

CHEM532 | Jan 23 2014

Molecular Vibrations

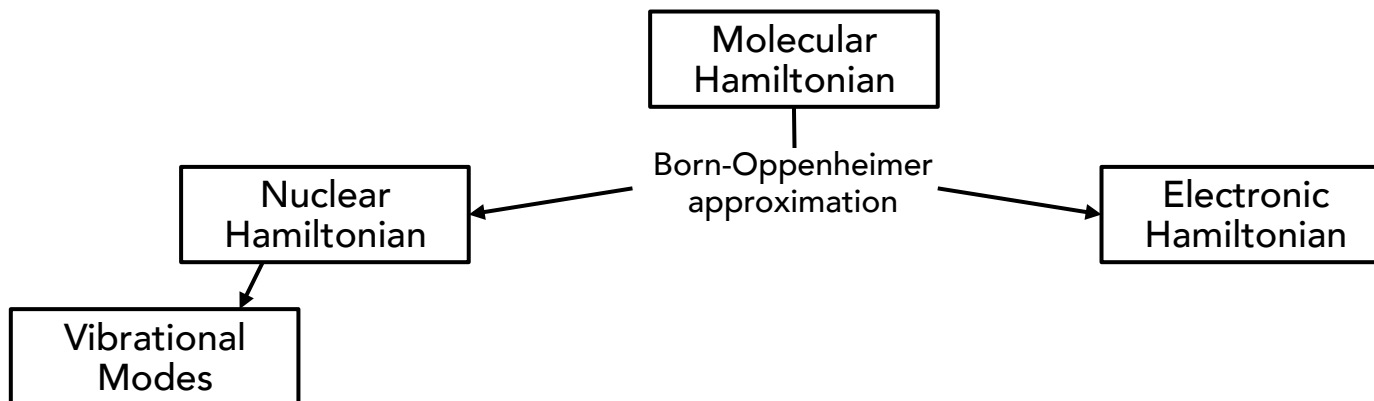
Francesco Evangelista
Emory University

Feedback

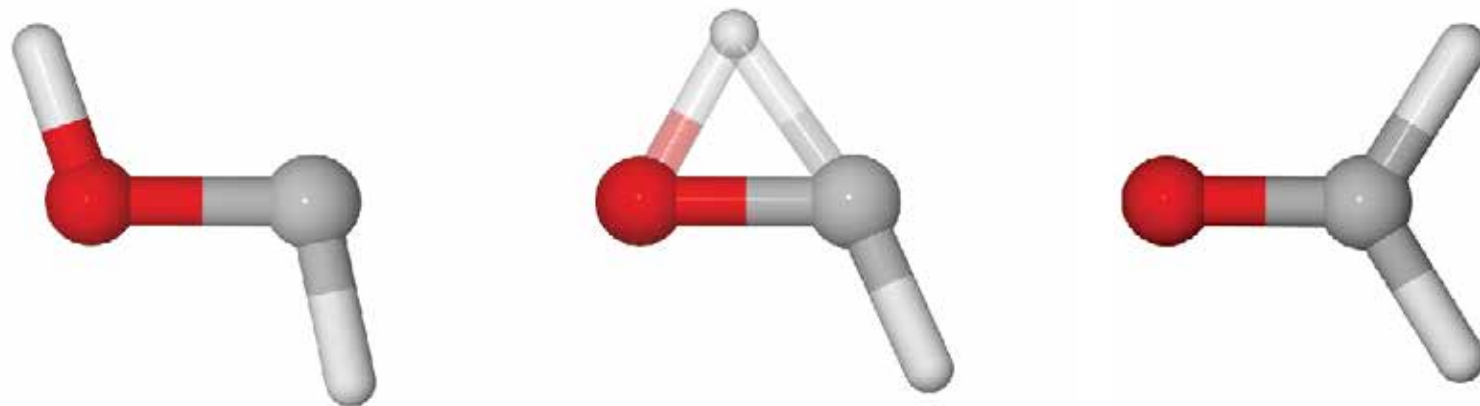
The Emerson Center account is ready to use. Please log in to `chem532@euch4e.chem.emory.edu`

