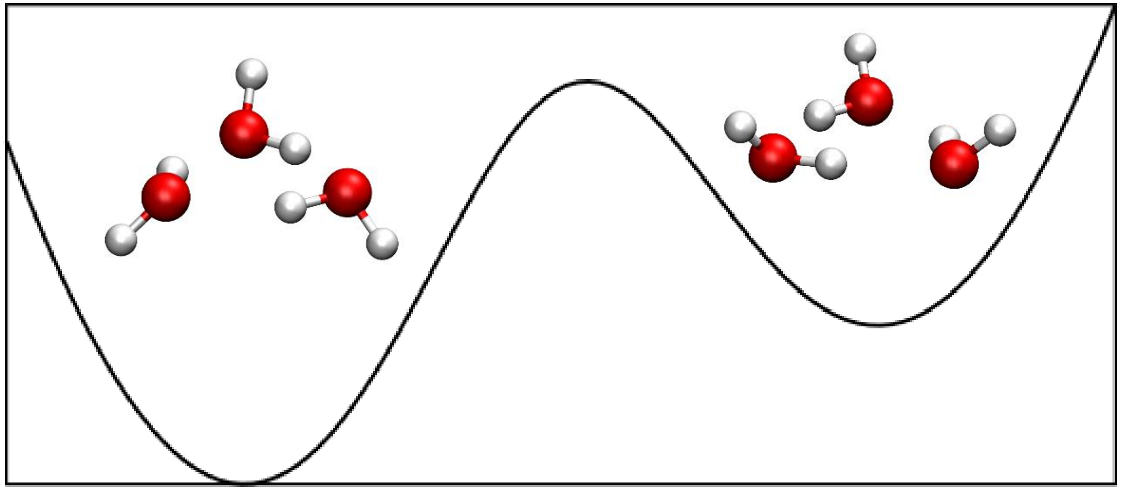


Tunneling splittings & vibrational spectra



1. Symmetric systems
2. Tunneling path asymmetry
3. Energy asymmetry (asymmetrically deuterated systems)

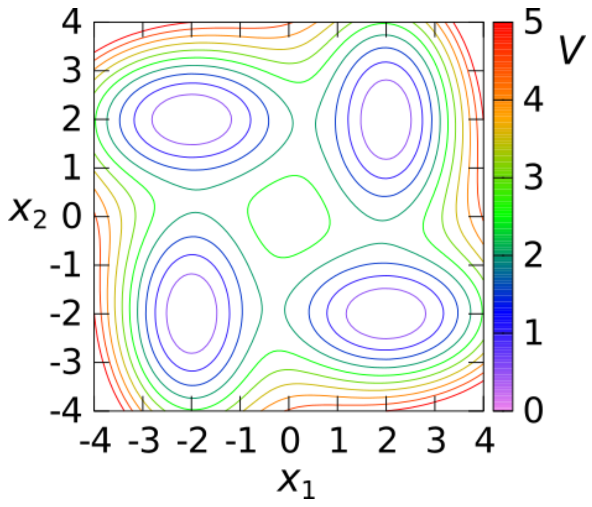
Tunneling splittings & vibrational spectra



1. Symmetric systems
2. Tunneling path asymmetry
3. Energy asymmetry (asymmetrically deuterated systems)
4. Energy & shape asymmetry

Tunneling splittings & vibrational spectra

- Physical systems with two or more energetically stable minima are ubiquitous in chemistry and physics.
- Bound states localized in such wells, separated by potential barriers, interact via tunneling, which results in observable shifts of their energies.
- These shifts are sensitive to PES away from the minima and can vary over many orders of magnitude even in a single system (*e.g.*, 3 orders of magnitude in water dimer for different pathways, or in water trimer and pentamer for different mode excitations).
- Variational methods are costly because basis set needs to cover regions between the wells sufficiently densely to obtain enough resolution to extract the energy shifts.
- Semiclassical *instanton method* : in full dimensionality
    - fewer PES evaluations
    - on-the-fly with accurate electronic structure methods
    - works better for high barriers and smaller energy shifts
    - black box: no basis set convergence, integral evaluations, …
    - can be combined with more accurate dynamical methods



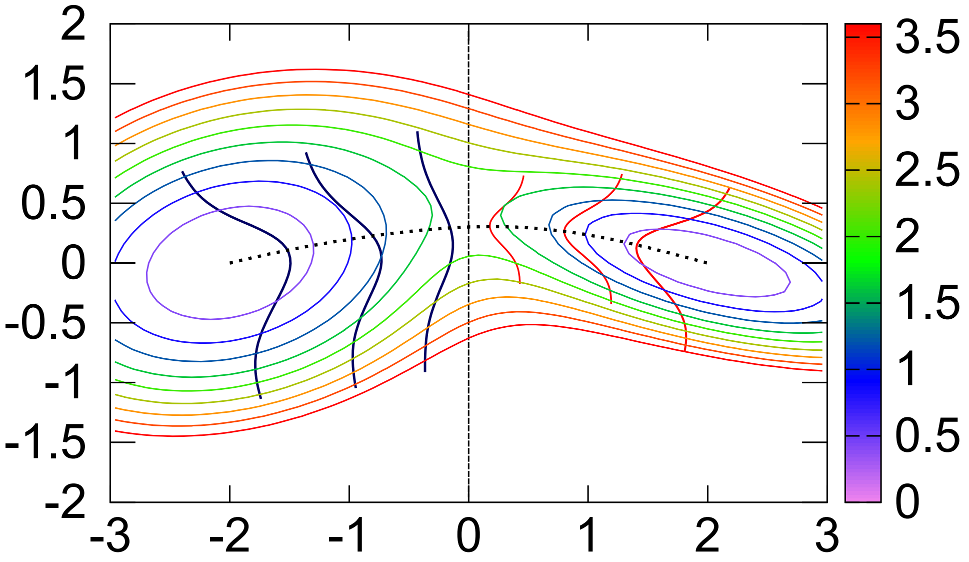
Instanton theory

ground state tunneling splittings

$$\Psi = \begin{pmatrix} \phi^{(L)} \\ \phi^{(R)} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} \mathbf{E}^{(L)} & \mathbf{h} \\ \mathbf{h}^{\top} & \mathbf{E}^{(R)} \end{pmatrix}$$

$$\mathbf{H}\Psi = E\Psi$$



HERRING FORMULA

$$h_{ij} = -\frac{1}{2}\int_{\Sigma}\left(\phi_i^{(L)}\frac{\partial}{\partial S}\phi_j^{(R)} - \phi_j^{(R)}\frac{\partial}{\partial S}\phi_i^{(L)}\right)d\Sigma$$

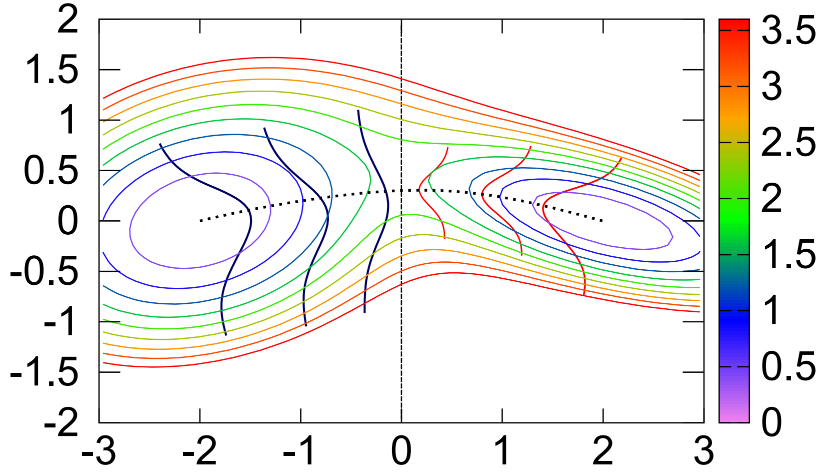
Erakovic, Cvitas, JCTC 2022.

Instanton theory
ground state tunneling splittings

MODIFIED WKB

Localized wavefunctions in Herring formula can be approximated using WKB:

$$h_{ij} = -\frac{1}{2}\int_{\Sigma}\left(\phi_i^{(\mathrm{L})}\frac{\partial}{\partial S}\phi_j^{(\mathrm{R})} - \phi_j^{(\mathrm{R})}\frac{\partial}{\partial S}\phi_i^{(\mathrm{L})}\right)d\Sigma$$



$$\phi = e^{-\frac{1}{\hbar}(W_0 + W_1\hbar)}$$

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_0}{\partial x_i} = 2V(\mathbf{x})$$

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_1}{\partial x_i} - \frac{1}{2}\frac{\partial^2 W_0}{\partial x_i \partial x_i} + E = 0$$

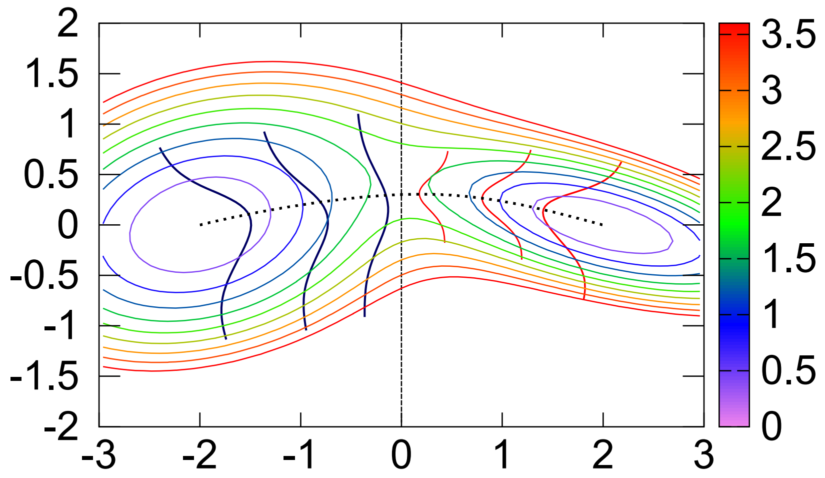
Mil'nikov, Nakamura, JCP 2005. *Erakovic, Cvitas, JCP* 2020.

Instanton theory
ground state tunneling splittings

MODIFIED WKB

Localized wavefunctions in Herring formula can be approximated using WKB:

$$h_{ij} = -\frac{1}{2}\int_{\Sigma}\left(\phi_i^{(\mathrm{L})}\frac{\partial}{\partial S}\phi_j^{(\mathrm{R})} - \phi_j^{(\mathrm{R})}\frac{\partial}{\partial S}\phi_i^{(\mathrm{L})}\right)d\Sigma$$



Hessian along characteristic

$$\frac{d}{d\tau}A + A^2 = \Omega^2(\tau)$$

$$\phi = e^{-\frac{1}{\hbar}(W_0 + W_1\hbar)}$$

Change in amplitude as exp(-Action)

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_0}{\partial x_i} = 2V(\mathbf{x})$$

Method of characteristics →

$$W_0(S,\Delta\mathbf{x}) = \int_0^S \sqrt{2V(S')}dS' + \frac{1}{2}\Delta\mathbf{x}^\top\mathbf{A}\,\Delta\mathbf{x}$$

→ Wavefunction in orthogonal plane

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_1}{\partial x_i} - \frac{1}{2}\frac{\partial^2 W_0}{\partial x_i \partial x_i} + E = 0$$

Equation of characteristic: Newton's equation of motion on inverted potential

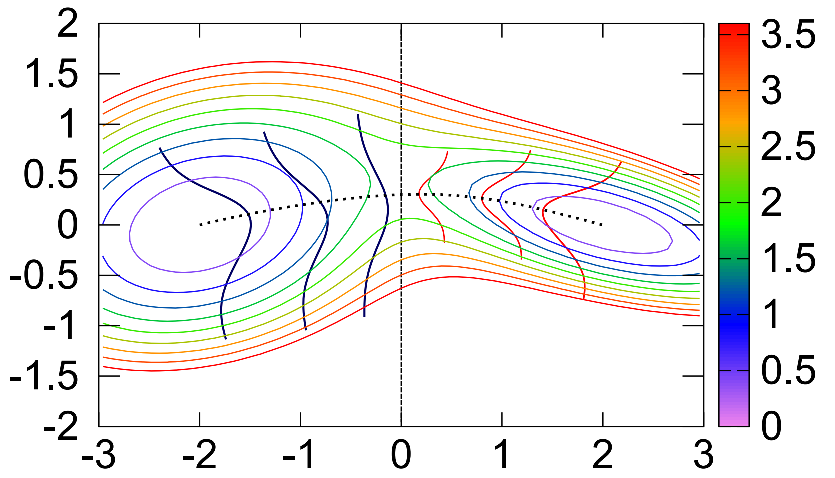
Mil'nikov, Nakamura, JCP 2005. *Erakovic, Cvitas, JCP* 2020.

Instanton theory
ground state tunneling splittings

MODIFIED WKB

Localized wavefunctions in Herring formula can be approximated using WKB:

$$h_{ij} = -\frac{1}{2}\int_{\Sigma}\left(\phi_i^{(\mathrm{L})}\frac{\partial}{\partial S}\phi_j^{(\mathrm{R})} - \phi_j^{(\mathrm{R})}\frac{\partial}{\partial S}\phi_i^{(\mathrm{L})}\right)d\Sigma$$



$$\frac{d}{d\tau}A + A^2 = \Omega^2(\tau)$$

$$\phi = e^{-\frac{1}{\hbar}(W_0 + W_1\hbar)}$$

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_0}{\partial x_i} = 2V(\mathbf{x}) \xrightarrow{\text{Method of characteristics}} W_0(S,\Delta\mathbf{x}) = \int_0^S \sqrt{2V(S')}dS' + \frac{1}{2}\Delta\mathbf{x}^{\top}\mathbf{A}\,\Delta\mathbf{x}$$

$$\frac{\partial W_0}{\partial x_i}\frac{\partial W_1}{\partial x_i} - \frac{1}{2}\frac{\partial^2 W_0}{\partial x_i \partial x_i} + E = 0 \xrightarrow{\text{Integration along characteristic}} W_1(S) = \frac{1}{2}\int_0^S \frac{\mathrm{Tr}(\mathbf{A}(S') - \mathbf{A}_0)}{\sqrt{2V(S')}}dS' \longrightarrow$$

Change in amplitude due to ZPE of orthogonal modes

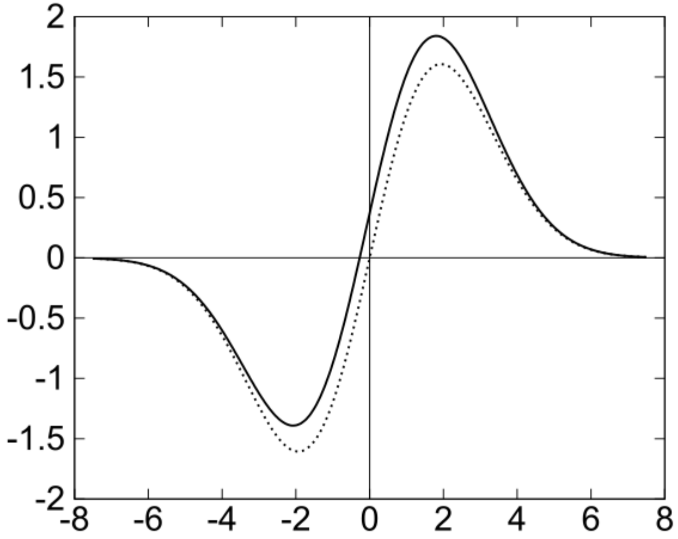
Instanton theory
excited state tunneling splittings

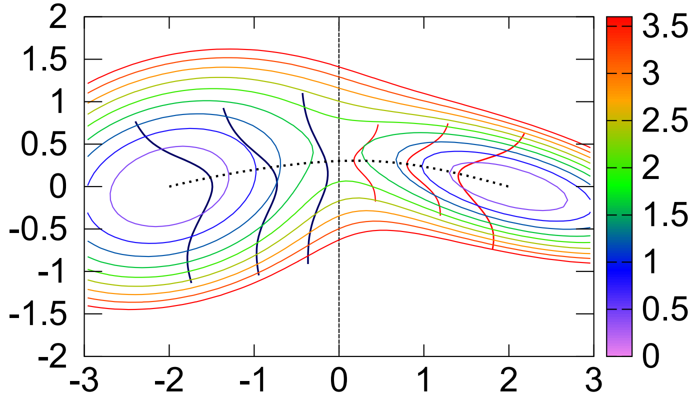
<u>MODIFIED WKB</u>

Excited vibrational states: $\phi^{(1)} = (F + \mathbf{U}^\top \Delta\mathbf{x})\phi^{(0)}$

Direction of nodal plane

Shift of node from the instanton path





$$\frac{d}{d\tau}U = \omega_e U - AU$$

$$\frac{d}{d\tau}A + A^2 = \Omega^2(\tau)$$

Instanton theory
ground state tunneling splittings

RING POLYMER INSTANTONS

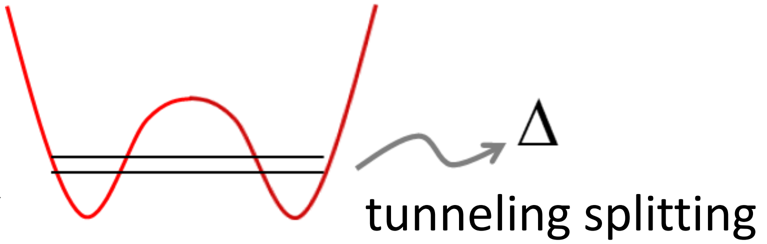
$$\lim_{\beta\to\infty} \frac{Q(\beta)}{Q_0(\beta)} = \frac{e^{-\beta(E_0-\Delta/2)} + e^{-\beta(E_0+\Delta/2)}}{2e^{-\beta E_0}} = \cosh\frac{\beta\Delta}{2}$$

low temperature

ratio of partition functions

$$\beta = \frac{1}{kT}$$

$$\Delta\tau = \beta_N = \beta/N$$



$$Q(\beta) = \mathrm{Tr}\left[e^{-\beta H}\right] \approx \left(\frac{1}{\beta_N 2\pi\hbar^2}\right)^{N/2} \int dx_1 \ldots dx_N \; e^{-S(x_1,\ldots x_n)/\hbar}$$

$$S(x_1,\ldots,x_N) = \sum_{i=1}^{N}\left(\frac{1}{2}\frac{(x_i - x_{i+1})^2}{\Delta\tau^2} + V(x_i)\right)\Delta\tau$$

