The MULTIMODE Approach to Molecular (Ro)Vibrations

- Review of Vibration SCF Theory

- Some elementary examples

- Post VSCF theories emphasis on VSCF/VCI

- MULTIMODE and the n-mode representation

- of the potential C_2H_4

- Torsional motion HOCO

- Local monomer theory

1. Hartree Theory — 2 mode

$$H = h_0(1) + h_0(2) + V(Q_1, Q_2)$$

$$h_0(i) = -\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\omega_i^2 Q_i^2 \, , \qquad i = 1, 2$$

$$[h_0(i) - \varepsilon_{n_i}]\phi_{n_i}^{(0)}(Q_i) = 0 \, ; \qquad \phi_{n_i}^{(0)} - H.O. \text{ wave functions}$$

Seek variationally optimum solution to

$$[H - E]\psi(Q_1, Q_2) = 0$$

of the "Hartree" product form

$$\psi(Q_1, Q_2) = \phi_{n_1}(Q_1)\,\phi_{n_2}(Q_2) \, ,$$

where $\langle \phi_{n_1} | \phi_{n_1} \rangle_{Q_1} = \langle \phi_{n_2} | \phi_{n_2} \rangle_{Q_2} = 1$

Use method of Lagrange multipliers (again)

Form the functional

$$E[\phi_{n_1}, \phi_{n_2}, \lambda_1, \lambda_2] = \langle \phi_{n_1}\phi_{n_2}|H|\phi_{n_1}\phi_{n_2}\rangle - \lambda_1[\langle \phi_{n_1}|\phi_{n_1}\rangle - 1]$$

$$- \lambda_2[\langle \phi_{n_2}|\phi_{n_2}\rangle - 1]$$

$$\frac{\delta F}{\delta \phi_{n_1}} = \frac{\delta E}{\delta \phi_{n_2}} = \frac{\delta E}{\delta \lambda_1} = \frac{\delta E}{\delta \lambda_2} = 0$$

Explicitly

$$\int dq_1 \, \delta\phi_{n_1}^* \, \langle\phi_{n_2}|H|\phi_{n_2}\rangle_{Q_2} |\phi_{n_1}\rangle - \lambda_1 \int \delta\phi_{n_1}^* |\phi_{n_1}\rangle dq_1 = 0$$

Must hold for any $\delta\phi_{n_1}^*$ ∴

$$[\langle\phi_{n_2}|H|\phi_{n_2}\rangle_{Q_2} - \lambda_1] \phi_{n_1}(Q_1) = 0$$

$\frac{1}{\varepsilon}$
1

$$[\langle\phi_{n_1}|H|\phi_{n_1}\rangle_{Q_1} - \lambda_2] \phi_{n_2}(Q_2) = 0$$

Insert expression for H:

$$\int dq_1 \, \delta\phi_{n_1}^* \Big[h_0(1) \langle\phi_{n_2}|\phi_{n_2}\rangle + \langle\phi_{n_2}|h_0(2)|\phi_{n_2}\rangle \cdot \phi_{n_1} + \langle\phi_{n_2}|V|\phi_{n_2}\rangle_{Q_2} \phi_{n_1}$$

"
2

$$-\lambda_1 \phi_{n_1} \Big] = 0$$

and analogous result for ϕ_{n_2}

$$\int dq_1 \, \delta\phi_{n_1}^* \, \phi_{n_1} = 0 \quad \text{condition to satisfy}$$

$$\frac{\delta E}{\delta \lambda_1} = 0 \quad ; \quad \langle\phi_{n_1}|\phi_{n_1}\rangle = 1 \; \therefore \; \langle\delta\phi_{n_1}|\phi_{n_1}\rangle = 0$$

Thus,

$$[h_0(1) + \langle\phi_{n_2}|V(1,2)|\phi_{n_2}\rangle_{Q_2} - \lambda_1] \phi_{n_1}(Q_1) = 0$$

$$h_0(2) + \langle\phi_{n_1}|V(1,2)|\phi_{n_1}\rangle_{Q_1} - \lambda_2] \phi_{n_2}(Q_2) = 0$$

Post Hartree

Recall for the two-mode example

$$H = h(1) + h(2) + V(1,2)$$

and the SCF eigenvalues equations are

$$[h(1) + V_{n_2,n_2}(1) - \varepsilon_{n_1}]\phi_{n_1}(1) = 0$$
$$[h(2) + V_{n_1,n_1}(2) - \varepsilon_{n_2}]\phi_{n_2}(2) = 0$$

These can be written as

$$h^{SCF}(1)\phi_{n_1}(1) = \varepsilon_{n_1}\phi_{n_1}(1)$$
$$h^{SCF}(2)\phi_{n_2}(2) = \varepsilon_{n_2}\phi_{n_2}(2)$$

where the definitions of the "SCF" Hamiltonians are obvious.

Thus,

$$H = h^{SCF}(1) + h^{SCF}(2) + V(1,2) - V_{n_2,n_2}(1) - V_{n_1,n_1}(2).$$

If we apply perturbation theory to this H using the SCF product function then

the perturbation is obviously $V(1,2) - V_{n_2,n_2}(1) - V_{n_1,n_1}(2)$. The current HW

and thus,

$$E^{(2)}_{n_1,n_2} = \sum_{m,l}{}' \frac{\left|\langle n_1,n_2 \left| V_{corr}(1,2) \right| m_1,m_2 \rangle\right|^2}{E^{(0)}_{n_1,n_2} - E^{(0)}_{m_1,m_2}},$$

where $E^{(0)}_{n_1,n_2} = \varepsilon_{n_1} + \varepsilon_{n_2}$; $E^{(0)}_{m_1,m_2} = \varepsilon_{m_1} + \varepsilon_{m_2}$ and where $|m_1,m_2\rangle$ are <u>virtual</u>

eigenstates of the SCF Hamiltonian $h^{SCF}(1) + h^{SCF}(2)$.

This is analogous to MP2 PT theory of electronic structure theory. It is referred to as CC-VSCF by Gerber and co-workers who developed and apply it extensively

Virtual State "CI" (VCI)

The VSCF Hamiltonian, if diagonalized in a basis, as is typical, generates not only the VSCF state of interest but additional states called "virtual states". These form a convenient orthonormal complete set is which to expand the exact wavefunctions, i.e.,

$$\psi_L = \sum_{n=0}^{N} C_{n_1,n_2...,L} \phi_{n_1}(Q_1)\phi_{n_2}(Q_2)...$$

In this expansion suppose **n** = 0 is the VSCF state

The Watson Hamiltonian - VSCF and VCI

$$\hat{H} = \frac{1}{2}\sum_{\alpha\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{2}\sum_k \frac{\partial^2}{\partial Q_k^2} - \frac{1}{8}\sum_\alpha \mu_{\alpha\alpha} + V(\mathbf{Q})_l, \qquad (1)$$

$$\left(T_l + \left\langle \prod_{i\neq l}^N \phi_{n_i}^{(i)} \middle| V + T_c \middle| \prod_{i\neq l}^N \phi_{n_i}^{(i)} \right\rangle - \epsilon_{n_l}^{(l)}\right)\phi_{n_l}^{(l)}(Q_l) = 0, \quad l = 1, N, \qquad (4)$$

$$\Psi_K^{VCI} = \Psi_{n_1,n_2,\dots,n_N}^{VSCF} + \sum_{n_1',n_2',\dots,n_N'} C_{n_1',n_2',\dots,n_N'}^K \Psi_{n_1',n_2',\dots,n_N'}^{Virtuals}$$

Issues:

The size of the Hamiltonian matrix

Potential matrix element - quadratures

Potential matrix elements

$$\left\langle \prod_{n'_i=1,}^{f} \phi_{n'_i}(Q_i) \middle| V(Q_1, Q_2, ..., Q_f) \middle| \prod_{n_i=1}^{f} \phi_{n_i}(Q_i) \right\rangle$$

Without some special form for the potential, e.g., a sum of products, these matrix elements are very time computationally intensive. (They are done by numerical quadratures, which is an active area of research.)

The Hamiltonian matrix

Direct diagonalization is feasible for matrices of order 50 K or so. Iterative diagonalization, e.g., block Davidson can deal with full matrices of order 100 K or bigger. Sparse matrices of order 1000 K can also be treated.

TABLE I. Comparison of VSCF, small VSCF-CI, exact V-CI, and previous exact (Ref. 13) vibrational energies (cm^{-1}) relative to the zero-point energy for nonrotating HO_2.

v_1	v_2	v_3	VSCF	VSCF-CI	V-CI	Exact
1	0	0	1071.47	1065.66	1065.49	1065.49
0	1	0	1331.69	1298.25	1296.38	1296.38
2	0	0	2104.78	2091.53	2091.12	2091.12
1	1	0	2414.82	2362.74	2359.53	2359.54
0	2	0	2699.67	2530.59	2516.68	2516.68
3	0	0	3104.99	3082.41	3081.02	3081.02
0	0	1	3259.83	3336.05	3333.68	3333.69
2	1	0	3459.34	3393.34	3387.01	3387.01
1	2	0	3791.72	3609.70	3589.80	3589.80
0	3	0	4102.21	3773.12	3725.78	3725.77
4	0	0	4076.39	4044.13	4041.28	4041.29
3	1	0	4469.92	4378.18	4368.56	4368.57
1	0	1	4351.48	4426.25	4421.44	4421.46
2	2	0	4843.90	4642.88	4615.59	4615.59
0	1	1	4529.21	4708.13	4688.32	4688.34
1	3	0	5198.27	4868.30	4817.05	4817.06
0	4	0	5530.71	5057.59	4944.46	4944.45
5	0	0	5025.99	4986.70	4975.91	4975.91
4	1	0	5450.63	5348.30	5332.50	5332.52
2	0	1	5393.68	5457.37	5447.89	5447.90
3	2	0	5860.99	5649.95	5610.66	5610.67
1	1	1	5630.15	5768.73	5743.02	5743.04
2	3	0	6253.28	5927.55	5850.96	5850.97
6	0	0	5979.67	5940.39	5888.69	5888.64
0	2	1	5842.03	5963.18	5911.88	5911.90
1	4	0	6625.87	6187.59	6052.08	6052.08
0	5	0	6974.53	6416.84	6155.50	6155.47

TABLE VI. Comparison of V-CI and exact (Ref. 14) vibrational energies (cm^{-1}) of H_2O for $J=0$.

v_s	v_b	v_a	V-CI	Exact	v_s	v_b	v_a	V-CI	Exact
				Even					
0	0	0	4 637.97	4 637.97	0	6	0	8 913.80	8 870.59
0	1	0	1 594.78	1 594.78	0	1	2	9 000.13	9 000.11
0	2	0	3 151.63	3 151.63	1	4	0	9 730.15	9 724.40
1	0	0	3 657.04	3 657.04	0	7	0	10 290.19	10 087.15
0	3	0	4 666.81	4 666.79	2	2	0	10 284.19	10 284.35
1	1	0	5 235.04	5 235.03	0	2	2	10 521.83	10 521.77
0	4	0	6 134.34	6 134.04	3	0	0	10 600.13	10 599.68
1	2	0	6 775.13	6 775.10	1	0	2	10 869.15	10 868.89
2	0	0	7 201.56	7 201.55	1	5	0	11 144.38	11 099.24
0	0	2	7 445.11	7 445.12	0	8	0	11 742.51	11 254.40
0	5	0	7 547.30	7 542.51	2	3	0	11 770.93	11 767.52
1	3	0	8 274.50	8 274.05	0	3	2	12 008.26	12 007.92
2	1	0	8 761.71	8 761.66	3	1	0	12 140.13	12 139.36
				Odd					
0	0	1	3 755.94	3 755.96	2	1	1	12 151.72	12 151.32
0	1	1	5 331.21	5 331.22	1	1	3	12 565.22	12 565.01
0	2	1	6 871.50	6 871.50	0	6	1	12 593.35	12 586.33
1	0	1	7 249.86	7 249.86	1	4	1	13 258.70	13 256.25
0	3	1	8 373.91	8 373.90	2	2	1	13 653.23	13 652.46
1	1	1	8 807.05	8 807.04	3	0	1	13 834.68	13 830.84
0	4	1	9 833.63	9 833.63	0	7	1	13 861.40	13 835.85
1	2	1	10 328.71	10 328.67	0	2	3	14 066.57	14 066.21
2	0	1	10 613.62	10 613.40	1	0	3	14 320.84	14 318.75
0	0	3	11 032.56	11 032.46	1	5	1	14 655.93	14 648.19
0	5	1	11 243.17	11 242.78					
1	3	1	11 813.46	11 813.23					

Advantages

- General for any "semi-rigid" molecule

- Straightforward for $J > 0$

  Examples: H_2O, H_2CO, CH_4, (C_2H_4)

Disadvantages

- Cannot describe torsional motion

- Numerical quadrature limits applications

Numerical Quadratures

$$\int_a^b dx\, f(x) \approx \sum_{i=1}^{m} w_i\, f(x_i)$$

x_i are <u>quadrature points</u> and w_i are <u>quadrature</u> <u>weights</u>

$$\int_a^b \int_c^d dy\, dx\, f(x,y) \approx \sum_{i=1}^{m} \sum_{j=1}^{n} w_j w_i\, f(x_i, y_j)$$

and obvious generalization for higher dimensions

$$\langle n_1' n_2' n_3' | V | n_1 n_2 n_3 \rangle \approx \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} w_k w_j w_i\, V(Q_i, Q_j, Q_k) \phi_{n'_1}(Q_i) \phi_{n_1}(Q_i) \phi_{n'_2}(Q_j) \phi_{n_2}(Q_j) \phi_{n'_3}(Q_k) \phi_{n_3}(Q_k)$$

Gaussian quadrature - exact for an integrand of known "polynomial order" - Gauss Hermite typically used for normal coordinate Hamiltonians.