The password is: `electron`

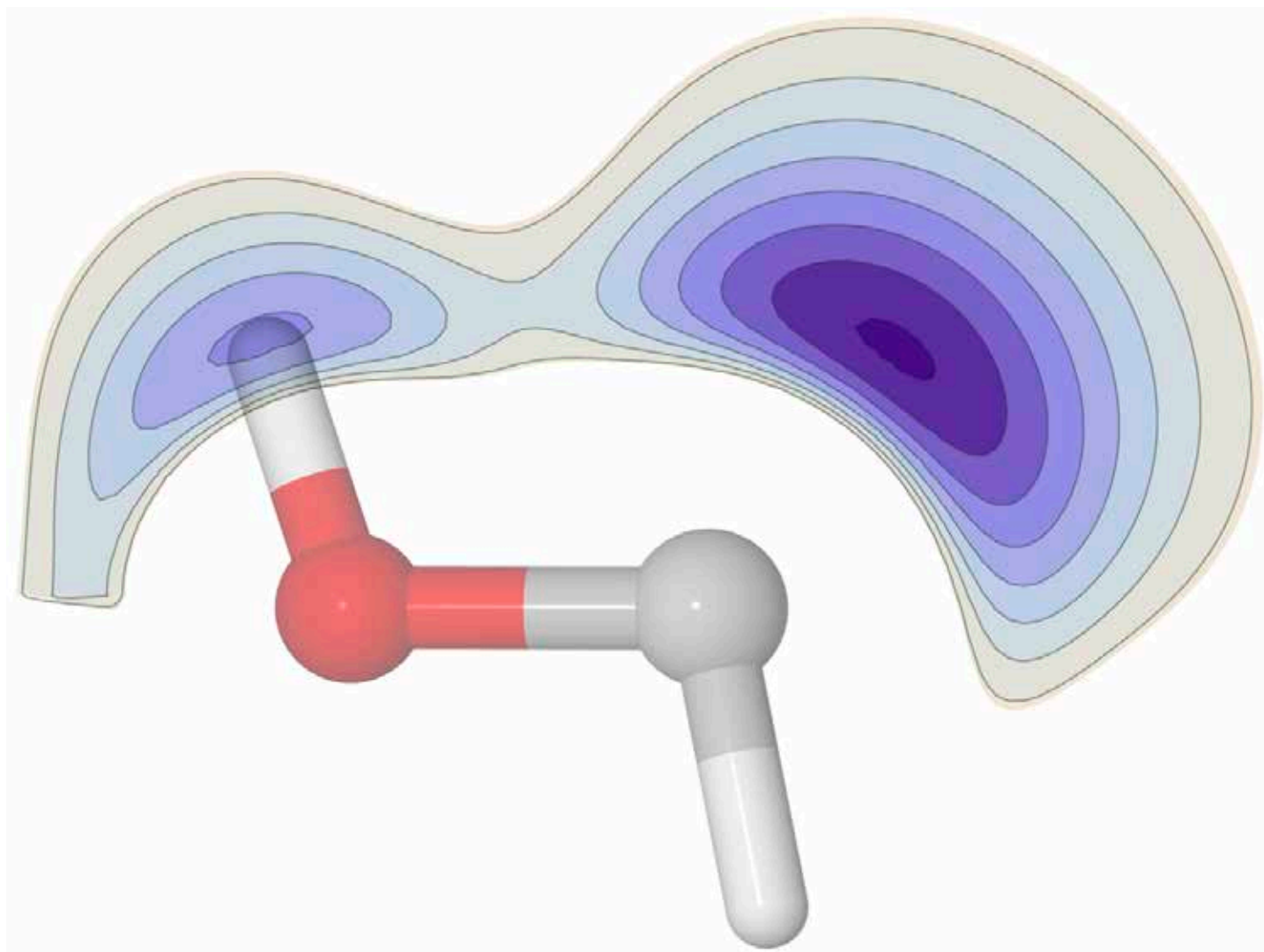
From Alex: You will see a README file and user folders including the one I made for myself (alexk) to test gaussian and orca. Gaussian works fine, and as far as I can tell orca only runs in serial. Please feel free to run tests of your own.



