Potential energy surfaces and quantum vibrational calculations in high dimensionality


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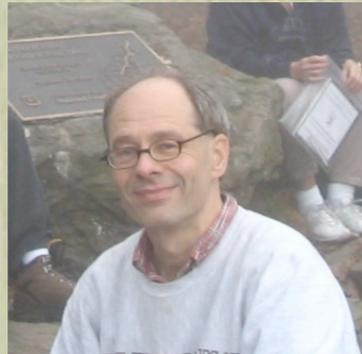
Bas
Braams

Yimin
Wang

Eugene

- Permutational symmetry for PESs in high dimensionality

- 'MULTIMODE' and new "high res" version

- H_5^+ (9 dofs)

- $(H_2O)_n$, $Cl^-(H_2O)_n$ (huge no of dofs)

- Challenges

Strategies for High Dimensional *Ab initio* Potential Energy Surfaces

- Global potentials that are invariant with respect to permutations of like atoms.

- The n-mode representation for use in vibrational "CI" calculations. (Discuss in the context of "MULTIMODE" code.)

Strategies for High Dimensional
## *Ab initio* Potential Energy Surfaces

- Global potentials that are invariant with respect to permutations of like atoms.

- The n-mode representation for use in vibrational "CI" calculations. (Discuss in the context of "MULTIMODE" code.)

# The PES as least-squares fits of *ab initio* energies.

Early example: H_2CO, ca 100 000 CCSD(T) and MRCI Energies
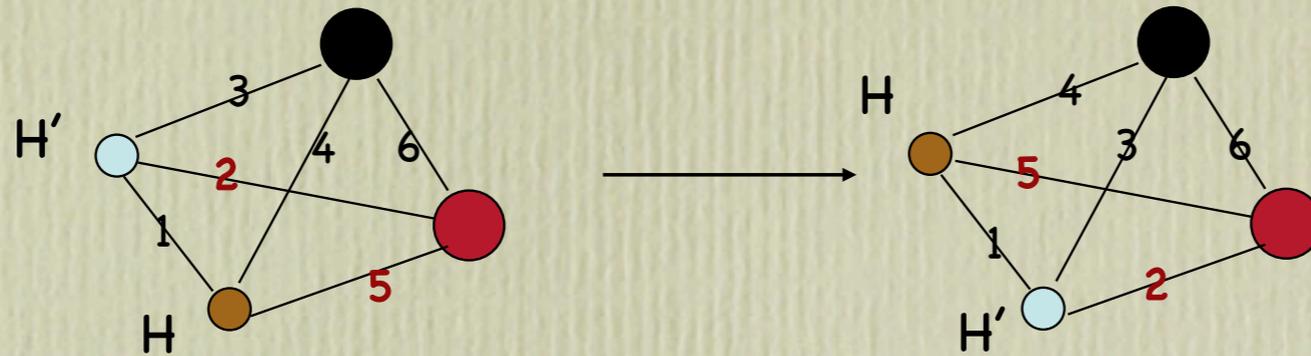
Electronic energies were replicated,

data set size doubled and fit was done

using

$$V = \sum_{m=0}^{N} C_{abcdef}[y_{12}^{a} y_{13}^{b} y_{14}^{c} y_{23}^{d} y_{24}^{e} y_{34}^{f}];$$

$$y_{ij} = exp(-r_{ij}/a)$$
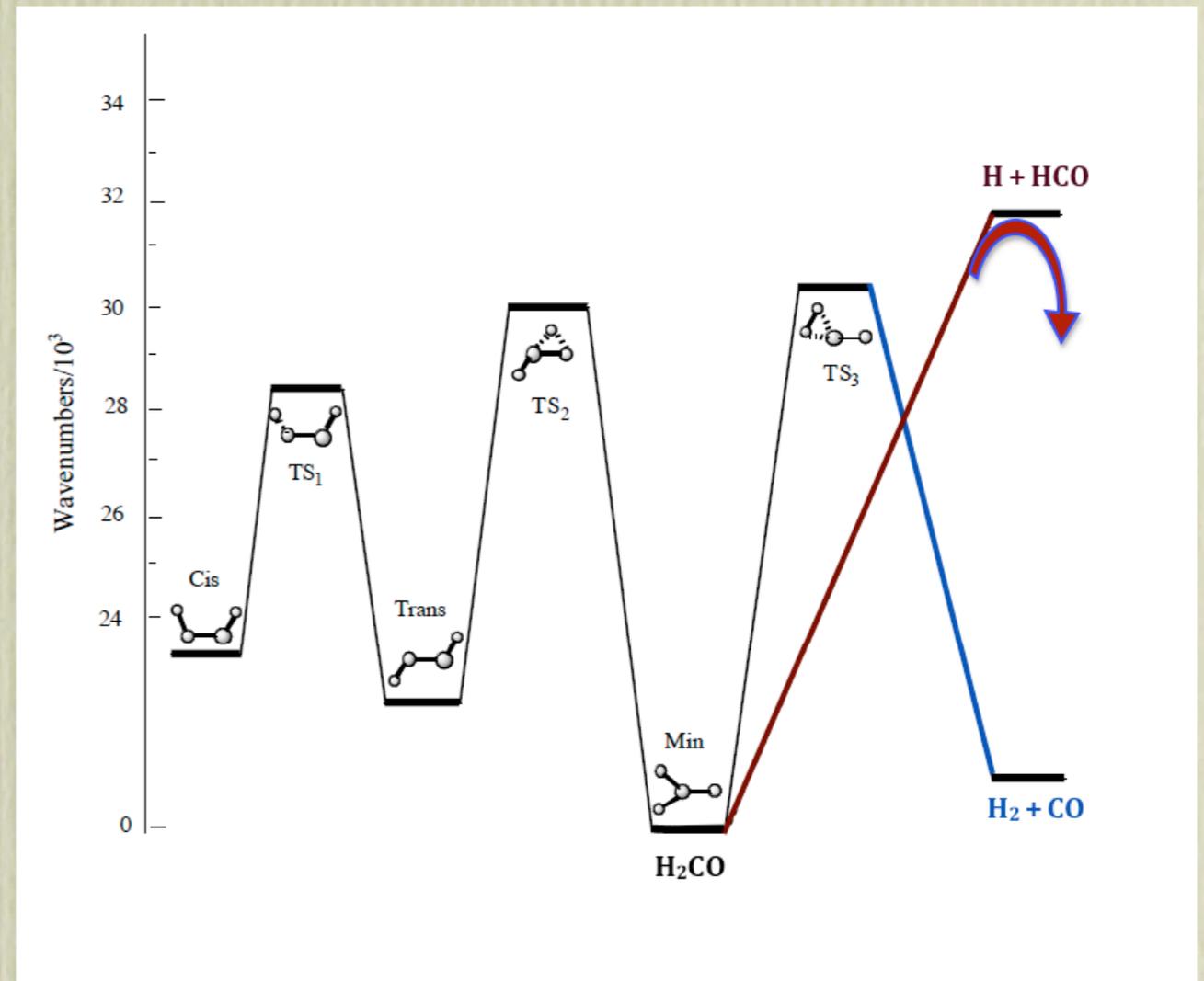
X.-B. Zhang, S.-L. Zou, L. B. Harding, and J. M. Bowman, J. Phys. Chem. A **108**, 8980

(2004).

Monomial Symmetrization: H₂CO Example

$$V(r_1 \cdots r_6) = \sum_{n_1, n_2 \ldots n_6} C_{n_1 \ldots n_6} S\{y_1^{n_1} y_2^{n_2} y_3^{n_3} y_4^{n_4} y_5^{n_5} y_6^{n_6}\}$$

$$y = 1 - e^{-a(r-r_0)}; \quad y = \frac{r - r_e}{r}; etc$$
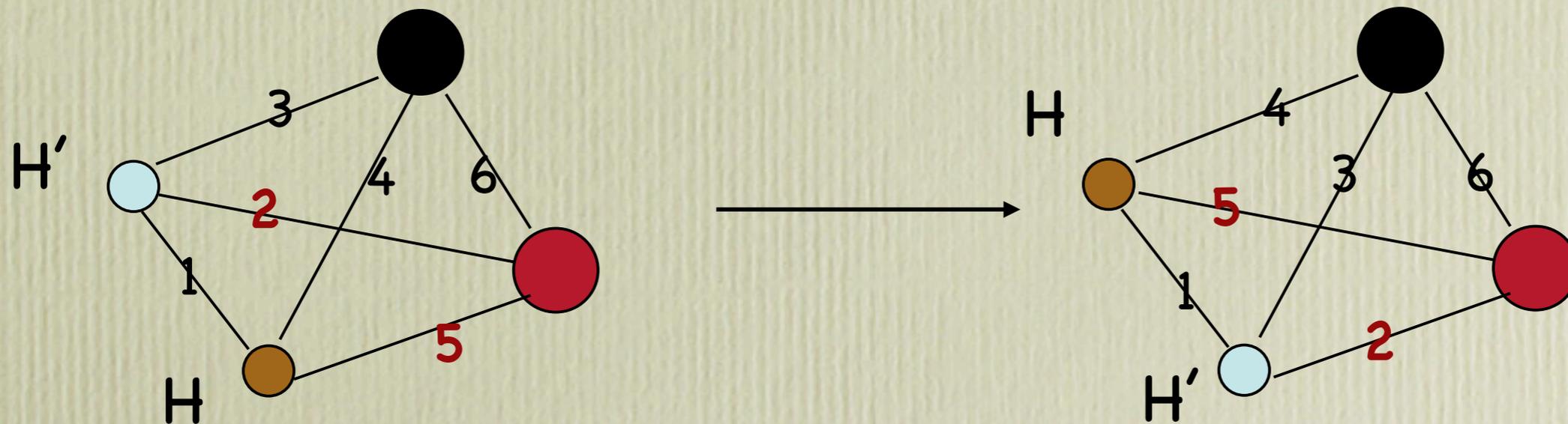
$$C_{n_1 \ldots n_6} y_1^{n_1} y_6^{n_6} (y_2^{n_2} y_3^{n_3} y_4^{n_4} y_5^{n_5} + y_2^{n_5} y_3^{n_4} y_4^{n_3} y_5^{n_2})$$

Potential expressions/fits should be invariant wrt permutations of like atoms

- Silly approach - replicate data for fit. Ok for H_2CO but impractical for CH_5^+.

- Monomial Symmetrization - systematic approach http://www.mcs.anl.gov/msa

$$V = \sum_{m=0}^{M} D_{abcdef...} \mathcal{S}[y_{12}^a y_{13}^b y_{14}^c y_{23}^d y_{24}^e y_{34}^f ...]$$

- Use a fitting basis of primary [p($\mathbf{y}$)] and secondary [q($\mathbf{y}$)[invariant polynomials obtained using symbolic algebra program "Magma". Library exists for up to ten atoms http://iopenshell.usc.edu/downloads/ezpes/.

$$V(\mathbf{y}) = \sum_{\alpha=1}^{N} \mathbf{c}_\alpha \mathrm{poly}_\alpha(\mathbf{p}(\mathbf{y})) \mathbf{q}_\alpha(\mathbf{y}),$$

- Many applications - CH_5^+, H_5^+, $(H_2O)_2$, $(H_2O)_3$, $H^+(H_2O)_2$, CH_4, $H+CH_4$, C_3H_2, ...

Permutational Invariant Fitting Bases

1. B. J. Braams, J. M. Bowman, Int. Rev. Phys. Chem. 28, 577-606 (2009). - Library

2. J. M. Bowman and S.-L. Zou, Chem. Phys. Lett. **368**, 421 (2003). C_2H_2

3. X.-B. Zhang, S.-L. Zou, L. B. Harding, and J. M. Bowman, J. Phys. Chem. A **108**, 8980
   (2004). H_2CO

4. J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, Molecular
   Potential Energy Functions (John Wiley, Chichester, 1984). XY_4

5. A. Schmelzer, J. Murrell, *Int. J. Quantum Chem.* **1985**, *28*, 287-295. XY_4

6. P. Cassam-Chenaï, F. Patras, *J. Math. Chem.* **2008**, *44*, 938 -966. XY_4

7. D. Opalkaa, W. J. Domcke, *J. Chem. Phys.* **2010**, *132*, 154108-1-14. XY_4

8. Z. Xie and J. M. Bowman, J. Chem. Theory Comput. 6, 26-34 (2010).

9. X. Huang, B. J. Braams, and J. M. Bowman, J. Chem. Phys. **122**, 044308 (2005).

10. H. Derksen and G. Kemper, Computational Invariant Theory (Springer Verlag, Berlin,
    Heidelberg,(New York, 2002).

11. W. Bosma, J. Cannon, and C. Playoust, *J. Comp. Symb. Comp.* 24, 235 (1997). –
    MAGMA

PES Fitting Details CH₅⁺

12 degrees of freedom, 15 variables in fit, $S_5 = 5! = 120$
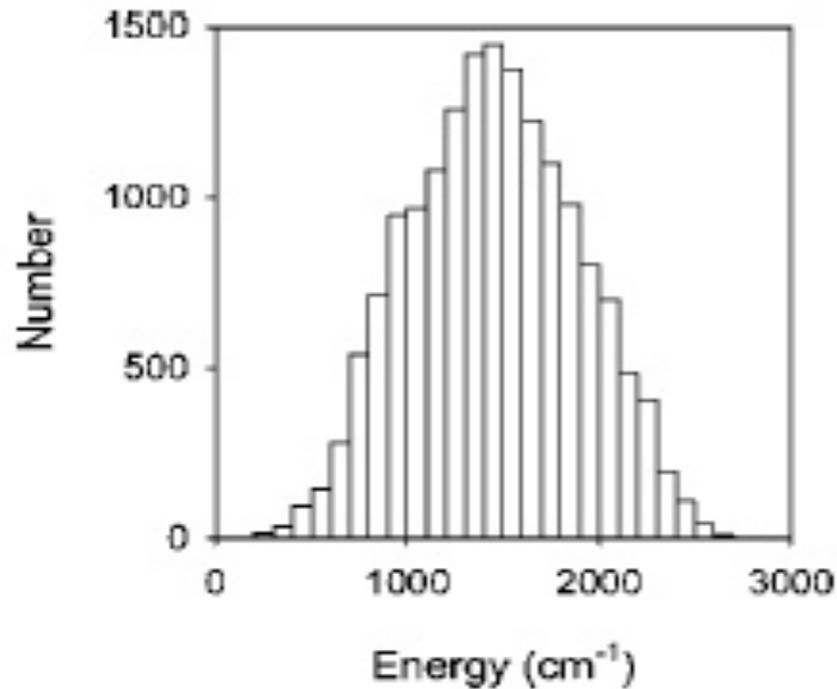
AIMD MP2/aVdZ

- Ab initio calculations do not sample all minima and saddle points.

- Better fits
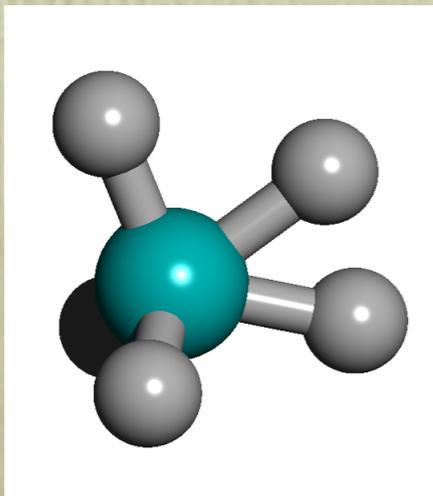
Supplement with many other high energy configs from MD and DMC – ca 30 000 CCSD(T)/avtz energies used in fit.

TABLE I. Comparison of harmonic vibrational frequencies (cm⁻¹) of CH_5^+, at the global minimum $C_s(I)$ geometry, at the $C_s(II)$ transition state geometry, and at the C_{2v} transition state geometry, from *ab initio* calculations and as determined from the PES.