Potential Optimized quadrature - specific to 1d cut potentials.

One Example: C_2H_4

"Exact" calculations (12 modes) recently reported[a] 10 days using 12 AMD 2.7GHz Shanghai processors. 4MR MULTIMODE calculations took 5.1 hrs single core

Table 2 Comparison of selected combination and overtone vibrational energies (cm^{-1}) for $J = 0$ with benchmark results for C_2H_4.

State	MULTIMODE	Benchmark[a]
$\nu_8 + \nu_{10}$	1750.1	1751.1
$2\nu_7$	1893.6	1895.2
$\nu_6 + \nu_8$	2157.7	2158.3
$\nu_3 + \nu_8$	2263.8	2264.2
$\nu_2 + \nu_7$	2564.4	2564.0
$3\nu_8$	2782.8	2784.9
$2\nu_{12}$	2870.5	2872.1
$\nu_3 + 2\nu_{10}$	2998.8	3000.3
$\nu_8 + \nu_{10} + \nu_{12}$	3185.1	3184.7
$\nu_8 + 3\nu_{10}$	3426.5	3426.1
$4 + 2\nu_6$	3474.3	3475.4
$\nu_7 + 2\nu_{10} + \nu_{12}$	4043.9	4043.2

[a]Gustavo Avila and Tucker Carrington, Jr. J. Chem. Phys. **135**, 064101 (2011). "Using a pruned basis, a non-product quadrature grid, and the exact Watson normal-coordinate kinetic energy operator to solve the vibrational Schrödinger equation for C_2H_4"

MULTIMODE APPROACH

n-mode representation of the potential

$$V(Q_1, \cdots Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{i \neq j} V_{i,j}^{(2)}(Q_i, Q_j) + \sum_{i \neq j \neq k} V_{i,j,k}^{(3)}(Q_i, Q_j, Q_k) + \cdots + \sum_{i \neq j \neq k, \ldots} V_{i,j,k,\ldots}^{(n)}(Q_i, Q_j, Q_k, \ldots)$$

$$\langle n_1' n_2' n_3' | V | n_1 n_2 n_3 \rangle = \sum_{i,j,k=1}^{3} \langle n_i' | V_i^{(1)}(i) | n_i \rangle \delta_{n_j' n_j} \delta_{n_k' n_k} + \langle n_1' n_2' | V_{1,2}^{(2)}(1,2) | n_1 n_2 \rangle \delta_{n_3' n_3} +$$

$$+ \langle n_1' n_3' | V_{1,3}^{(2)}(1,3) | n_1 n_3 \rangle \delta_{n_2' n_2} + \langle n_2' n_3' | V_{2,3}^{(2)}(2,3) | n_2 n_3 \rangle \delta_{n_1' n_1} .$$

For an N-mode molecule there are

$$\frac{N!}{(N-2)!2!}, \quad 2MR$$

$$\frac{N!}{(N-3)!3!}, \quad 3MR \qquad \text{potential grids}$$

$$\frac{N!}{(N-4)!4!}, \quad 4MR$$
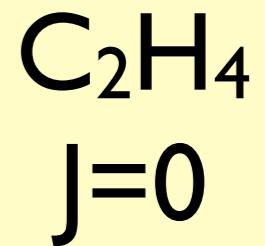
State	Ref[5]	Basis(1)	Basis(2)	Basis(3)	State	Ref[5]	Basis(1)	Basis(2)	Basis(3)
zpe	11004.79	11003.98	11003.98	11004.21					
ν_{10}	821.74	821.15	821.19	822.26	ν_8	926.81	926.13	926.18	927.25
ν_7	947.22	946.49	946.54	947.67	ν_4	1025.93	1025.28	1025.32	1026.25
ν_6	1223.76	1223.46	1223.47	1224.16	ν_3	1341.37	1341.42	1341.44	1342.04
ν_{12}	1440.20	1439.67	1439.70	1440.47	ν_2	1623.53	1623.17	1623.28	1624.42
$2\nu_{10}$	1655.51	1654.22	1654.72	1658.11	$\nu_8 + \nu_{10}$	1751.09	1750.05	1750.34	1753.07
$\nu_7 + \nu_{10}$	1775.36	1774.18	1774.48	1777.32	$\nu_4 + \nu_{10}$	1849.44	1848.32	1848.57	1851.04
$2\nu_8$	1855.72	1854.04	1854.62	1858.37	$\nu_7 + \nu_8$	1869.38	1866.06	1866.62	1870.66
$2\nu_7$	1895.21	1893.58	1894.20	1898.15	$\nu_4 + \nu_8$	1949.81	1946.54	1946.96	1950.11
$\nu_4 + \nu_7$	1964.46	1961.19	1961.65	1964.98	$\nu_6 + \nu_{10}$	2040.33	2038.34	2038.60	2040.98
$2\nu_4$	2049.11	2047.54	2047.97	2050.78	$\nu_6 + \nu_8$	2158.35	2157.66	2157.82	2159.62
$\nu_3 + \nu_{10}$	2165.84	2164.88	2165.11	2167.19	$\nu_6 + \nu_7$	2173.18	2172.44	2172.62	2174.53
$\nu_4 + \nu_6$	2250.59	2249.87	2249.99	2251.60	$\nu_{10} + \nu_{12}$	2259.26	2256.73	2256.99	2259.58
$\nu_3 + \nu_8$	2264.23	2263.77	2263.95	2265.77	$\nu_3 + \nu_7$	2285.87	2285.37	2285.58	2287.53
$\nu_8 + \nu_{12}$	2362.40	2361.04	2361.32	2364.12	$\nu_3 + \nu_4$	2363.47	2363.20	2363.32	2364.77
$\nu_7 + \nu_{12}$	2381.19	2379.82	2380.12	2383.10	$\nu_2 + \nu_{10}$	2435.60	2434.08	2434.56	2438.78
$2\nu_6$	2447.67	2446.56	2446.79	2448.62	$\nu_4 + \nu_{12}$	2468.14	2467.01	2467.16	2469.08
$3\nu_{10}$	2494.40	2492.97	2495.03	2519.85	$\nu_2 + \nu_8$	2542.41	2542.01	2542.37	2546.03
$\nu_3 + \nu_6$	2562.94	2562.51	2562.60	2563.76	$\nu_2 + \nu_7$	2564.38	2564.04	2564.38	2567.71
$\nu_8 + 2\nu_{10}$	2585.30	2583.95	2585.23	2608.24	$\nu_7 + 2\nu_{10}$	2612.42	2610.83	2612.13	2635.96
$\nu_2 + \nu_4$	2646.03	2645.42	2645.69	2648.89	$\nu_6 + \nu_{12}$	2659.38	2658.13	2658.26	2659.86

Continued on next page

C_2H_4
$J=0$

Ref. 5

Exact

the ZPE (zero-point energy). Results for 4-mode and 5-mode approximations to the PES. Only states symmetric wrt to reflection in the plane of the molecule are included.

Assig.	4-mode	5-mode	Bench	Assig	4-mode	5-mode	Bench
ZPE	−0.5	−0.1	11004.8	ν_{10}	−1.1	−0.1	821.7
ν_6	−0.8	0.0	1223.8	ν_3	−0.5	0.0	1341.4
ν_{12}	−1.0	−0.1	1440.2	ν_2	−1.0	−0.1	1623.6
ν_{10}	−2.2	−0.2	1655.5	$2\nu_8$	−2.6	−0.3	1855.6
$\nu_7 + \nu_8$	−5.6	−0.6	1869.3	$2\nu_7$	−2.5	−0.3	1895.1
$\nu_4 + \nu_8$	−4.9	−0.5	1949.7	$\nu_4 + \nu_7$	−5.1	−0.5	1964.3
$\nu_6 + \nu_{10}$	−3.2	−0.2	2040.3	$2\nu_4$	−2.2	−0.3	2048.9
$\nu_3 + \nu_{10}$	−2.5	−0.2	2165.8	$\nu_{10} + \nu_{12}$	−3.8	−0.3	2259.2
$\nu_2 + \nu_{10}$	−3.3	−0.3	2435.6	$2\nu_6$	−1.8	−0.1	2447.6
$3\nu_{10}$	−4.2	−0.4	2494.3	$\nu_3 + \nu_6$	−1.9	−0.1	2562.9
$\nu_6 + \nu_{12}$	−2.6	−0.2	2659.3	$2\nu_3$	−2.7	−0.1	2680.9
$\nu_4 + 2\nu_{10}$	−3.6	−0.5	2683.4	$\nu_7 + \nu_8 + \nu_{10}$	−10.3	−0.9	2699.4
$2\nu_7 + \nu_{10}$	−5.4	−0.5	2729.6	$\nu_3 + \nu_{12}$	−7.6	−0.2	2774.9
$\nu_4 + \nu_8 + \nu_{10}$	−3.4	−0.8	2775.9	$\nu_4 + \nu_7 + \nu_{10}$	−9.2	−0.8	2793.7
$\nu_2 + \nu_6$	−2.8	−0.2	2832.7	$\nu_6 + 2\nu_{10}$	−5.4	−0.5	2867.5
$2\nu_{12}$	−2.7	−0.2	2872.1	$2\nu_4 + \nu_8$	−4.6	−0.4	2874.3
$\nu_2 + \nu_3$	−1.8	−0.2	2958.0	ν_{11}	0.8	−0.3	2984.1
$\nu_3 + 2\nu_{10}$	−4.7	−0.4	3000.2	ν_1	−0.2	0.0	3019.7
$\nu_4 + \nu_6 + \nu_{10}$	−4.5	−0.4	3072.9	ν_5	1.4	−0.3	3077.0
$2\nu_{10} + \nu_{12}$	−4.7	−0.4	3095.0	$\nu_6 + 2\nu_8$	−3.7	−0.4	3095.6
ν_9	−5.9	−0.4	3098.2	$\nu_6 + \nu_7 + \nu_8$	−0.8	−0.6	3105.1
$\nu_6 + 2\nu_7$	−4.4	−0.4	3123.4	$\nu_4 + \nu_6 + \nu_8$	−7.7	−0.7	3181.8
$\nu_3 + 2\nu_8$	−6.9	−0.4	3189.1	$\nu_4 + \nu_6 + \nu_7$	−5.7	−0.7	3190.9
$\nu_3 + \nu_7 + \nu_8$	−7.8	−0.7	3203.6	$\nu_3 + 2\nu_7$	−4.2	−0.4	3230.9
$2\nu_2$	−3.9	−0.3	3238.3	$2\nu_6 + \nu_{10}$	−5.8	−0.4	3259.2
$\nu_2 + 2\nu_{10}$	−5.2	−0.4	3268.0	$2\nu_4 + \nu_6$	−4.5	−0.4	3274.3
$\nu_3 + \nu_4 + \nu_8$	−6.8	−0.6	3283.3	$2\nu_8 + \nu_{12}$	−6.5	−0.7	3285.7
$\nu_7 + \nu_8 + \nu_{12}$	−9.5	−1.0	3297.0	$\nu_3 + \nu_4 + \nu_7$	−6.5	−0.6	3299.2
$2\nu_7 + 2\nu_{12}$	−6.0	−0.6	3322.2	$4\nu_{10}$	−6.4	−0.6	3340.4
$\nu_3 + 2\nu_4$	−6.5	−0.4	3382.2	$\nu_3 + \nu_6 + \nu_{10}$	−4.9	−0.3	3382.6
$\nu_4 + \nu_8 + \nu_{12}$	−7.7	−0.9	3387.0	$\nu_4 + \nu_7 + \nu_{12}$	−9.8	−0.9	3399.8
$\nu_2 + 2\nu_8$	−4.5	−0.5	3462.0	$\nu_3 + \nu_6 + \nu_{12}$	−8.6	−0.5	3473.4
$\nu_2 + \nu_7 + \nu_8$	−7.8	−0.9	3476.3	$2\nu_4 + \nu_{12}$	−4.6	−0.4	3493.0
$\nu_2 + 2\nu_7$	−4.3	−0.5	3504.3	$\nu_{10} + \nu_{11}$	−13.9	−2.2	3800.3
$\nu_1 + \nu_{10}$	−4.4	−0.4	3833.6	$\nu_2 + \nu_{10} + \nu_{12}$	−15.5	−0.6	3885.2
$\nu_9 + \nu_{10}$	−7.2	−0.5	3918.8	$\nu_6 + \nu_7 + \nu_8 + \nu_{10}$	−10.6	−1.1	3929.2
$3\nu_{10} + \nu_{12}$	−7.0	−1.0	3929.5	$\nu_2 + 2\nu_6$	−6.8	−0.4	4042.3

Torsional Motion

- MM-RP

- Polysherical, Jacobi, "valence" coords

These are more demanding calculations owing to the presence of one or more very large amplitude mode. Here I discuss recent work on HOCO* as a relevant example.