Discretized path integral formulation

Langer, 1967; Miller, 1975; Vainshtein, Zakharov, Novikov, Shifman, 1982

Instanton theory

ground state tunneling splittings

RING POLYMER INSTANTONS

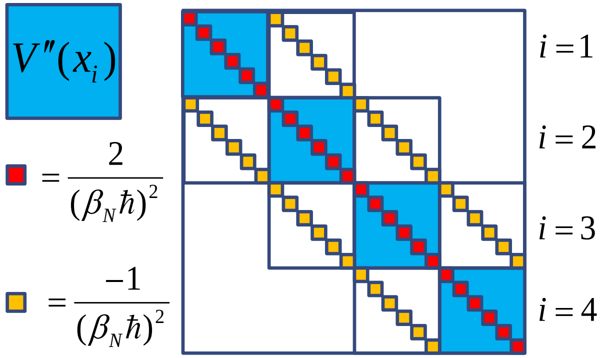
$$\lim_{\beta\to\infty}\frac{Q(\beta)}{Q_0(\beta)}=\frac{e^{-\beta(E_0-\Delta/2)}+e^{-\beta(E_0+\Delta/2)}}{2e^{-\beta E_0}}=\cosh\frac{\beta\Delta}{2}$$

low temperature

ratio of partition functions

$$Q(\beta)=\mathrm{Tr}\left[e^{-\beta H}\right]\approx\left(\frac{1}{\beta_N 2\pi\hbar^2}\right)^{N/2}\int dx_1\ldots dx_N\; e^{-S(x_1,\ldots x_n)/\hbar}$$

Discretized path integral formulation



Dominant contribution:

$$S(x)\approx S(x_{\min})+\frac{1}{2}S''(x_{\min})(x-x_{\min})^2$$

Minimal action => Newton's equation of motion on inverted potential

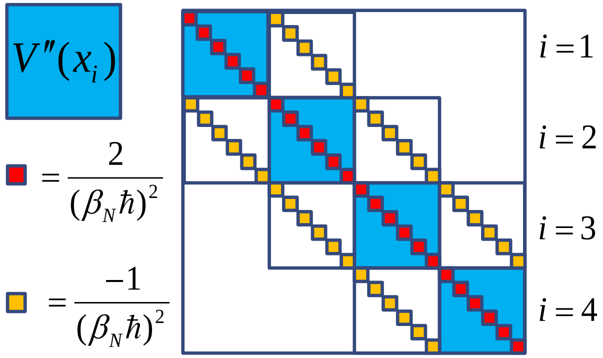
$$S(x_1,\ldots,x_N)=\sum_{i=1}^{N}\left(\frac{1}{2}\frac{(x_i-x_{i+1})^2}{\Delta\tau^2}+V(x_i)\right)\Delta\tau$$

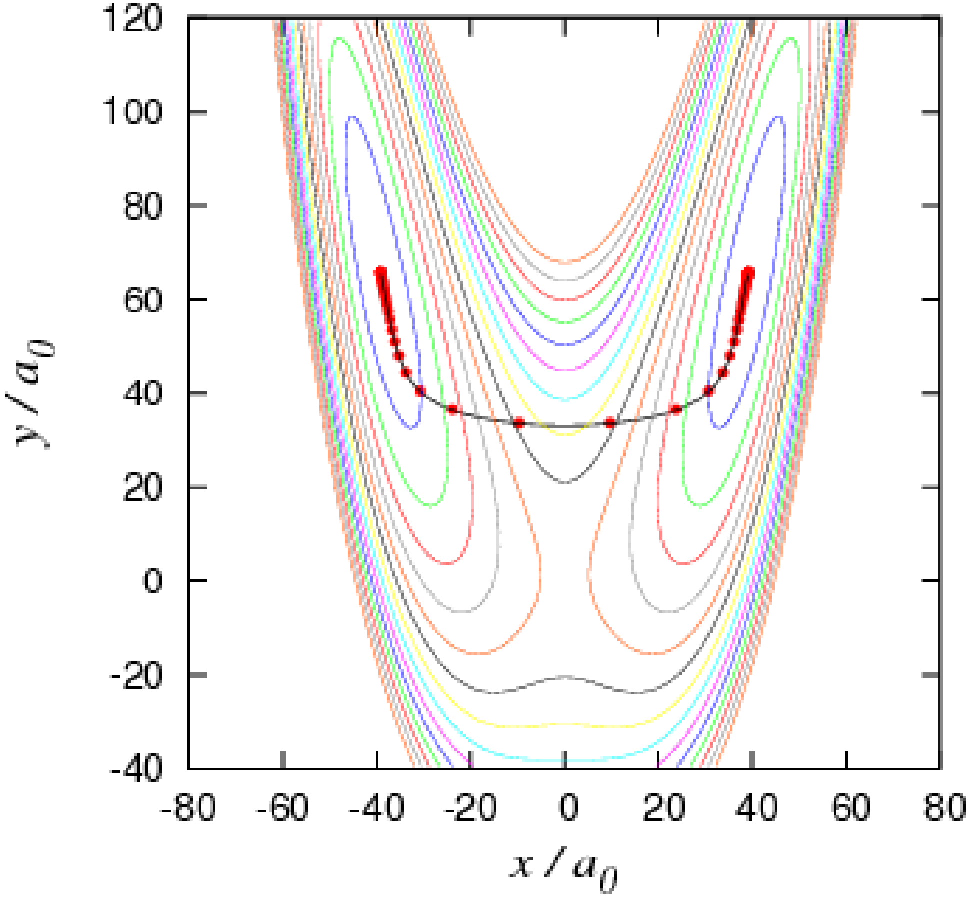
Langer, 1967; Miller, 1975; Vainshtein, Zakharov, Novikov, Shifman, 1982

Instanton theory
ground state tunneling splittings

RING POLYMER INSTANTONS

Discretized path integral formulation





JACOBI FIELD INSTANTONS

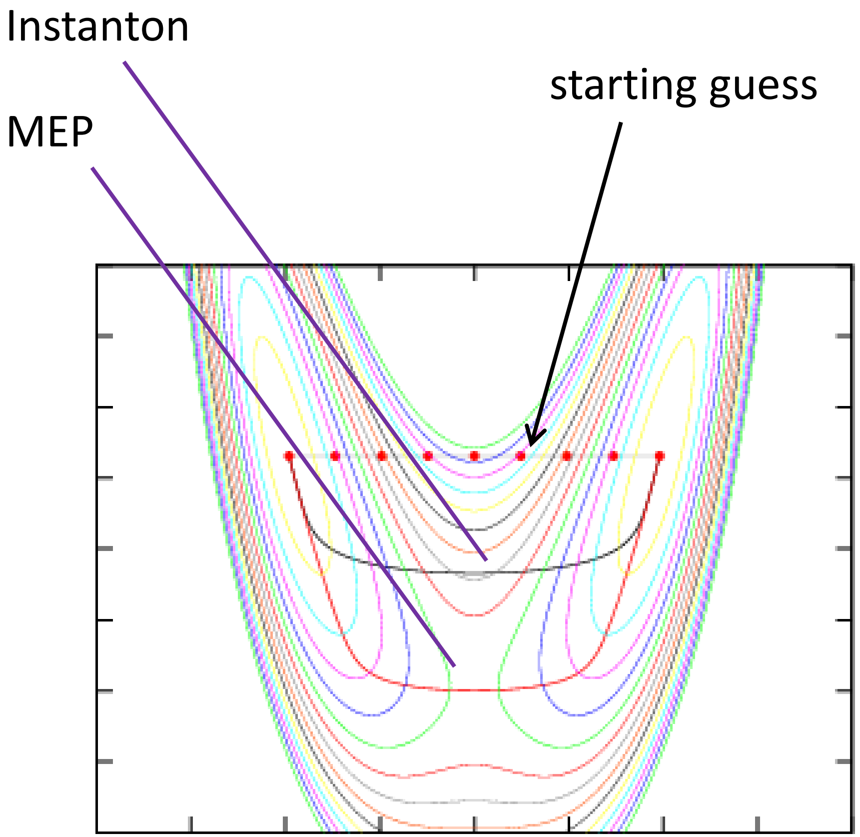
Continuous path integral formulation

$$\frac{d}{d\tau}A + A^2 = \Omega^2(\tau)$$

Langer, 1967; Miller, 1975; Vainshtein, Zakharov, Novikov, Shifman, 1982

Instanton theory
implementation

MINIMUM ACTION PATH SEARCH



- Minimization of Jacobi action :

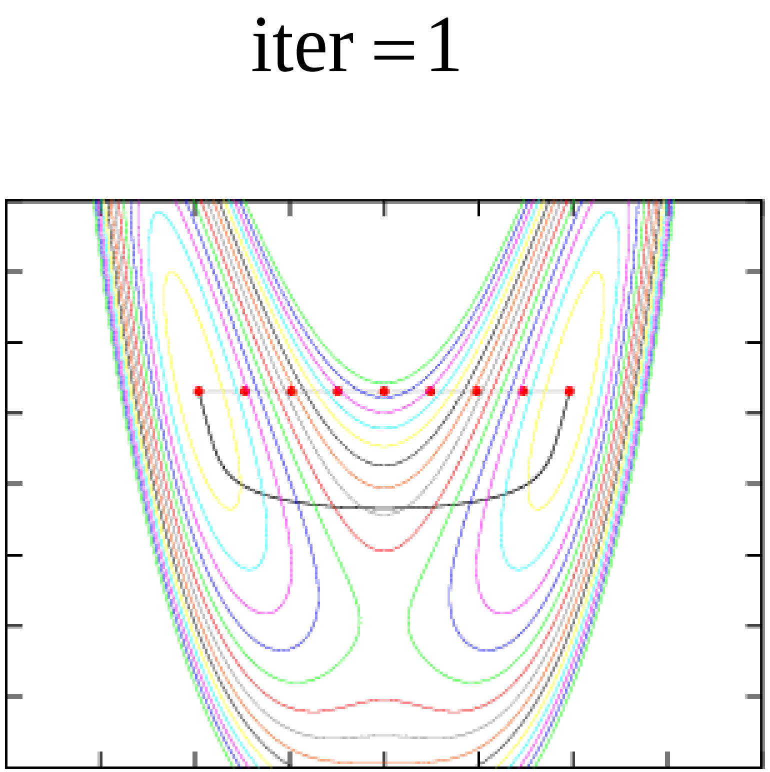
$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string



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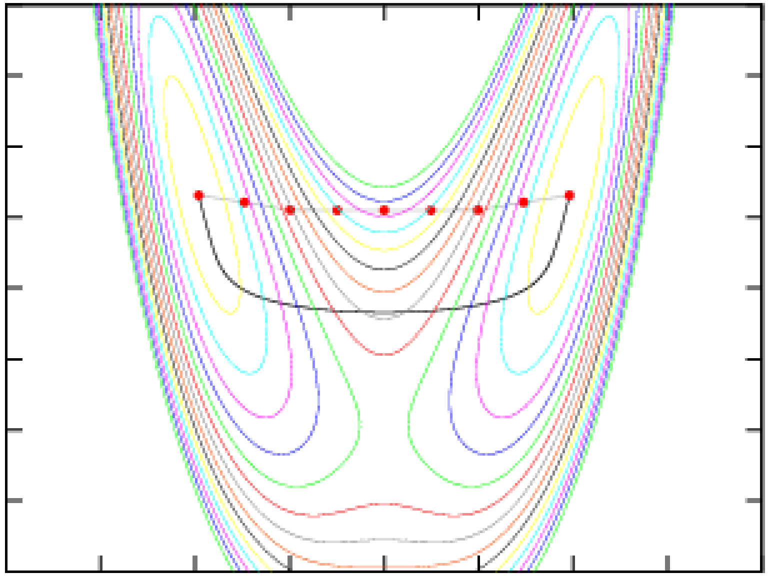
Instanton theory
implementation

LBFGS + string

iter = 2



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}\,|x_{i+1} - x_i|$$

- L-BFGS in *N* x *f* degrees of freedom.

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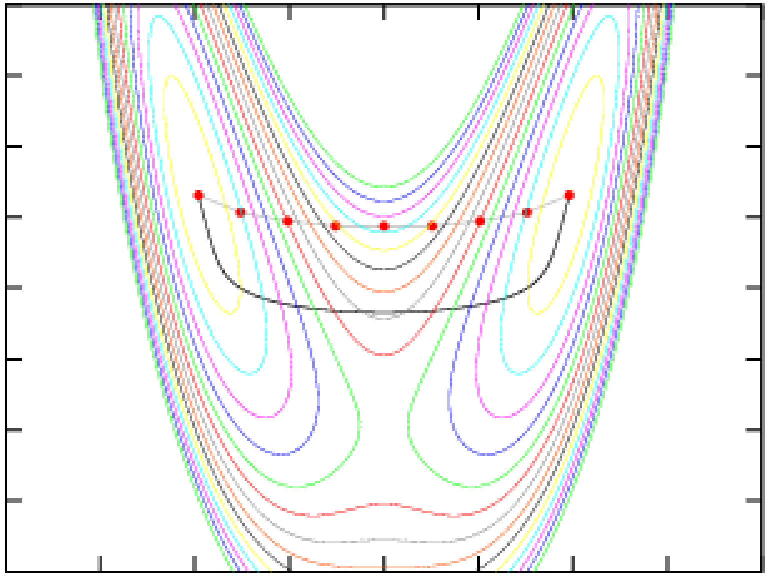
Instanton theory
implementation

LBFGS + string

$$\mathrm{iter} = 3$$



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

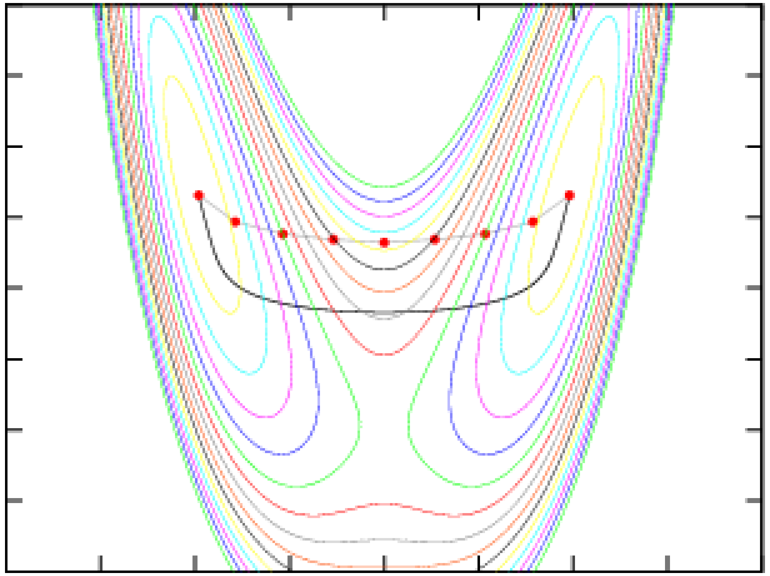
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

iter = 4



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p \mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}} |x_{i+1} - x_i|$$

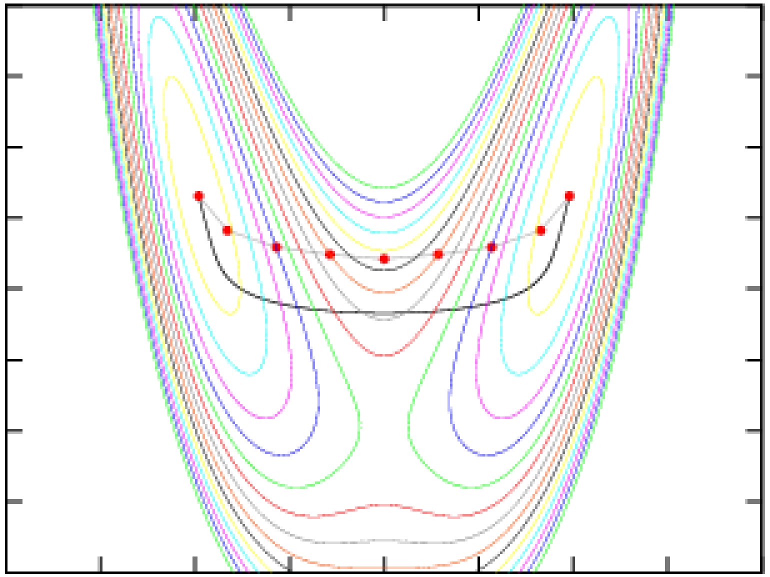
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

$\text{iter} = 5$



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}\,|x_{i+1} - x_i|$$

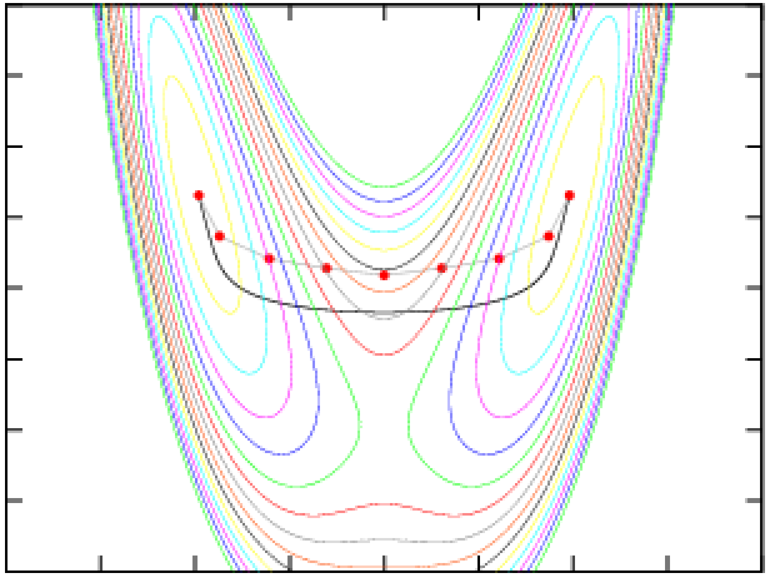
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

iter = 6



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

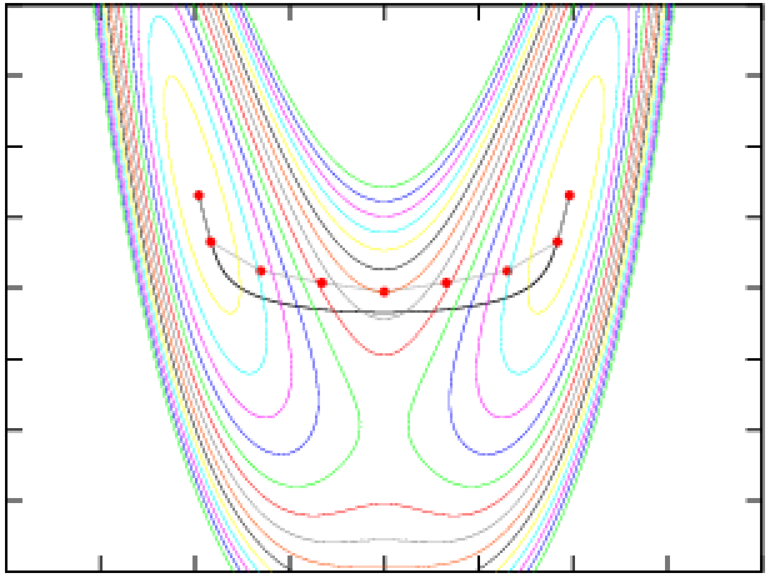
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

iter = 7



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} \mathrm{p}\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}\,|x_{i+1} - x_i|$$