Mode[a]	C_s(I)		C_s(II)		C_{2v}	
	Ab initio[b]	PES[c]	*Ab initio*[b]	PES[c]	*Ab initio*[b]	PES[c]
1	3273	3274	3279	3282	3284	3282
2	3171	3167	3134	3128	3168	3162
3	3035	3028	3077	3070	2910	2903
4	2719	2713	2737	2731	2747	2737
5	2523	2519	2499	2497	2682	2675
6	1581	1577	1611	1607	1476	1477
7	1499	1498	1502	1504	1456	1456
8	1474	1476	1479	1477	1411	1405
9	1301	1314	1337	1340	1320	1340
10	1289	1289	1146	1156	1252	1253
11	749	749	944	941	471	470
12	245	238	216i	218i	584i	592i

## *Ab initio* global potential-energy surface for $H_5^+ \rightarrow H_3^+ + H_2$

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roughly 100 000 CCSD(T)/aug-cc-pVTZ energies
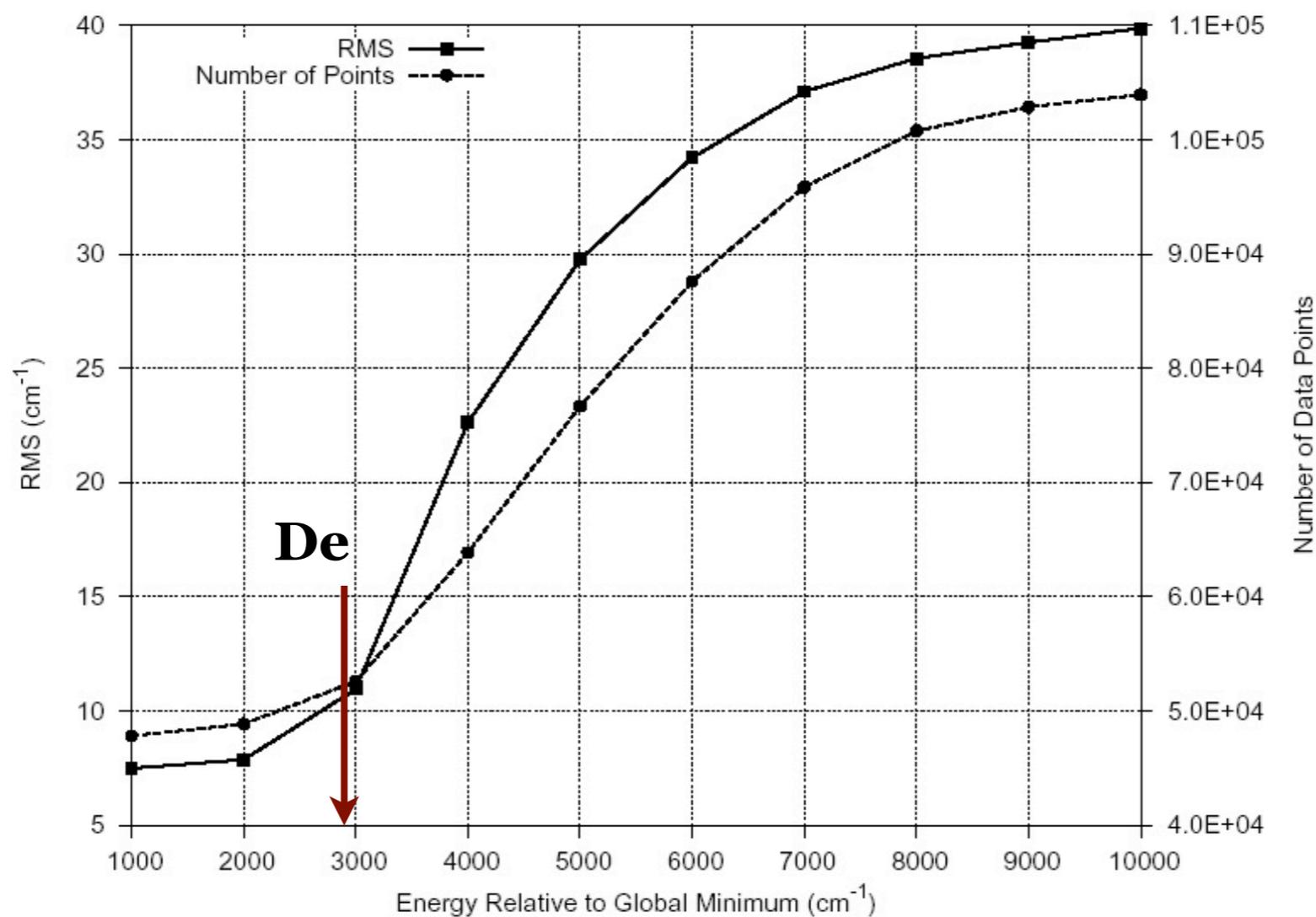
# The Potential Landscape - The Big Picture
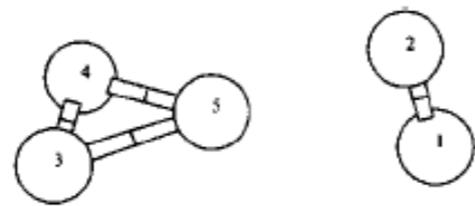
(a) 1-C$_{2v}$
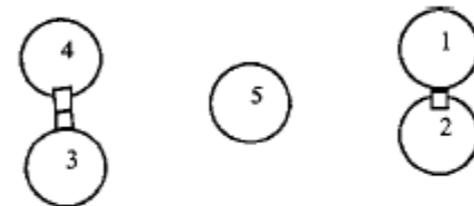
(b) 2-D$_{2d}$
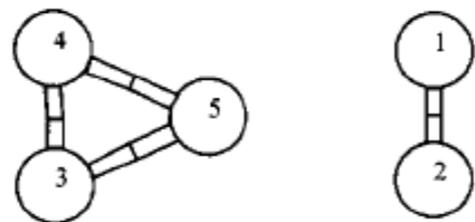
(c) 3-C$_{2v}$
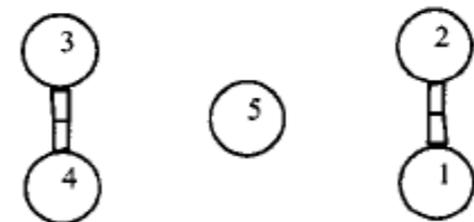
(d) 4-D$_{2h}$

(e) 5-C$_{2v}$
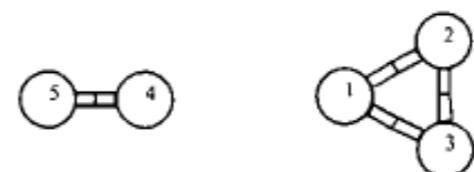
(f) 6-C$_{2v}$

(g) 7-C$_{2v}$

(h) 8-C$_{2v}$

(i) 9-C$_s$

(j) 10-C$_{3v}$

(a) 1-C_{2v} (b) 2-D_{2d}

(c) 3-C_{2v} (d) 4-D_{2h}

(e) 5-C_{2v} (f) 6-C_{2v}
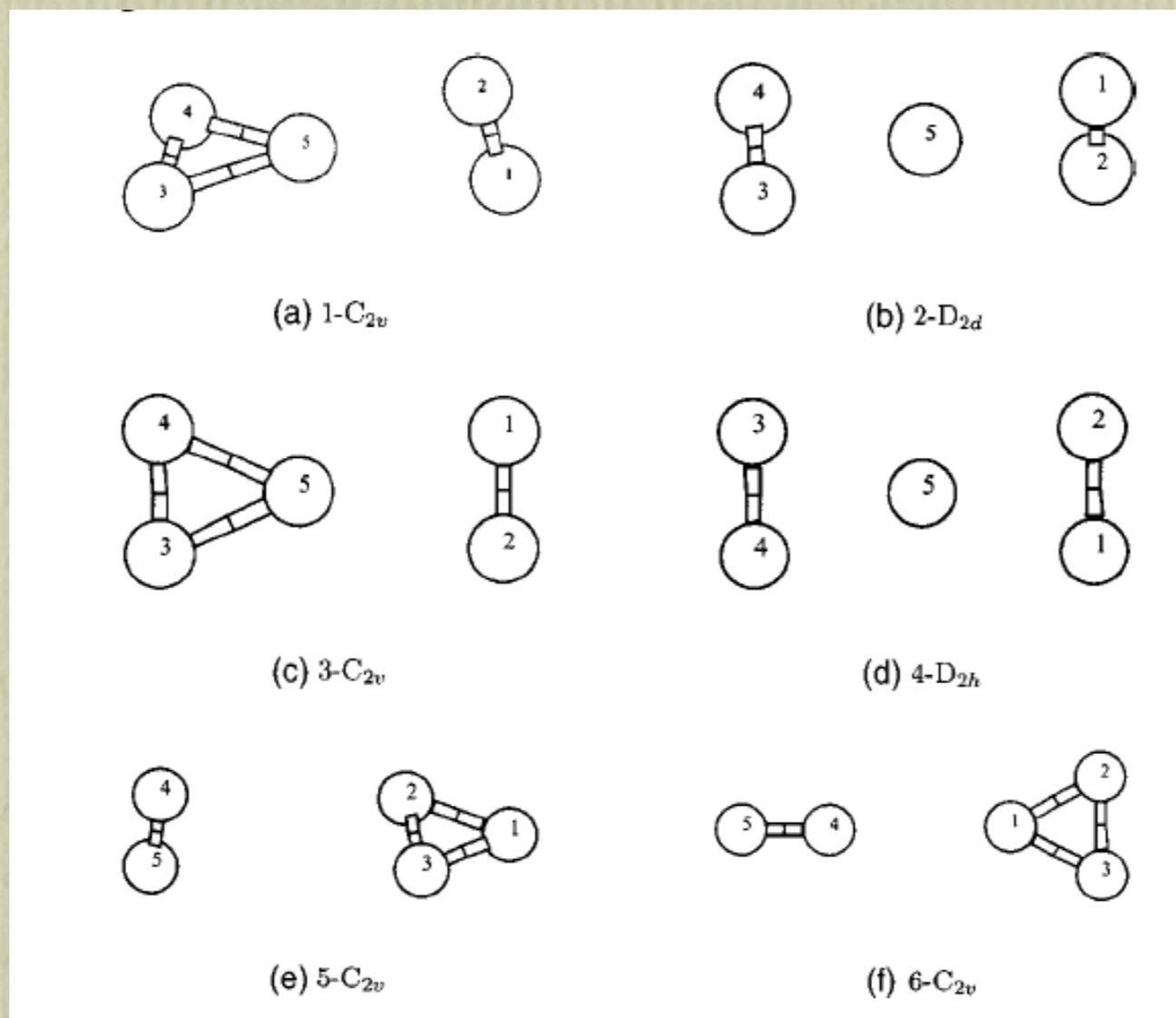
TABLE IV. Energy comparison for ten known stationary points among indicated *ab initio* calculations, current PES, and a previously reported PES. The value for 1-C_{2v} is the absolute global minimum energy in hartree. Other values are the energies in wave numbers relative to the global minimum.

Conformer	1-C_{2v}	2-D_{2d}	3-C_{2v}	4-D_{2h}	5-C_{2v}	6-C_{2v}	7-C_{2v}	8-C_{2v}	9-C_s	10-C_{3v}
CC-R12[a]	−2.531 794	61.5	96.6	182.2						
QCISD[b]	−2.530 509	64.1	95.5	181.9	1543.6	2299.0	1672.2	2663.3	2171.3	2834.5
CCSD(T)[c]	−2.527 994	48.4	96.4	162.8	1526.8	2282.7	1653.9	2646.3	2130.7	2873.2
PES[c]	−2.528 015	52.2	103.0	160.2	1565.9	2408.3	1677.2	2498.7	2105.9	2712.5
Previous PES[d]	−2.518 215	27.9	89.5	146.5	1970.9	2125.2	1988.9	2496.8	2540.5	2801.9

(i) 9-C_s (j) 10-C_{3v}

# Zero-point energies from Diffusion Monte Carlo

$$\Psi(t) = \sum_{n=0} \langle \chi_n | \Psi(0) \rangle \chi_n e^{-i(E_n - E_0)t}; \quad H\chi_n = E_n \chi_n$$

Let $\tau = it$

$$\Psi(\tau) = \sum_{n=0} \langle \chi_n | \Psi(0) \rangle \chi_n e^{-(E_n - E_0)\tau}$$

$$\xrightarrow[\tau \to \infty]{} \langle \chi_0 | \Psi(0) \rangle \chi_0$$

$$\frac{\langle \Psi(\tau) | H | \Psi(\tau) \rangle}{\langle \Psi(\tau) | \Psi(\tau) \rangle} \xrightarrow[\tau \to \infty]{} E_0$$
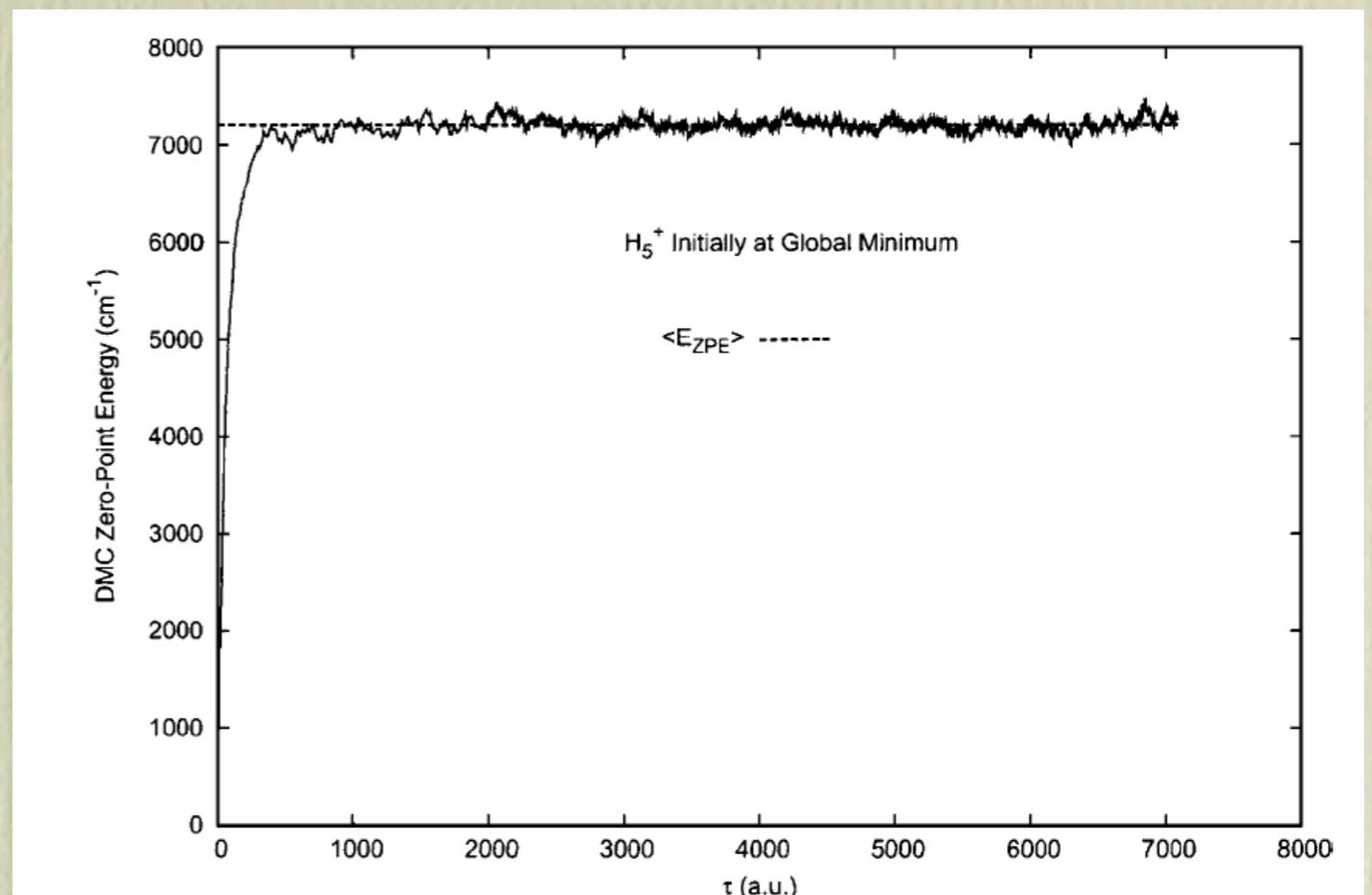
Solve using Monte Carlo "Birth/Death" Method