**Variational Calculations of Vibrational Energies and IR Spectra of trans- and cis-HOCO Using New ab Initio Potential Energy and Dipole Moment Surfaces**

Yimin Wang, Stuart Carter, and Joel M. Bowman*

MULTIMODE-"Reaction Path"

The reaction path Hamiltonian is quite complex
In vibrational work it is given in terms a torsional
mode and rectilinear normal modes orthogonal to it

Then the n-mode representation of the PES is made

$$
\begin{aligned}
V(s; Q_1, Q_2, \ldots, Q_{3N-7}) = {} & V^{(0)}(s) + \sum_i V_i^{(1)}(s; Q_i) + \sum_{ij} V_{ij}^{(2)}(s; Q_i, Q_j) + \\
& \sum_{ijk} V_{ijk}^{(3)}(s; Q_i, Q_j, Q_k) + \sum_{ijkl} V_{ijkl}^{(4)}(s; Q_i, Q_j, Q_k, Q_l) + \\
& \sum_{ijklm} V_{ijklm}^{(5)}(s; Q_i, Q_j, Q_k, Q_l, Q_m) + \cdots
\end{aligned} \tag{1}
$$

MULTIMODE-Reaction Path
Some examples

H_5^+ : Mid- and far-IR spectra of H_5^+ and D_5^+ compared to the predictions of anharmonic theory, T. C. Cheng, L. Jiang, K. R. Asmis, Y. Wang, J. M. Bowman, A. Ricks, and M. A. Duncan, J. Phys. Chem. Lett. **3**, 3160 (2012).

H_2O_2 Multimode calculations of rovibrational energies and dipole transition intensities for polyatomic molecules with torsional motion: Application to H_2O_2, S. Carter, A. R. Sharma, and J. M. Bowman, J. Chem. Phys. **135**, 014308 (2011). DOI: 10.1063/1.3604935

HOCO Variational Calculations of Vibrational Energies and IR Spectra of *trans* and *cis*-HOCO Using New *ab initio* Potential Energy and Dipole Moment Surfaces, Y. Wang, S. Carter, and J. M. Bowman, J. Phys. Chem. A. dx.doi.org/10.1021/jp309911w

Variational Calculations of Vibrational Energies and IR Spectra of *trans*- and *cis*-HOCO Using New ab Initio Potential Energy and Dipole Moment Surfaces

Yimin Wang, Stuart Carter, and Joel M. Bowman*

Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States

ABSTRACT: We report ab initio potential energy and dipole moment surfaces that span the regions describing the minima of *trans*- and *cis*-HOCO and the barrier separating them. We use the new potential in three types of variational calculations of the vibrational eigenstates, for zero total angular momentum. Two use the code MULTIMODE (MM) in the so-called single-reference and reaction path versions. The third uses the exact Hamiltonian in diatom–diatom Jacobi coordinates. The single-reference version of MM is limited to a description of states that are localized at each minimum separately, whereas the reaction-path version and the Jacobi approach describe localized and delocalized states. The vibrational IR spectrum for zero total angular momentum is also reported for the *trans* and *cis* fundamentals and selected overtone and combination states with significant oscillator strength.
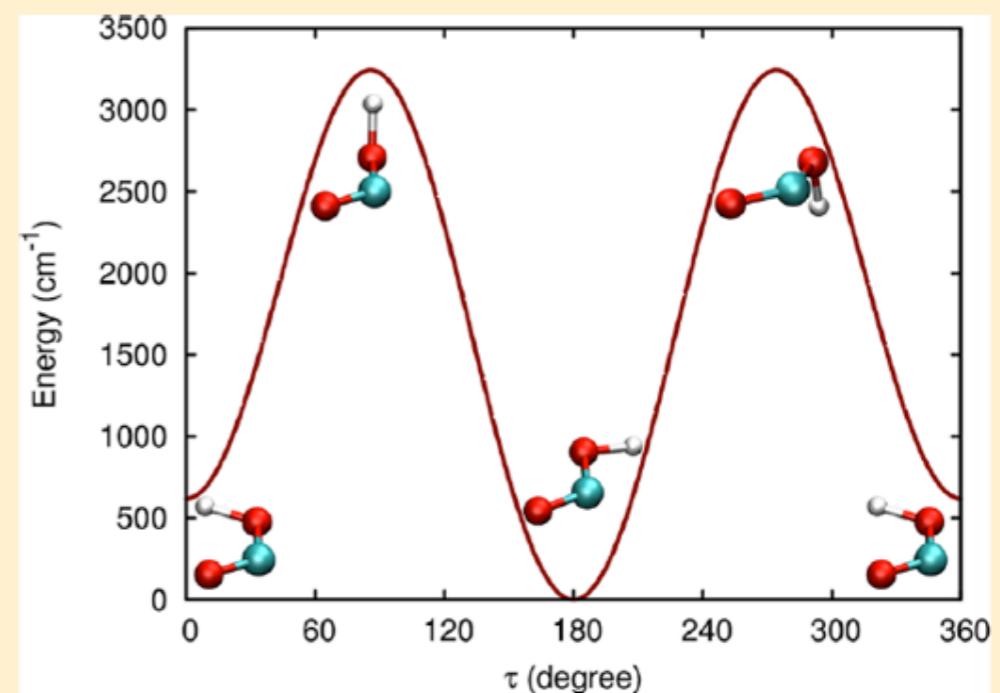
Hamiltonian in a Tetratomic Jacobi coordinate

$$\hat{H} = \hat{T}_{r_1} + \hat{T}_{r_2} + \hat{T}_R + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + \frac{\hat{l}^2}{2\mu_R R^2} + V(r_1, r_2, R, \theta_1, \theta_2, \phi)$$

$$\begin{cases} \dfrac{1}{\mu_1} = \dfrac{1}{m_a} + \dfrac{1}{m_b} \\[2mm] \dfrac{1}{\mu_2} = \dfrac{1}{m_c} + \dfrac{1}{m_d} \\[2mm] \dfrac{1}{\mu_R} = \dfrac{1}{m_a + m_b} + \dfrac{1}{m_c + m_d} \end{cases}$$
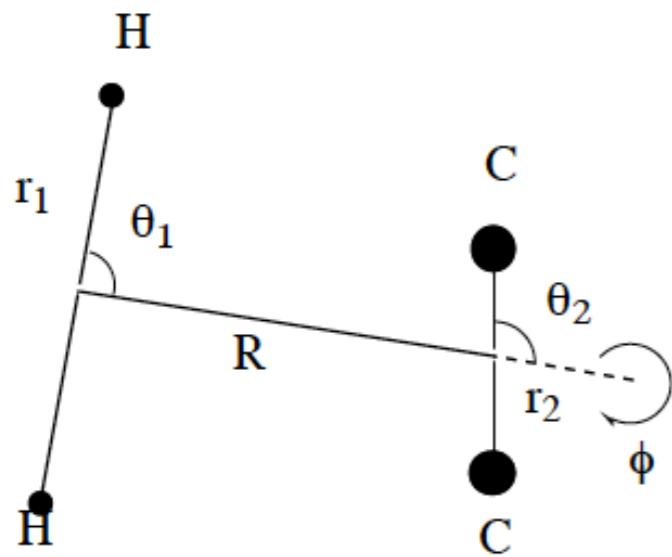
Total angular momentum $(\hat{J})$

$$\hat{H} = \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu_R R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} - \frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + V(\vec{r}_1, \vec{r}_2, \vec{R})$$

where

$$\hat{j}_{12} = \hat{j}_1 + \hat{j}_2$$
$$\hat{J} = \hat{j}_{12} + \hat{l} = \hat{j}_1 + \hat{j}_2 + \hat{l}$$

For $J = 0$,

$$\hat{H} = \frac{\hat{j}_{12}^2}{2\mu_R R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} - \frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + V(\vec{r}_1, \vec{r}_2, \vec{R})$$

Truncation/recoupling Approach

Full-dimensional quantum calculations of acetylene-vinylidene isomerization.

S. Zou, J. M. Bowman, and A. Brown, JCP, 118, 10012 (2003)

$$\hat{H}_{6D} = \hat{H}_{4D} + \hat{H}_{2D} + \hat{j}_1^2 \left(\frac{1}{2\mu_1 r_1^2} - \frac{1}{2\mu_1 r_{1e}^2} \right) + \hat{j}_2^2 \left(\frac{1}{2\mu_1 r_2^2} - \frac{1}{2\mu_2 r_{2e}^2} \right)$$

$$+ V(R, r_1, r_2, \theta_1, \theta_2, \phi) - V_{4D}(R, \theta_1, \theta_2, \phi; r_{1e}, r_{2e}) - V_{2D}(r_1, r_2)$$

Diagonalize H_{4D} (large coupled angular basis x R-basis
Diagonalize H_{2D}. Then use reduced basis from each to set up and diagonalize H_{6D}.

Table 2. Fundamentals and Zero-Point Energy (cm^{-1}) of *trans*-HOCO′

	description	MM-RP	Jacobi	MM-SR	CcCR/5MR[a]	VPT2[a]	VPT2[b]	expt
ZPE		4547.4	4546.2	4546.5	4549.8	4559.2		
ν_1	OH stretch	3639.9	3639.6	3639.5	3634.4	3640.7	3641	3635.7[c]
ν_2	CO′ stretch	1855.5	1855.5	1855.3	1862.2	1862.2	1854	1852.6[d]
ν_3	HOC bend	1210.0	1209.7	1209.2	1214.2	1213.7	1217	1194[b]
ν_4	OC stretch	1049.4	1049.7	1050.2	1052.8	1053.0	1057	1048[b]
ν_5	OCO′ bend	612.4	612.7	612.5	616.9	616.6	614	629[b]
ν_6	torsion	500.3	502.4	505.0	484.6	497.5	507	

[a]Reference 3. [b]Reference 2. [c]Reference 35. [d]Reference 36.

Table 3. Fundamentals and Zero-Point Energy (cm^{-1}) of *cis*-HOCO′

	description	MM-RP	Jacobi	MM-SR	CcCR/5MR[b]	VPT2[b]	VPT2[c]	expt[c]
ZPE		5101.1	5100.1	5099.8				
		4480.3	4481.3	4480.0	4485.7	4491.4		
ν_1	OH stretch	3438.4[a]	3438.3[a]	3436.5[a]	3452.3	3450.8	3458	
		3444.7[a]	3443.5[a]	3442.4[a]				
ν_2	CO′ stretch	1817.6	1819.0	1819.0	1824.1	1823.4	1815	
ν_3	HOC bend	1268.7	1271.4	1271.5	1280.2	1284.4	1282	1290
ν_4	OC stretch	1037.6	1040.0	1040.0	1042.4	1045.9	1042	1040
ν_5	OCO′ bend	594.5	596.8	596.8	601.2	601.7	596	605
ν_6	torsion	552.5	553.6	554.3	540.2	566.5	545	

[a]Mixed states, see text for details. [b]Reference 4. [c]Reference 2.