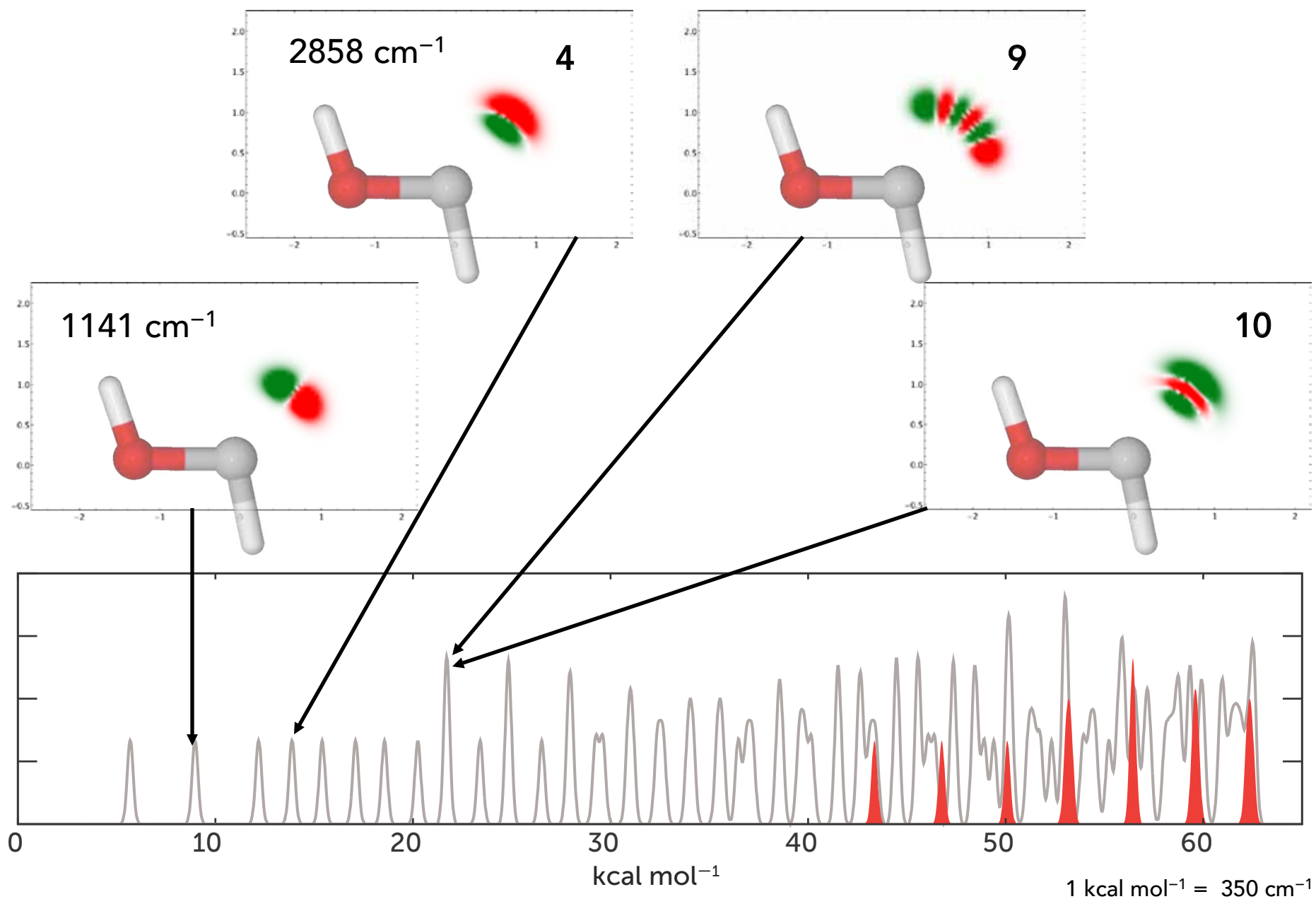
Stationary Points on the Potential Energy Surface