$H_5^+ \rightarrow H_3^+ + H_2$

$H_3^+ + H_2$

H_5^+

DMC result using PES: $D_0 = 6.33 \pm .03$ kcal/mol

Present D_e is low by 0.28 kcal/mol
So, our estimate would be 6.6 kcal/mol
(HO Result is 5.57 kcal/mol)

*Exp1 = 6.6 $\pm$0.3, Exp2 = 7.0 $\pm$0.1
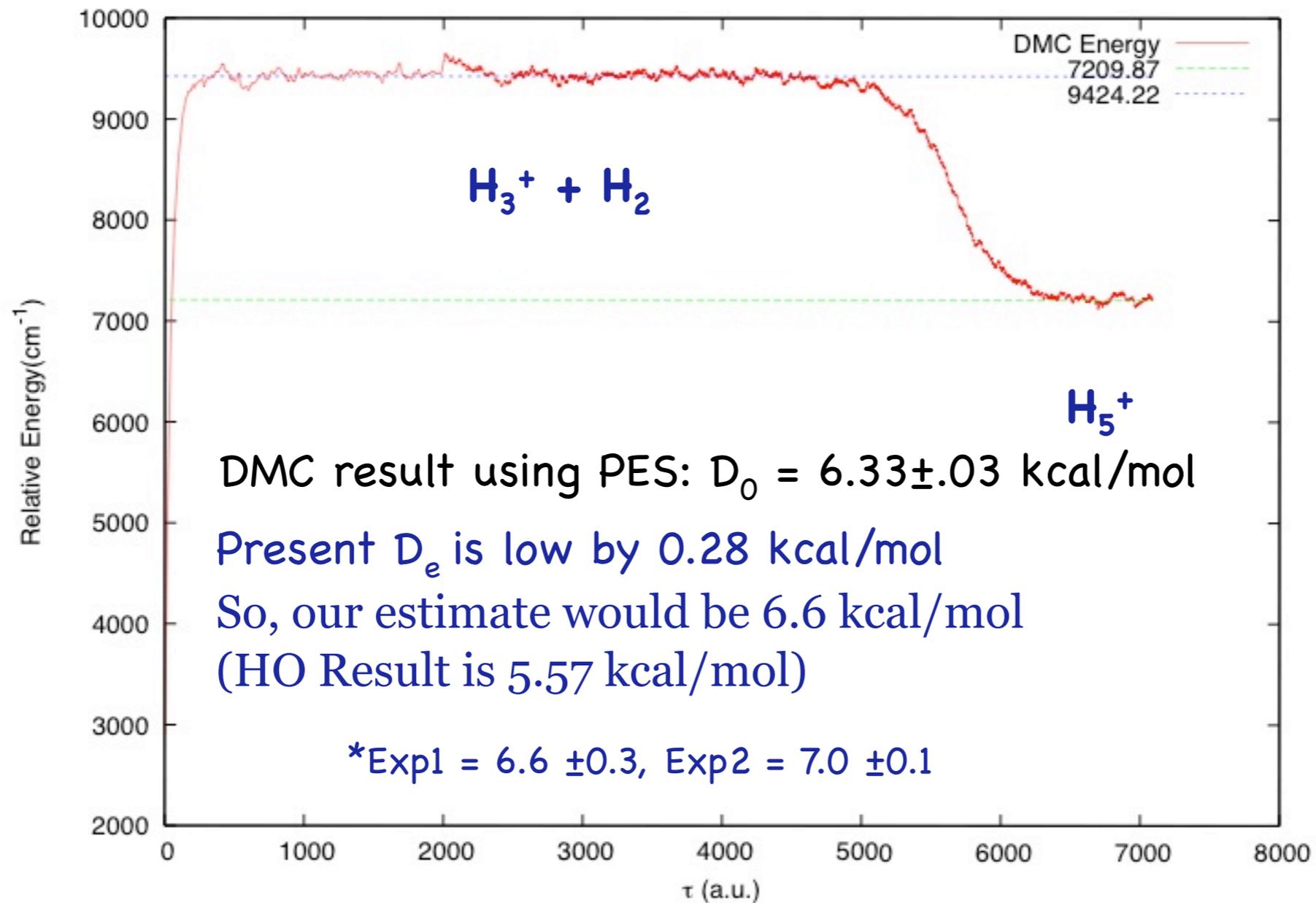
Application of the PES (and dipole moment surface) to (low-res) spectroscopy and new experiments

Major challenge for a rigorous method

- 9 degrees of freedom
- expected to highly fluxional
- very low D_o

Our goal is "the best we can currently do" - realistic, predictive and interpretive.

We apply the code 'MULTIMODE' to do this.

MULTIMODE BASICS

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

$$\mu_{\alpha\beta} = (\mathbf{I'}^{-1})_{\alpha\beta}; \quad \mathbf{I'}_{\alpha\beta} = I_{\alpha\beta}^{(0)} + \Delta_{\alpha\beta}(Q_k) \qquad \pi_\alpha = -i\sum_{k,l}\zeta_{kl}^\alpha Q_k \frac{\partial}{\partial Q_l}$$

$$\Psi_{n_1,n_2,,...,n_N}^{VSCF}(Q_1,Q_2,...Q_N) = \prod_{i=1}^N \phi_{n_i}^{(i)}(Q_i),$$

$$[T_l + <\prod_{i\neq l}^N \phi_{n_i}^{(i)} \mid V + T_c \mid \prod_{i\neq l}^N \phi_{n_i}^{(i)} > -\varepsilon_{nl}^{(l)}]\phi_{nl}^{(l)}(Q_l) = 0, l = 1,N$$

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

MULTIMODE BASICS

n-mode representation of the potential (and μ)

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

For example for a 3-mode molecule using a 2MR for V

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

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

Quadratures are 1,2,3,...,n-dimensional

H$_2$O Tests, J = 0 and 3MR is exact)

TABLE VI. Comparison of V-CI and exact (Ref. 14) vibrational energies (cm^{-1}) of H$_2$O 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					

H$_2$O Tests (cont) J > 0

TABLE VII. Comparison of adiabatic rotation V-CI(AR) and exact (Ref. 14) rovibrational energies (cm^{-1}), relative to the zero-point energy, for H$_2$O for $J=1$.

	$K_a=0$ $K_c=1$					$K_a=1$ $K_c=0$					$K_a=1$ $K_c=1$			
v_s	v_b	v_a	Exact	AR	v_s	v_b	v_a	Exact	AR	v_s	v_b	v_a	Exact	AR
0	0	0	23.79	23.34	0	0	0	42.37	42.37	0	0	0	37.14	37.47
0	1	0	1618.59	1617.90	0	1	0	1640.54	1640.54	0	1	0	1634.00	1635.76
0	2	0	3175.44	3174.29	0	2	0	3201.91	3201.91	0	2	0	3196.09	3197.49
1	0	0	3680.44	3679.97	1	0	0	3698.48	3698.48	1	0	0	3693.28	3693.63
0	0	1	3779.53	3778.20	0	0	1	3797.01	3796.00	0	0	1	3791.74	3792.47
0	3	0	4690.58	4688.93	0	3	0	4723.54	4723.56	0	3	0	4717.47	4719.58
1	1	0	5258.46	5257.74	1	1	0	5279.73	5279.73	1	1	0	5274.21	5275.01
0	1	1	5354.83	5353.14	0	1	1	5375.31	5375.31	0	1	1	5369.72	5371.02
0	4	0	6157.77	6155.98	0	4	0	6201.08	6201.26	0	4	0	6194.80	6197.67
1	2	0	6798.53	6797.38	1	2	0	6824.13	6824.15	1	2	0	6818.32	6819.79

INVITED TOPICAL REVIEW

Variational quantum approaches for computing vibrational energies of polyatomic molecules

Joel M. Bowman[a]*, Tucker Carrington[b] and Hans-Dieter Meyer[c]
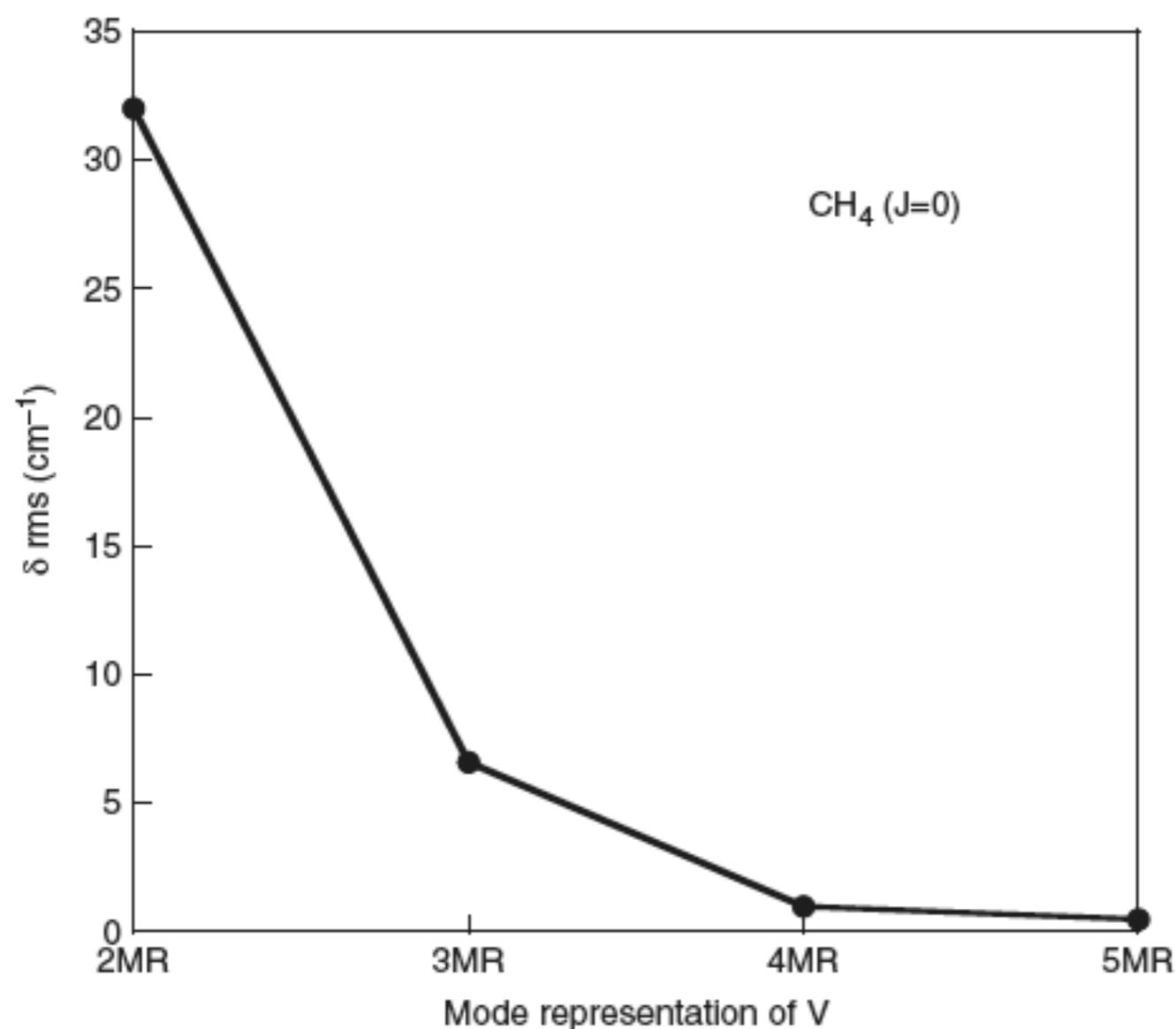
Figure 1. Root mean square difference between nMR MULTIMODE energies and benchmark ones [158] versus n for roughly 50 energies $4500\,cm^{-1}$ above the zero-point energy.

Table 4. Comparison of 5MR MULTIMODE rovibrational energies of CH_4 (cm^{-1}) for $J=1$ with benchmark results of [158].

State	Benchmark	MULTIMODE
Zero point	10.43	10.43
(00)(01) A2	1312.41	1312.50
(00)(01) F2	1317.25	1317.34
(00)(01) F1	1326.73	1326.82
(00)(01) E	1327.03	1327.12
(00)(10) F2	1543.79	1543.88
(00)(10) F1	1543.91	1544.01
(00)(02) F1	2600.02	2600.58
(00)(02) F1	2615.61	2616.36
(00)(02) E	2622.05	2622.82
(00)(02) F2	2626.64	2627.37
(00)(02) A2	2634.83	2635.61
(00)(02) F2	2641.58	2642.25
(00)(02) F1	2644.03	2644.68
(00)(11) E	2835.80	2836.67
(00)(11) F1	2837.85	2838.73
(00)(11) F2	2843.53	2844.39
(00)(11) A2	2848.87	2849.75
(00)(11) F2	2856.65	2857.36
(00)(11) E	2858.02	2858.73
(00)(11) F1	2860.39	2861.11
(00)(11) A1	2862.34	2863.06
(10)(00) F1	2924.16	2924.32
(01)(00) A2	3022.81	3023.02
(01)(00) F2	3023.36	3023.58
(01)(00) F1	3024.50	3024.72
(01)(00) E	3024.56	3024.78
(00)(20) F1	3074.26	3074.68
(00)(20) F2	3075.80	3076.22
(00)(20) F1	3075.82	3076.50

High Resolution "MULTIMODE"

Calculations of rovibrational energies and dipole transition intensities for polyatomic molecules using MULTIMODE

Stuart Carter,[1] Amit R. Sharma,[2] Joel M. Bowman,[2,a)] Pavel Rosmus,[3,b)] and Riccardo Tarroni[4]

$$R^2 = 3 \sum_m \sum_{m'} |\langle \Psi_r^{Jm}(\mathbf{Q}, \alpha, \beta, \gamma) | \mu_z^s | \Psi_{r'}^{J'm'}(\mathbf{Q}, \alpha, \beta, \gamma) \rangle|^2$$

$$\Psi_r^{J0}(\mathbf{Q}, \alpha, \beta, \gamma) = \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} \sum_k \sum_v C_{rv}^{|k|} \Phi_v^{|k|}(\mathbf{Q}) D_{0,k}^J(\pm)$$

$$
\begin{aligned}
\mu_\alpha(Q_1, Q_2, \ldots, Q_N) = {} & \sum_i \mu_{\alpha i}^{(1)}(Q_i) + \sum_{ij} \mu_{\alpha ij}^{(2)}(Q_i, Q_j) + \\
& \sum_{ijk} \mu_{\alpha ijk}^{(3)}(Q_i, Q_j, Q_k) + \sum_{ijkl} \mu_{\alpha ijkl}^{(4)}(Q_i, Q_j, Q_k, Q_l) + \\
& \sum_{ijklm} \mu_{\alpha ijklm}^{(5)}(Q_i, Q_j, Q_k, Q_l, Q_m) + \cdots
\end{aligned}
$$

H₂CS 4MR

State	Symmetry	MM	RVIB4[a]
ν_1	A_1	2970.54	2970.72
ν_2	A_1	1457.18	1457.42
ν_3	A_1	1058.89	1058.87
ν_4	B_1	990.31	990.51
ν_5	B_2	3024.40	3024.59
ν_6	B_2	990.73	990.95

[a]Reference 43.

TABLE IV. $J=1$ vibrational wavenumbers (cm⁻¹) for the fundamentals of H₂CS.