Table 4. Overtones (cm^{-1}) of *trans*- and *cis*-HOCO

	trans-HOCO			*cis*-HOCO		
	MM-RP	Jacobi	MM-SR	MM-RP	Jacobi	MM-SR
$2\nu_1$		7117.4	7118.7		6645.6	6644.9
$2\nu_2$	3685.7	3685.3	3683.7	3612.0	3614.1	3614.8
$2\nu_3$	2400.6	2398.3	2398.2	2523.8	2528.6	2528.5
$2\nu_4$	2079.7	2080.2	2076.3	2061.8	2066.2	2067.3
$2\nu_5$	1227.4	1228.5	1228.0	1190.8	1194.9	1194.7
$2\nu_6$	970.8	979.4	999.2	1057.7	1062.9	1073.8
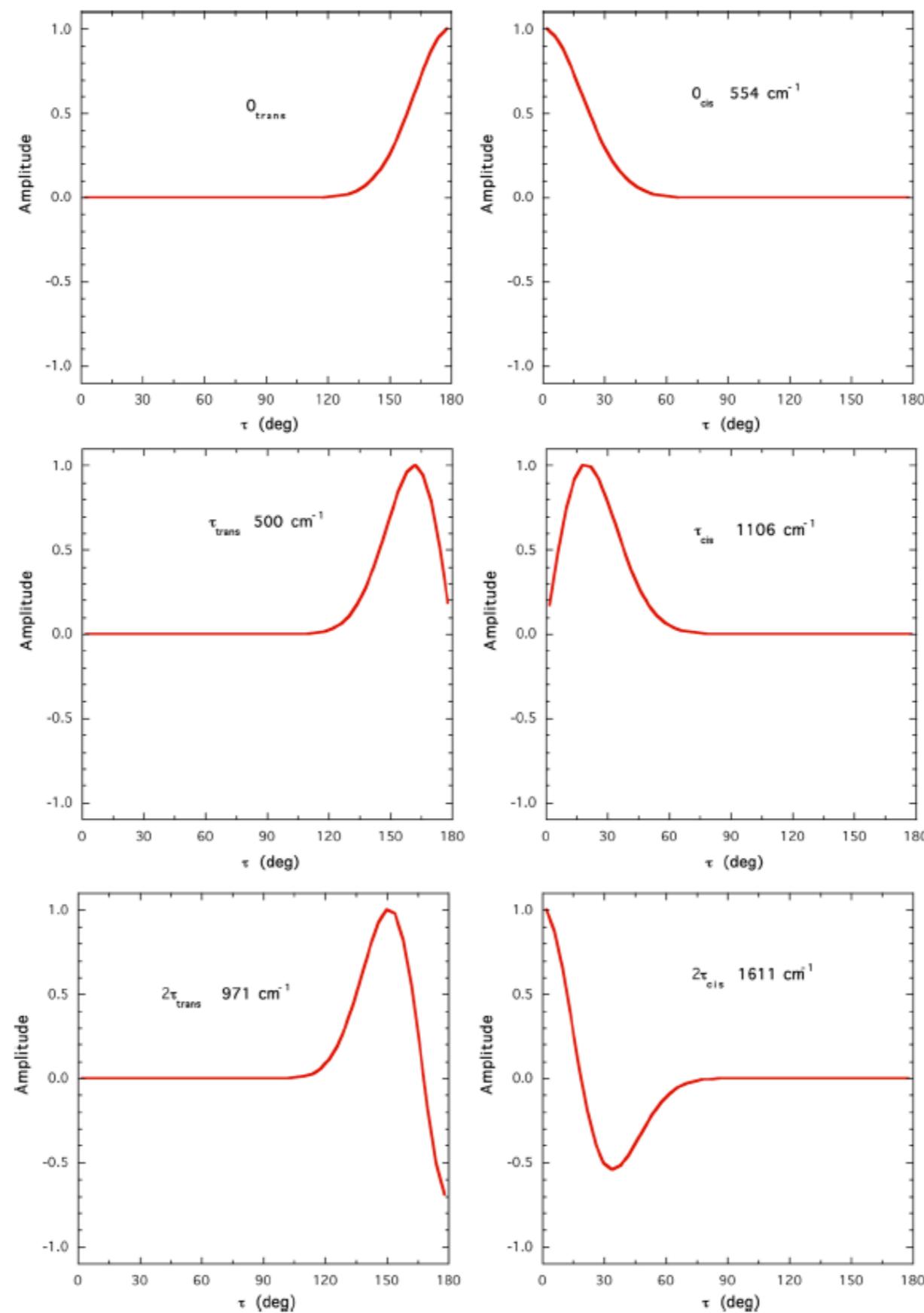
Figure 4. Torsional wave functions.

The Problem: Exponential scaling

Given an f-mode Hamiltonian H=T+V(*1,2,...,f*) and a direct-(Hartree) product form for the wavefunction

$$\{\phi^{(1)}(1)\} \times \{\phi^{(2)}(2)\} \cdots \times \{\phi^{(f)}(f)\}.$$

The resulting "CI" is of huge dimension and excited states are of course essential. V is high dimensional and so if we use a DVR a direct product grid is easily of the order 10^f.
A spectral approach require f-dimensional quadratures.

Current QM Approaches and Limits

- Watson Hamiltonian/RPH VSCF/VCI n-mode representation

  CH_4, H_2O_2, $OH^-(H_2O)$, CH_3OH, etc.

- MCTDH - $H_5O_2^+$, Malonaldehyde, ... also n-mode rep

- Heroic - Watson Hamiltonian

  CH_5^+, C_2H_4

- VSCF/MP2 or VPT2 - small biomolecules, water complexes

Variational quantum approaches for computing vibrational energies of polyatomic molecules], J. M. Bowman, T. Carrington, and H.-D. Meyer, Mol. Phys. **106**, 214 (2008).

A local approach for large molecules and molecular assemblies

Water and water clusters specifically the quantum intramolecular OH-stretch and bend modes
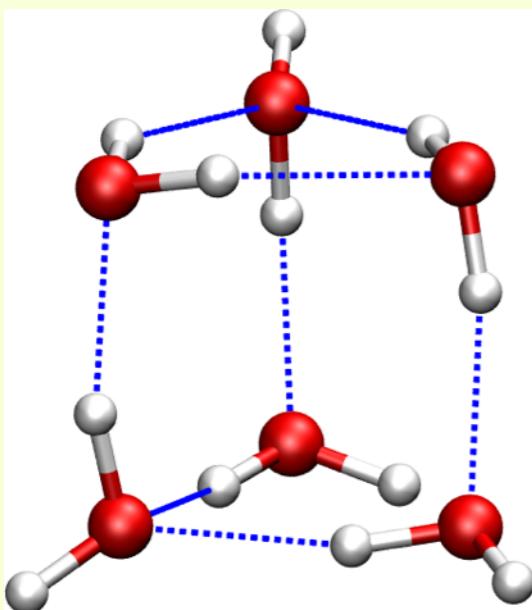
The hexamer has 42 vibrational degrees of freedom, of which 18 are intramolecular ones. The 20-mer has 60 intramolecular modes.
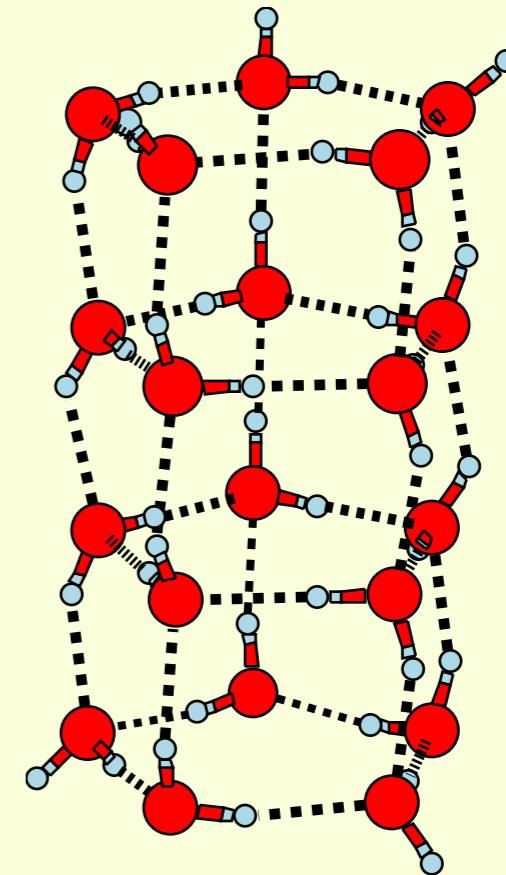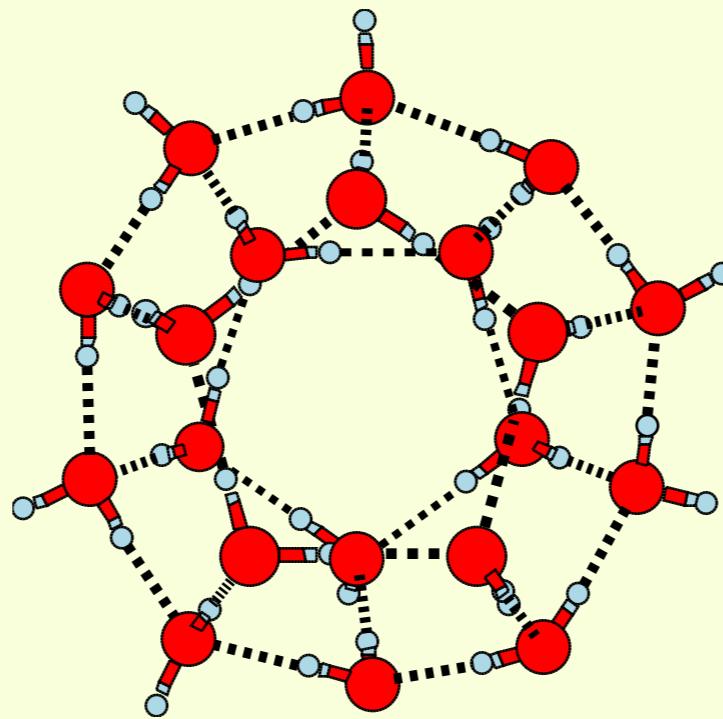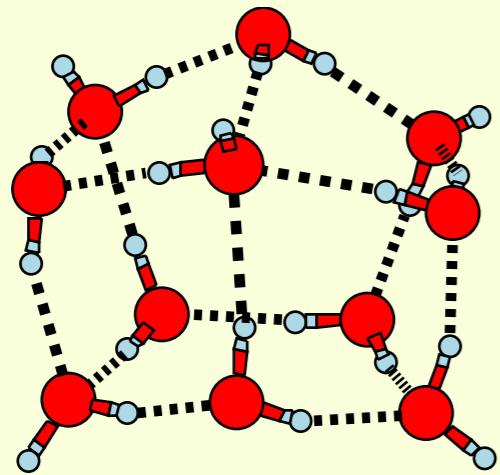
Divide and Conquer Local Approach
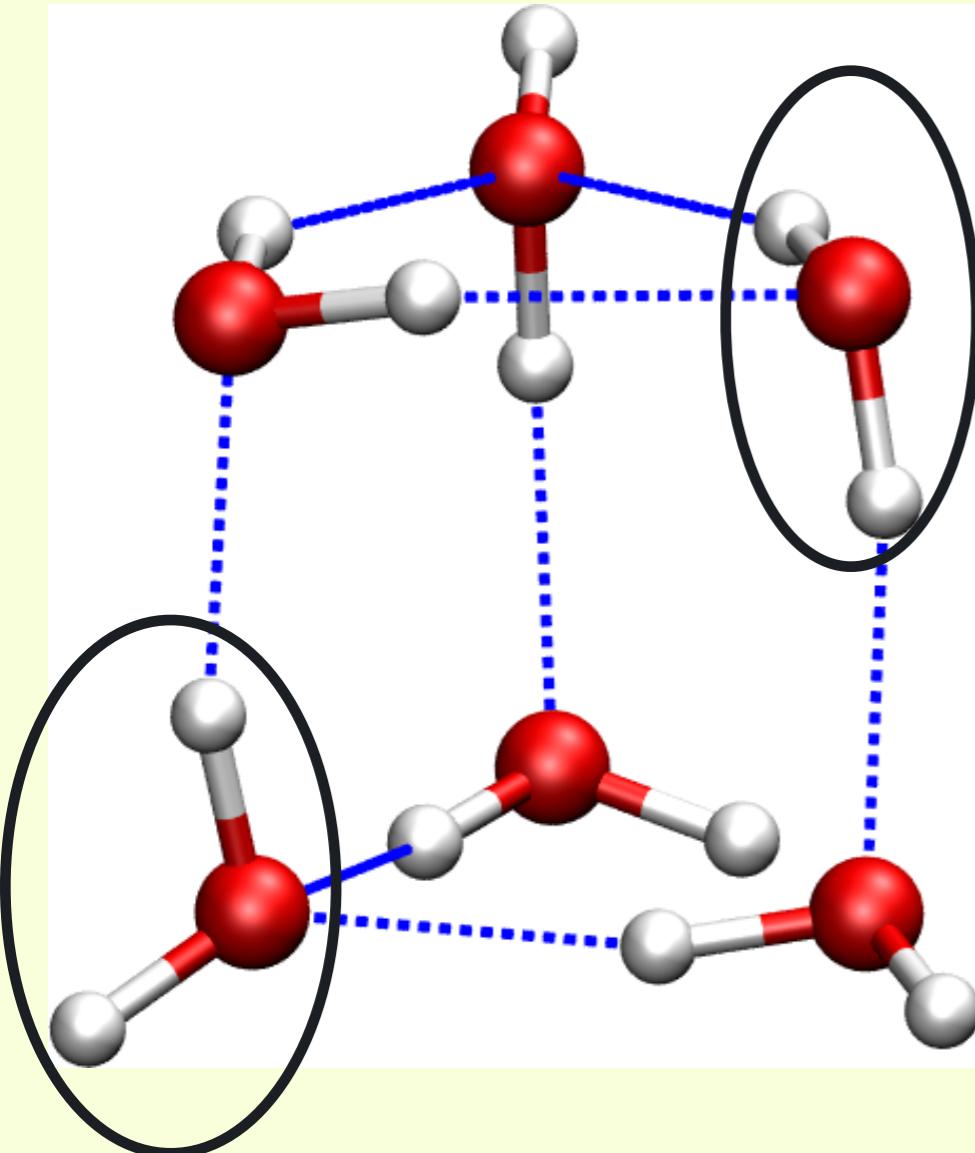
Six perturbed monomers. Do a normal mode analysis for each monomer with other monomers fixed. Separate the 9-modes into 6 hindered trans and rotation and 3 intramolecular modes.

Solve exact Sch. eq. in 3-modes for each monomer m using MULTIMODE.

$$[T_m + U_m(Q_m) - \varepsilon_{n_m}]\chi_{n_m}(Q_m) = 0,$$

Divide and Conquer Local Approach

Water dimer

T. Salmi, V. Hänninen, A. L. Garden, H. G. Kjaergaard, J. Tennyson, and L. Halonen, J. Phys. Chem. A **112**, 6305 (2008).

Water trimer

B. Auer, T. Salmi, V. Hänninen, A. L. Garden, H. G. Kjaergaard, J. Tennyson, and L. Halonen, J. Phys. Chem. A **113**, 9124 (2009).