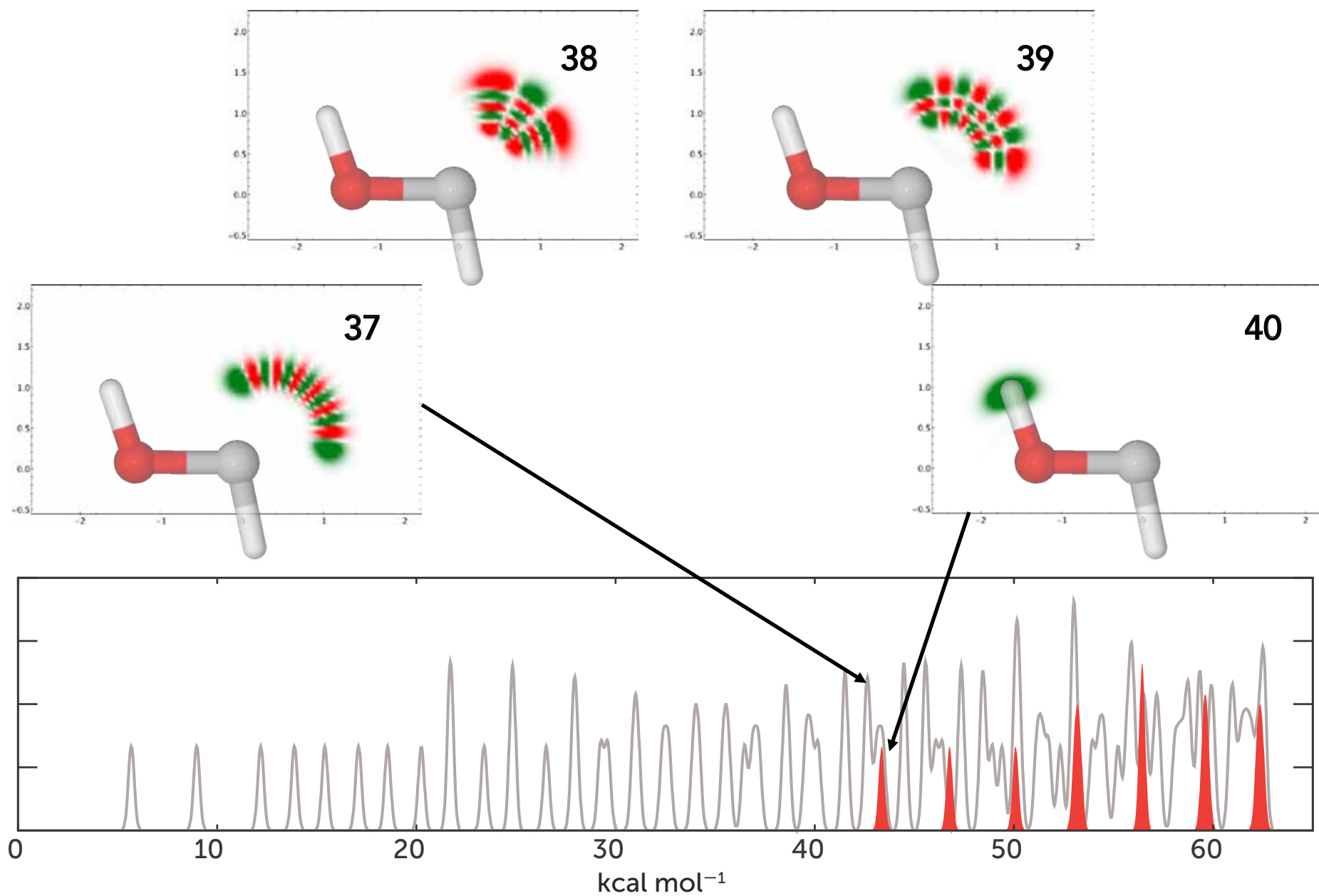
Stationary Points on the Potential Energy Surface



Solutions to the nuclear vibrational problem (using DVR)