State	k_a	k_c	MM	RVIB4[a]
ν_0	0	1	1.1436	1.1436
ν_1	0	1	1.1411	1.1436
ν_2	0	1	1.1426	1.1438
ν_3	0	1	1.1366	1.1381
ν_4	0	1	1.1436	1.1426
ν_5	0	1	1.1416	1.1434
ν_6	0	1	1.1414	1.1416
ν_0	1	1	10.2961	10.2714
ν_1	1	1	10.2767	10.1649
ν_2	1	1	10.4065	10.3608
ν_3	1	1	10.2835	10.2606
ν_4	1	1	0.6336	0.6374
ν_5	1	1	10.0851	10.1712
ν_6	1	1	19.8654	19.8586
ν_0	1	0	10.3309	10.3063
ν_1	1	0	10.3119	10.2068
ν_2	1	0	10.4412	10.3985
ν_3	1	0	10.3180	10.2942
ν_4	1	0	0.6329	0.6351
ν_5	1	0	10.1209	10.2046
ν_6	1	0	19.8709	19.8623

[a]Reference 43.

Exp

J = 3

Theory
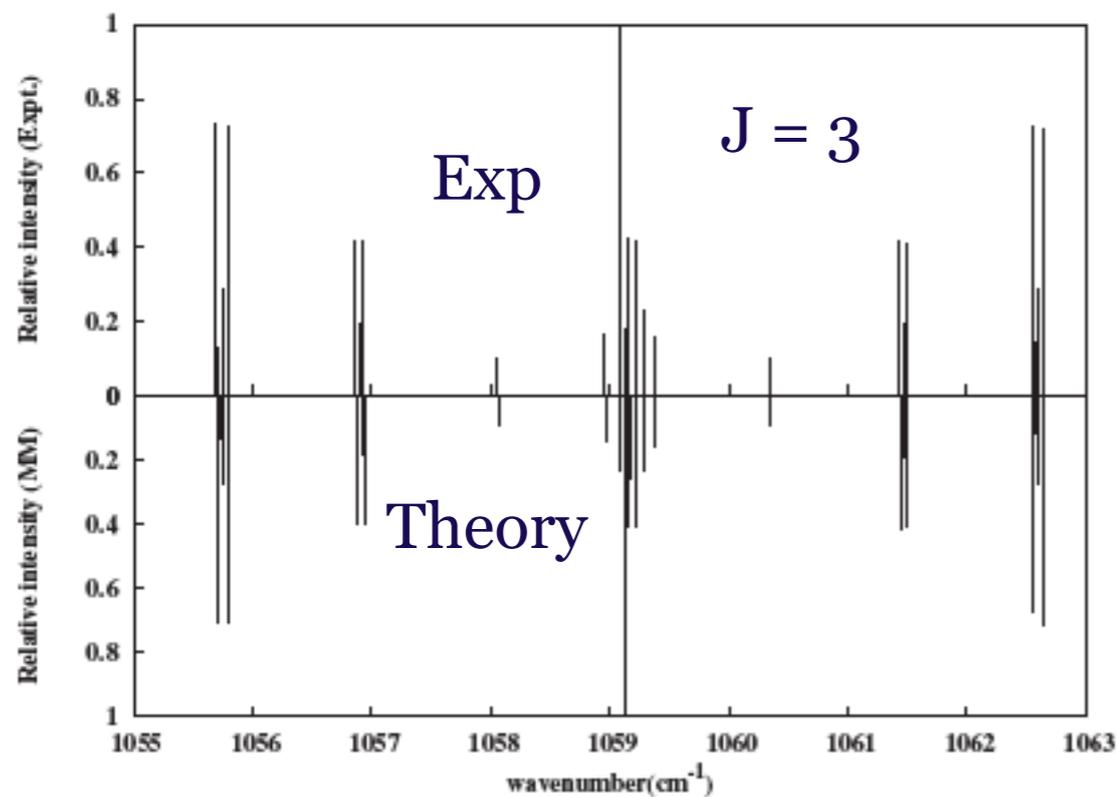
J. M. Flaud, W. J. Lafferty, A. Perrin, Y. S. Kim, H. Beckers, and H. Willner, J. Quant. Spectrosc. Radiat. Transf. **109**, 995 (2008).
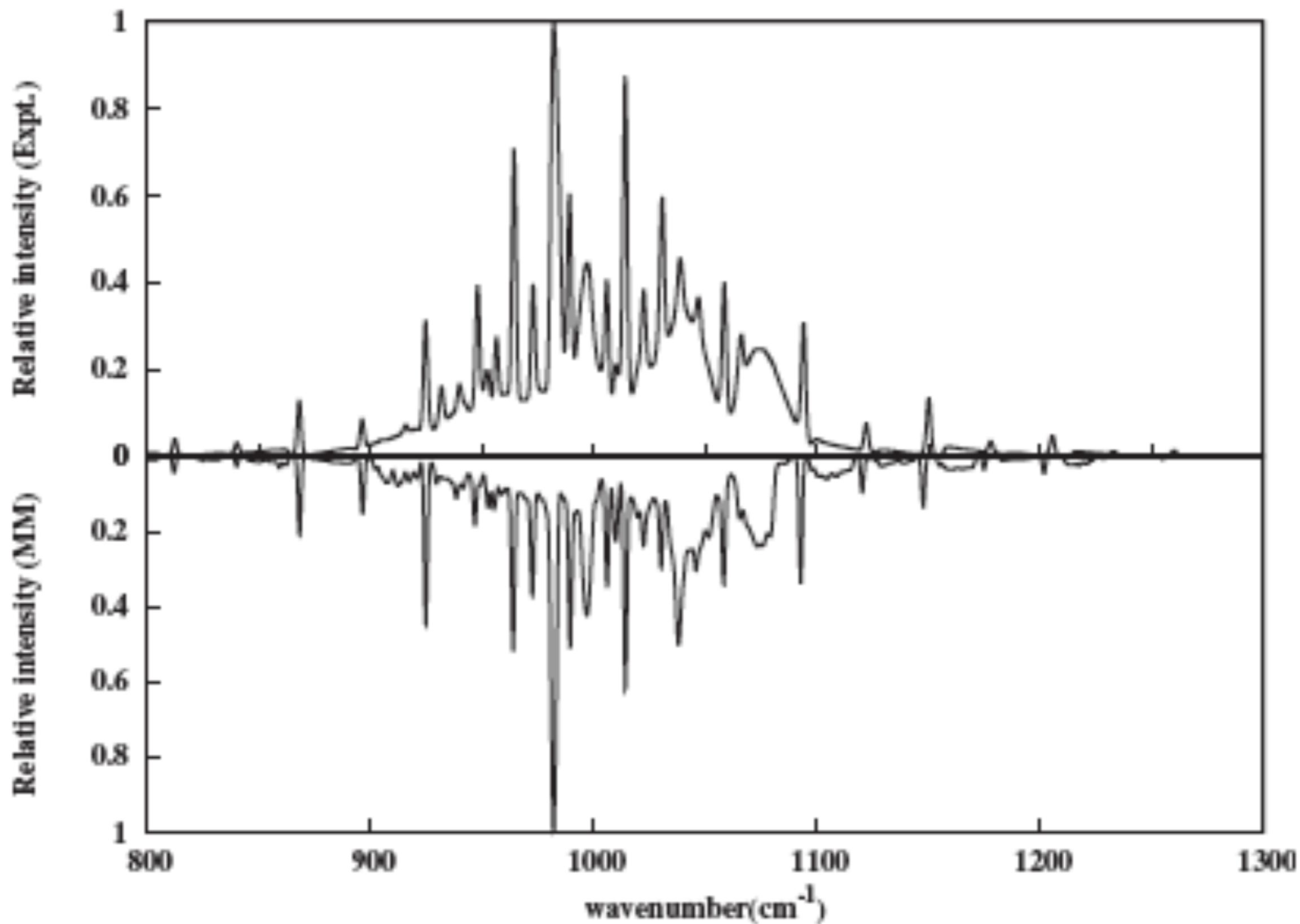
FIG. 4. Comparison of H_2CS experimental spectrum taken at 293 K with MM synthetic spectra ($J=20$, at 2 cm^{-1} resolution).

H₂CO 4MR

TABLE VII. Comparison of MM anharmonic fundamentals (cm⁻¹) for H₂CO ($J=0$) with RVIB4 and experimentally observed band centers.

Mode number	Symmetry	MM	RVIB4[a]	Band center
ν_1	A_1	2781.3	2782.9	2782.4575[b]
ν_2	A_1	1746.6	1747.4	1746.0089[c]
ν_3	A_1	1500.0	1499.8	1500.1747[d]
ν_4	B_1	1166.7	1165.8	1167.2563[d]
ν_5	B_2	2842.7	2841.7	2843.9685[b]
ν_6	B_2	1250.5	1249.9	1249.0947[d]

[a]Reference 65.
[b]Reference 66.
[c]References 67 and 68.
[d]Reference 69.
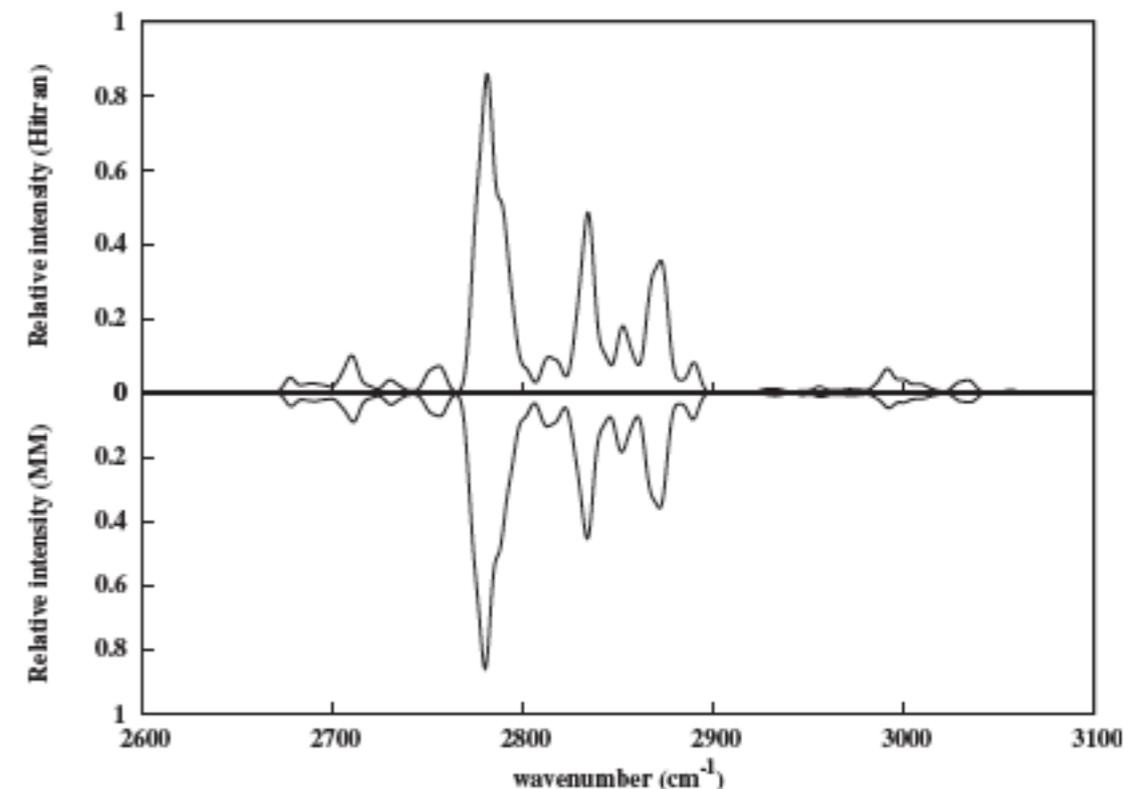
FIG. 7. A portion of the spectrum showing the $J=3$ transitions of the 3.6 μm band (ν_1 and ν_5 band) of H₂CO.

[50] A. Perrin, D. Jacquemart, F. K. Tchana, and N. Lacome, J. Quant. Spectrosc. Radiat. Transf. 110, 700 (2009).

PES: S. Carter, N. C. Handy, and J. Demaison, Mol. Phys. 90, 729 (1997).

DMS: New fit to ca 14 000 dipole values CCSD(T)/aVTZ

Return to H_5^+ and D_5^+ IR Spectra

Shared-Proton Mode Lights up the Infrared Spectrum of Fluxional Cations H_5^+ and D_5^+

Timothy C. Cheng,[†] Biswajit Bandyopadyay,[†] Yimin Wang,[†] Stuart Carter,[†,§] Bastiaan J. Braams,[†,#] Joel M. Bowman,*[,†] and Michael A. Duncan*[,†]

Some History

Kraemer, W. P.; Špirko, V.; Bludsky, O. Extended Ab-Initio Study of the Vibrational Dynamics of H_5^+ and D_5^+ Including All Vibrational-Modes. *J. Mol. Spectrosc.* **1994**, *164*, 500–509.

Ab initio force field, adiabatic treatment of vibrations. Proton fundamental 622 cm⁻¹

Okumura, M.; Yeh, L. I.; Lee, Y. T. Infrared Spectroscopy of the Cluster ions H·$(H_2)n$. *J. Chem. Phys.* **1988**, *88*, 79–81.

Predissociation "action" spectroscopy - low resolution peaks at 3520, 3904, 4232 cm⁻¹

The present theory and exp

- Exp by Mike Duncan UGA, still predissociation action spectra, but higher resolution and also new results for D_5^+. (Very new exps also at Felix)

- New Dipole Moment Surface by us

- MM-RPH calculations

- Diffusion Monte Carlo with fixed node approximation for "shared" proton stretch

- Approximate "vibrational" spectra from 0 to 5000 cm^{-1}.

MULTIMODE "RPH/TORSION"

$$H = T + V(s, Q_1, Q_2, \ldots, Q_N)$$

T is the very complex kinetic energy operator that contains
all the couplings between the large amplitude mode s and
the orthogonal normal modes. s can be and most often is
a torsional angle.

$$V(s, Q_1, Q_2, \ldots, Q_N) = V(s) + \sum_i V_i^{(2)}(s, Q_i) + \sum_{ij} V_{ij}^{(3)}(s, Q_i, Q_j) + \ldots$$

Begin, as usual, with a VSCF reference Hamiltonian.