Calculation of Overtone O−H Stretching Bands and Intensities of the Water Trimer

Teemu Salmi,[†] Henrik G. Kjaergaard,[‡] and Lauri Halonen*,[†]

Ab initio force fields and internal coordinate Hamiltonian for the monomers.

Intramolecular Fundamentals of the Water Dimer
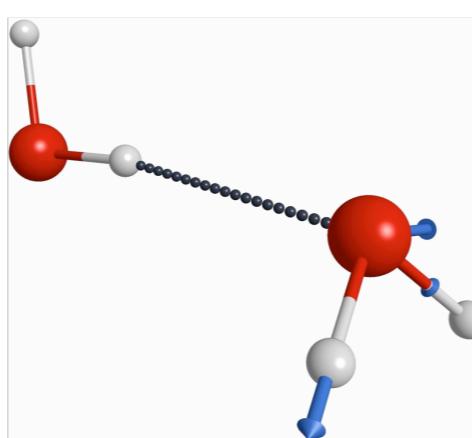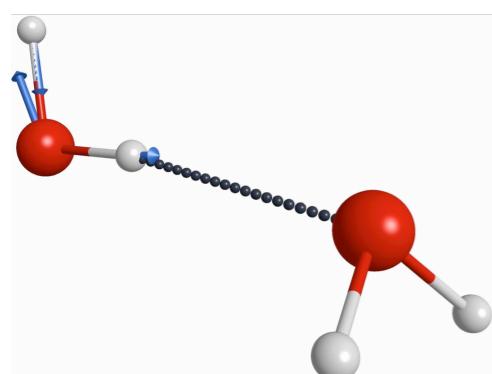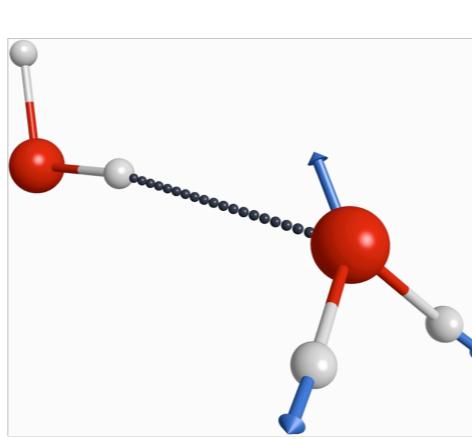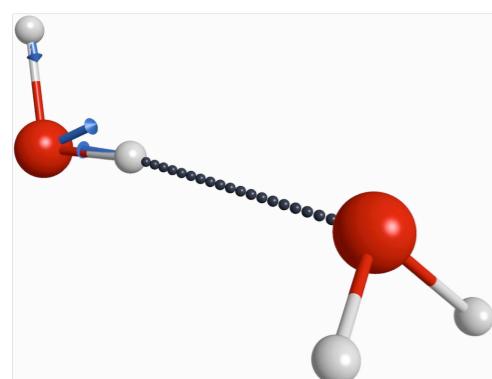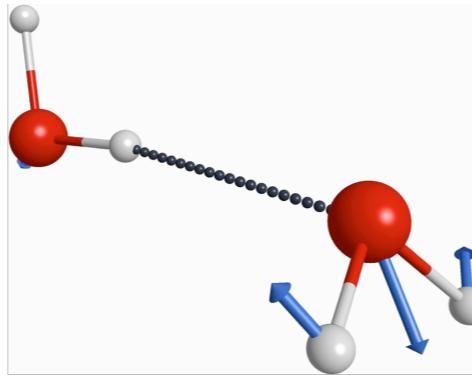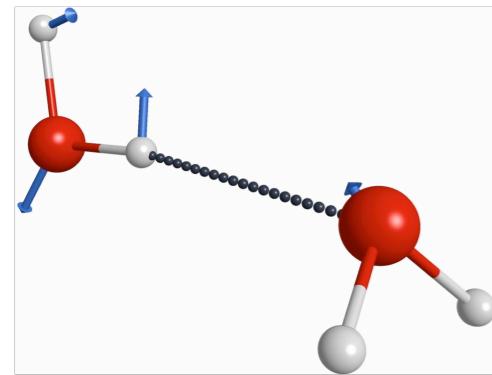
MODE	"EXACT"[a]	LOCAL
D-bend	1588[b]	1595
A-bend	1603	1602
D-OH$_1$	*3573*	3550
D-OH$_2$	3627	3637
A-OH$_1$	3709	3701
A-OH$_2$	3713	3724

[a]8-mode MM; cm^{-1}

Tests for the Water Trimer
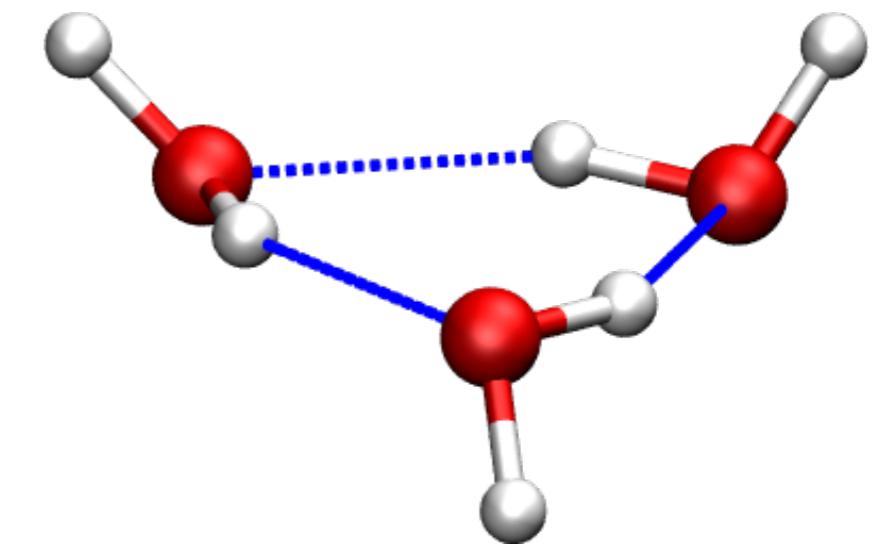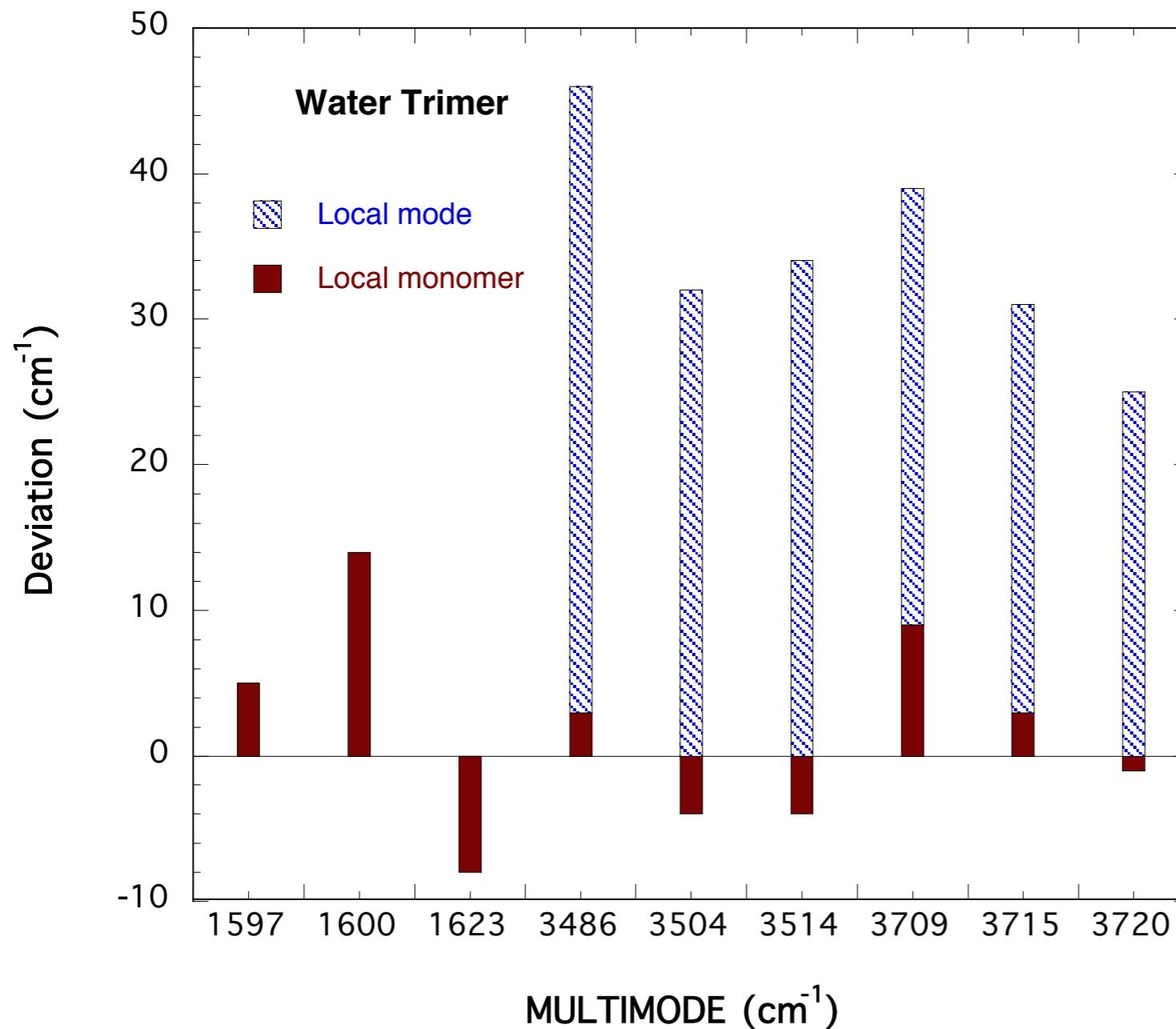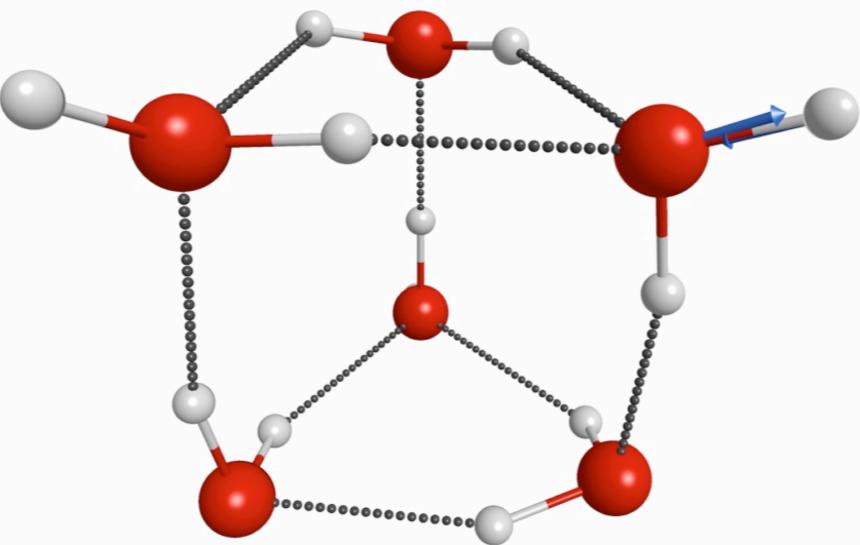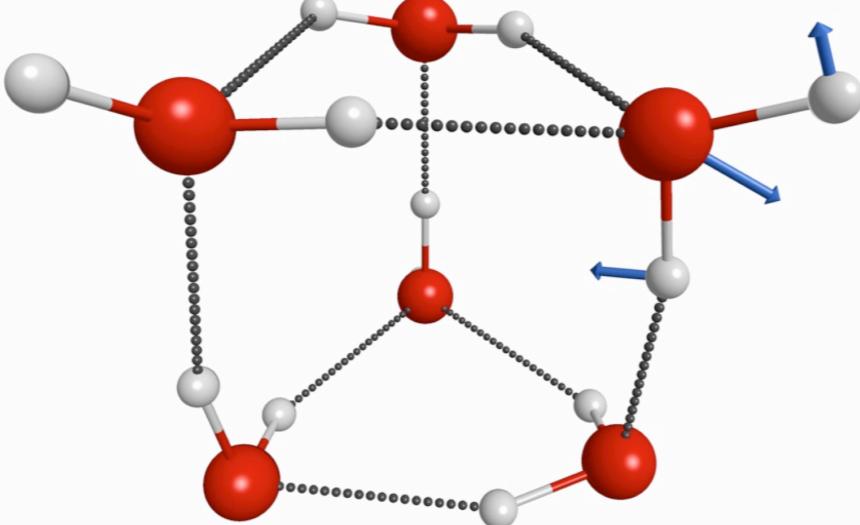
IR Spectra of Hexamer Isomers