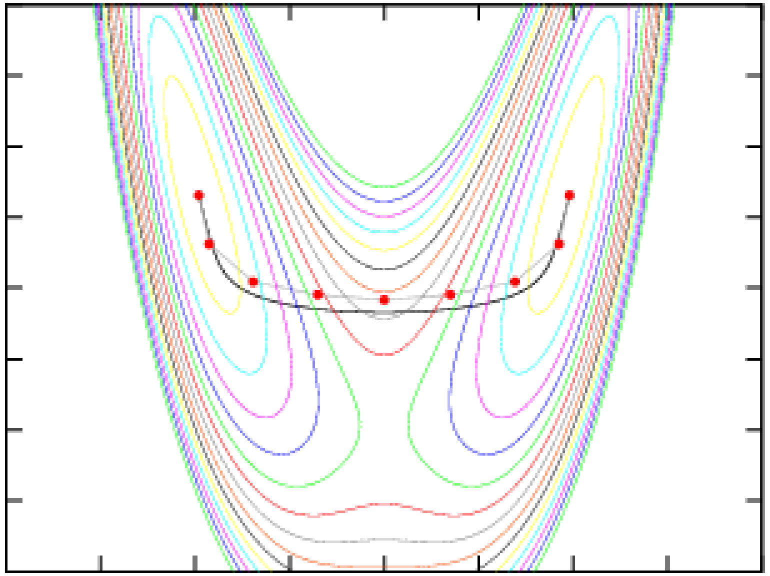
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

$$\text{iter} = 8$$



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

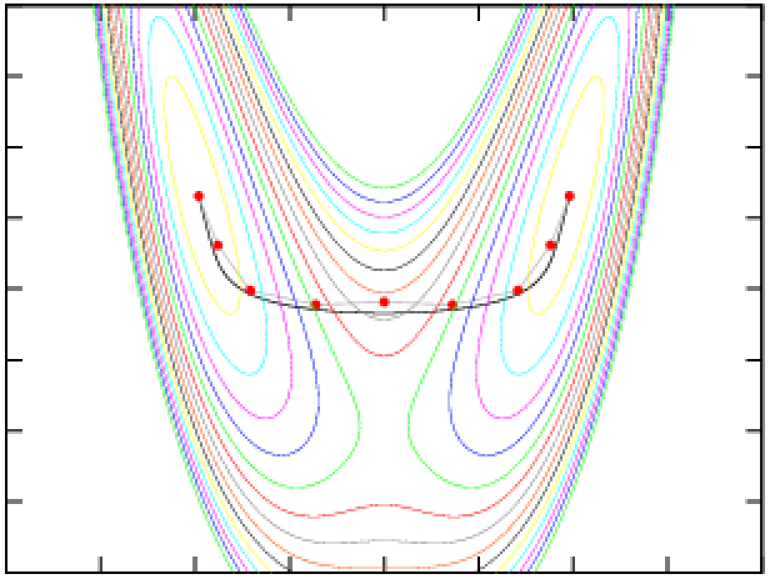
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

iter = 9



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

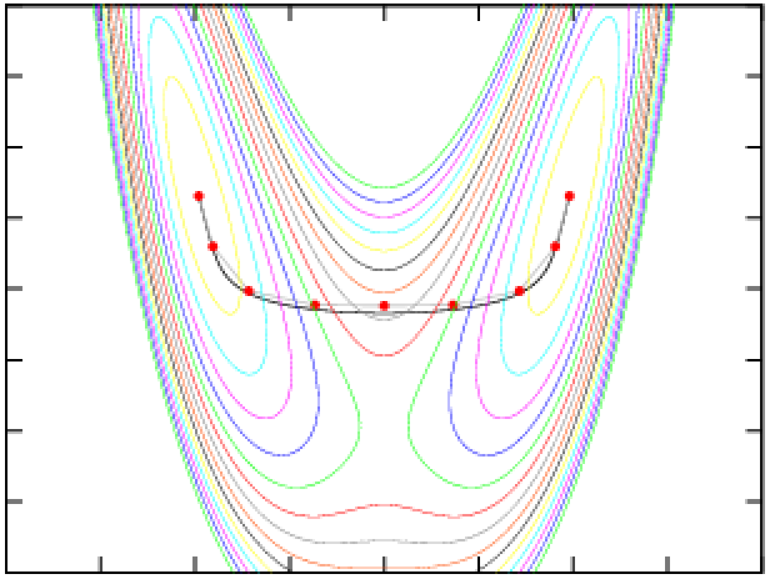
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

$\text{iter} = 10$



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}|x_{i+1} - x_i|$$

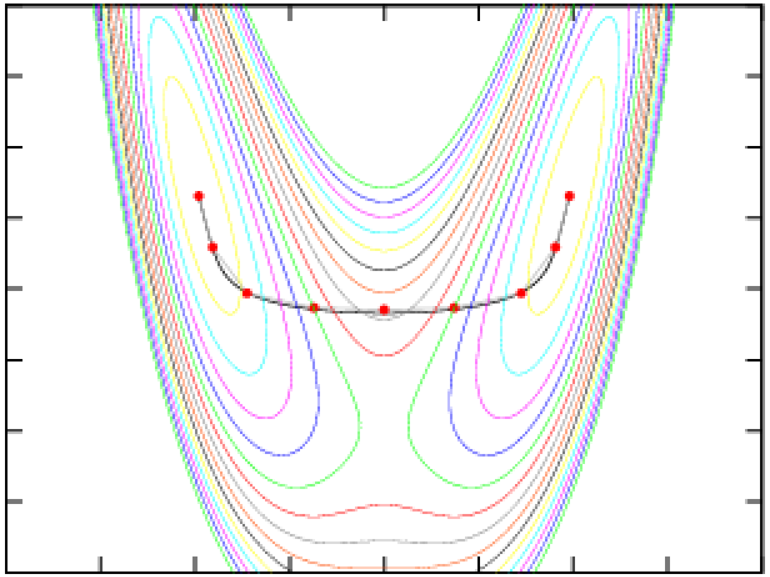
- L-BFGS in N x f degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

$$\mathrm{iter} = 11$$



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}\,|x_{i+1} - x_i|$$

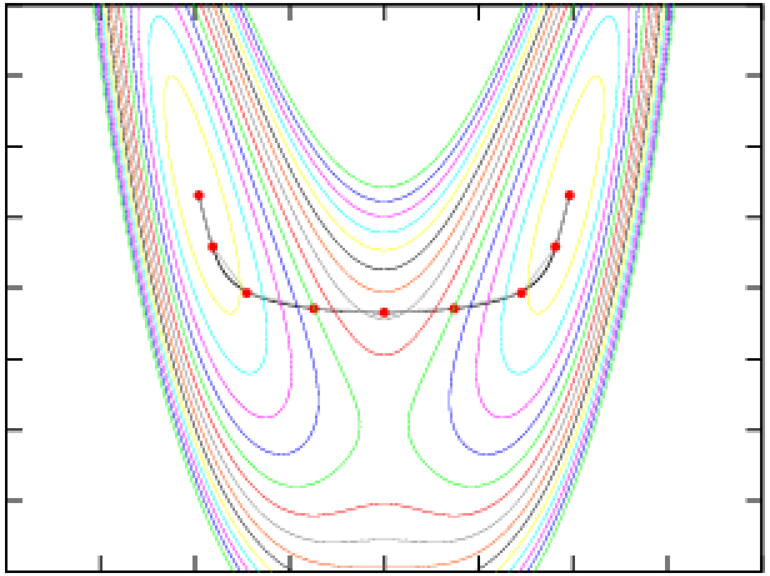
- L-BFGS in $N \times f$ degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

LBFGS + string

iter = 12



- Minimization of Jacobi action :

$$S_A = \int_{x_1}^{x_N} p\mathrm{d}x = \sum_i \sqrt{2\frac{V(x_{i+1}) + V(x_i)}{2}}\,|x_{i+1} - x_i|$$

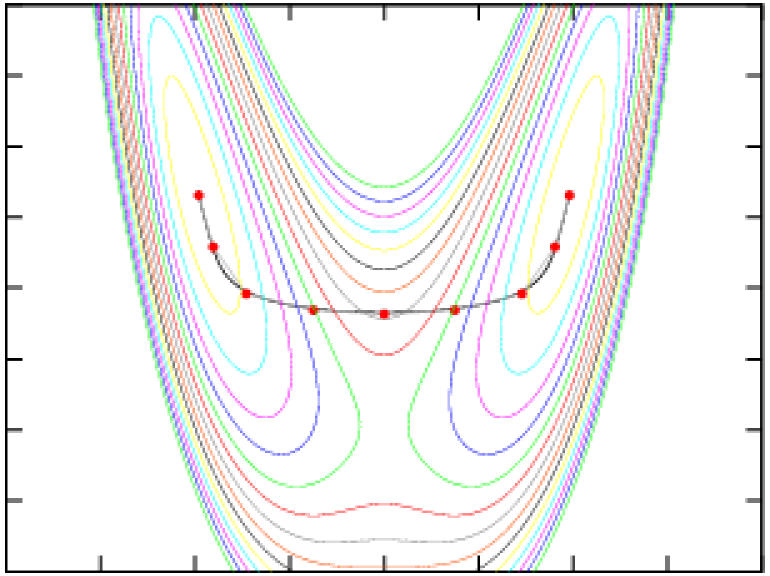
- L-BFGS in *N* x *f* degrees of freedom.

- string method: *Cvitas, Althorpe, JCTC* 2016.
- quadratic string method: *Cvitas, JCTC* 2018.

Instanton theory
implementation

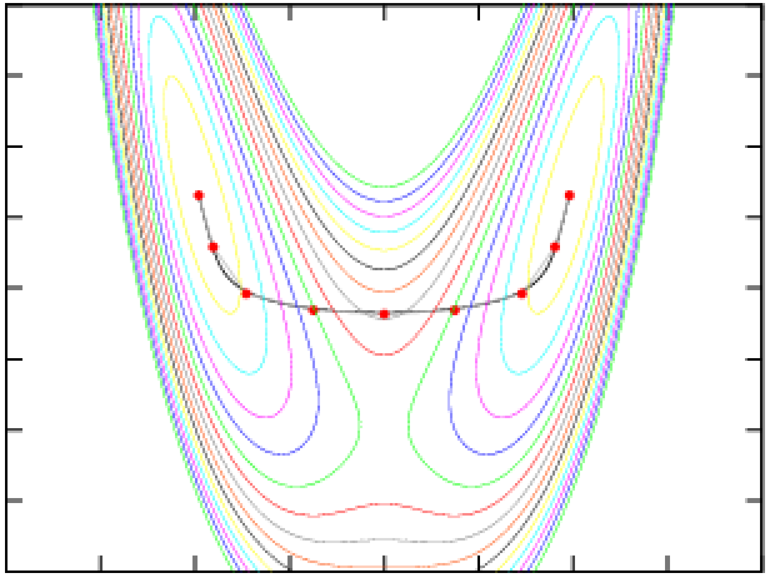
LBFGS + string

$$\text{iter} = 13 - 17$$



1) Evaluate Hessians at beads along MAP.
2) Interpolate Hessian matrix elements.
3) Solve : $$\frac{d}{d\tau}A + A^2 = \Omega^2(\tau)$$
4) Interpolate *A*.
5) Solve : $$\frac{d}{d\tau}U = \omega_e U - AU$$
6) Evaluate tunneling matrix elements *h*.

Instanton theory
implementation



Can be computed using instantons

$$\left\langle \phi_i^{(\mathrm{L/R})} \middle| \hat{H} \middle| \phi_j^{(\mathrm{R/L})} \right\rangle$$

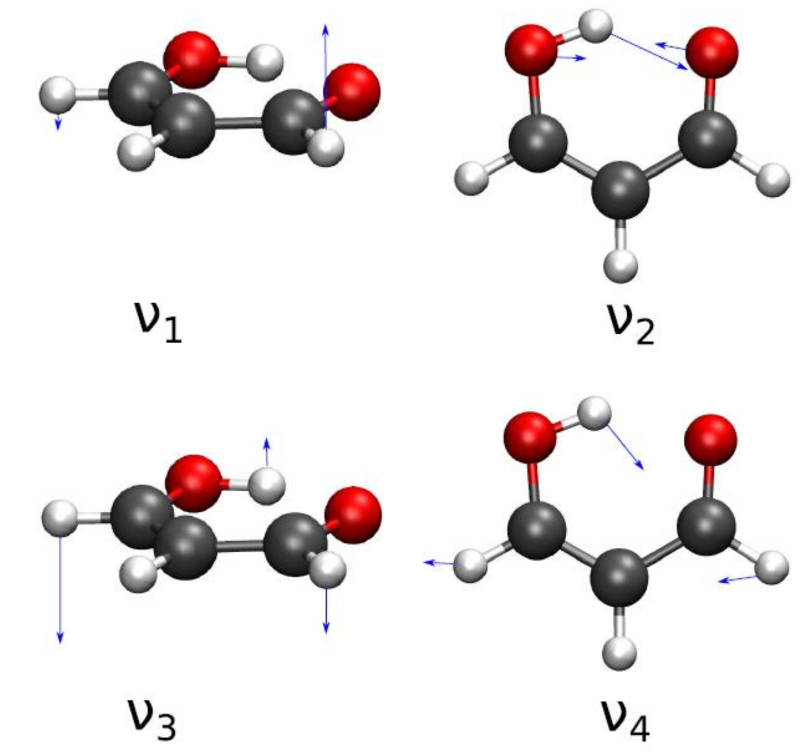
$$\mathbf{H} = \begin{pmatrix} \mathbf{E}^{(\mathrm{L})} & \mathbf{h} \\ \mathbf{h}^{\top} & \mathbf{E}^{(\mathrm{R})} \end{pmatrix}$$

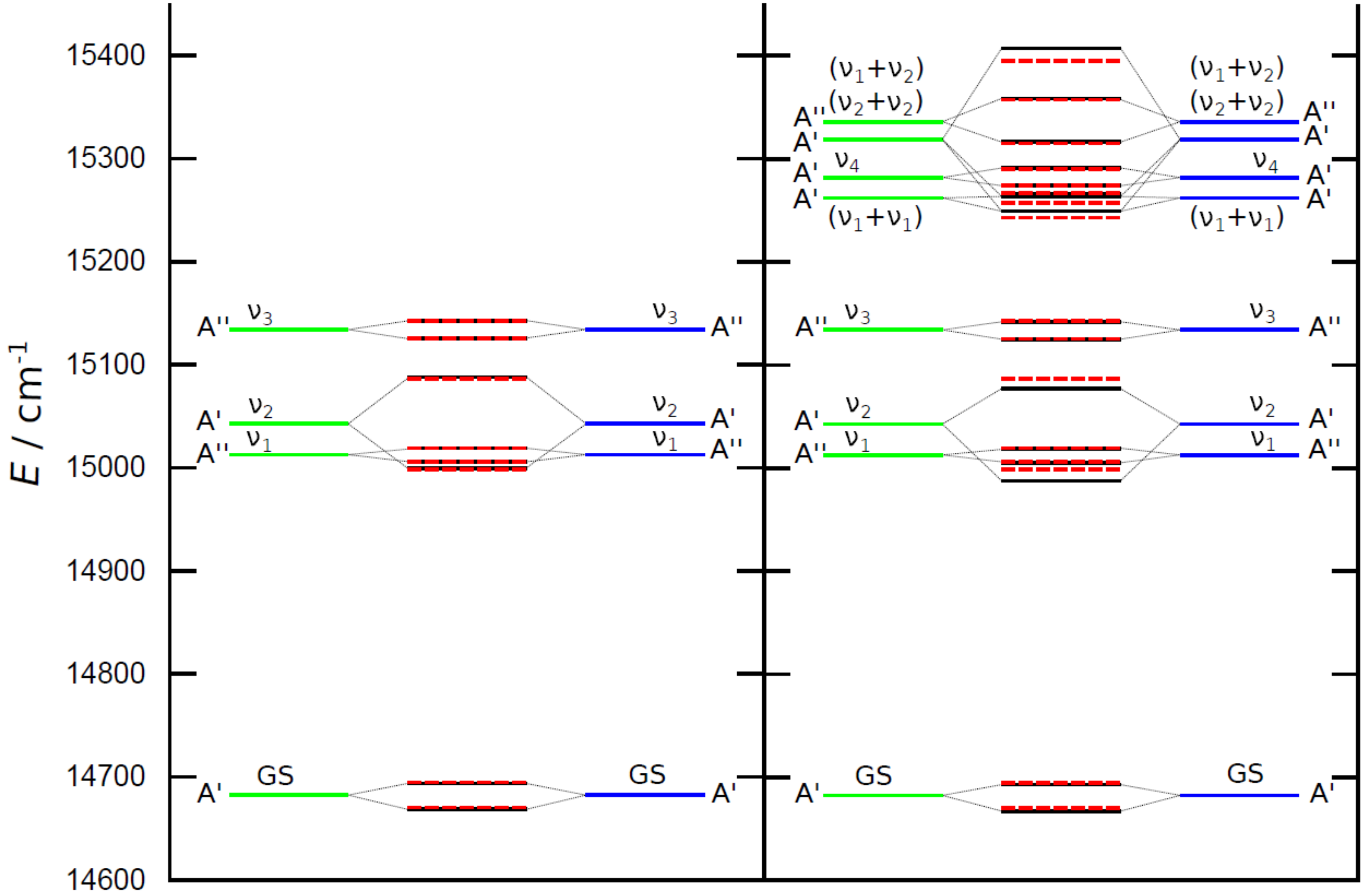
$$\left\langle \phi_i^{(\mathrm{L/R})} \middle| \hat{H} \middle| \phi_j^{(\mathrm{L/R})} \right\rangle$$

Diagonal energies calculated using Vibrational Configuration interaction (VCI).