*Carter and Handy (2002), Miller, Handy, Adams (1988), Hougen, Bunker, Johns (1970)

H$_5^+$ low energy stationary points
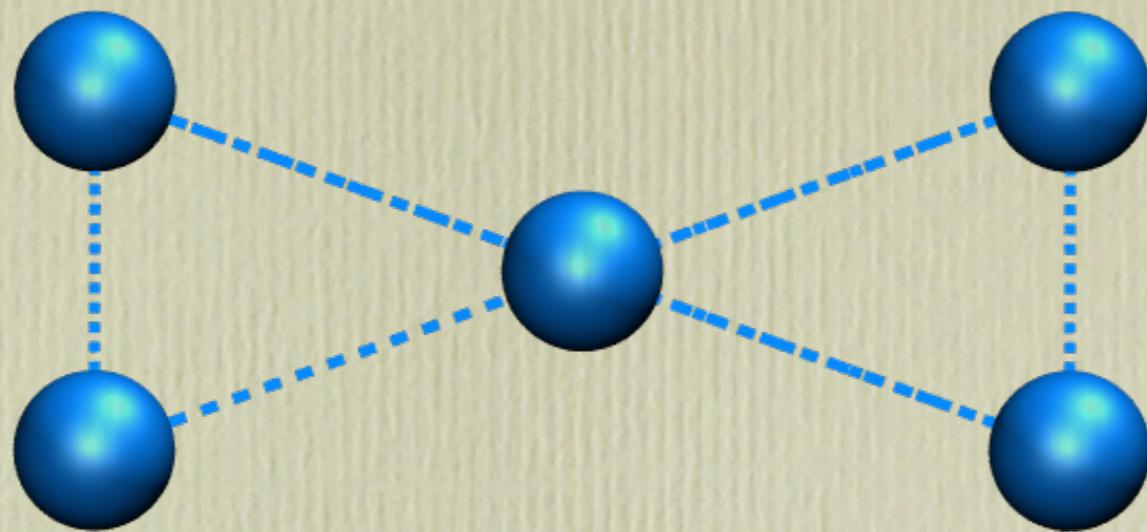
160 cm^{-1}
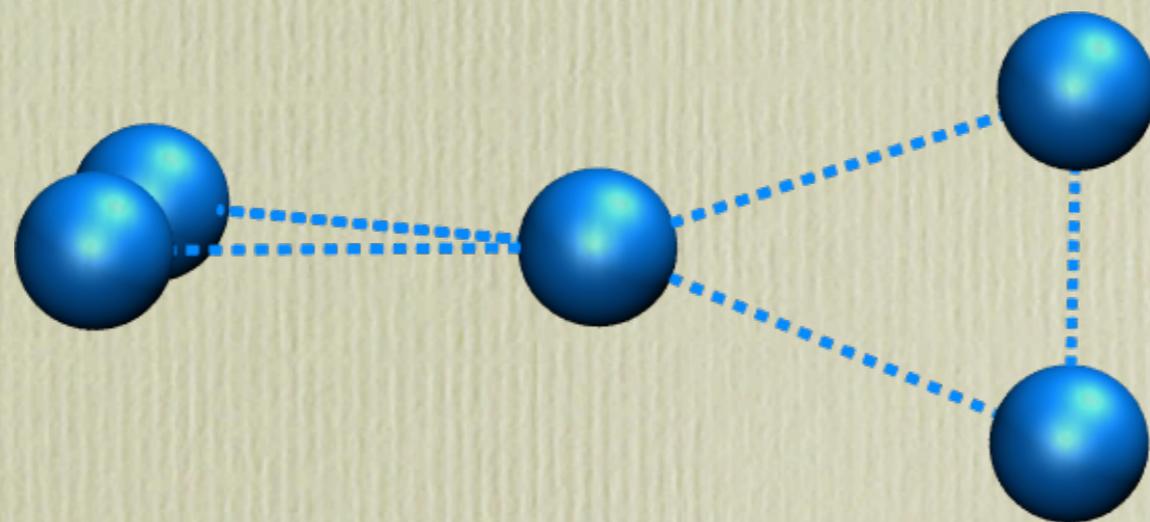
5^2
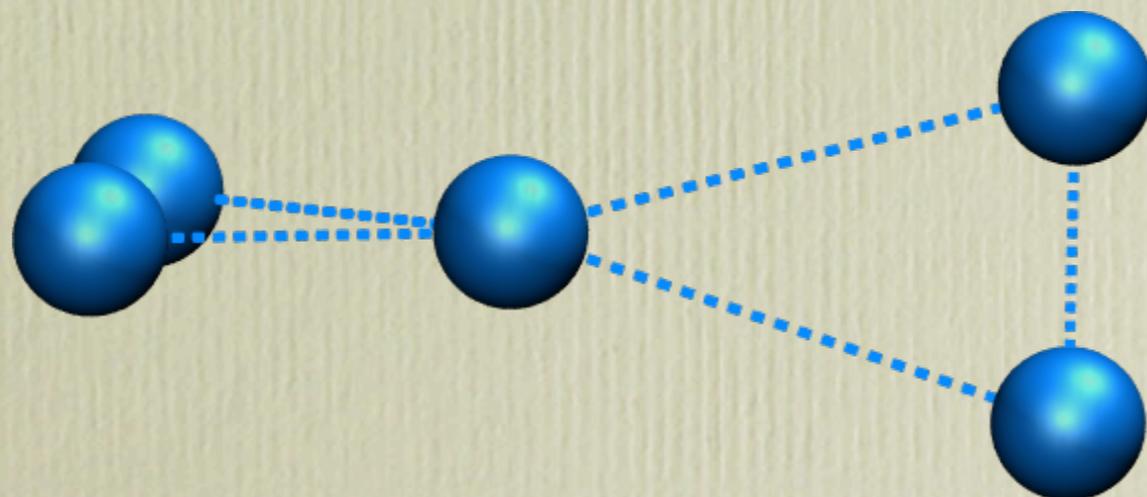
0

Actually Two Large Amplitude Motions
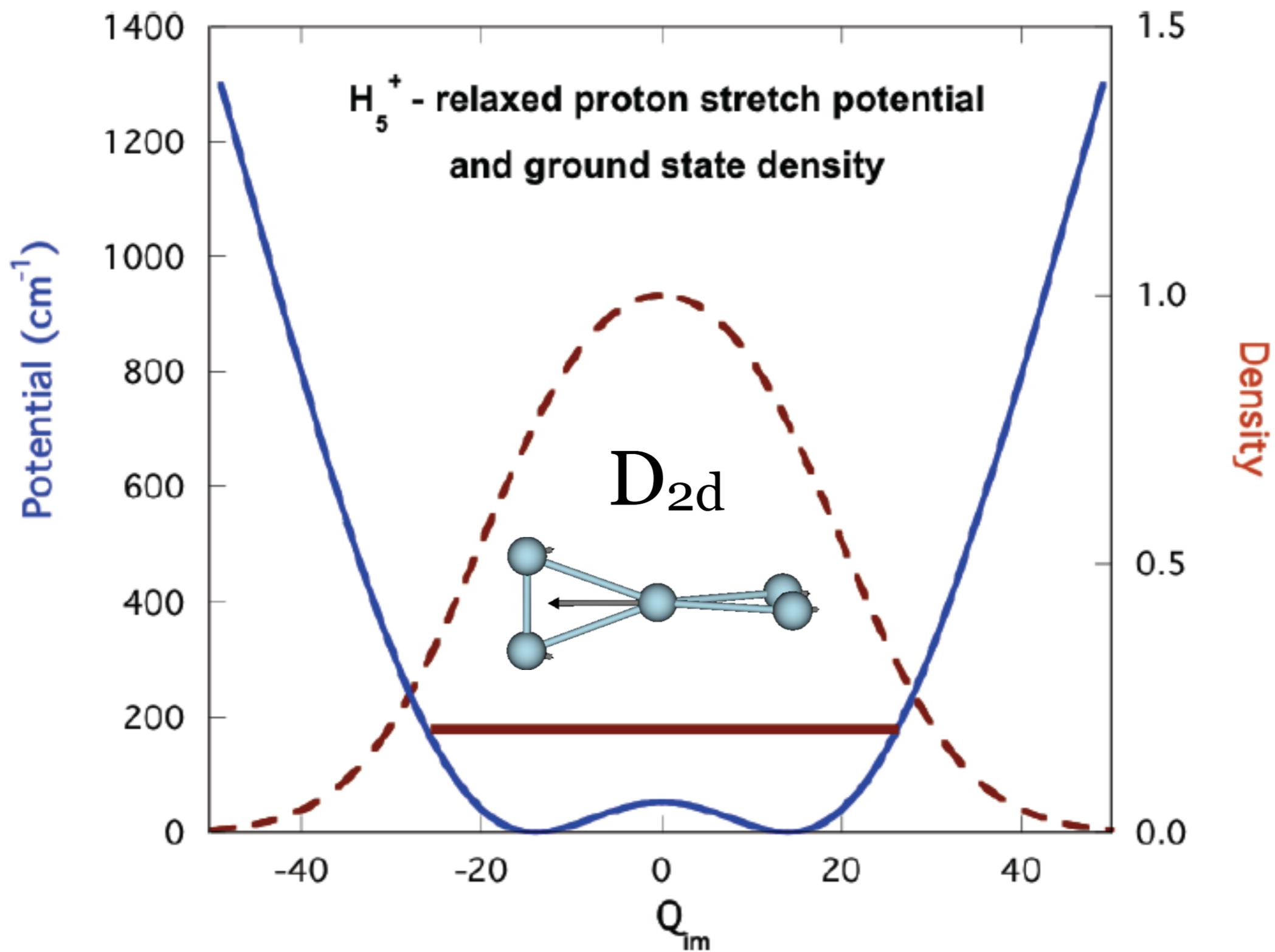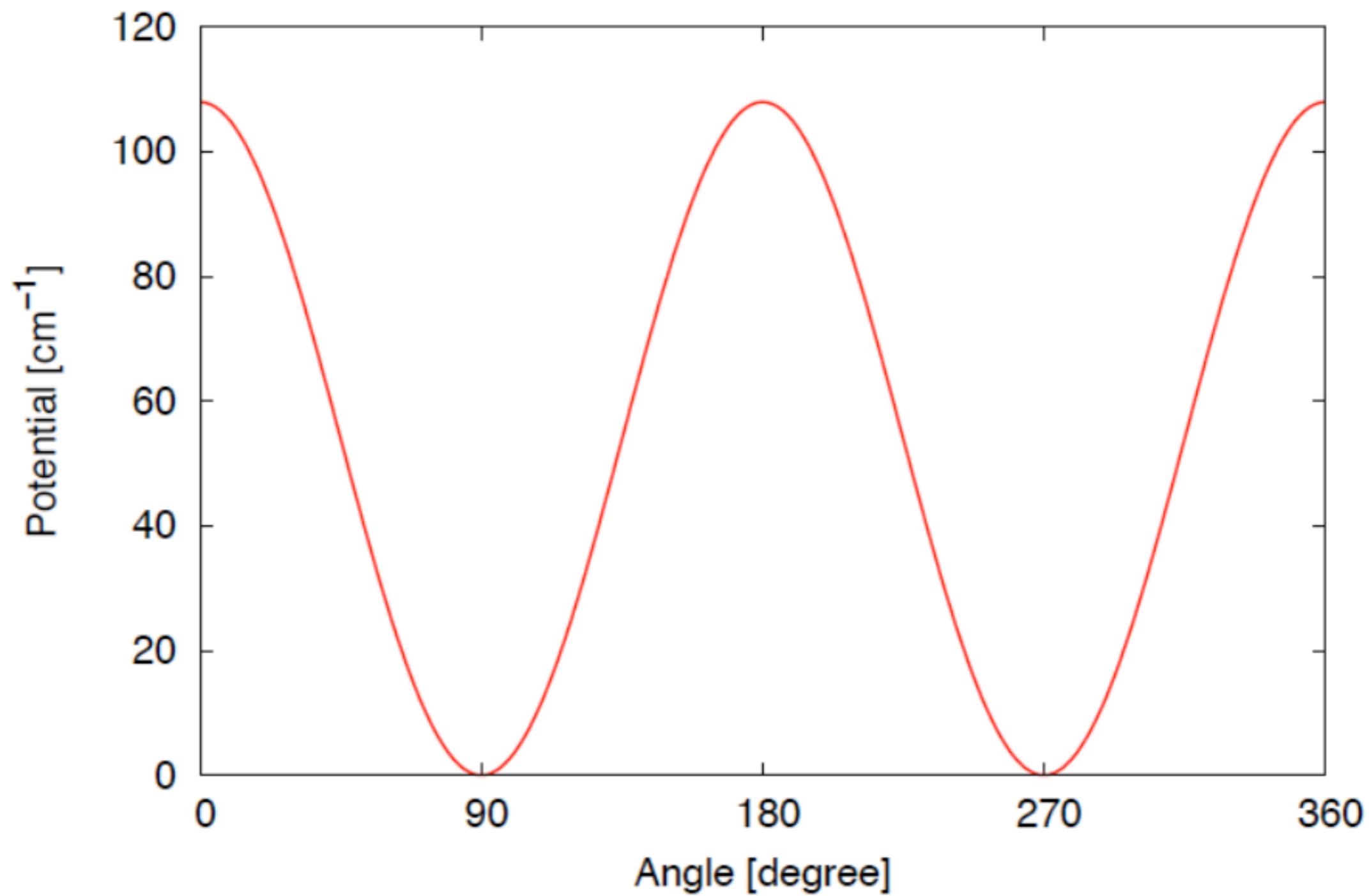
Benchmark DMC Calculations

Diffusion Monte Carlo Calculations

In the present Diffusion Monte Carlo (DMC) calculations energies were obtained using an ensemble of 20 000 Gaussian random "walkers". After equilibrating, which typically took 2 000 time steps, propagation continued for an additional 80 000 steps. The zero-point energy is calculated using the standard expression

$$E_R(\tau) = <V> - \alpha \frac{[N(\tau) - N(0)]}{N(0)},$$

where $N(t)$ is the number of "walkers" at (imaginary) time t, $<V>$ is the average of the potential over all walkers. The total number of walkers is kept approximately constant by the feedback parameter α which is adjustable but which is essentially the inverse of the time step. In the present calculations α equals 0.1 a.u.

Fixed-node DMC calculations were performed as above with the addition of a nodal surface which forces a node in the wavefunction by eliminating walkers that cross the surface. A standard re-crossing correction was also applied. In the present application for the first excited proton-stretch state the node was placed (in Cartesian coordinates) at the midpoint of a vector defined by the centers of mass of the two H_2 units, shown in
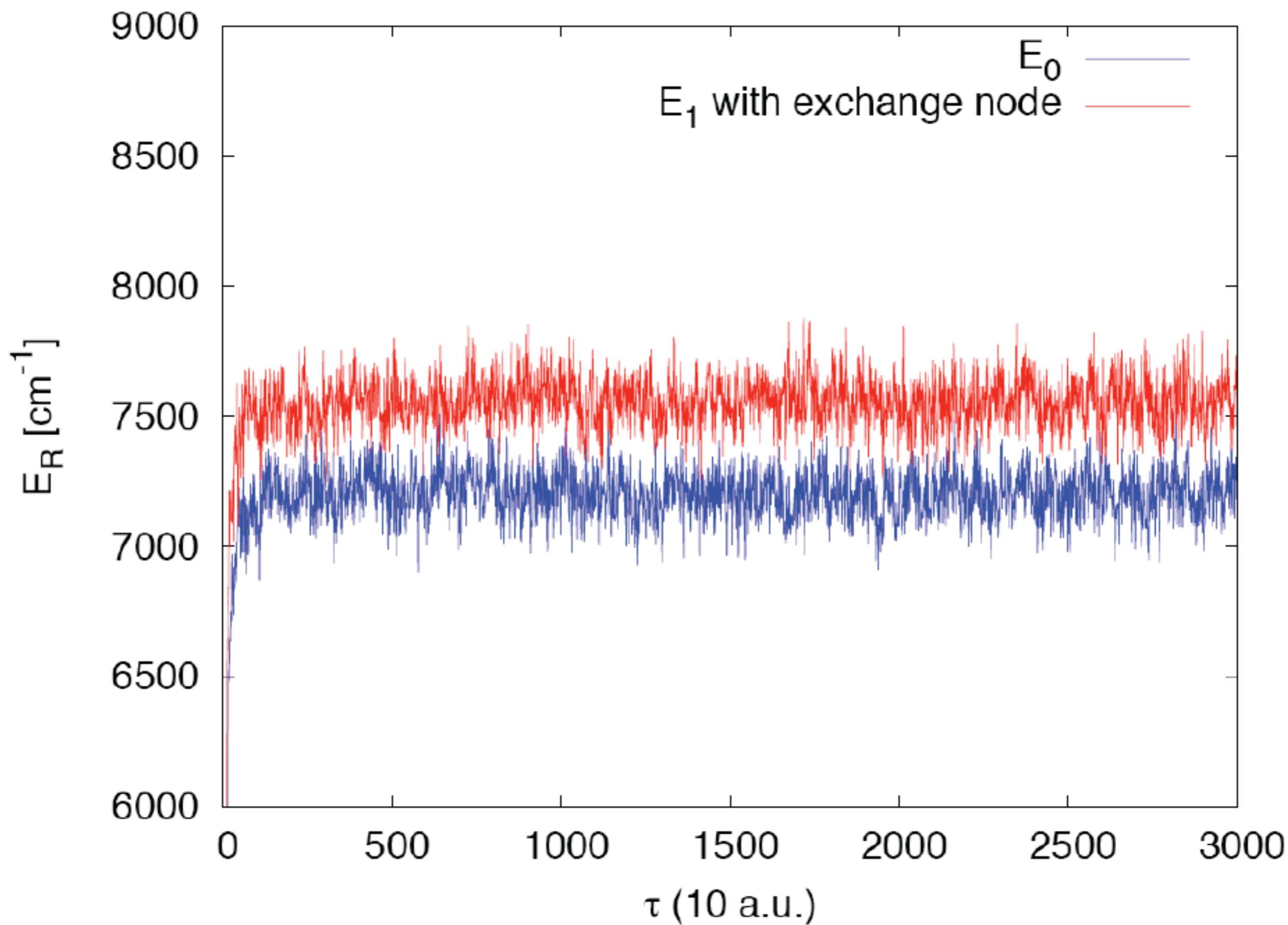
Results