Ring
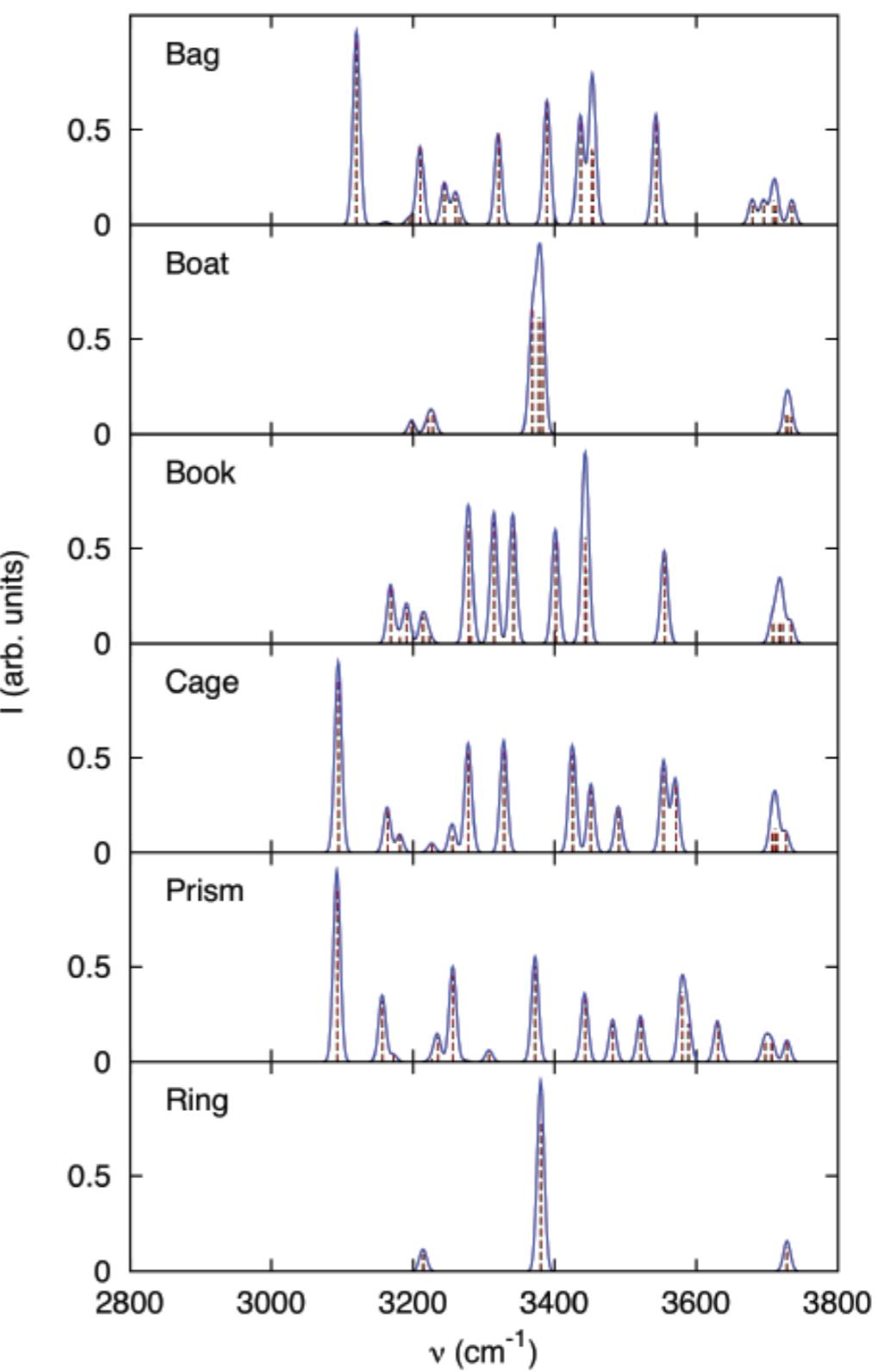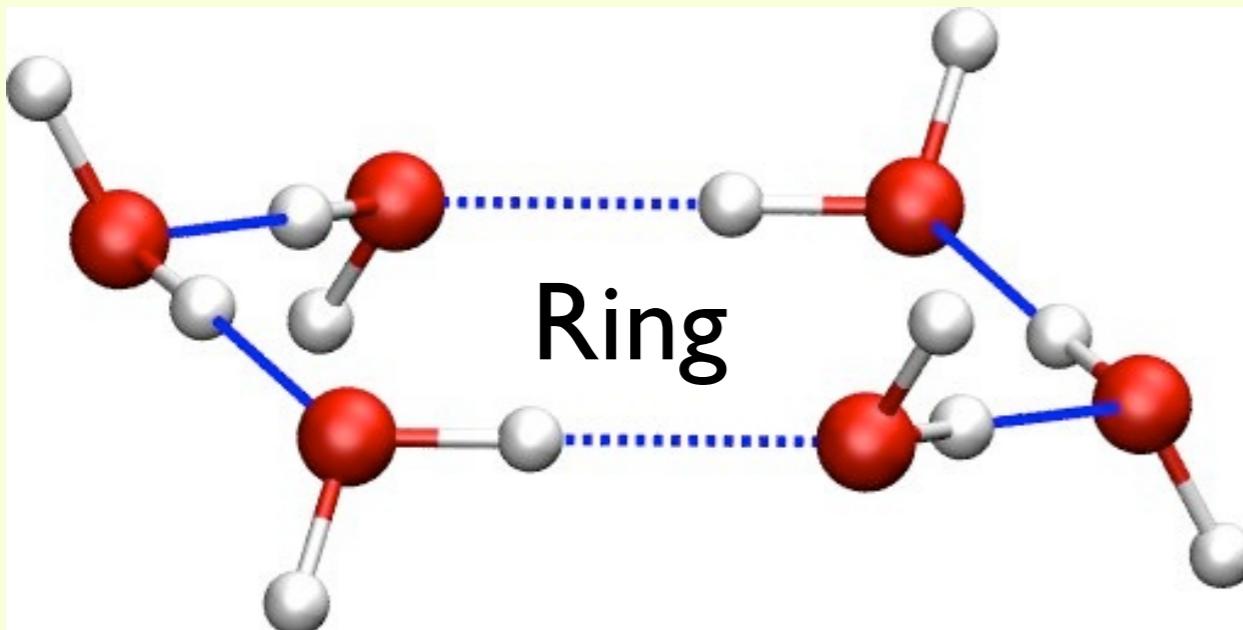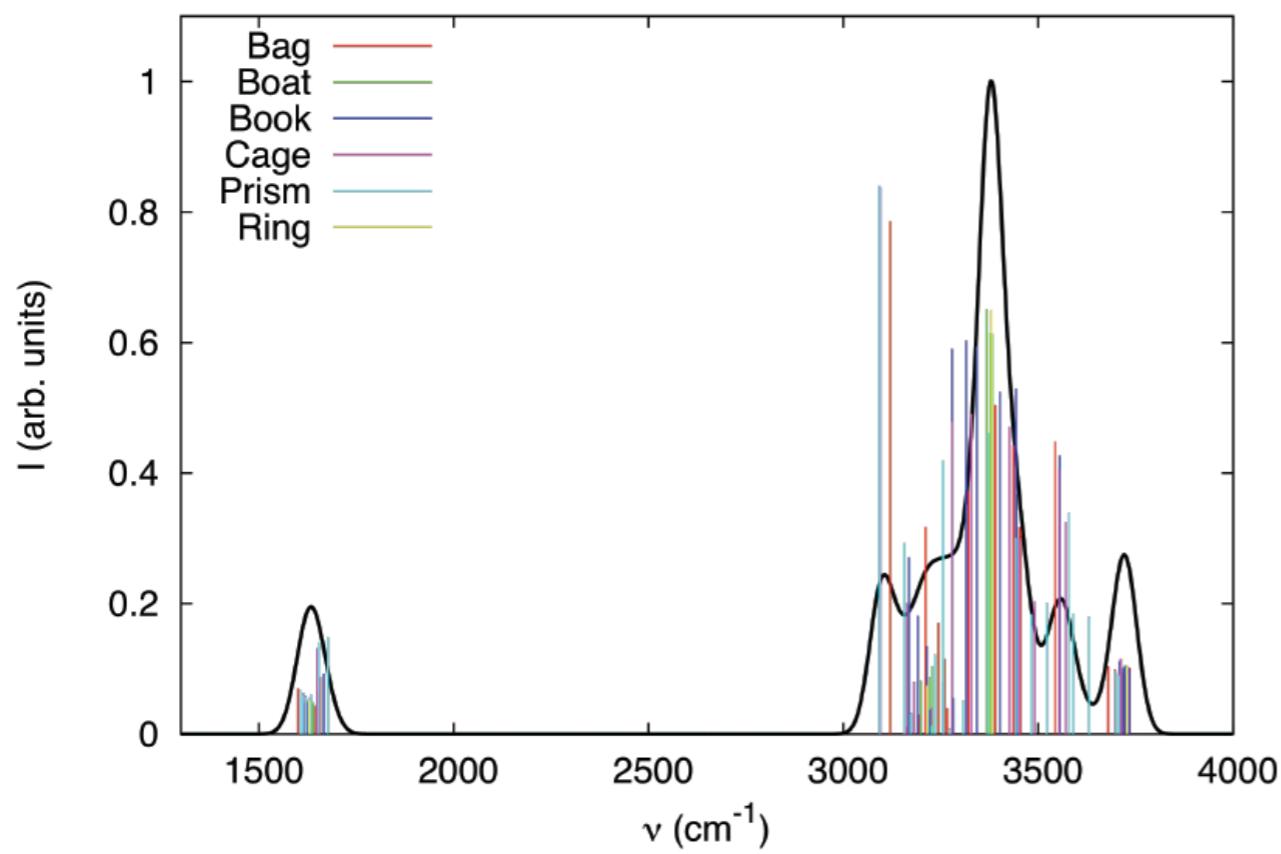
Wang and Bowman, J.C.P. (2011)