Malonaldehyde

- PES: *Wang et al, JCP* 1999.
- Experiment : TS = 21.6 cm^{-1}
  Baba et al, JCP 1999.

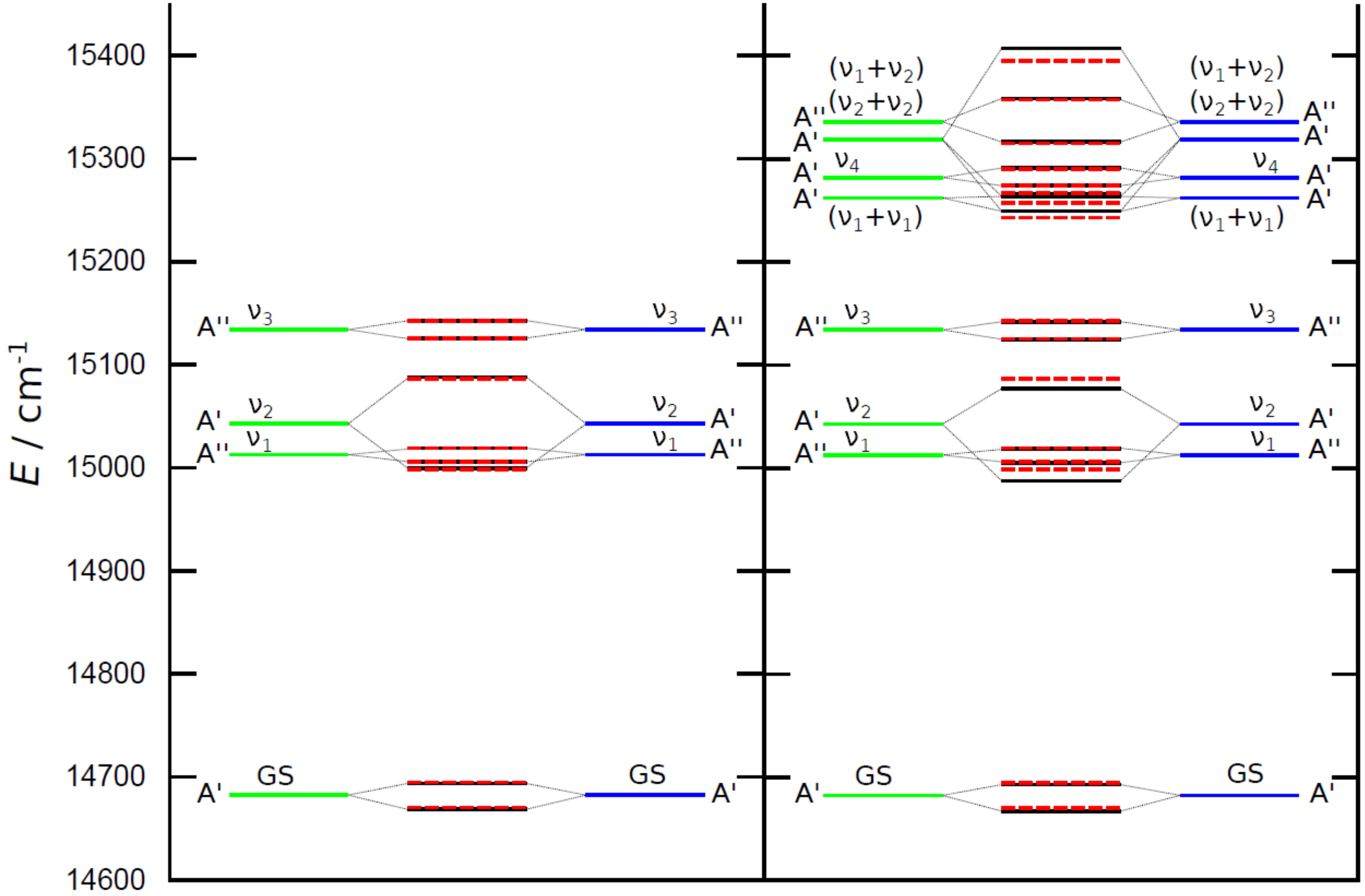




Erakovic, Cvitas, JCTC 2022.

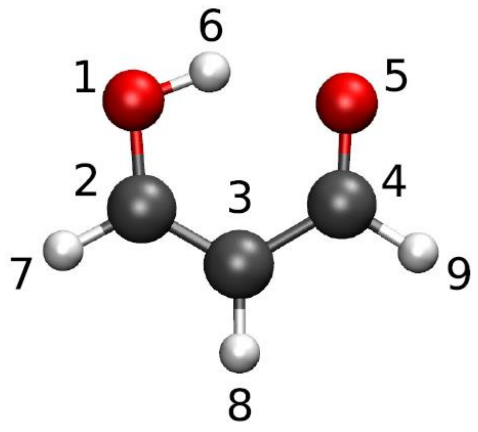
Malonaldehyde

	TS (cm^{-1})	TS (MCTDH)
GS	24.6	23.5
	(25.7)	
ν_1	13.4	6.7
ν_2	88.4	69.9
	(89.4)	
ν_3	17.1	16.3
ν_4	15.6	18.8
ν_5	24.4	21.1
ν_7	39.5	33.3
ν_8	15.6	14.6
ν_{11}	22.1	19.5
ν_{11}	22.1	19.5
$\nu_1 + \nu_1$	15.6	18.8
	(17.3)	
$\nu_1 + \nu_2$	42.6	49.5



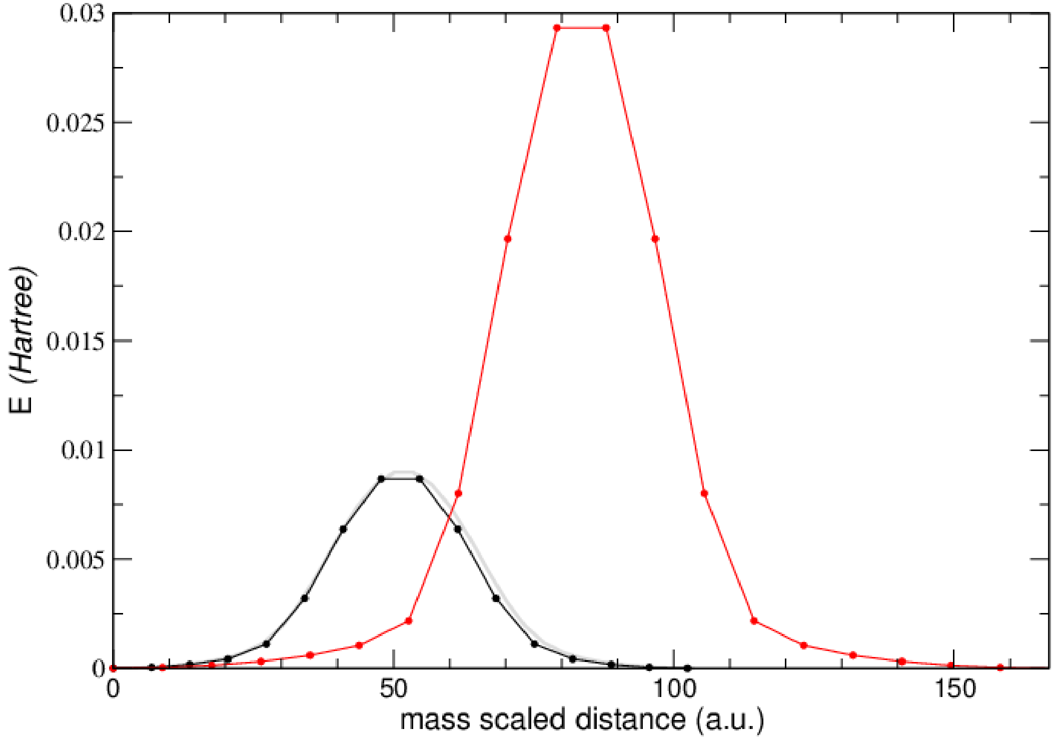
Hammer, Manthe, JCP 2012. *Schroder, Meyer, JCP* 2014. *Erakovic, Cvitas, JCTC* 2022.

Malonaldehyde on-the-fly



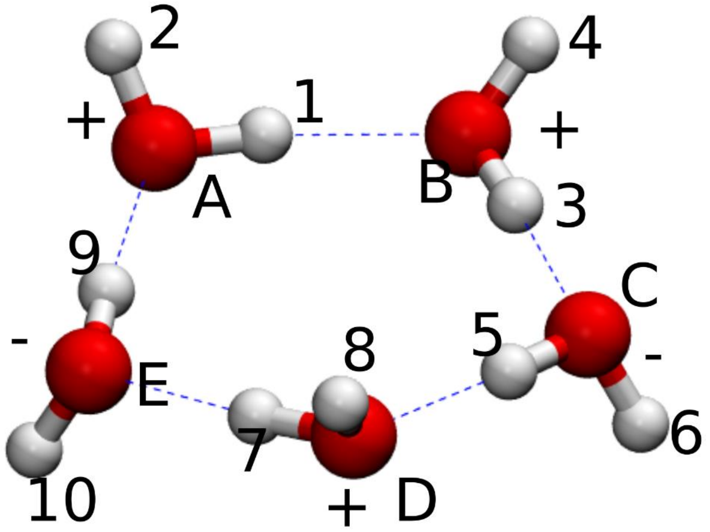
- On-the-fly calculation of S_0 and S_1 state of malonaldehyde.
- Collaboration with Marin Sapunar & Nađa Došlić
- Cfour: CCSDT + cc-pVDZ
- N = 16 beads (S_0) and 20 beads (S_1)
- Experiment: S_1 splitting ±19 cm^{-1} of ground state (*Arias, Wasserman, Vaccaro, JCP 1997*).
- Exp(S_0) : 21.6 cm^{-1} (*Baba et al, JCP 1999*).

	Δ (cm^{-1})	Action ($\hbar$)
S_0(Bow)	24.6	6.13
S_0	20.6	5.85
S_1	2.9(−2)	13.40



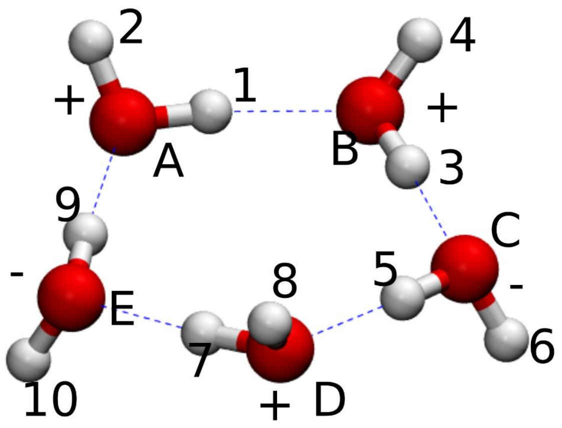
Water pentamer

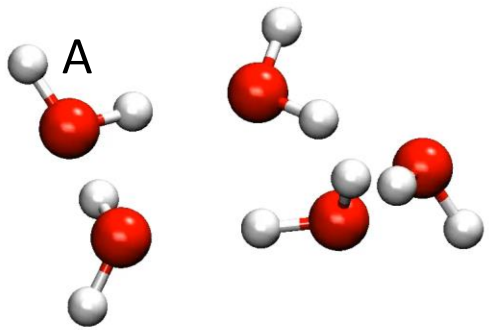
- Potential: MB-pol (*Babin et al, 2013*)
  WHBB (*Wang et al, 2009*)
- Recent experiments: *Cole et al 2016*; *Harker et al, 2005; Brown et al, 1998; Liu et al 1997; Cruzan et al, 1998*



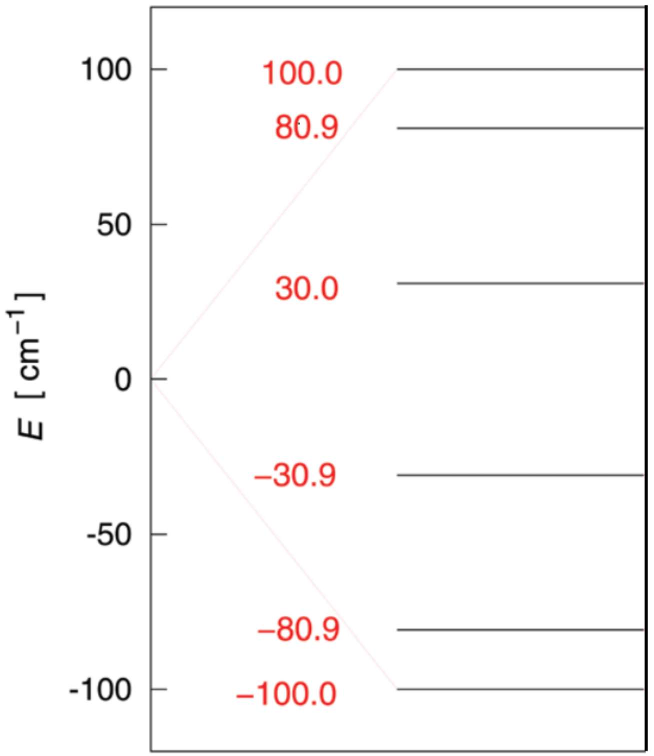
- G_{320} analysed by Walsh & Wales, 1996
- Label minima using notation: UUDUD
- 5 positions for majority monomer
- 2 for U/D of majority monomer (DDUDU)
- 2^5 positions of hydrogens (bifurcations)
- $5 \times 2 \times 2^5 = 320$ equivalent minima

Water pentamer



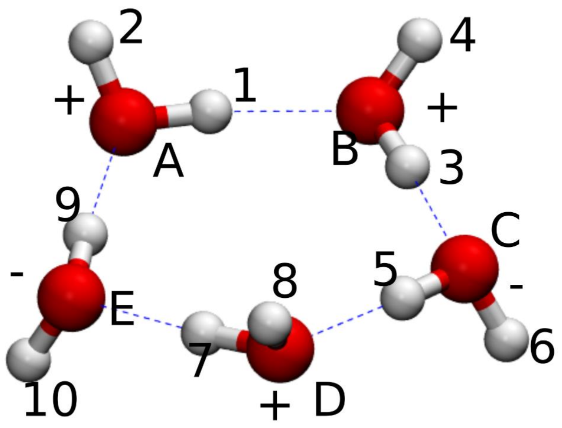


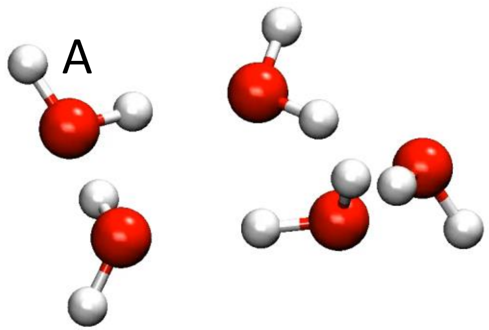
Flip A / B :



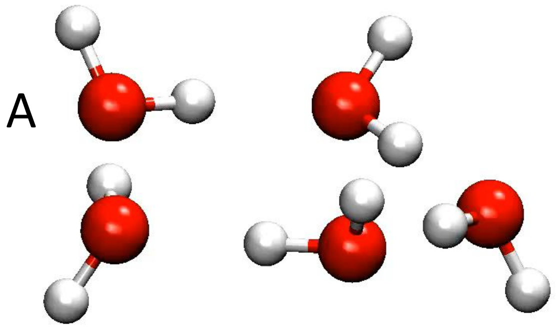
Cvitas, Richardson, PCCP 2019.

Water pentamer



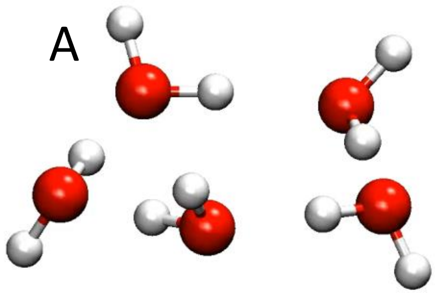


Flip A / B :



Bifur A / B :

Water pentamer



equivalent to A flip

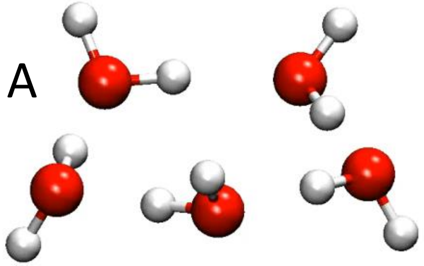
(A+E) = (A) + E

Action = 16.30 < (14.76 + 1.64) = 16.40 a.u.

	h / cm^{-1}	Action
A / B	50	1.64
A / B	4.7(-4)	14.76
A+E / C+B	5.0(-4)	16.30
B+C / E+A	2.2(-4)	15.65
C+BD / E+AD	1.7(-4)	17.27

Water pentamer

A

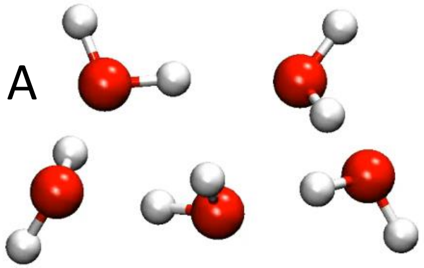


A+BCDE

Action = 28.63 a.u.

Water pentamer

A



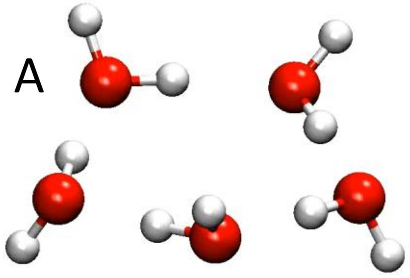
A+BCDE

Action = 28.63 a.u.

↓

0.06% contribution

A



equivalent to A flip

↓ ↓ ↓

A+BCDE = (A+E) + (D) + (C) + (B) :

Action = 16.30 + 3 x 1.64 = 21.22 a.u.

Cvitas, Richardson, PCCP 2019.