	H$_5^+$		D$_5^+$	
	DMC	MM-RPH	DMC	MM-RPH
Zero-point energy	7210	7244	5152	5174
υ_{H+}	334	382	222	257
$\Delta\upsilon_{torsion}$	80	66	32	28
$2\upsilon_{H+}$	---	1718	---	1241
$3\upsilon_{H+}$	---	2751	---	1821, 1834

Fig. S2 Cuts of the dipole moment components along the D_{2h} saddle point "IR active" normal modes. Q_1 is the imaginary frequency proton-transfer mode.
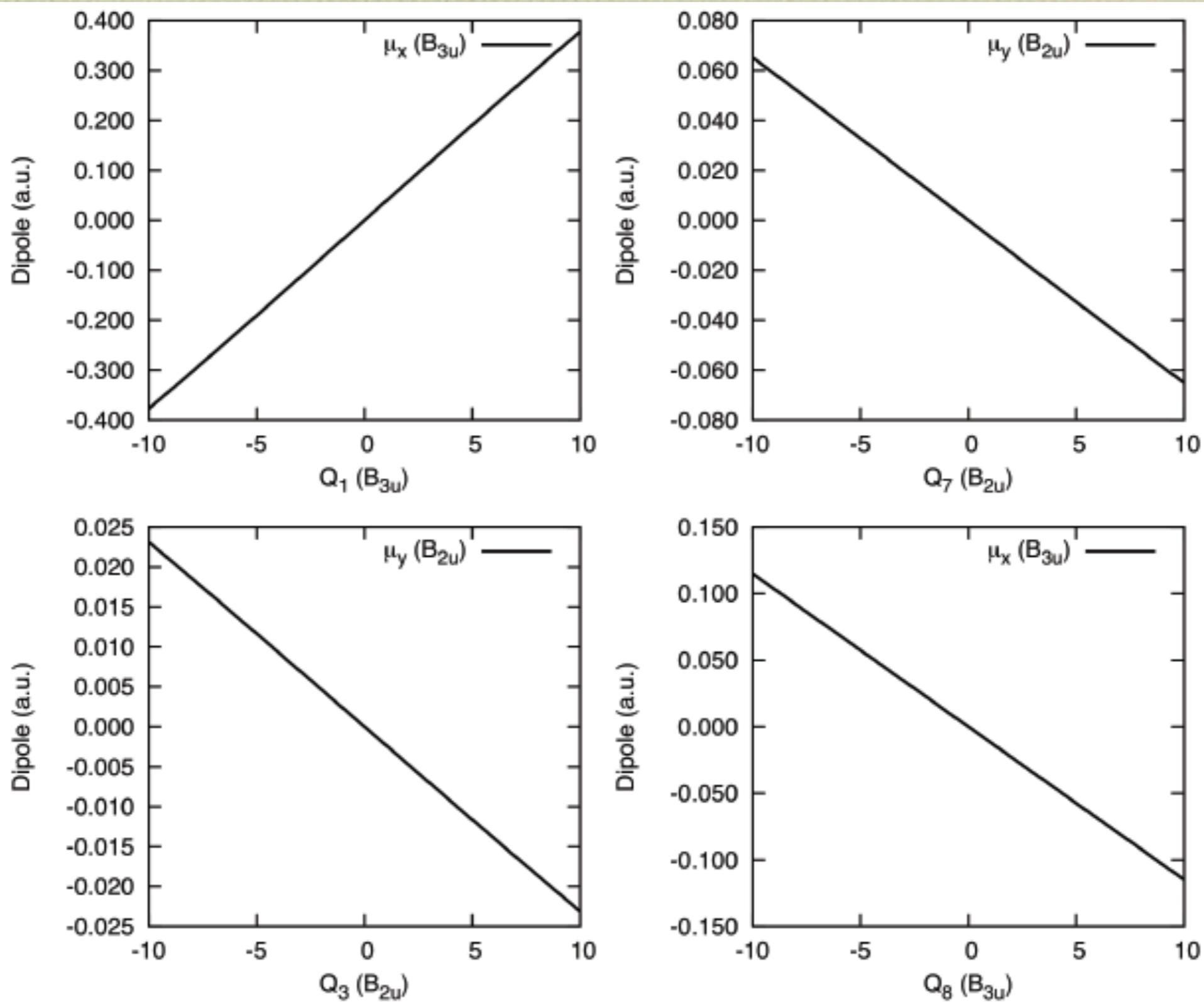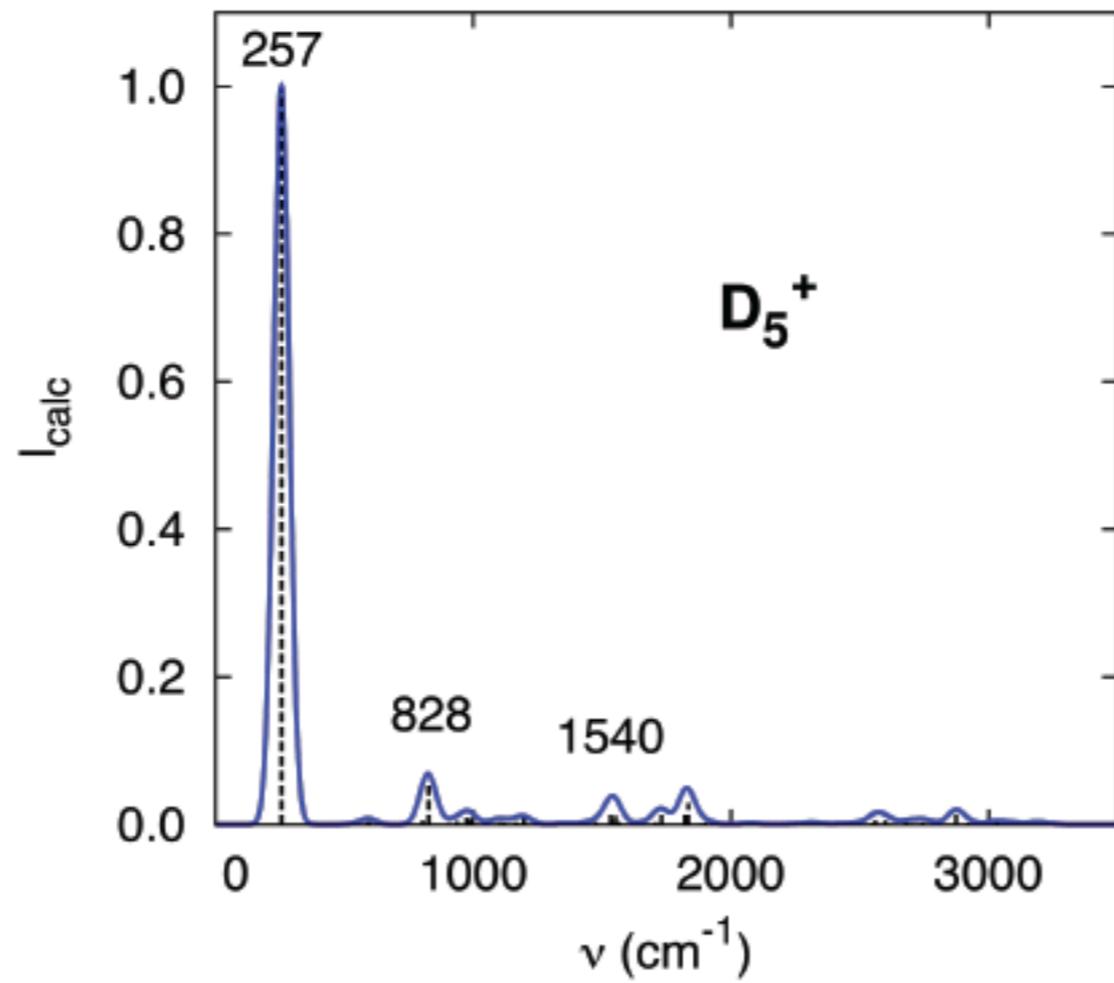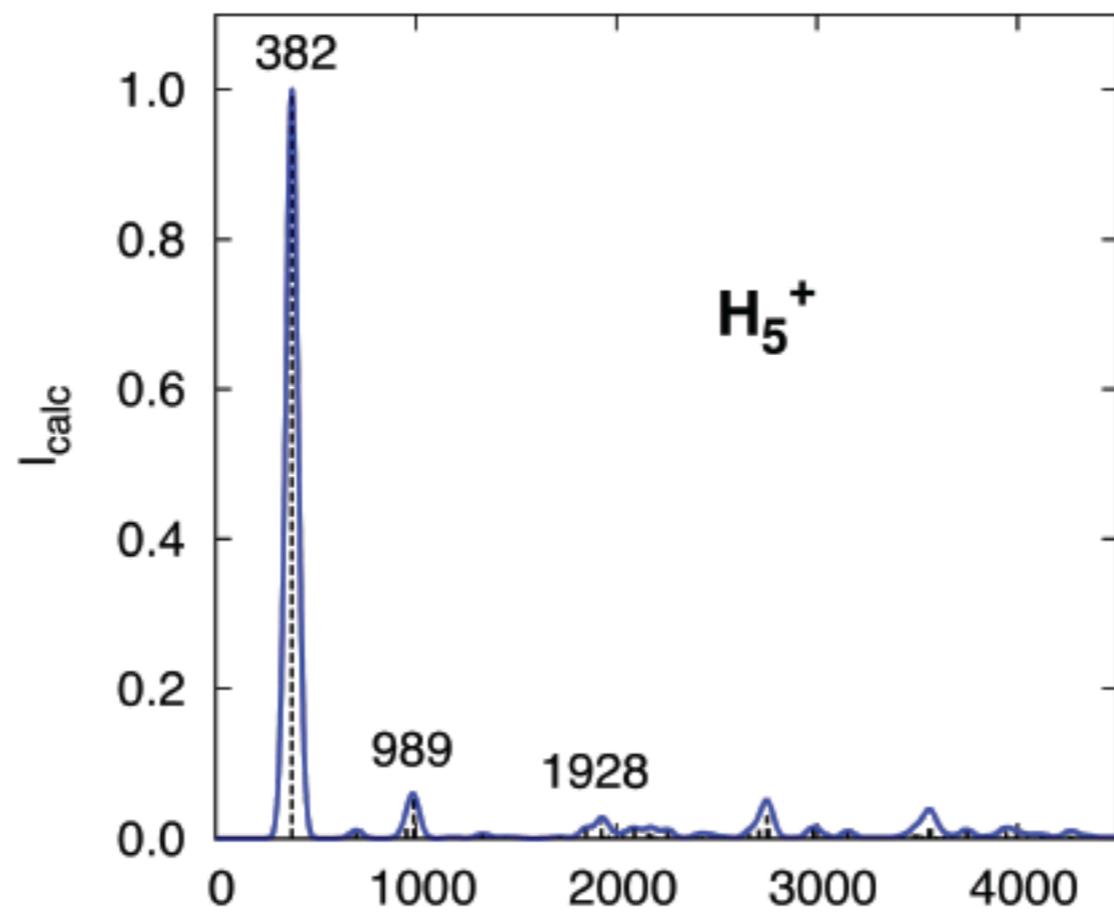
Comparison between Theory and Exp for $\nu > D_o$
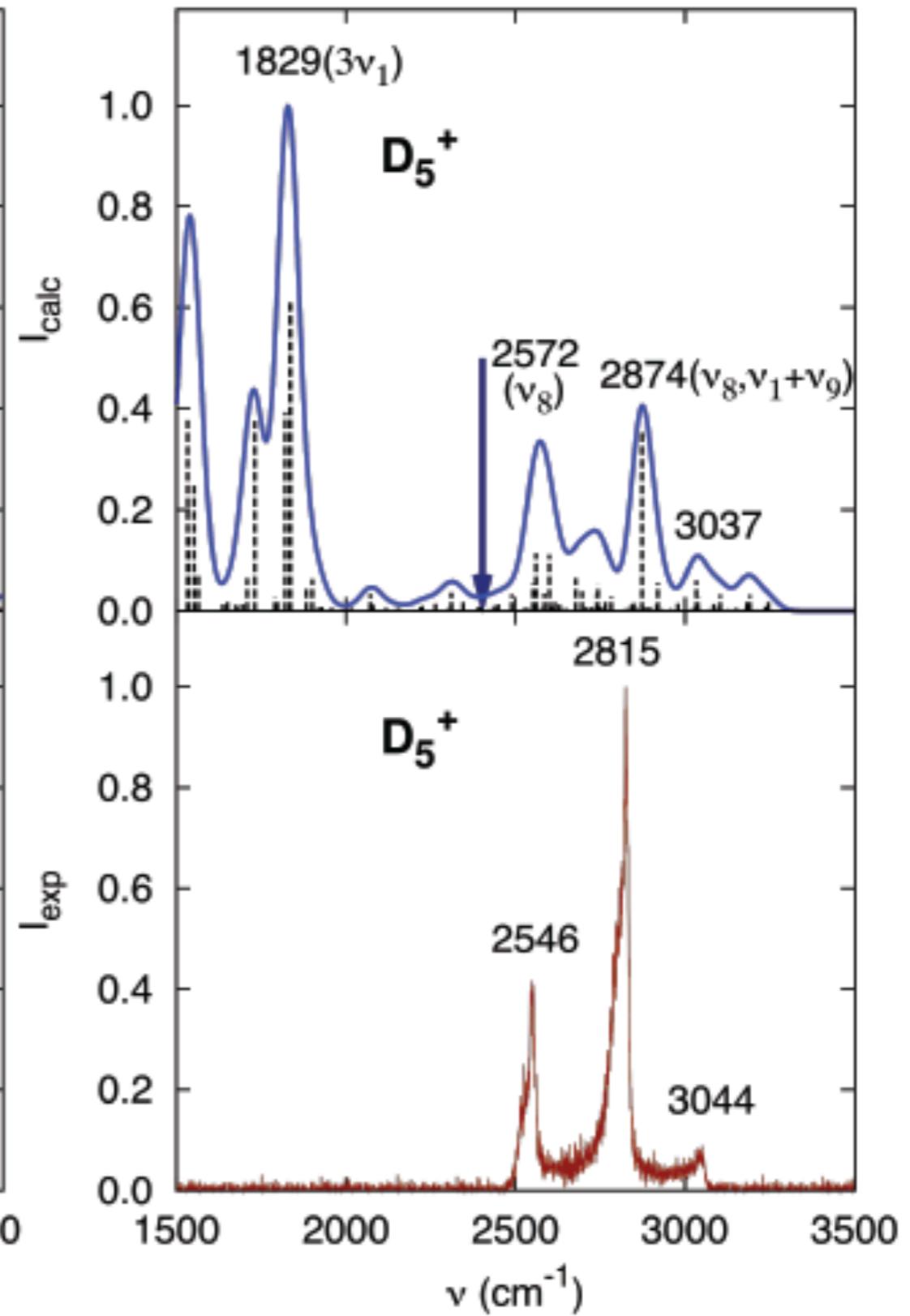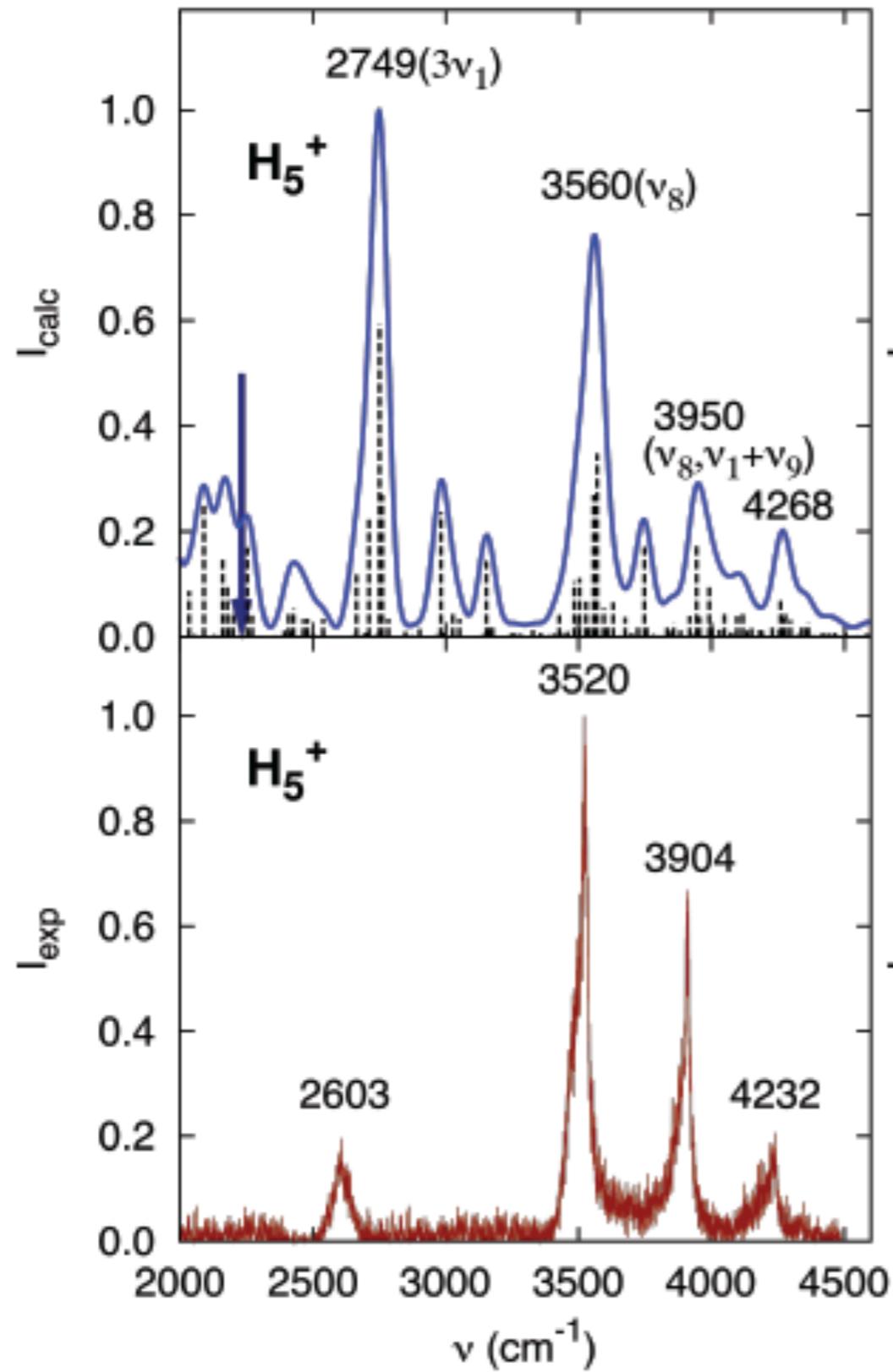
New Experiments at Felix

