

Electronic Supplementary Information

Theoretical Study on the Difference of OH Vibrational Spectra between $\text{OH}^-(\text{H}_2\text{O})_3$ and $\text{OH}^-(\text{H}_2\text{O})_4$

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Within the truncated functional space defined in the text, concrete expression of the 0-th order Hamiltonian H_0 in text eq.(2) is given as follows;

$$\begin{aligned}
 H_0 &= \sum_I^{N_{\text{unit}}} H_0^I \\
 &\approx \sum_I^{N_{\text{unit}}} |0\rangle \langle 0| + \sum_I^{N_{\text{unit}}} \sum_k^{I_{\text{state}}} \hat{T}_k^I |0\rangle \langle 0| (\hat{T}_k^I)^t \\
 &\quad + \sum_I^{N_{\text{unit}}} \sum_{J>I}^{N_{\text{unit}}} \sum_k^{I_{\text{state}}} \sum_l^{J_{\text{state}}} \hat{T}_k^I \hat{T}_l^J |0\rangle \langle 0| (\hat{T}_k^I)^t (\hat{T}_l^J)^t,
 \end{aligned}
 \tag{A-1}$$

where E_k^I is the energy of k -th vibrational state of unit I . Here the following orthogonal conditions are assumed as,

$$\langle \Phi_k^I | H_0 | \Phi_l^J \rangle = \delta_{I,J} \delta_{k,l} E_k^I, \quad \langle \Phi_k^I | \Phi_l^J \rangle = \delta_{I,J} \delta_{k,l}. \tag{A-2}$$

These conditions are valid for our calculations because we are considering the fundamental OH stretching energy region and the proton transfer effects are negligible in $\text{OH}^-(\text{H}_2\text{O})_3$ and $\text{OH}^-(\text{H}_2\text{O})_4$. As a result, H_0 contributes only to the diagonal part of the total Hamiltonian matrix.

On the other hand, the interaction part V_{LLC} , contributes both to the diagonal and the off-diagonal parts. In particular, for diagonal part, all coupling terms included in V_{LLC} give finite values, which result in the diagonal corrections for eigenvalues of H_0 . For the off-diagonal parts, there exist the selection rules, which depend on the combination of the unit and state numbers of the excitation operators for bra and ket, and the unit number of the coupling terms. Here it is enough to consider the upper triangle elements of the Hamiltonian matrix because the matrix is real symmetric.

In the following, we summarize the selection rule for the coupling terms in V_{LLC} in making the off-diagonal part of the Hamiltonian. For simplicity, we describe the direct product basis functions defined in text eq. (5) as;

$$\hat{T}_m^M |0\rangle \equiv |\hat{T}_m^M\rangle, \quad \langle 0 | (\hat{T}_m^M)^t \equiv \langle \hat{T}_m^M |, \quad T_m^M T_n^N |0\rangle \equiv |T_m^M T_n^N\rangle, \quad \text{and} \quad \langle 0 | (\hat{T}_m^M)^t (\hat{T}_n^N)^t \equiv \langle \hat{T}_m^M \hat{T}_n^N | \quad (M < N).
 \tag{A-3}$$

1). Bra is the ground state basis and ket is a single unit excited basis:

$$\langle 0 | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I) (q_j^J - q_{j,eq}^J) | T_m^M \rangle = 0, \quad \text{if } (I \neq M \text{ and } J \neq M)$$

2). Bra is a single unit excited state basis and ket is a single unit excited basis:

$$\langle T_k^K | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I) (q_j^J - q_{j,eq}^J) | T_m^M \rangle = 0,$$

$$\text{2-1) if } \{K = M \text{ and } (K \neq I \text{ and } K \neq J)\}$$

Note that when $K=M$, only $k \neq m$ are off-diagonal elements.

2-2)

$$\text{if } [K \neq M \text{ and } \{(K \neq I \text{ and } K \neq J) \text{ or } (M \neq I \text{ and } M \neq J)\}]$$

3). Bra is the ground state basis and ket is a double units excited basis:

$$\langle 0 | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I) (q_j^J - q_{j,eq}^J) | T_m^M T_n^N \rangle = 0,$$

$$\text{if } \{(M \neq I \text{ and } M \neq J) \text{ or } (N \neq I \text{ and } N \neq J)\}$$

4). Bra is a single unit excited basis and ket is a double units excited basis:

$$\langle T_k^K | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I)(q_j^J - q_{j,eq}^J) | T_m^M T_n^N \rangle = 0,$$

$$4-1) \text{ if } (K \neq M \text{ and } K \neq N)$$

$$4-2) \text{ if } \{K = M \text{ and } (N \neq I \text{ and } N \neq J)\}$$

$$4-3) \text{ if } \{K = N \text{ and } (M \neq I \text{ and } M \neq J)\}$$

$$4-4) \text{ if } [K = M \text{ and } \{(K \neq I \text{ and } K \neq J) \text{ and } (k \neq m)]$$

$$4-5) \text{ if } [K = N \text{ and } \{(K \neq I \text{ and } K \neq J) \text{ and } (k \neq n)]$$