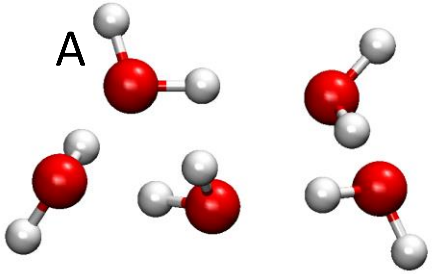
Water pentamer

	composed of	equivalent to
A + BCDE	(A+E) + D + C + B	(A+E) + 3 x A
A + CDE	(A+E) + D + C	(A+E) + 2 x A
A + DE	(A+E) + D	(A+E) + A
B + ACDE	(B+C) + D + E + A	(B+C) + 3 x A
B + CDE	(B+C) + D + E	(B+C) + 2 x A
B + CD	(B+C) + D	(B+C) + A
C + ABDE	(C+BD) + E + A	(C+BD) + 2 x A
C + BDE	(C+BD) + E	(C+BD) + A
D + ABCE	B + (D+CE) + A	(C+BD) + 2 x A
D + BCE	B + (D+CE)	(C+BD) + A
E + ABCD	(E+AD) + C + B	(C+BD) + 2 x A
E + ACD	(E+AD) + C	(C+BD) + A

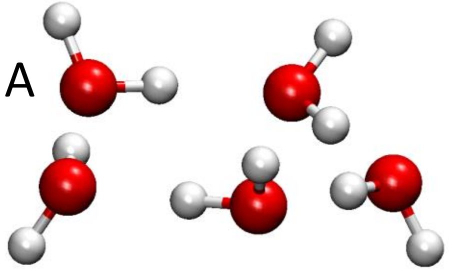
	h / cm^{-1}	Action
A / B	50	1.64
A / B	4.7(-4)	14.76
A+E / C+B	5.0(-4)	16.30
B+C / E+A	2.2(-4)	15.65
C+BD / E+AD	1.7(-4)	17.27

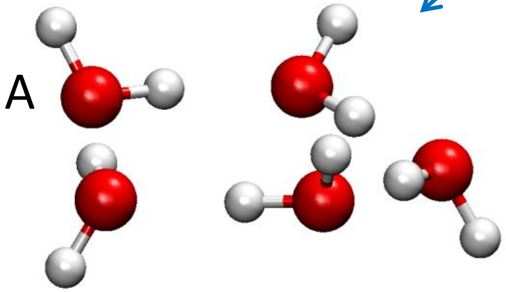
Cvitas, Richardson, PCCP 2019.

Water pentamer



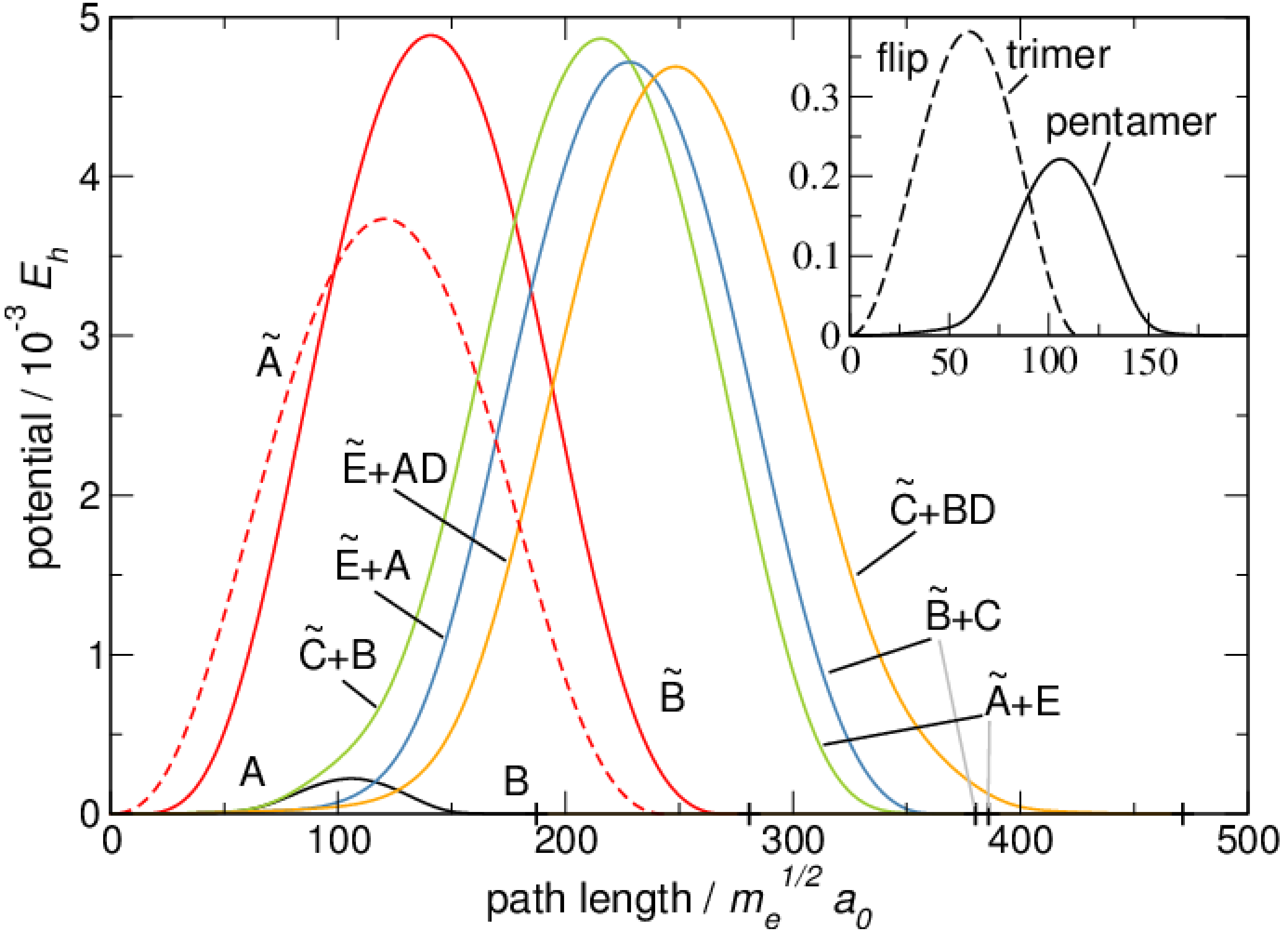
	h / cm^{-1}	Action
A / B	50	1.64
A / B	4.7(-4)	14.76
A+E / C+B	5.0(-4)	16.30
B+C / E+A	2.2(-4)	15.65
C+BD / E+AD	1.7(-4)	17.27





Cvitas, Richardson, PCCP 2019.

Water pentamer



	h / cm^{-1}	Action
A / B	50	1.64
A / B	4.7(-4)	14.76
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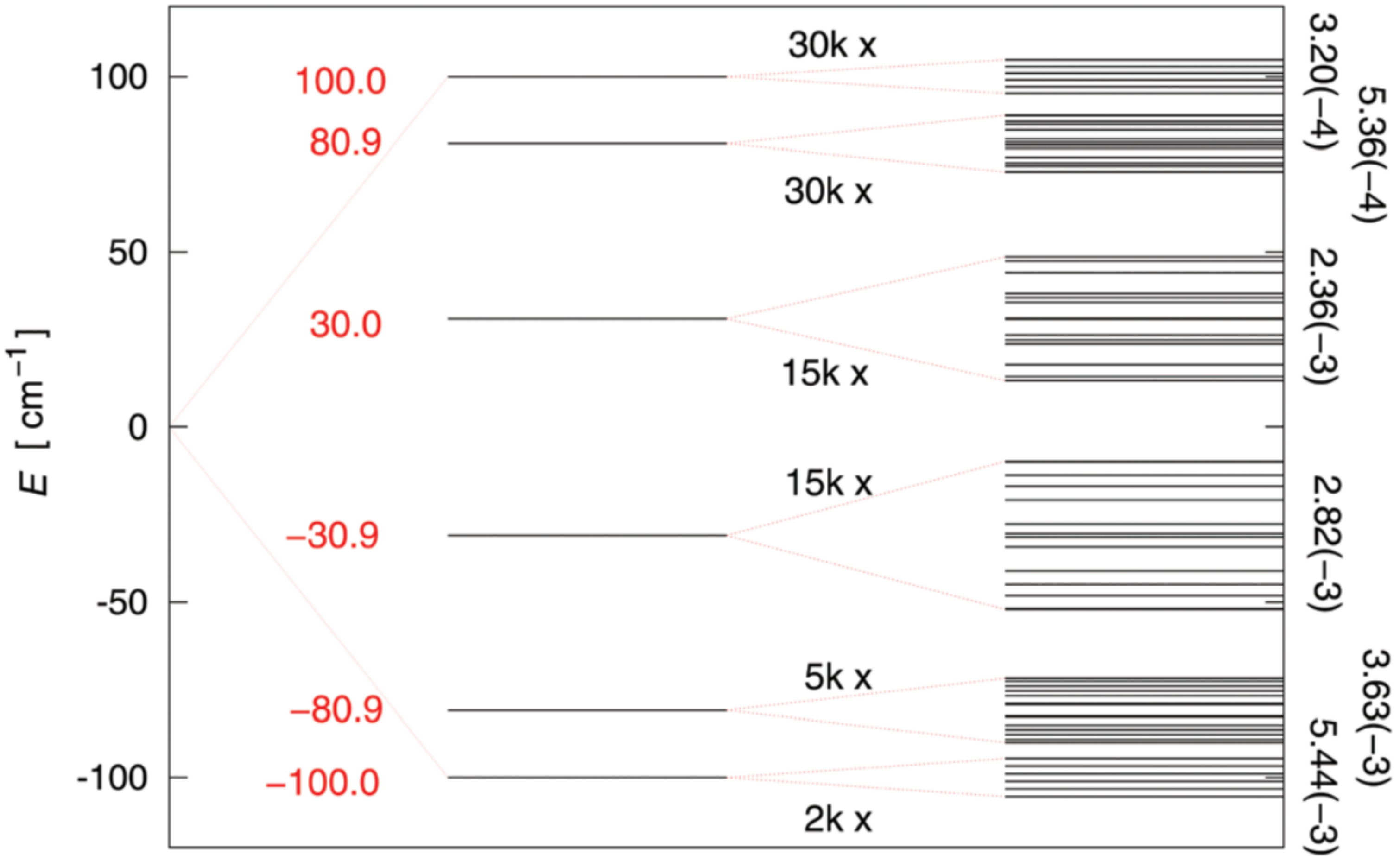
C+BD / E+AD	1.7(-4)	17.27

Cvitas, Richardson, PCCP 2019.

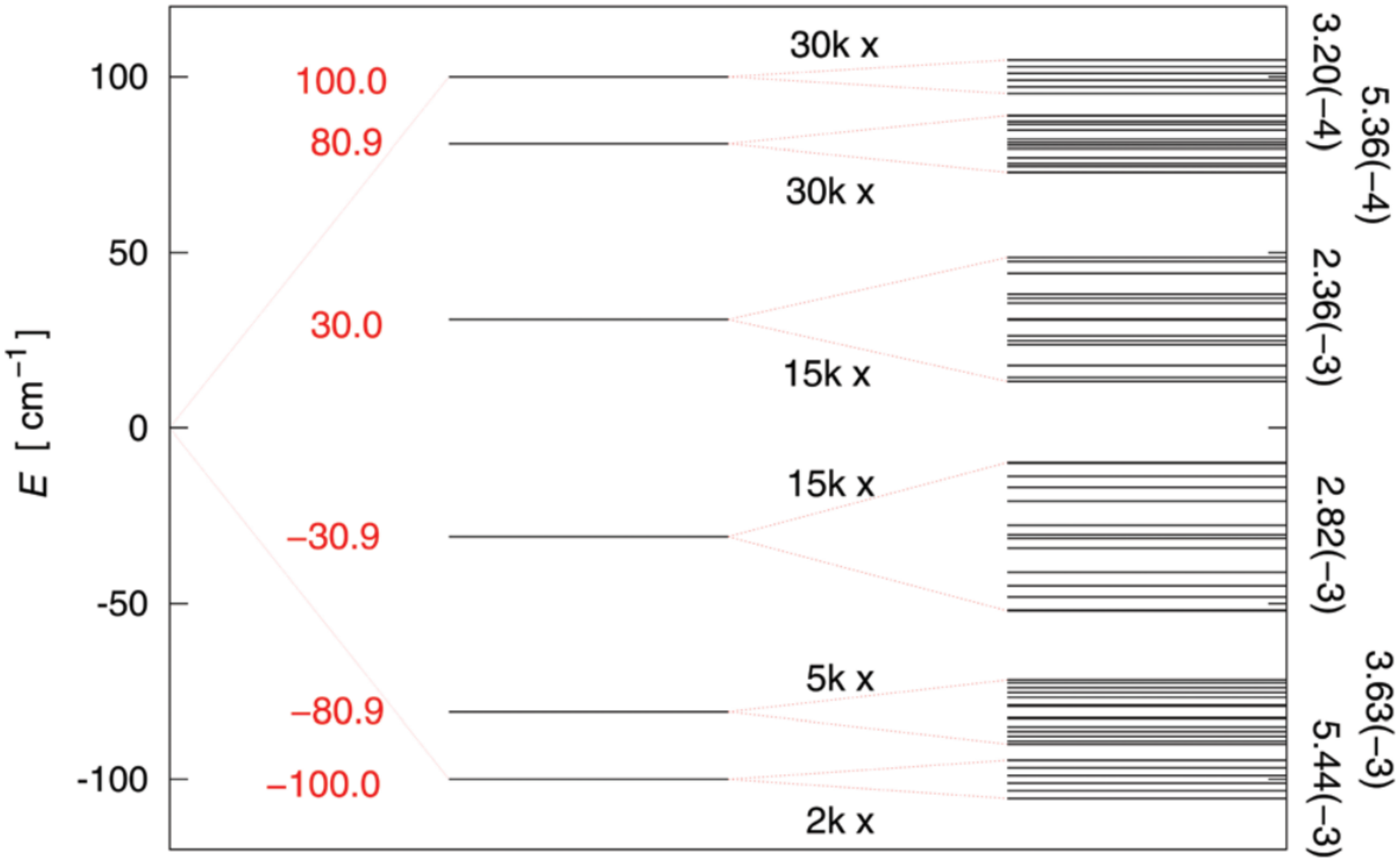
Water pentamer



- Number 320 minima.
- Apply each symmetry operation on every minimum *i*, determine index *j* of the resulting minimum, and place *h* at H_{ij} in the tunnelling matrix H.
- Diagonalize H to obtain energy levels.
- State symmetries, degeneracies and nuclear-spin weights can be obtained from eigenvectors to deduce allowed transitions and their intensity patterns.

Cvitas, Richardson, PCCP 2019.

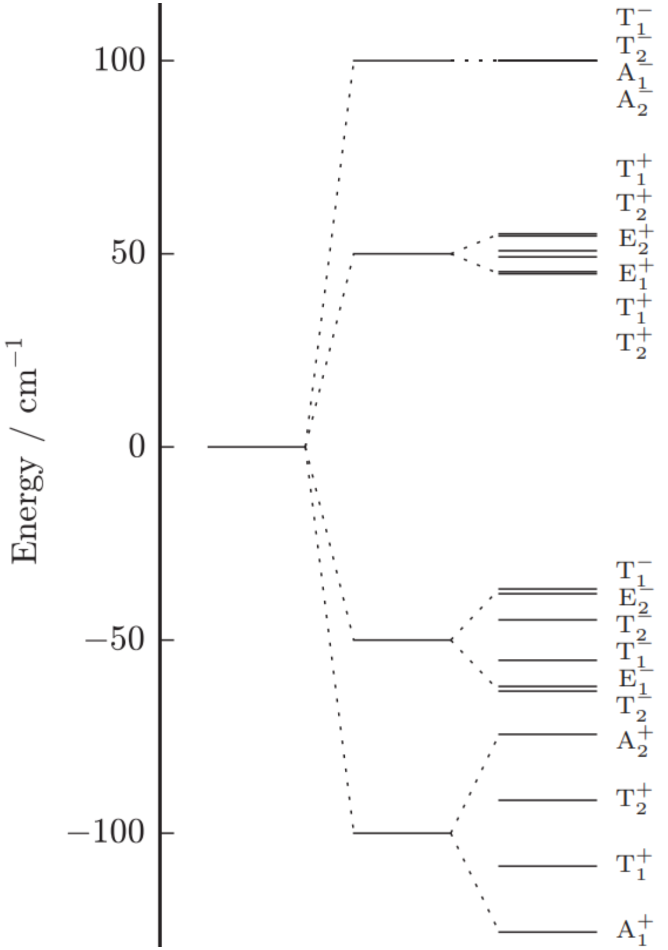
Water pentamer

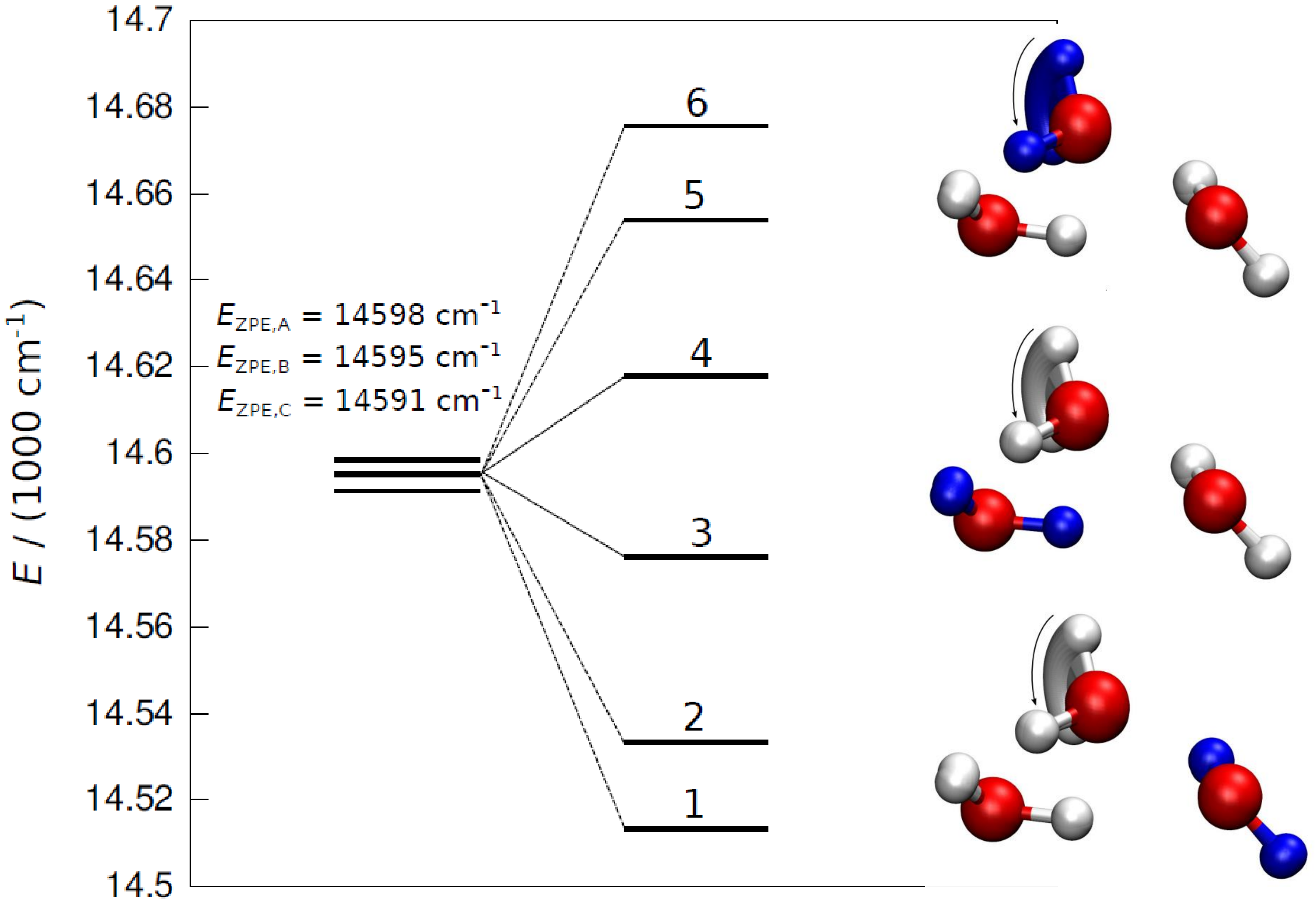


- Mechanism other than A are responsible for marked decrease in the splitting for higher flip states. Decrease 17 x.
- Lowest flip state width increases 2.9x due to other mechanisms.
- Anomalous splitting pattern in intermediate flip states (unequal spacing).
- Width of the lowest flip state is $1.0\text{x}10^{-3}$ cm^{-1} ($1.6\text{x}10^{-4}$ cm^{-1}). Factor of 6.9 x . (In trimer: 3.8 x $9.6\text{x}10^{-3}$).
- Sextet splitting in D-pentamer is $2.5\text{x}10^{-6}$ cm^{-1}. Experiment: splitting $< 1.0\text{x}10^{-5}$ cm^{-1}.
- KIE(H/D) bifurcation widths: 400 x
- KIE($^{16}O/^{18}O$) bifurcation widths: 1.11 x

Cvitas, Richardson, PCCP 2019. *Brown, Keutsch, Saykally, JCP* 1998.