$H_5^+ \rightarrow H_3^+ + H_2$

Exp: Knut Asmis, Torsten Wende, Allen Ricks, Mike Duncan

Nov. 3, 2010
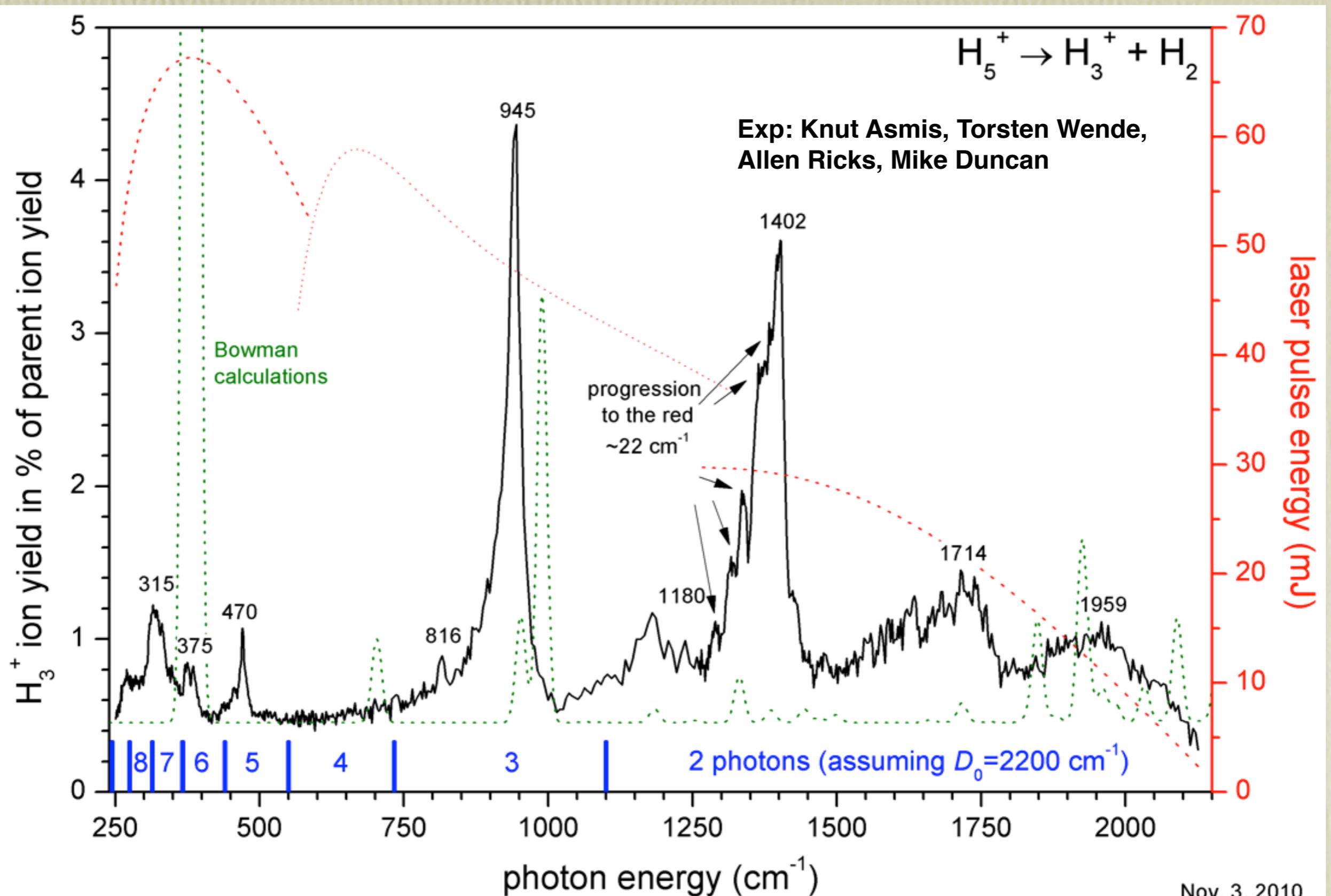
Approximate Quantum Models for Intramolecular Vibrations (Yimin Wang)

I. Local mode approximation
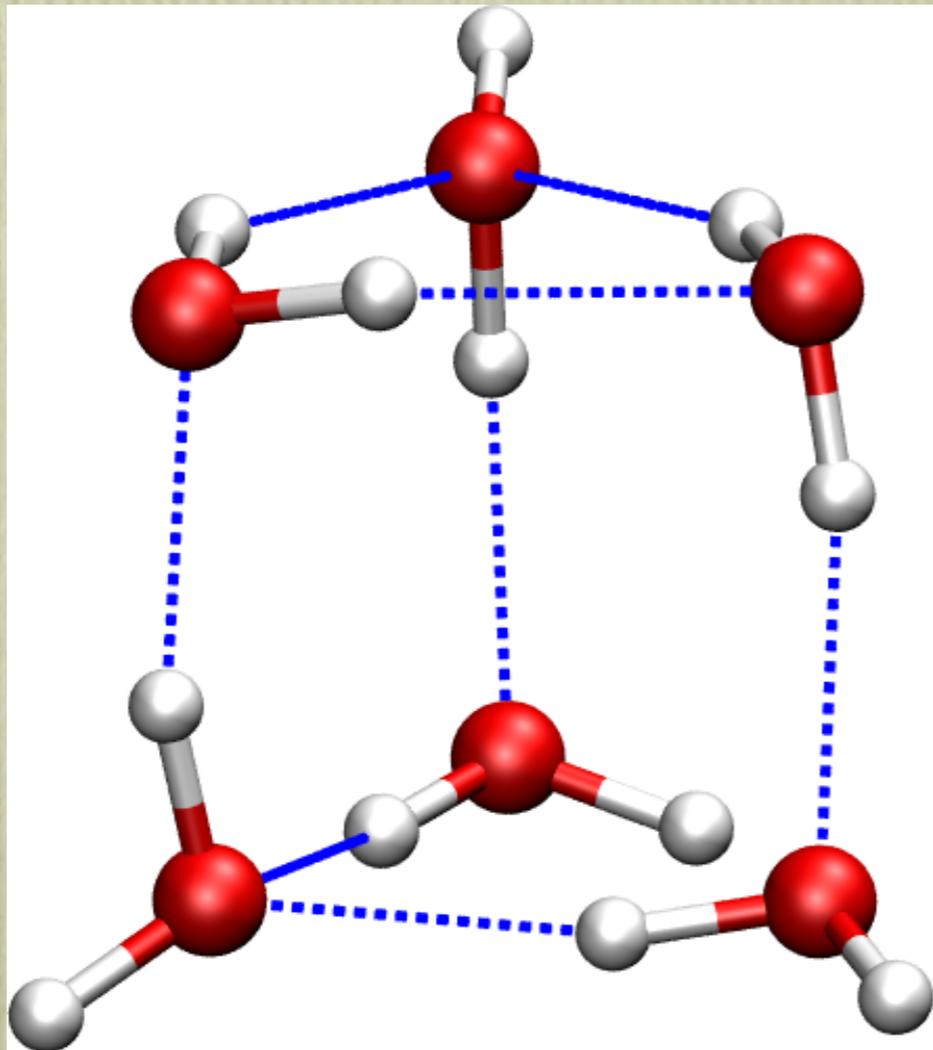
$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr_i^2} + V_i(r_i) - E_{n_i}]\phi_{n_i}(r_i) = 0$$

Twelve local modes - sample all minima in principle, maybe with MD, RPMD, CMD, IVR.

Local Monomer Model (similar to Halonen and Kjaergaard)
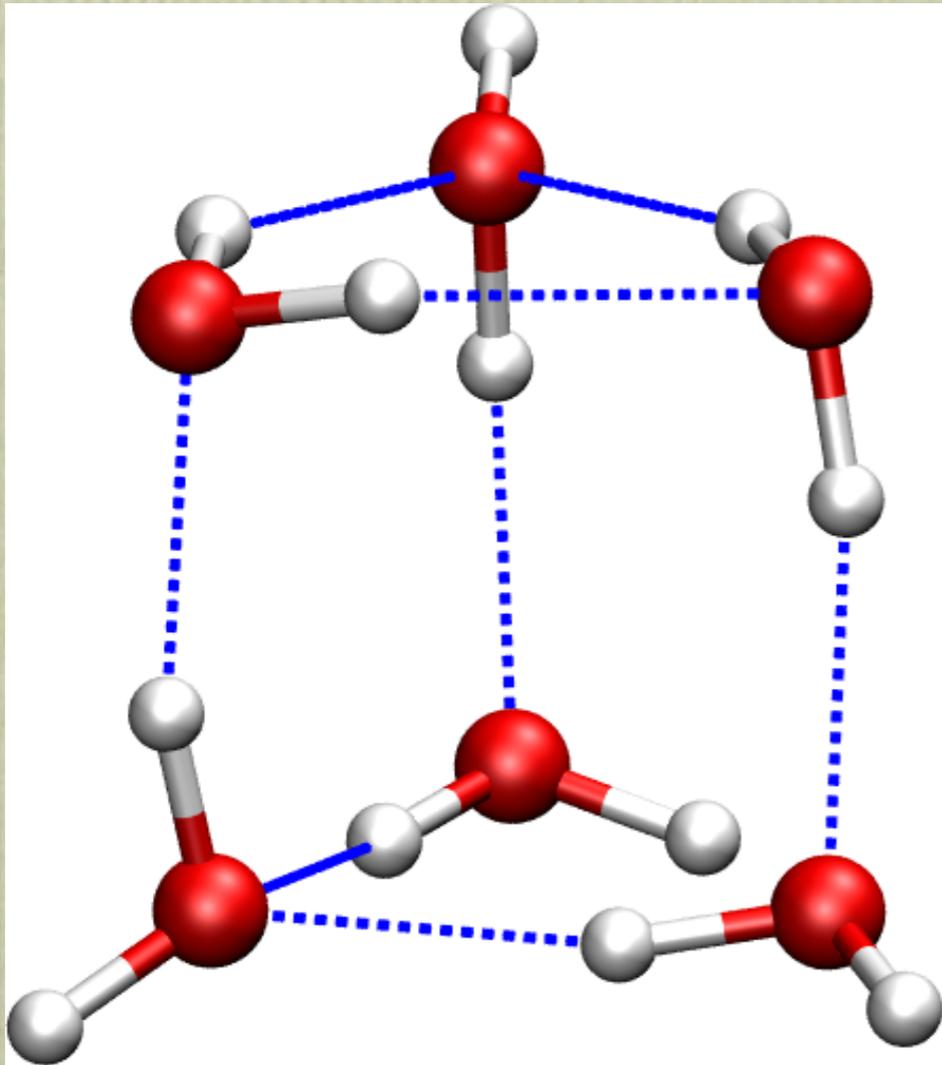
Six perturbed monomers. Do standard normal mode analysis for each. Separate the 9-modes into 6 hindered trans and rotation and 3 intramolecular modes.

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

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

Obviously more accurate than local-mode for stretches, also get bending modes.