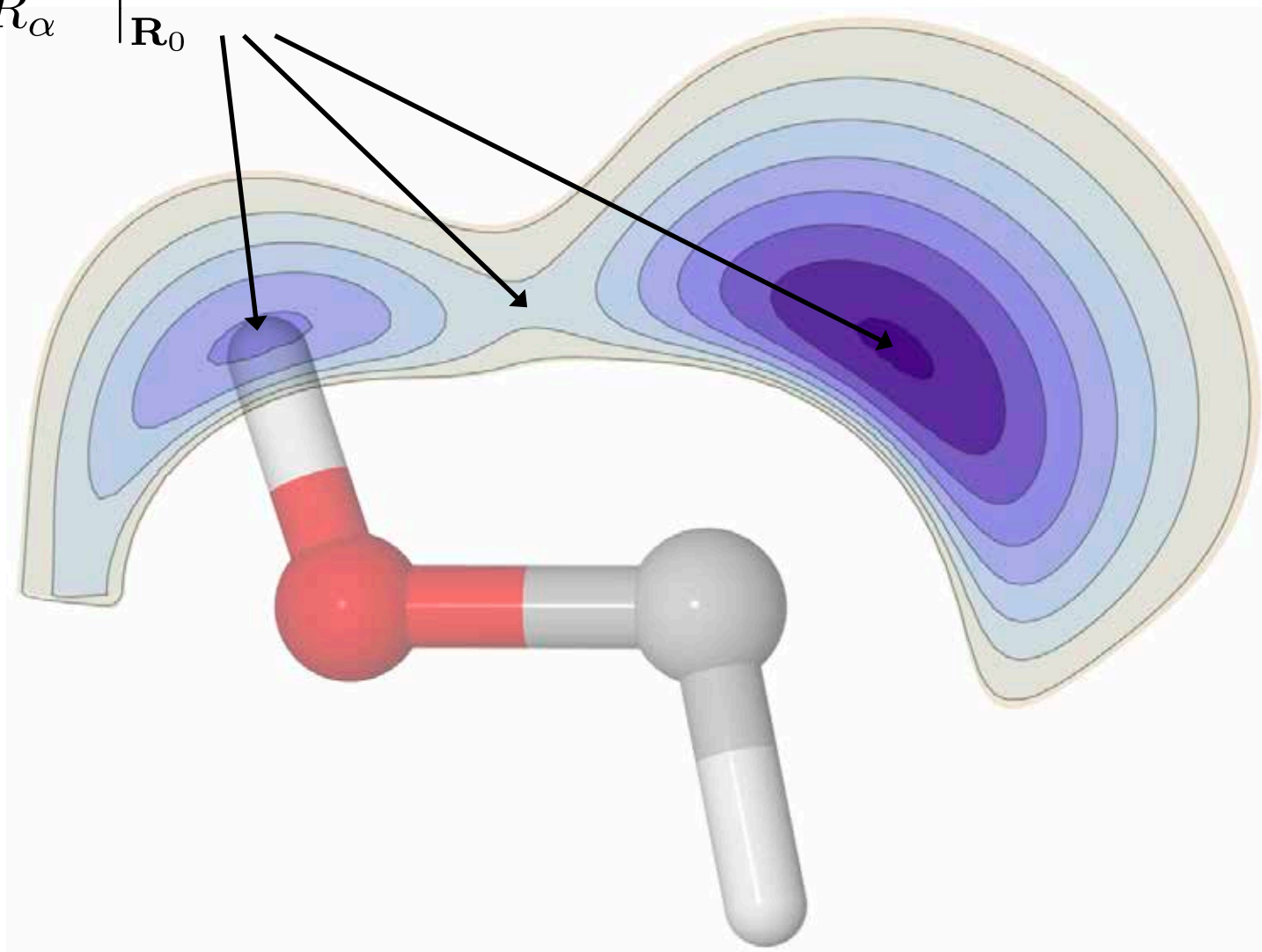


Solutions to the nuclear vibrational problem (using DVR)



Stationary Points on the Potential Energy Surface

$$\left. \frac{\partial E_n(\mathbf{R})}{\partial R_\alpha} \right|_{\mathbf{R}_0} = 0, \text{ for } \alpha = 1, \dots, 3M.$$



Water Harmonic Vibrational Frequency Analysis

VIBRATIONAL FREQUENCIES

0:	0.00	cm** ⁻¹
1:	0.00	cm** ⁻¹
2:	0.00	cm** ⁻¹
3:	0.00	cm** ⁻¹
4:	0.00	cm** ⁻¹
5:	0.00	cm** ⁻¹
6:	1616.11	cm** ⁻¹
7:	3781.46	cm** ⁻¹
8:	3887.37	cm** ⁻¹

Sym. Species	No	Approximate type of mode	Selected Freq. Value	Rating	Infrared Value	Phase	Raman Value	Phase	Comments
a ₁	1	Sym str	3657	A	3656.65	gas	3654	gas	
a ₁	2	Bend	1595	A	1594.59	gas			
b ₁	3	Anti str	3756	A	3755.79	gas			