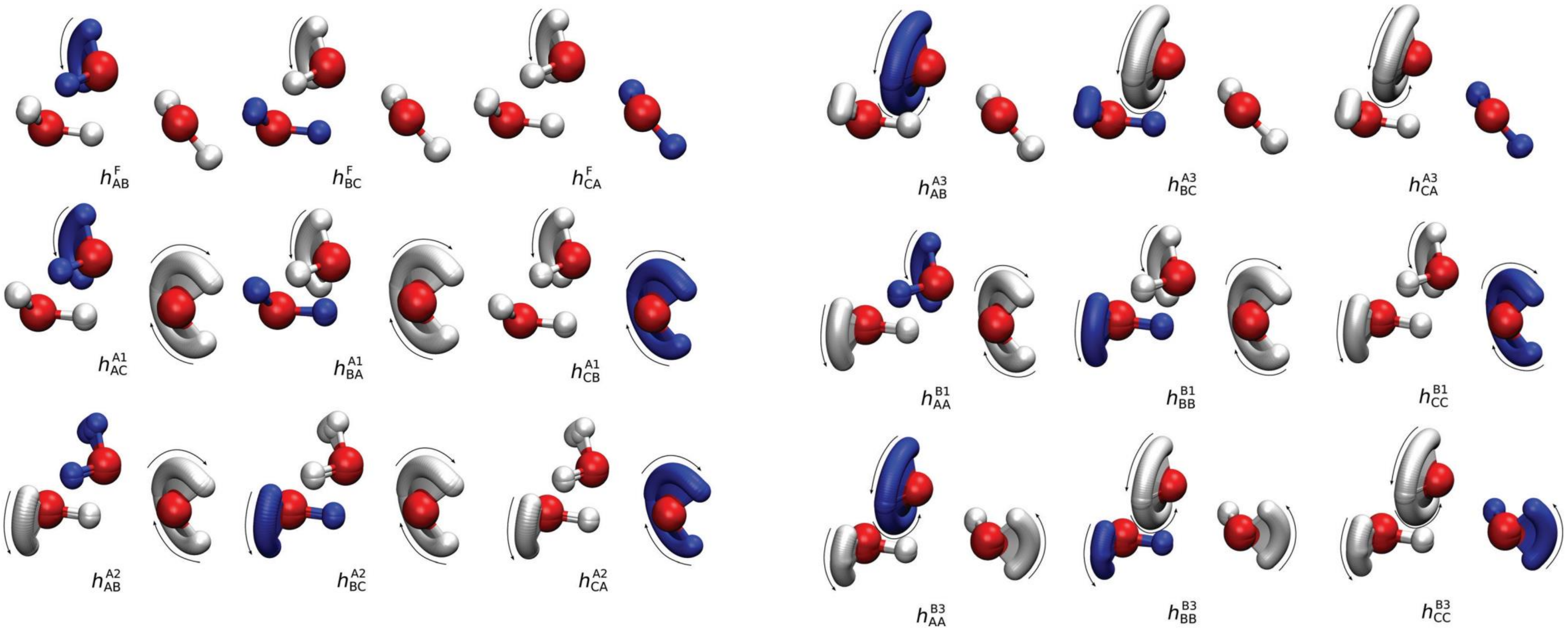
Water trimer: $D_2O(H_2O)_2$





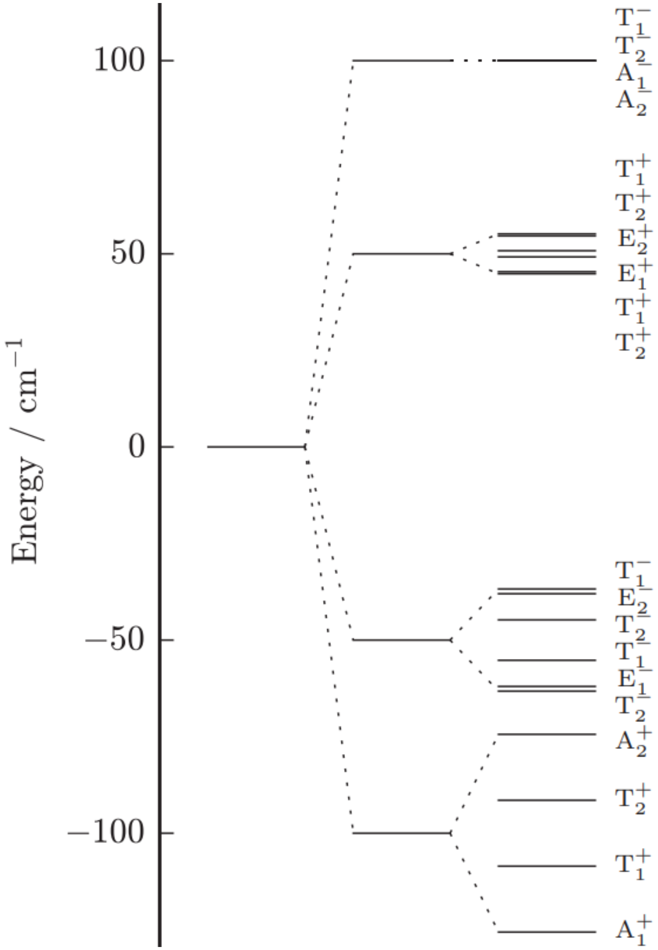
Erakovic, Cvitas, PCCP 2021.

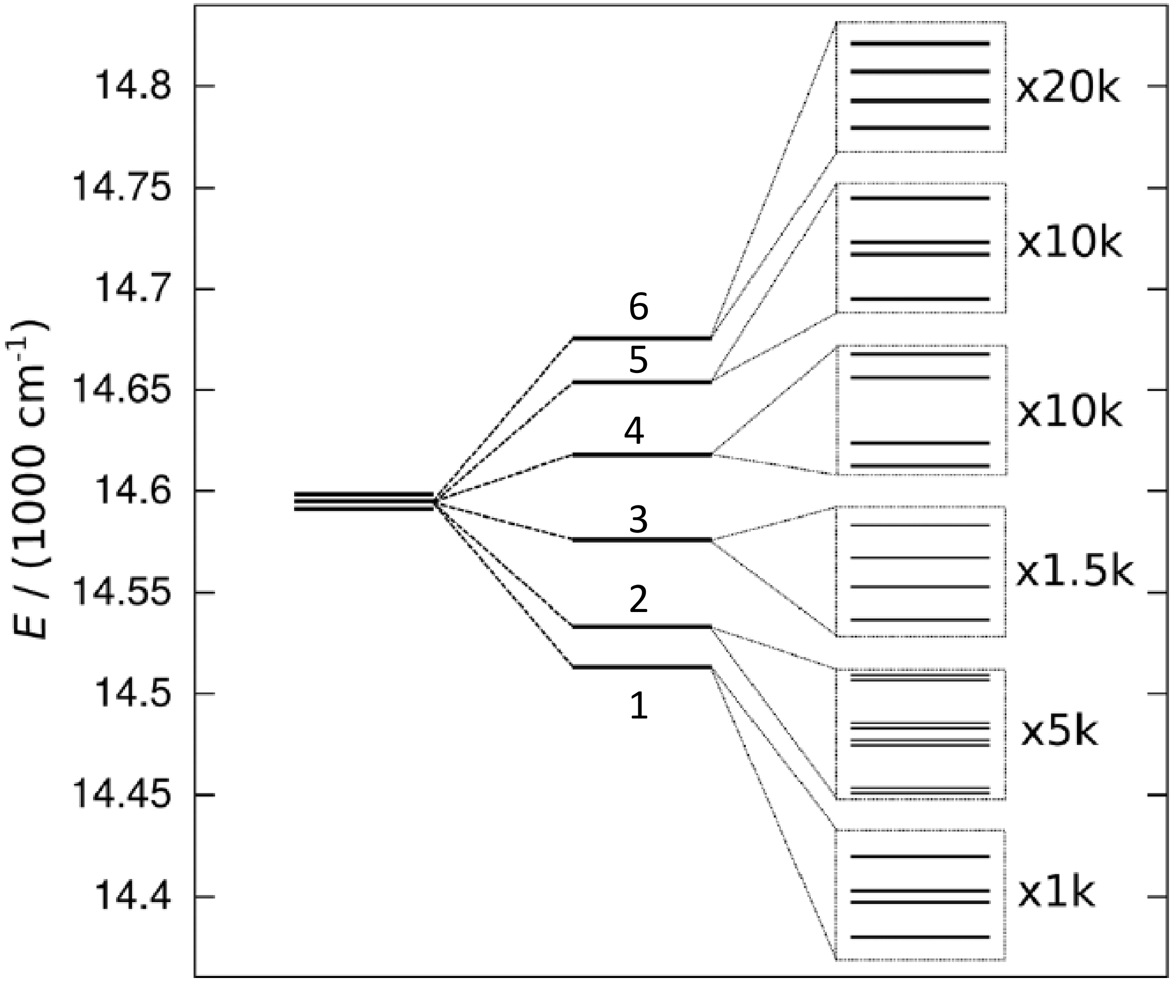
Water trimer: $D_2O(H_2O)_2$



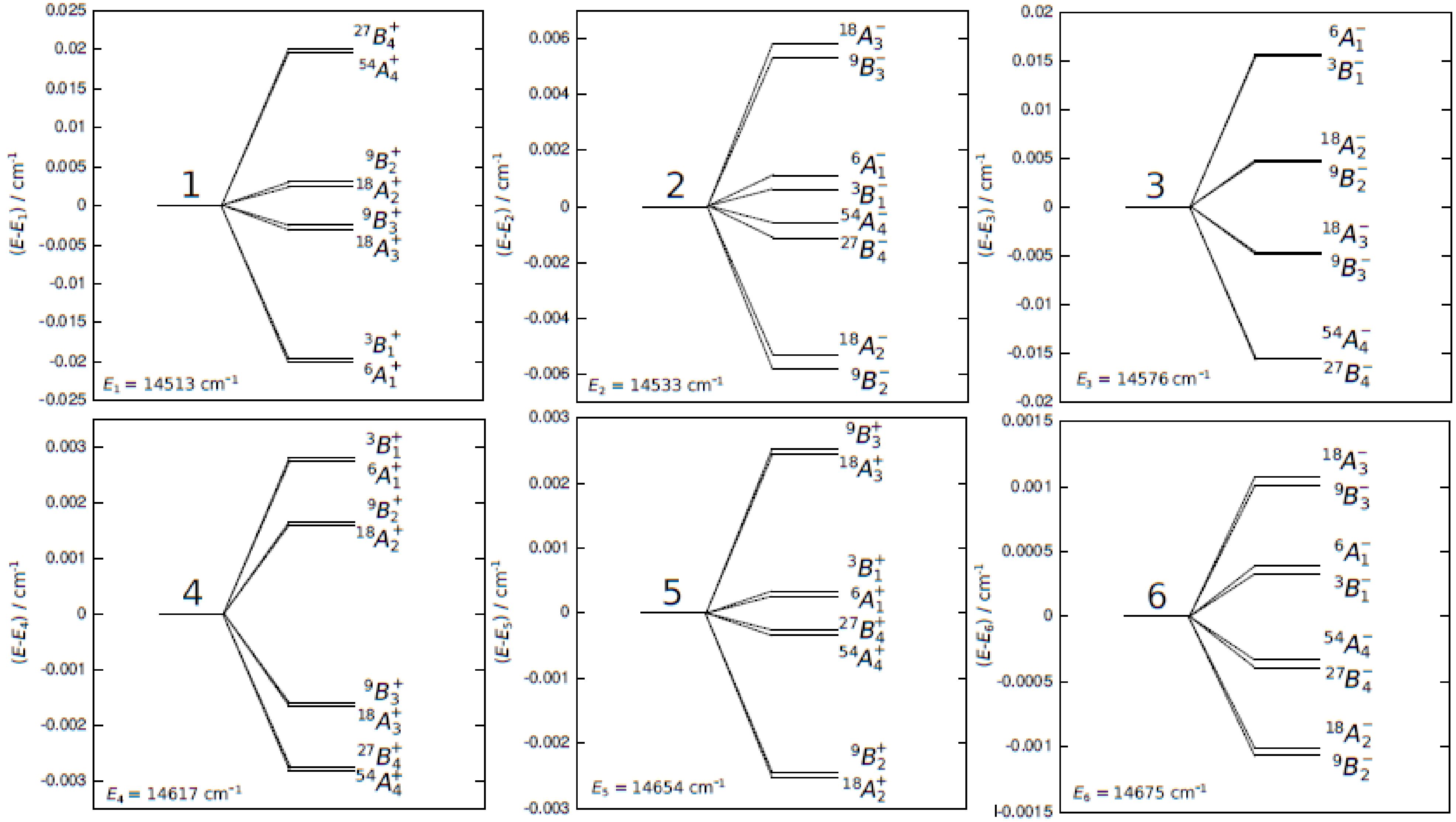
Erakovic, Cvitas, PCCP 2021.

Water trimer: $D_2O(H_2O)_2$



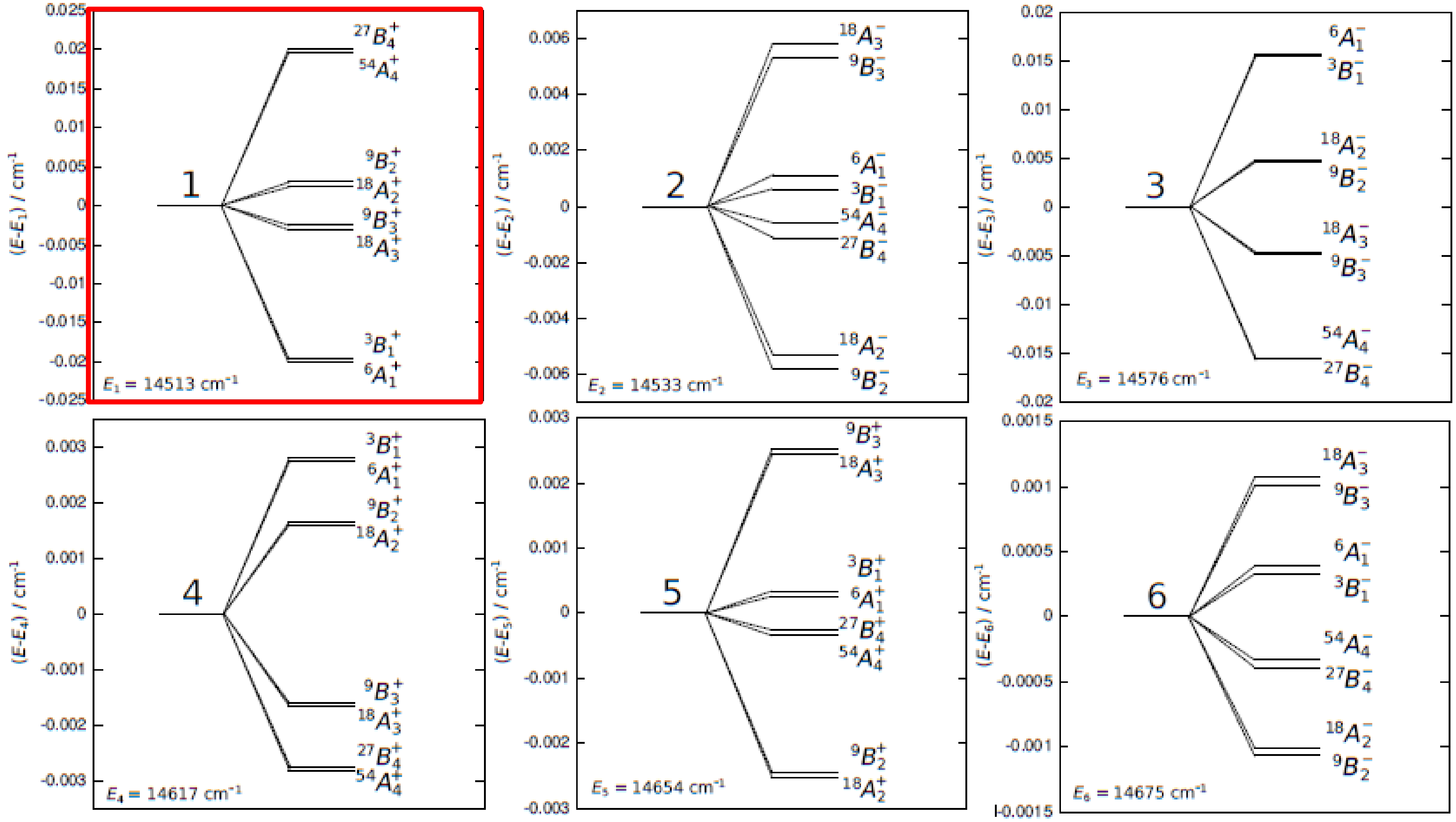


Water trimer: $D_2O(H_2O)_2$



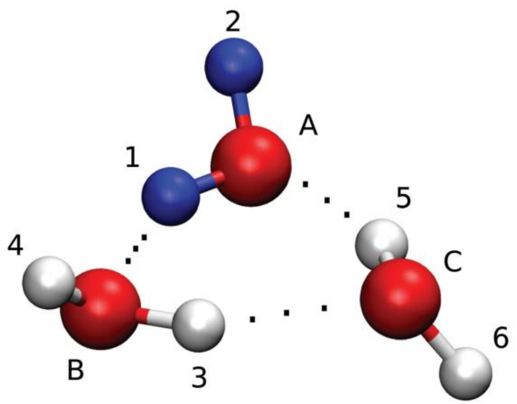
Erakovic, Cvitas, *PCCP* 2021.