Tests for the Water Trimer
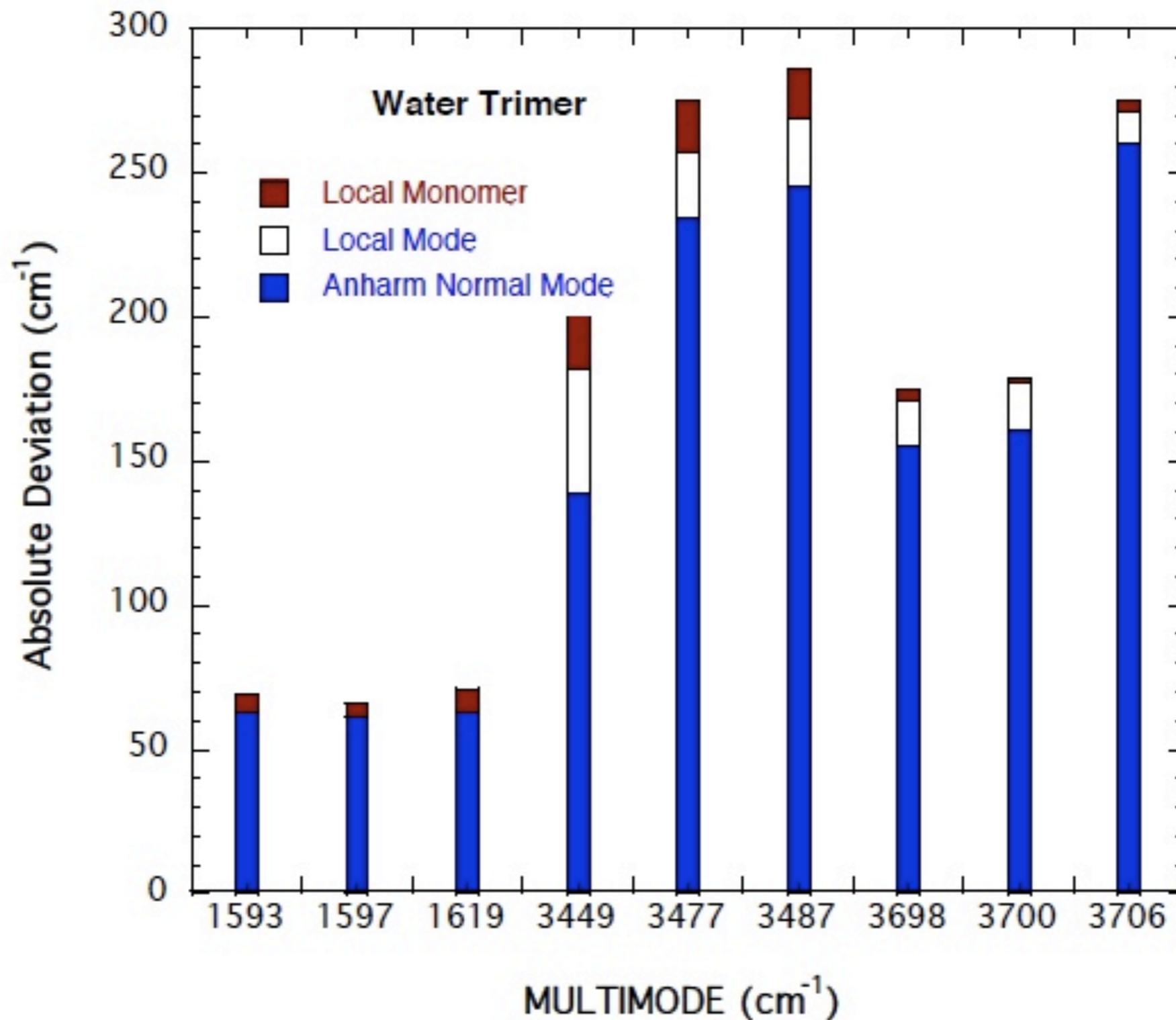
First Test: The Dimer Energies (cm^{-1}) and Intensities

MM-4MR	LMon	MM-Int	LMon-Int
1589.62	1594.53	5.49	4.64
1604.43	1602.50	2.00	2.81
3144.32	*3152.80*	*0.07*	*0.06*
3167.12	*3168.41*	*0.42*	*0.44*
3549.07	3550.07	20.05	18.87
3637.31	3637.29	0.59	0.84
3701.07	3700.52	6.03	6.07
3723.45	3724.35	5.83	5.66

Hydration of Ions (Eugene Kamarchik)
Using a new water potential (Yimin Wang)

$$V(0_{Cl}, 1_{H_2O}, 2_{H_2O}, \ldots, N_{H_2O}) = V(0_{Cl}) + \sum_{i=1}^{N} V_{1-body}(i_{H_2O})$$

$$+ \sum_{i=1}^{N} V(0_{Cl}, i_{H_2O}) + \sum_{i=1}^{N} \sum_{j>i}^{N} V_{2-body}(i_{H_2O}, j_{H_2O})$$

$$+ \sum_{i=1}^{N} \sum_{j>i}^{N} \sum_{k>j}^{N} V_{3-body}(i_{H_2O}, j_{H_2O}, k_{H_2O})$$

$$+ \text{ higher order terms.}$$

sodium/water potential

Uses the same *N*-body decomposition as the chloride/water potential.

6th order invariant polynomial fit to 11,649 CCSD(T)/aVTZ points.

points are from 1-, 2-, and 3-dimensional cuts along normal modes + trajectories on a lower order surface

rms of 11.5 cm^{-1}

# Structures and Local Monomer Results

optimized clusters

$(H_2O)_2Cl^-$ $(H_2O)_3Cl^-$ $(H_2O)_4Cl^-$

$(H_2O)_{14}Cl^-$ $(H_2O)_2Na^+$ $(H_2O)_3Na^+$
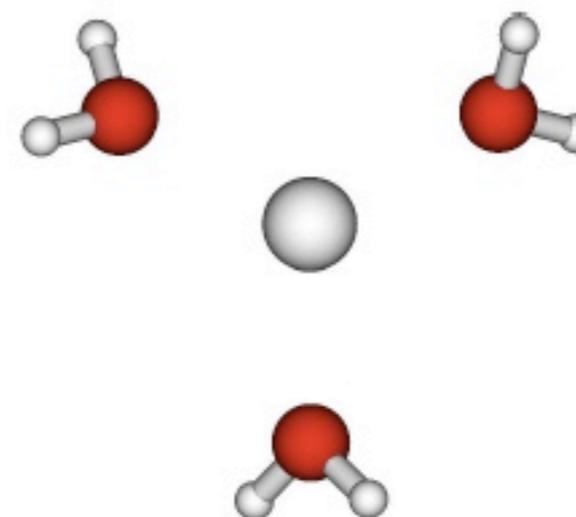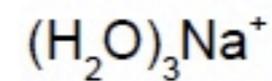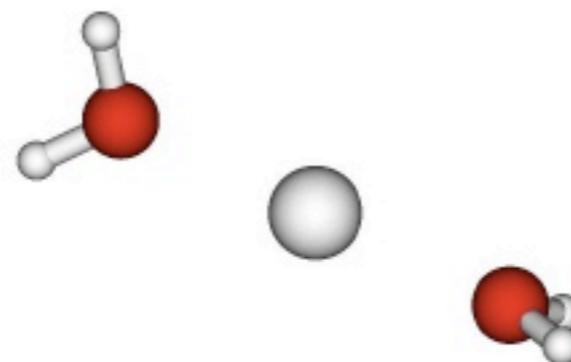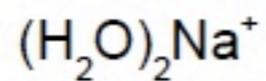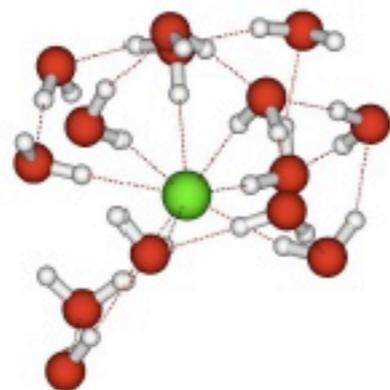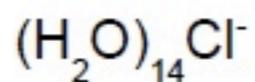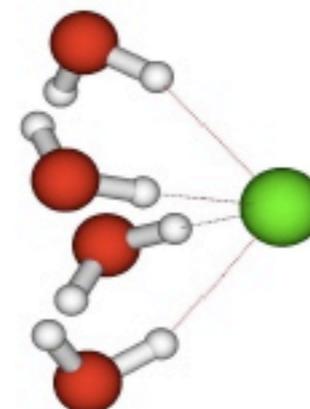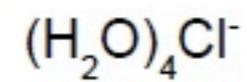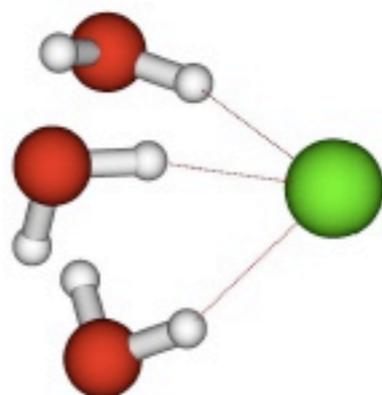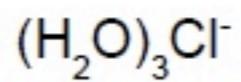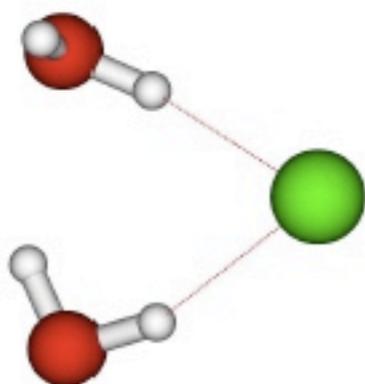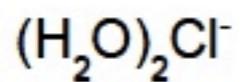
Local Monomer Energies

$(H_2O)_3Cl^-$ local monomer frequencies

TABLE V: Local-monomer model VCI vibrational energies of the water monomers in $(H_2O)_3Cl^-$. All three monomers are equivalent. All frequencies are in cm^{-1}.

Mode	LMM-VCI H_2O (2-body)	LMM-VCI H_2O (2 and 3-body)
ν_{bend}	1663	1664
ν_{sym}	3179	3219
$2\nu_{bend}$	3290	3301
ν_{asym}	3603	3584
$\nu_{bend} + \nu_{sym}$	4786	4832
$3\nu_{bend}$	4884	4913
$\nu_{bend} + \nu_{asym}$	5254	5239
$2\nu_{sym}$	6061	6193
$2\nu_{bend} + \nu_{sym}$	6346	6408
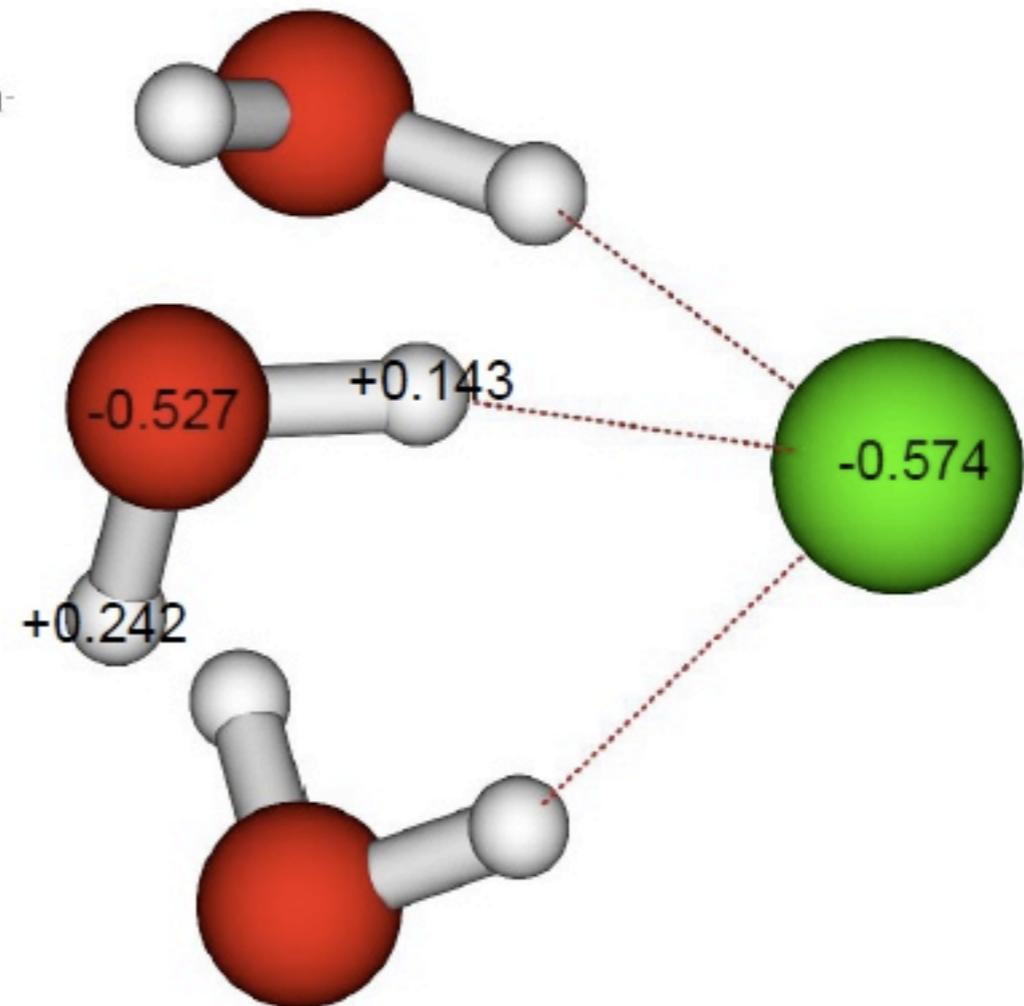
$(H_2O)_3Na^+$ local monomer frequencies

BLE V: Local-monomer model VCI vibrational energies of the water monomers in $(H_2O)_3Na^+$.

three monomers are equivalent. All frequencies are in cm^{-1}.

| Mode	LMM-VCI H_2O (2-body)	LMM-VCI H_2O (2 and 3-body)
ν_{bend}	-	1650
$2\nu_{bend}$	-	3263
ν_{sym}	-	3629
ν_{asym}	-	3706
$3\nu_{bend}$	-	4842
$\nu_{bend} + \nu_{sym}$	-	5251
$\nu_{bend} + \nu_{asym}$	-	5322
$4\nu_{bend}$	-	6387
$2\nu_{bend} + \nu_{sym}$	-	6836
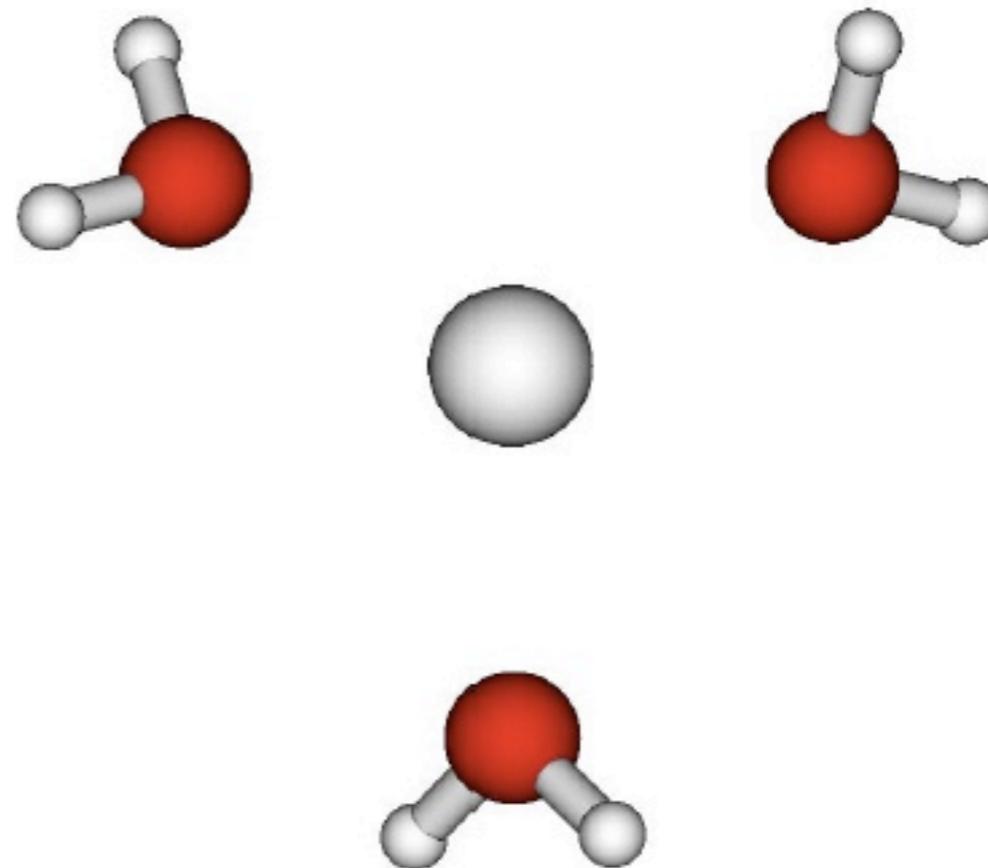
Challenges for the future

"High Res" *ab initio* spectroscopy for floppy molecules

- Floppy means large amplitude motion
  Could also mean isomerization

- This requires extensive PES coverage
  Extensive PES coverage is beyond the quartic force field

- Vibrational approach becomes far more difficult as wavefunctions extend well beyond the global minimum.

- Spectroscopy means J > 0 so need ro-vibrational wavefunctions.

Acknowledgments

Financial support from NSF, DOE, and ONR