IR Spectra Larger Clusters
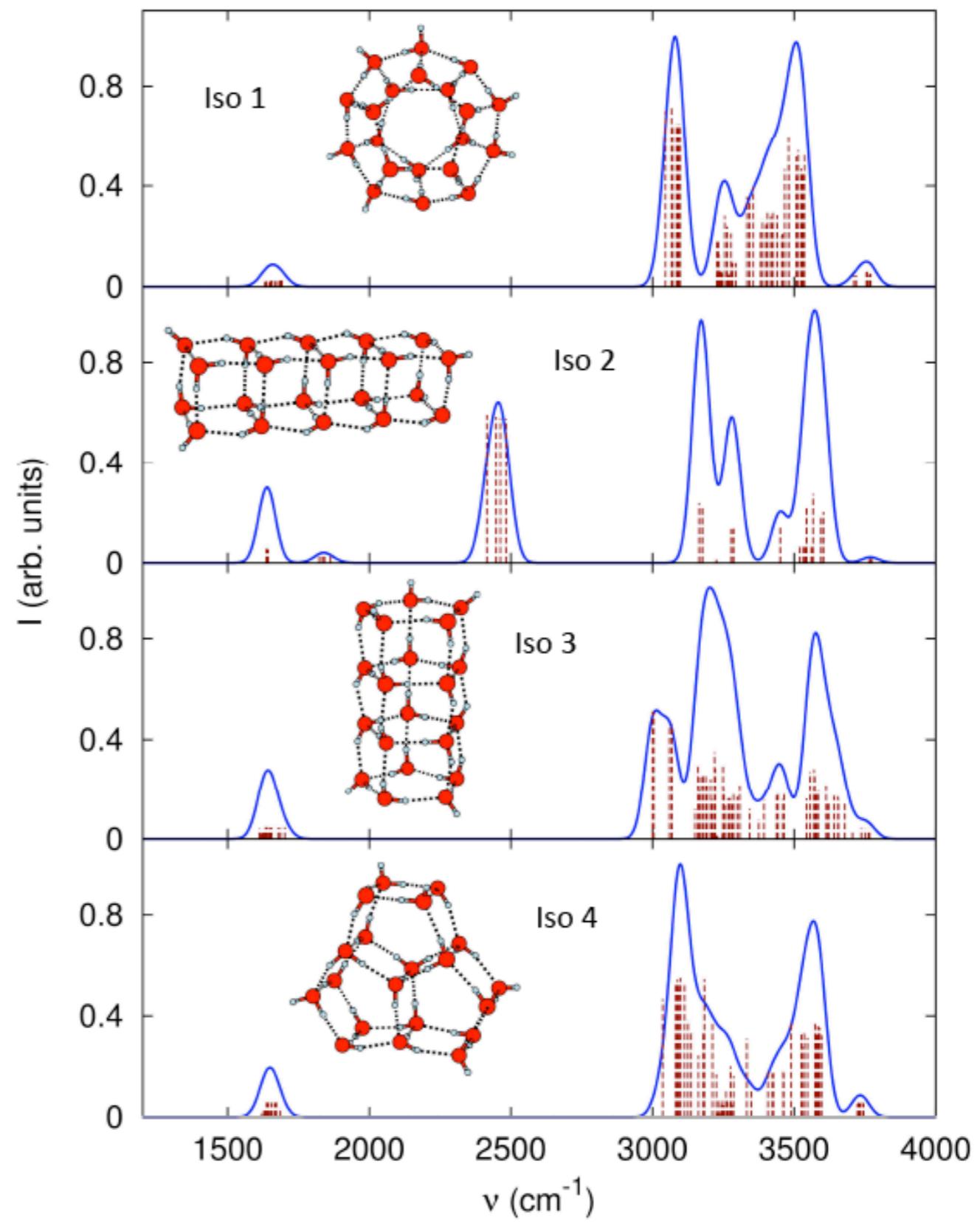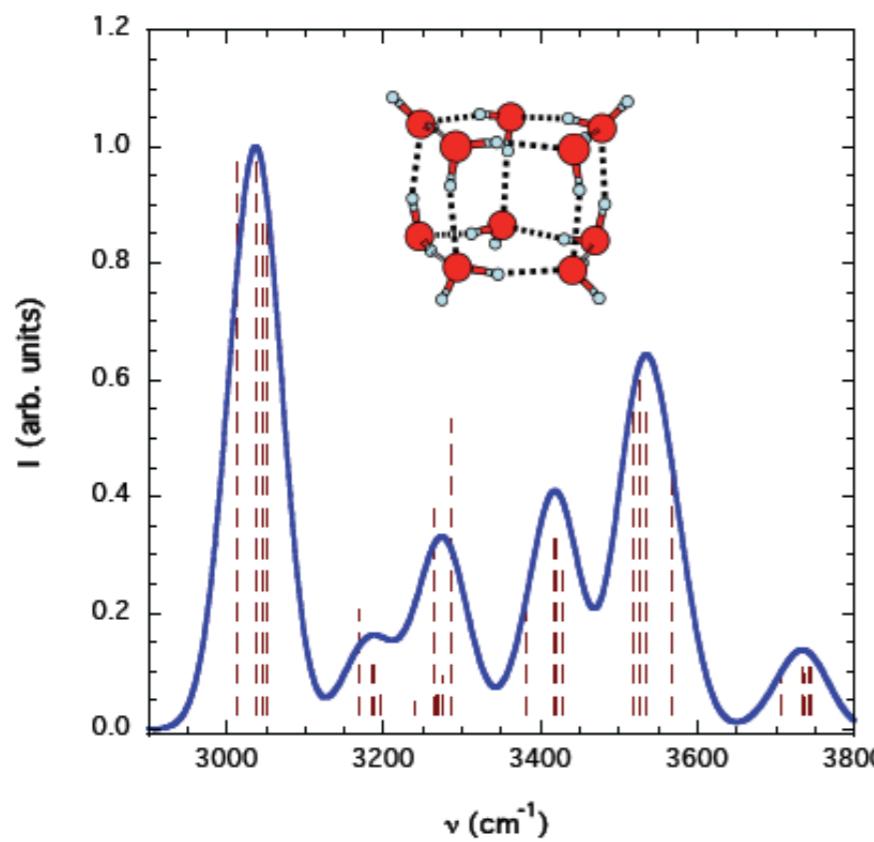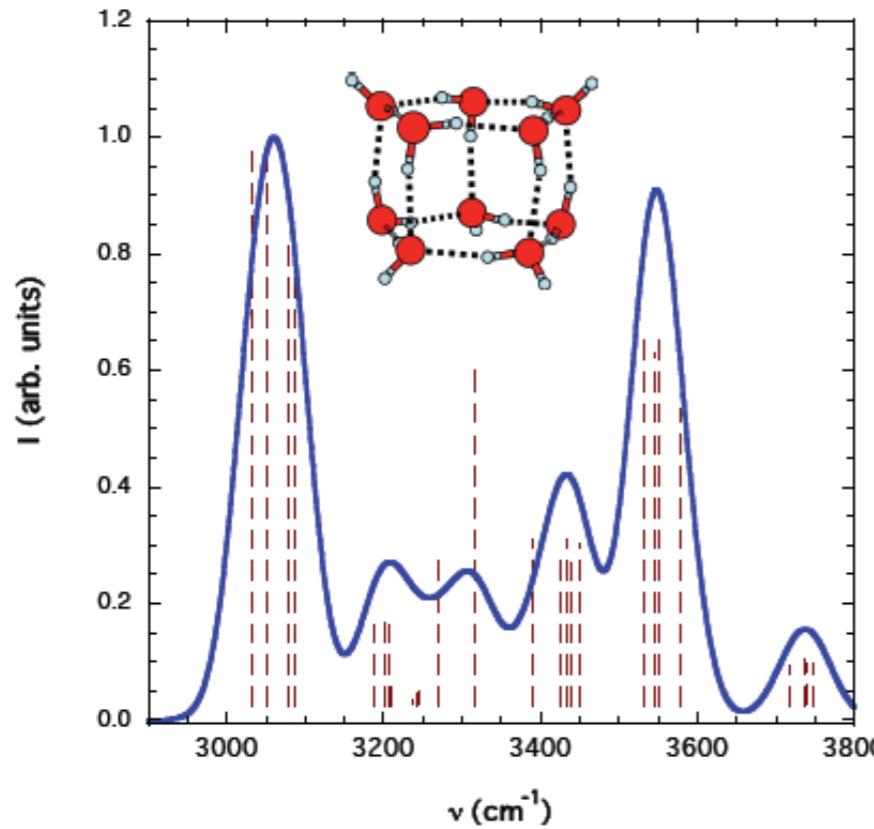
Quantum Calculations of Intramolecular IR Spectra of Ice Models Using Ab Initio Potential and Dipole Moment Surfaces