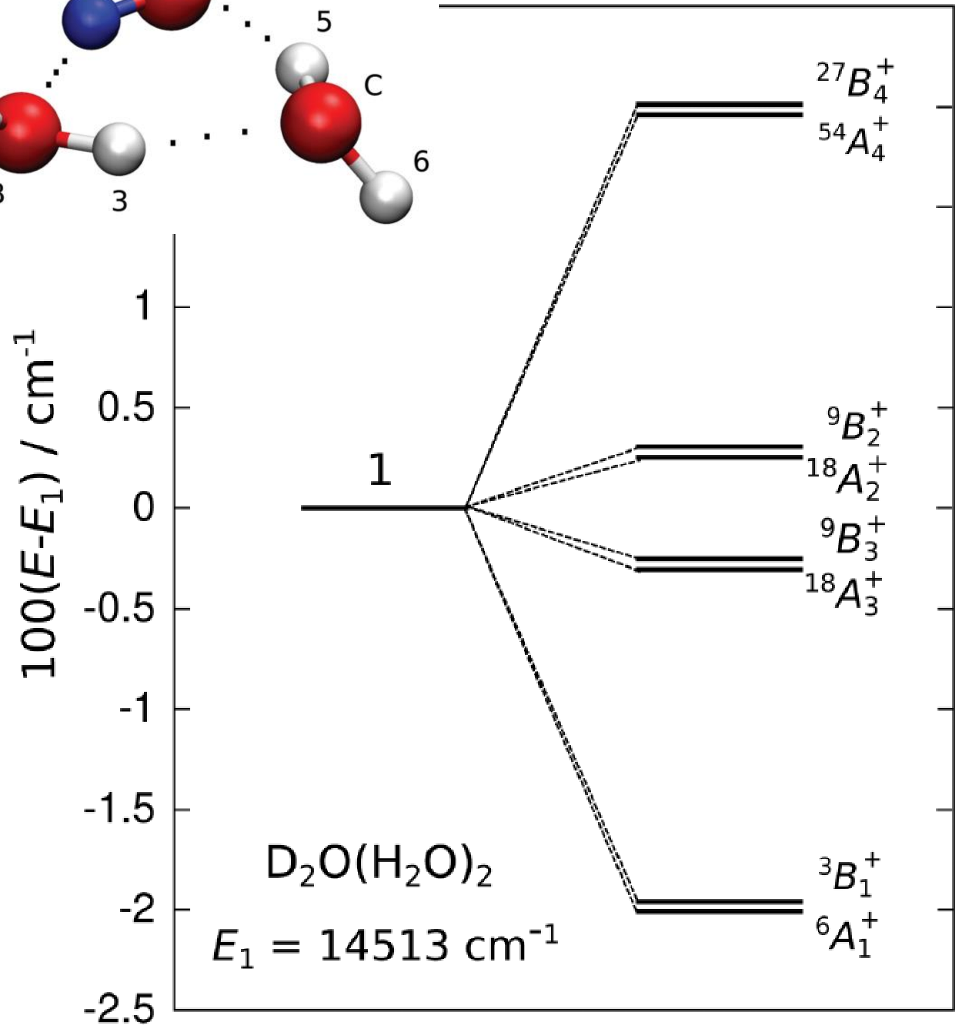
Water trimer: $D_2O(H_2O)_2$

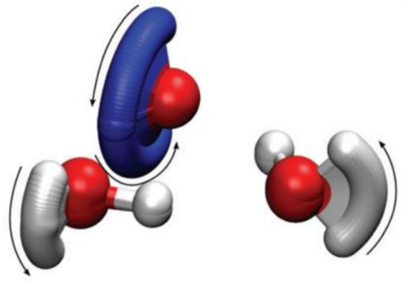


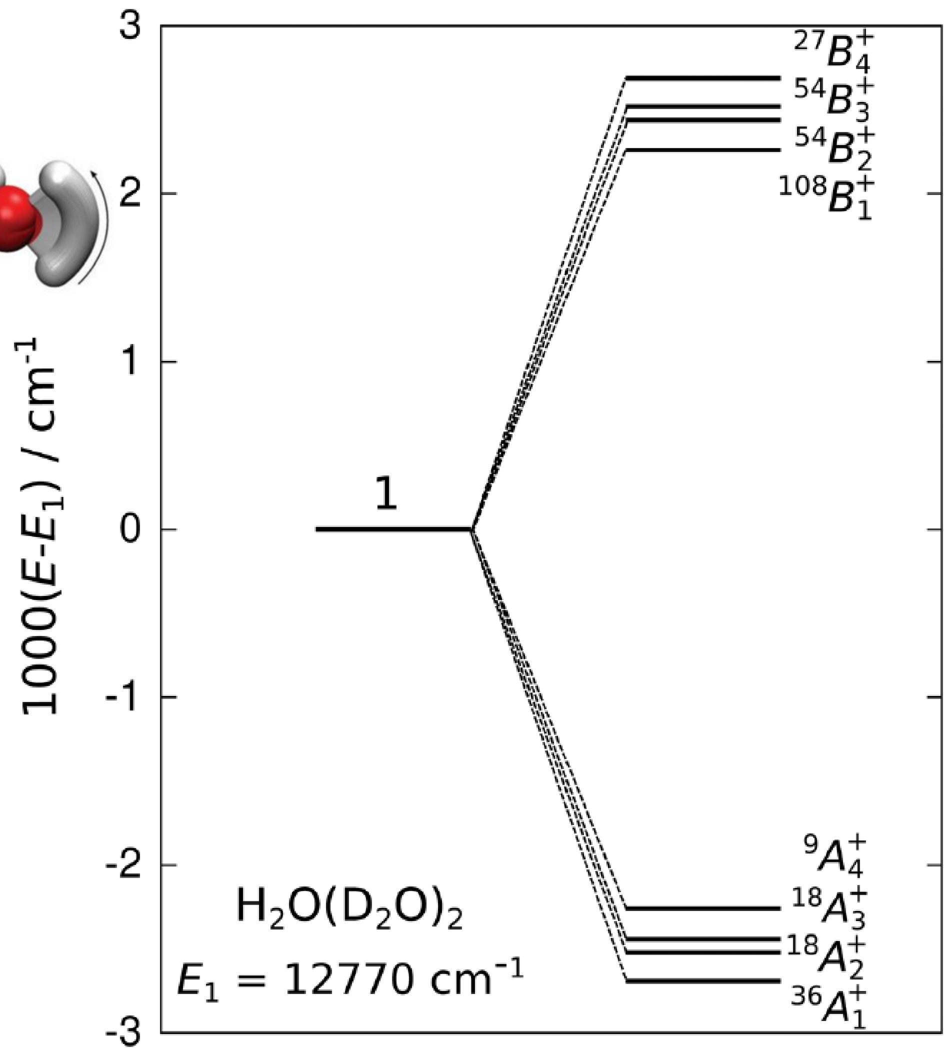
Erakovic, Cvitas, PCCP 2021.

Water trimer: $D_2O(H_2O)_2$





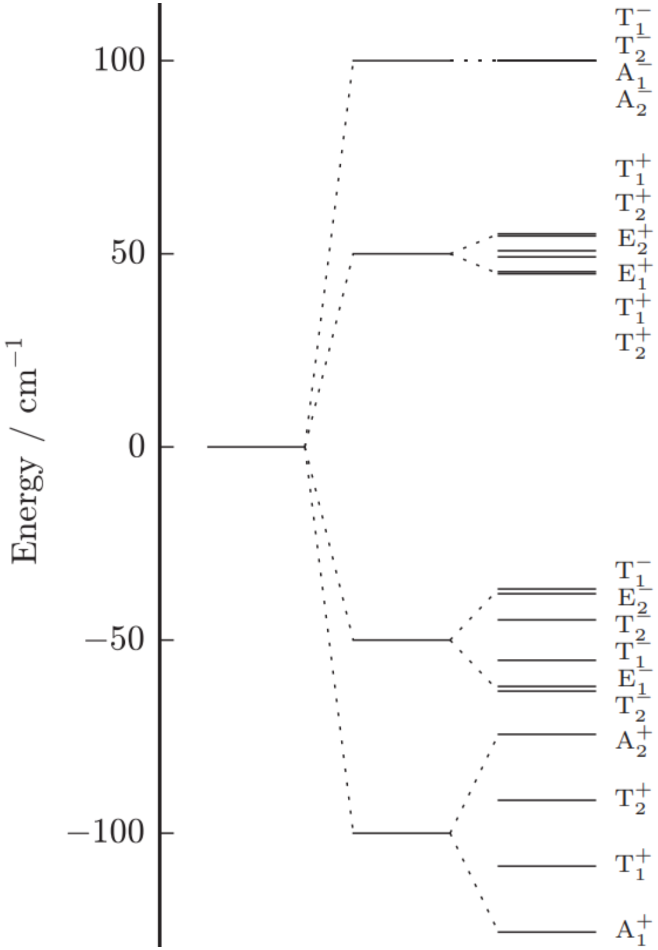


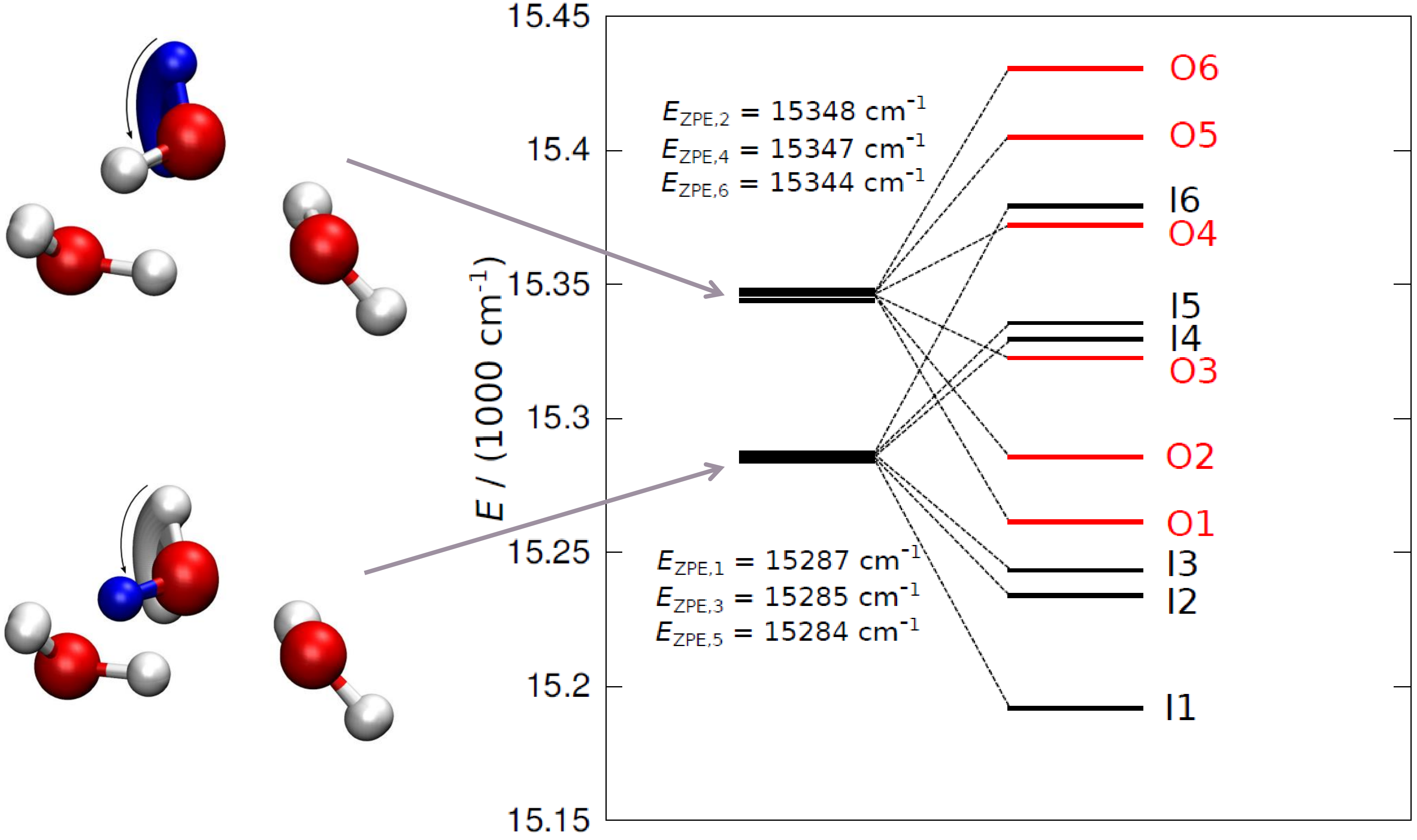


Erakovic, Cvitas, PCCP 2021.