Source: [Shimanouchi, 1972](#)

IR SPECTRUM

Mode	freq (cm** ⁻¹)	T**2	TX	TY	TZ
6:	1614.69	79.207738	(5.381799	7.088298	0.000000)
7:	3782.74	5.035175	(1.407960	1.747233	0.000000)
8:	3888.68	48.568450	(-5.460797	4.329913	0.000000)

Water Harmonic Vibrational Frequency Analysis

----- INNER ENERGY

The inner energy is: $U = E(\text{el}) + E(\text{ZPE}) + E(\text{vib}) + E(\text{rot}) + E(\text{trans})$

Summary of contributions to the inner energy U:

Electronic energy	...	-76.42591080 Eh	
Zero point energy	...	0.02115266 Eh	13.27 kcal/mol
Thermal vibrational correction	...	0.00000302 Eh	0.00 kcal/mol
Thermal rotational correction	...	0.00141627 Eh	0.89 kcal/mol
Thermal translational correction	...	0.00141627 Eh	0.89 kcal/mol

Total thermal energy

		-76.40192257 Eh	
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----- ENTHALPY

The enthalpy is $H = U + kB*T$ (kB is Boltzmann's constant)

Total free energy	...	-76.40192257 Eh	
Thermal Enthalpy correction	...	0.00094421 Eh	0.59 kcal/mol

Total Enthalpy

	...	-76.40097836 Eh	
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----- ENTROPY

The entropy contributions are $T*S = T*(S(\text{el})+S(\text{vib})+S(\text{rot})+S(\text{trans}))$

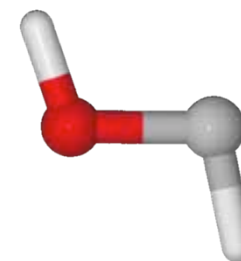
The entropies will be listed as multiplied by the temperature to get units of energy

Electronic entropy	...	0.00000000 Eh	0.00 kcal/mol
Vibrational entropy	...	0.00000341 Eh	0.00 kcal/mol
Rotational entropy	...	0.00459453 Eh	2.88 kcal/mol
Translational entropy	...	0.01644380 Eh	10.32 kcal/mol

Final entropy term

	...	0.02104175 Eh	13.20 kcal/mol
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HOCH Harmonic Vibrational Frequency Analysis



IR SPECTRUM

Mode	freq (cm** ⁻¹)	T**2	TX	TY	TZ
6:	1089.93	116.861108	(-0.228493	-0.884066	-10.771598)
7:	1211.59	136.106325	(11.455775	-2.194162	-0.239159)
8:	1322.43	68.062148	(8.146421	-1.297519	-0.120080)
9:	1502.96	24.143184	(3.571669	3.357960	-0.332374)
10:	2843.50	139.529313	(-2.205131	11.567634	-0.925497)
11:	3672.18	64.982917	(-2.954974	7.484039	-0.490103)

Table 1 | Comparison of computed and experimental vibrational frequencies

Vibrational description*	ω (I_{rel})	ν	Expt. (I_{rel})
<i>trans</i> -H-C-OH (1t)			
78% ν_1 (OH str.) + 8% [$\nu_3 + 2\nu_6$]	3,765.4 (57)	3,561.6	3,500.6 (43)
84% [$\nu_4 + \nu_5 + \nu_6$]		3,520.8	
83% [$3\nu_5$]		3,516.0	
72% [$\nu_3 + \nu_4$] + 15% ν_2 (CH str.) + 14% [$\nu_3 + \nu_5$]		2,785.5	2,776.2 (16)
55% ν_2 (CH str.) + 18% [$\nu_3 + \nu_4$]	2,876.6 (99)	2,706.5	2,703.3 (37)
96% ν_3 (HOC def. + HCO def.)	1,513.7 (13)	1,475.1	1,465.5 (10)
92% ν_4 (CO str.)	1,334.1 (39)	1,300.5	1,297.1 (53)
97% ν_5 (HOC def. - HCO def.)	1,220.0 (100)†	1,183.5	1,183.2 (100)
97% ν_6 (twist)	1,094.3 (82)	1,058.9	1,048.5 (88)

HOCH Harmonic Vibrational Frequency Analysis