Hanchao Liu, Yimin Wang, and Joel M. Bowman*
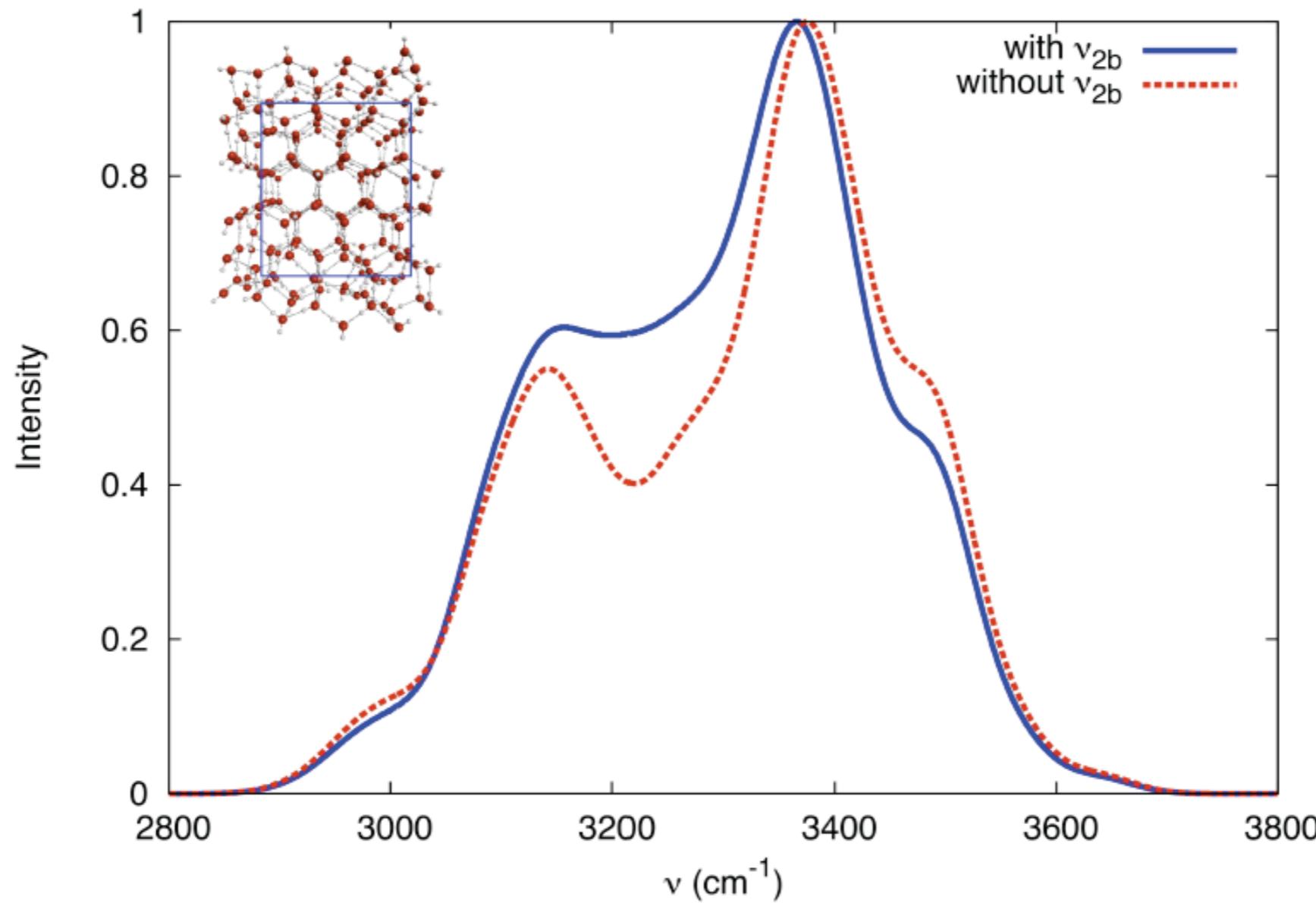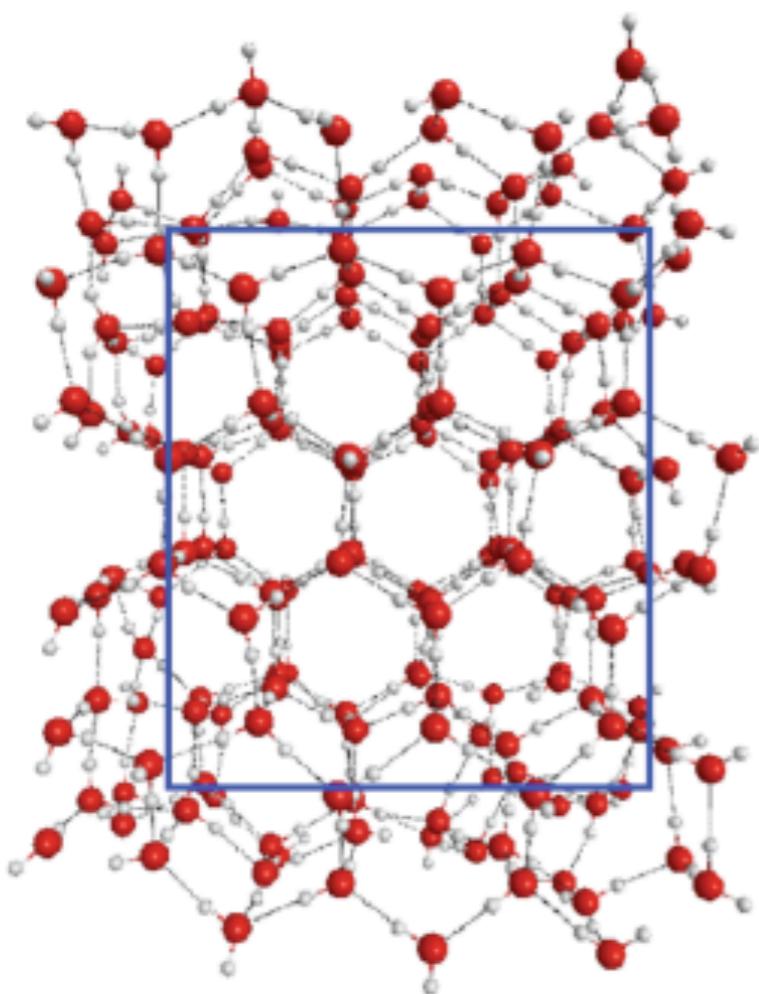
Ice Ih   ASW
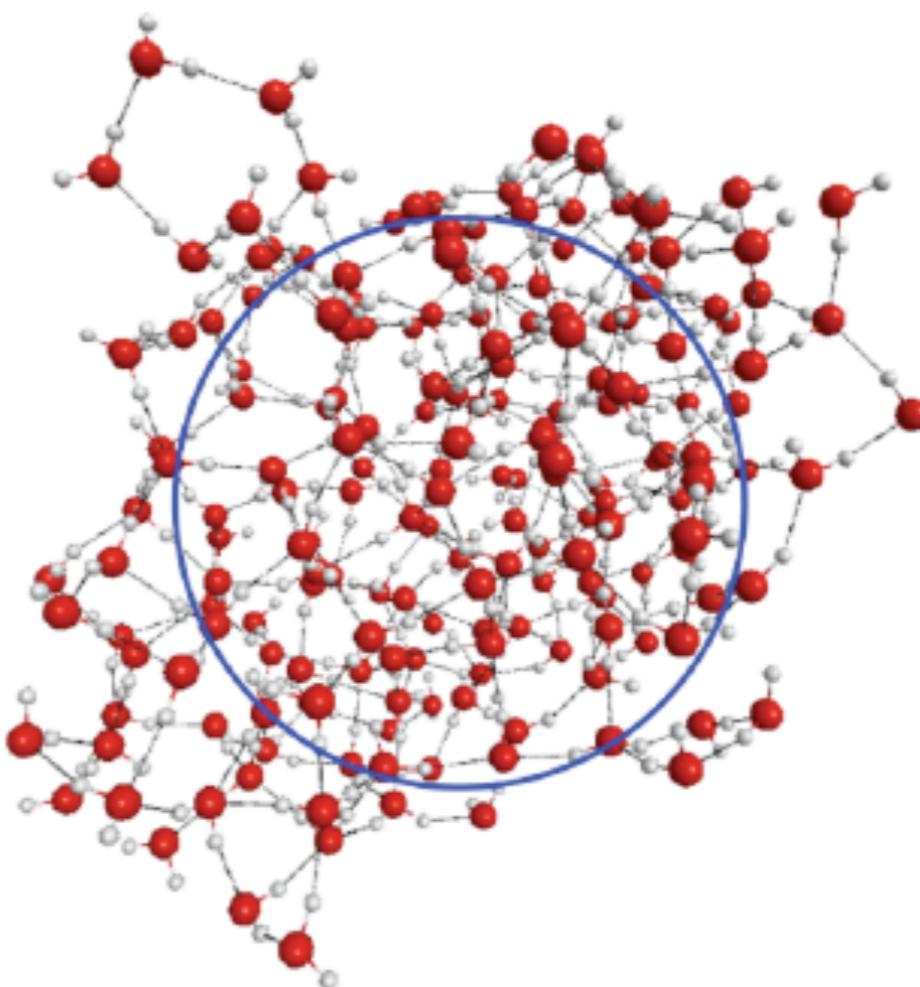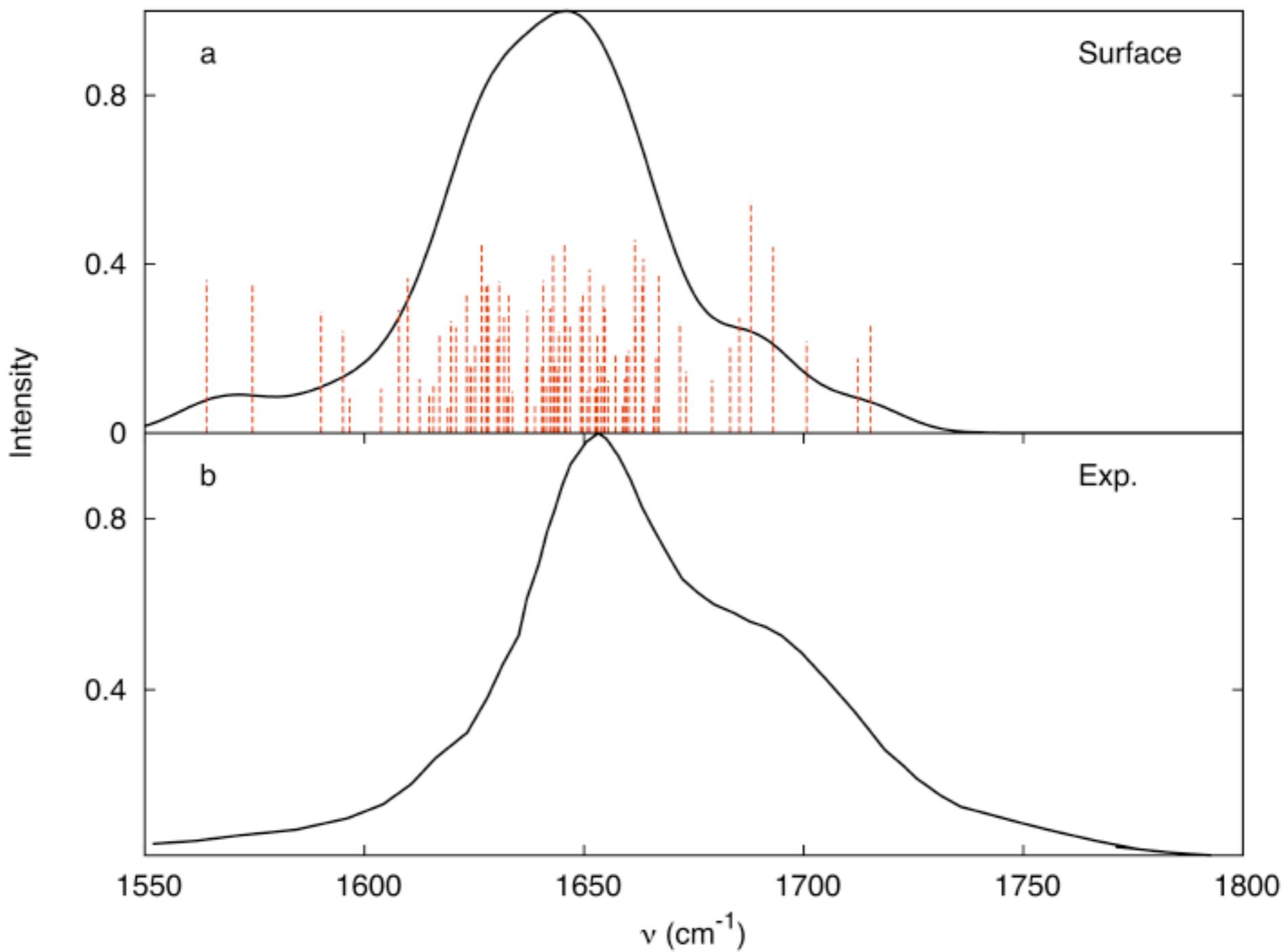
Figure 3. IR spectra of intramolecular bend modes of hexagonal ice. a) Local-monomer calculation for 87 monomers on the surface of 192-mer cluster. b) Experimental surface spectra in the bending region of crystalline ice at 120 K. (Ref.
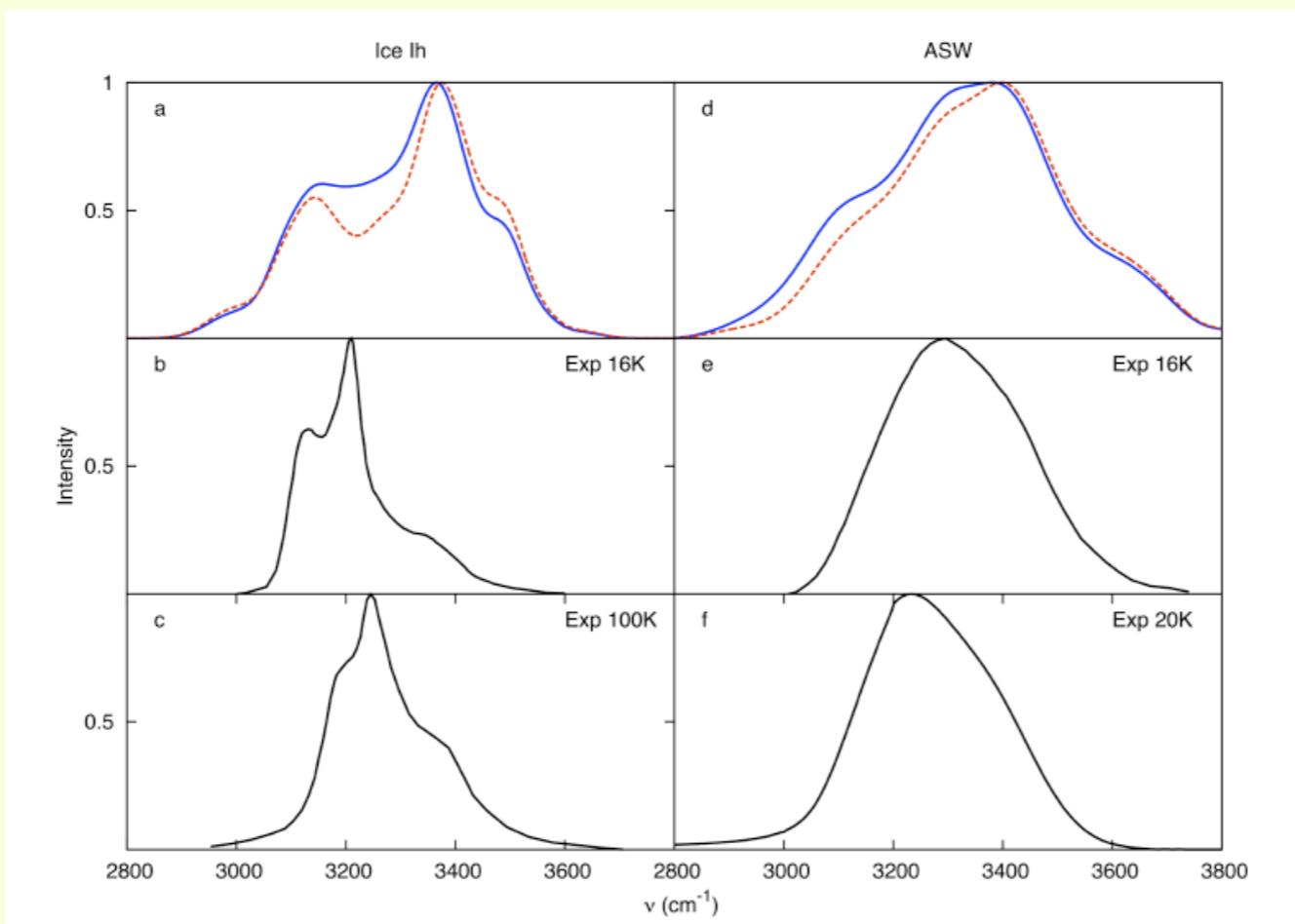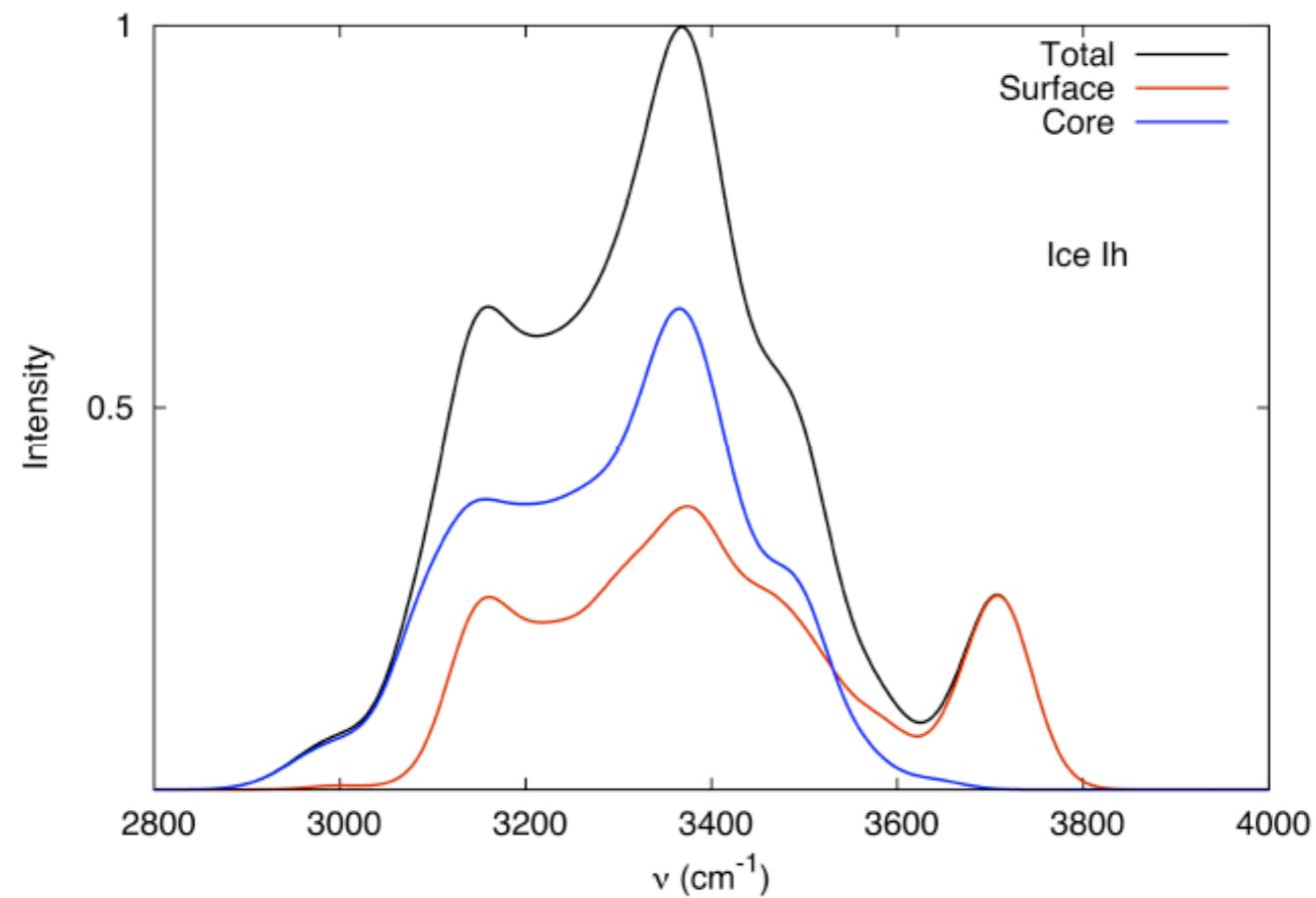
References

MULTIMODE: a code to calculate rovibrational energies of polyatomic molecules

JOEL M. BOWMAN*, STUART CARTER and
XINCHUAN HUANG

Cherry L. Emerson Center for Scientific Computation and
Department of Chemistry, Emory University, Atlanta, GA 30322, USA