Water trimer: $HOD(H_2O)_2$

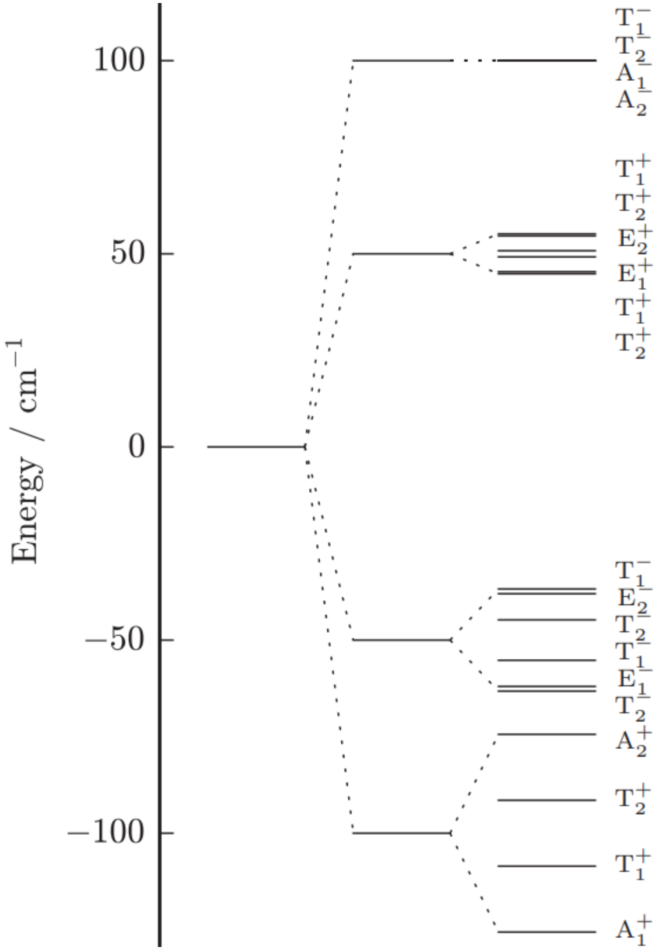
- I = in-bond D
- O = out-of-bond D

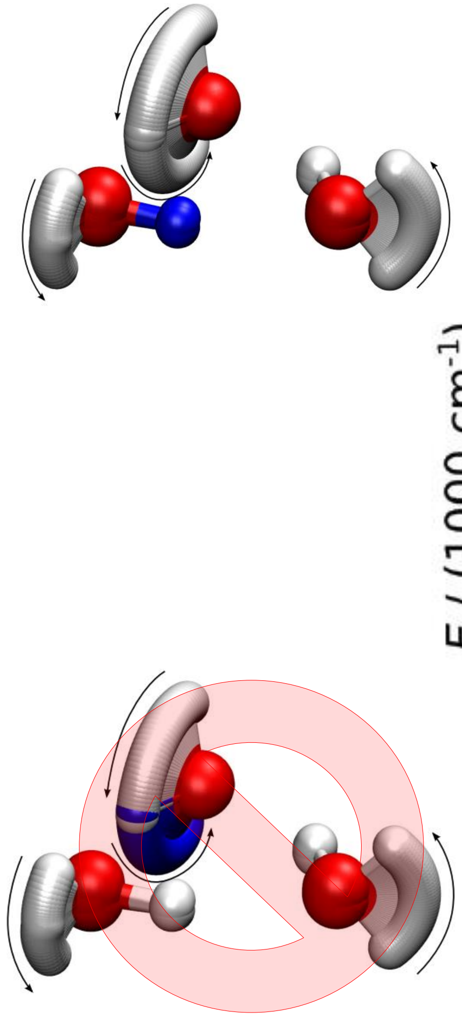


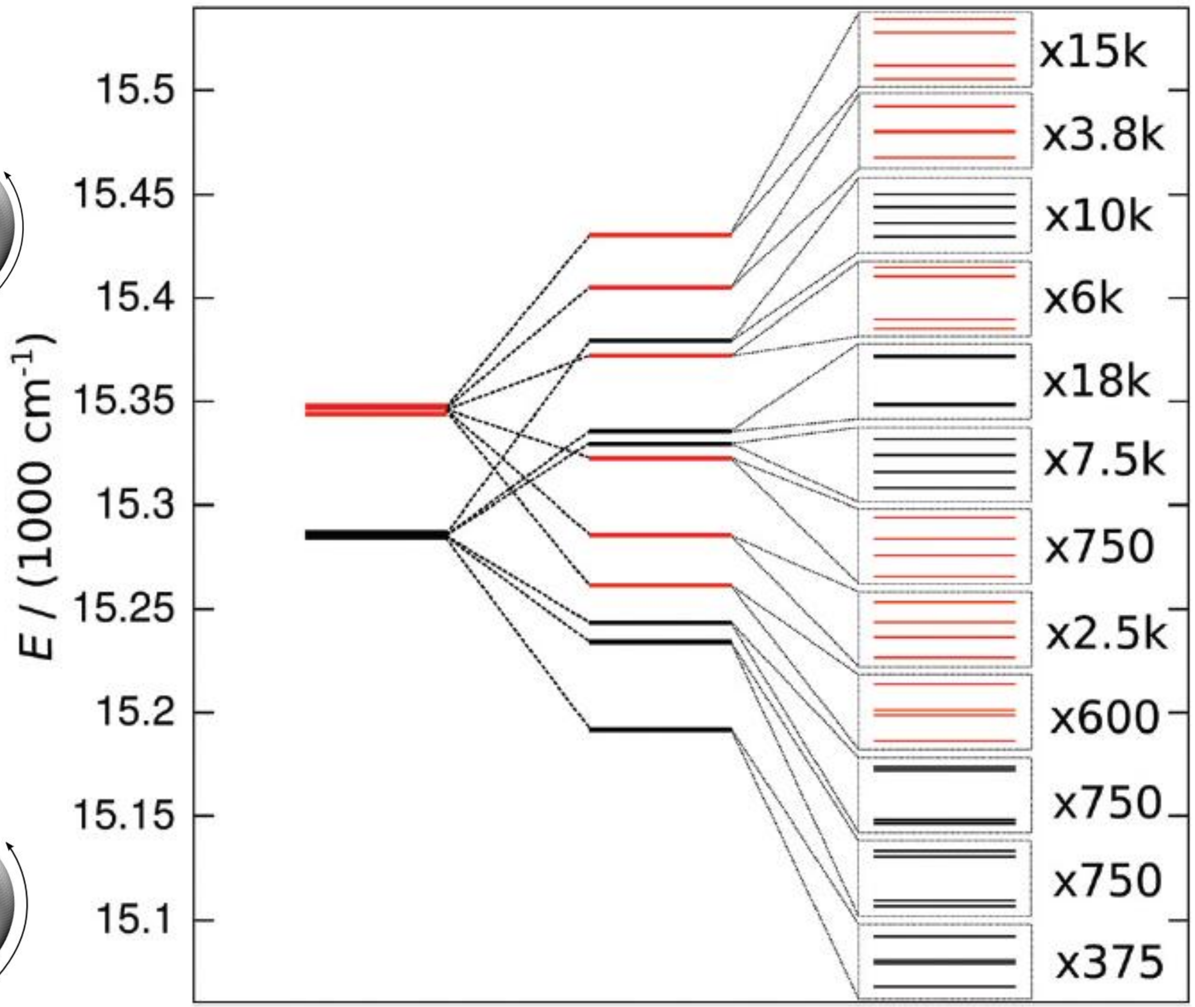


Erakovic, Cvitas, PCCP 2021.

Water trimer

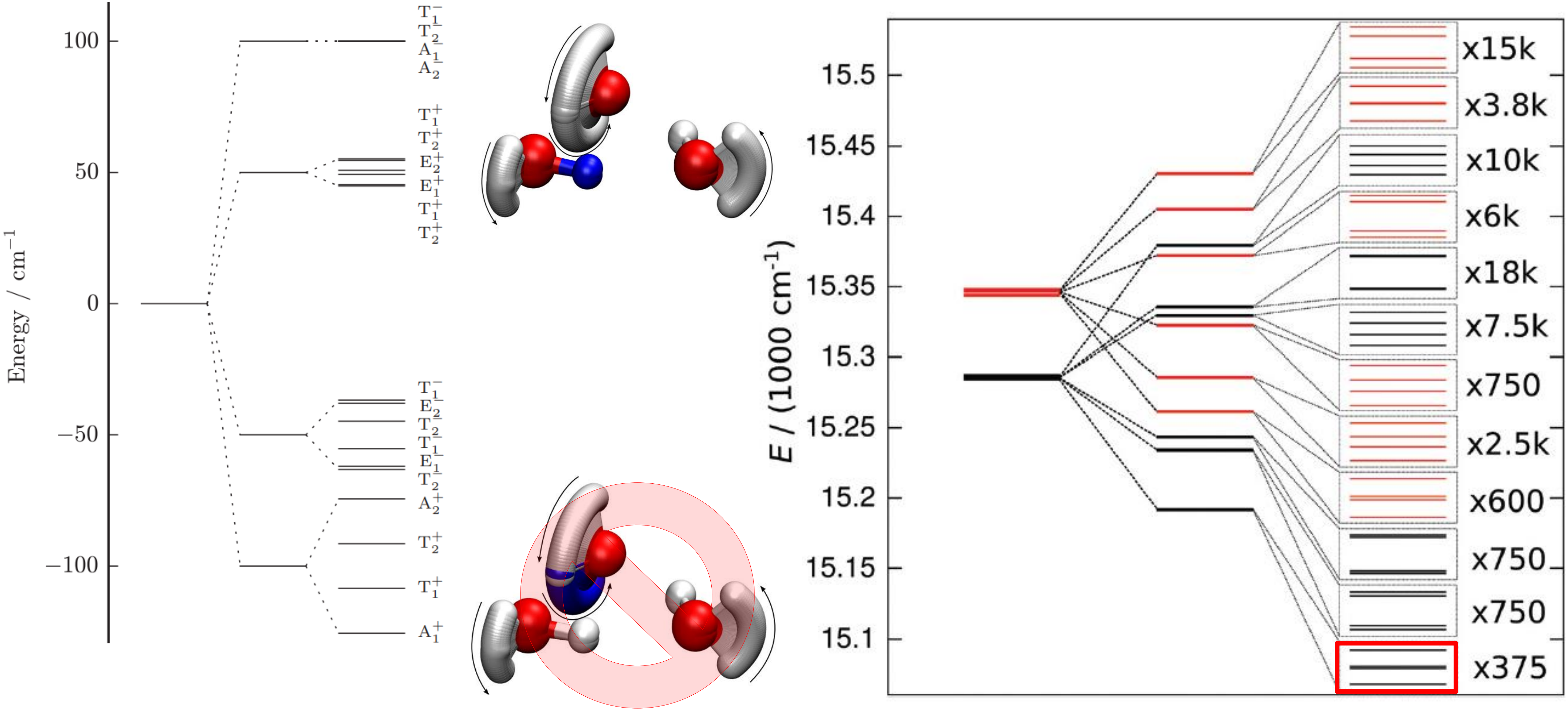






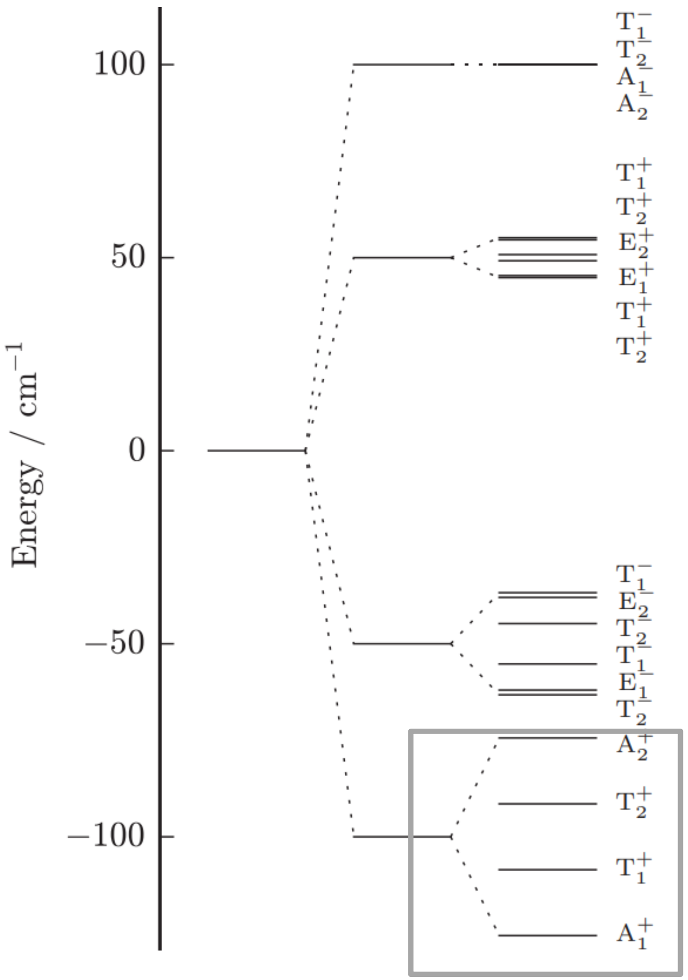
Erakovic, Cvitas, PCCP 2021.

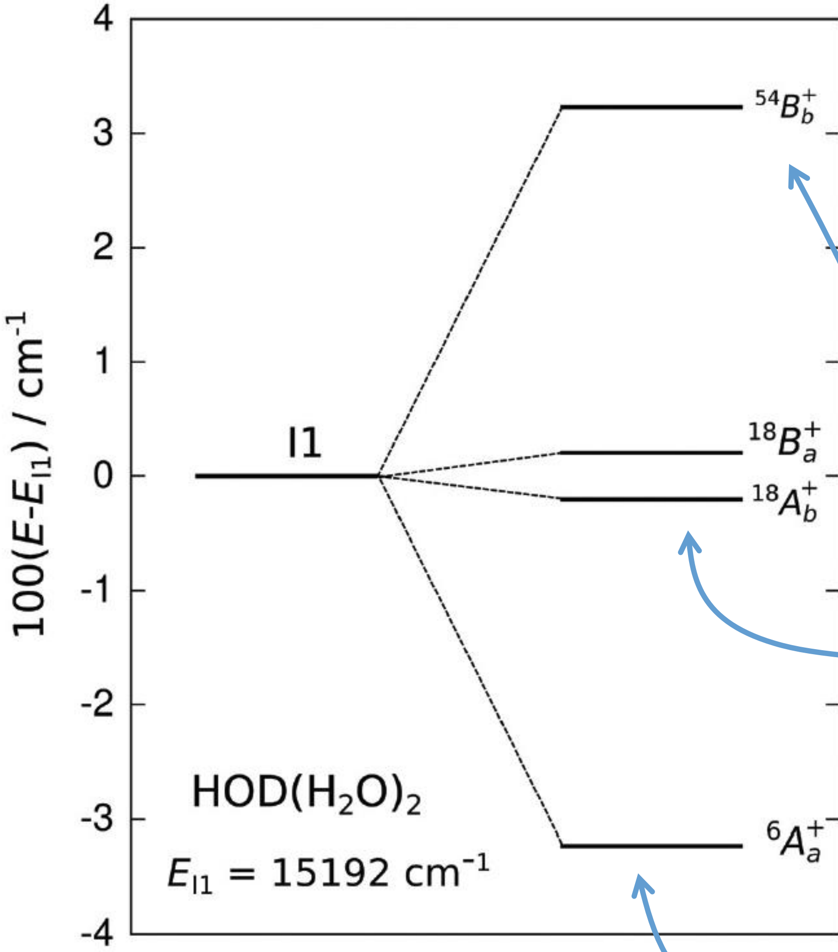
Water trimer



Erakovic, Cvitas, PCCP 2021.

Water trimer



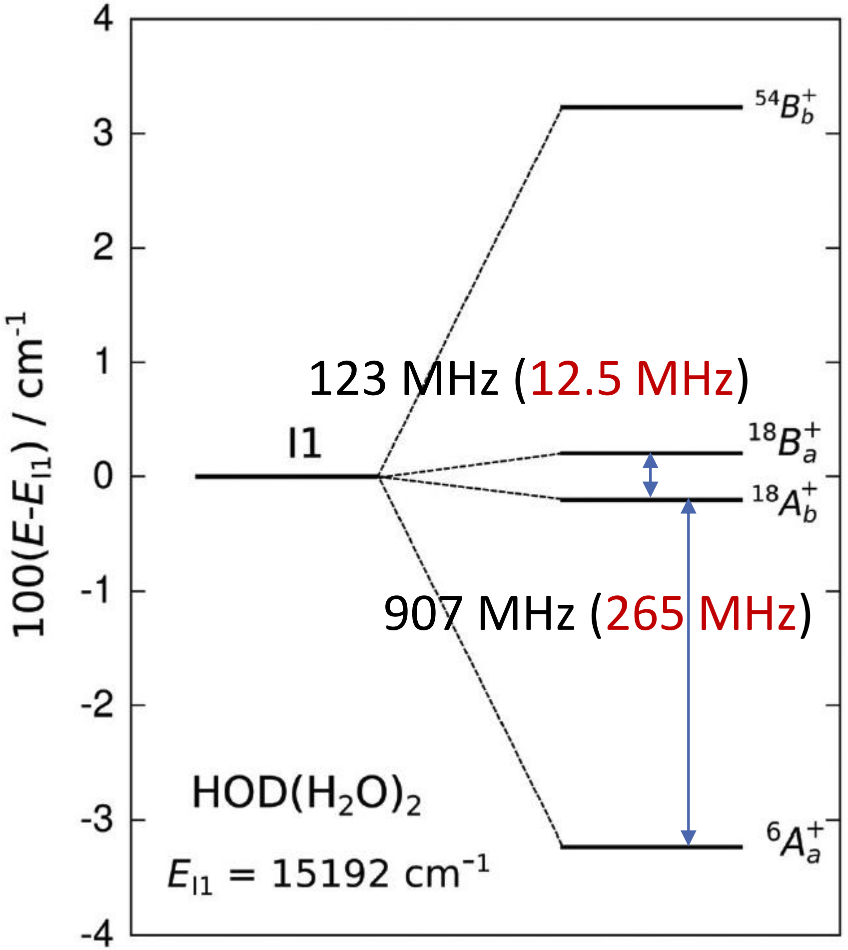


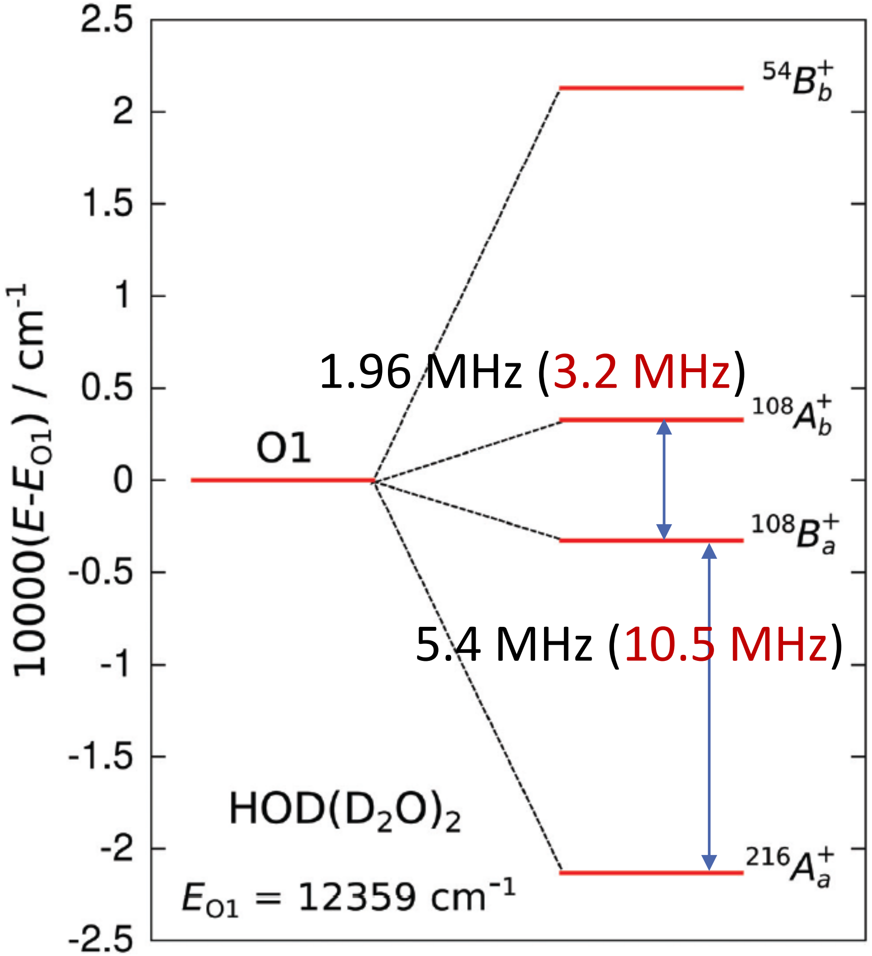
- From correlation table to G_{48} :
- $A_2^+ = B_b^+$
- $T_1^+ = A_a^+ + A_b^+ + B_a^+$
- $T_2^+ = A_b^+ + B_a^+ + B_b^+$
- $A_1^+ = A_a^+$

Erakovic, Cvitas, PCCP 2021.

Water trimer

- Lowest two levels in $(H_2O)_3$: 1100 MHz (289.4 MHz), and in $(D_2O)_3$: 3.9 MHz (5 MHz).
- Level of agreement comparable to homoisotopic trimers.
- The splitting of intermediate levels in $HOD(D_2O)_2$ is 6.5 x (7.6 x) smaller than the full width.





Erakovic, Cvitas, PCCP 2021.

Liu, Brown, Viant, Cruzan, Saykally, Mol. Phys. 1996.

Summary

- Tunneling matrix (TM) elements can be calculated using modified WKB for systems with asymmetric tunnelling paths and that are asymmetric in shape and energy.
- Theory can treat non-equivalent excitations in different wells.
- Instanton theory can be combined with higher-level quantum methods, such as VCI.
- Excited states come at no additional cost.
- Tunneling splittings in malonaldehyde quantitavely match exact quantum calculations.
- Instanton theory can semi-quantitatively describe TS in water pentamer and partially deuterated water trimer.
- TS in excited states of water clusters are within reach.
- Instantons are complementary to variational calculations because they work better for high barriers and small TM elements.
- Calculating TM elements using instanton theory is computationally cheap and relies on few potential evaluations, which leaves room for application to high-dimensional systems or using high-quality electronic potentials on-the-fly.

Outlook

- Extension of the theory to treat higher vibrational excitations.
- Inclusion of rotational degrees of freedom in the treatment.
- Application of the methodology to treat decay and rates.

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Thank you

for listening