5). Bra is a double units excited basis and ket is a double units excited basis:

$$\langle T_k^K T_l^L | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I)(q_j^J - q_{j,eq}^J) | T_m^M T_n^N \rangle = 0,$$

$$5-1)$$

$$\text{if } \{(K \neq M \text{ and } K \neq N) \text{ and } (L \neq M \text{ and } L \neq N)\}$$

$$5-2)$$

$$\text{if } \{(K = M \text{ and } L = N) \text{ and } (K \neq I \text{ and } K \neq J) \text{ and } (L \neq I \text{ and } L \neq J)\}$$

$$5-3)$$

$$\text{if } \{(K = M \text{ and } L = N) \text{ and } (K = I \text{ or } K = J) \text{ and } (L \neq I \text{ and } L \neq J) \text{ and } (l \neq n)\}$$

$$5-4)$$

$$\text{if } \{(K = M \text{ and } L = N) \text{ and } (K \neq I \text{ and } K \neq J) \text{ and } (L = I \text{ or } L = J) \text{ and } (k \neq m)\}$$

$$5-5)$$

$$\text{if } [(K = M \text{ and } L \neq N) \text{ and } \{(L = I \text{ and } N = J) \text{ or } (L = J \text{ and } N = I)\} \text{ and } (k \neq m)]$$

$$5-6)$$

$$\text{if } \{K = N \text{ and } (L = J \text{ and } M = I) \text{ and } (k \neq n)\}$$

In all other cases, the contributions of the V_{LLC} to the total Hamiltonian matrix elements are calculated by utilizing the DIPJ0DVR program (J. R. Henderson, C. R. Le Sueur and J. Tennyson, *Comput. Phys. Commun.*, 1993, **75**, 379) with the local water wavefunctions and by the finite difference method with the local OH⁻ 1-dimensional wavefunction. For example, the expectation value of

$$\langle 0 | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I)(q_j^J - q_{j,eq}^J) | 0 \rangle$$

is obtained from the product of the expectation values of the local unit wavefunctions as follow;

$$\langle 0 | C_{ij}^{IJ} (q_i^I - q_{i,eq}^I)(q_j^J - q_{j,eq}^J) | 0 \rangle = C_{ij}^{IJ} \langle \Phi_0^I | (q_i^I - q_{i,eq}^I) | \Phi_0^I \rangle \cdot \langle \Phi_0^J | (q_j^J - q_{j,eq}^J) | \Phi_0^J \rangle.$$

Transition moments

By solving the eigenvalue problem of the total Hamiltonian matrix, energies of vibrational states and corresponding wavefunctions are obtained. For the calculation of the intensity given in the text eq. (7), both the excitation energy and transition moment vector are needed. The transition moment vector between initial ground state Ψ_0 and the final excited state Ψ_f is written as follows;

$$\langle \Psi_0 | \hat{\boldsymbol{\mu}} | \Psi_f \rangle = \langle \Psi_0 | \sum_I^{N_{unit}} \hat{\boldsymbol{\mu}}^I(q_1^I, q_2^I, q_3^I) | \Psi_f \rangle, \quad (\text{A-4})$$

where the dipole moment function (DMF), $\hat{\boldsymbol{\mu}}$, is assumed as the sum of DMFs of the all monomer units, and the wavefunctions are given by the liner combination of the direct product basis functions as,

$$\Psi = c_0 | 0 \rangle + \sum_I^{N_{unit}} \sum_k^{Istate} c_k^I | \hat{T}_k^I \rangle + \sum_I^{N_{unit}} \sum_{J>I}^{N_{unit}} \sum_k^{Istate} \sum_l^{Jstate} c_{k,l}^{I,J} | \hat{T}_k^I \hat{T}_l^J \rangle. \quad (\text{A-5})$$

Note that the above $\{c\}$ are the expansion coefficients and different from the expansion coefficients $\{C\}$ of coupling terms.

In the evaluation of (A-5), depending on the combination of the unit and state numbers of the excitation operators for bra and ket, and the unit number of the DMF, some types of segment becomes zero due to the above definition of $\hat{\boldsymbol{\mu}}$ and the orthogonal relation in (A-3).

1). Bra is the ground state basis:

$$\langle 0 | \hat{\boldsymbol{\mu}}^I | \hat{T}_m^M \rangle = 0 \quad \text{if } (I \neq M), \quad \langle 0 | \hat{\boldsymbol{\mu}}^I | \hat{T}_m^M \hat{T}_n^N \rangle = 0 \quad (\forall M, N)$$

2). Bra is a single unit excited basis:

$$\langle \hat{T}_m^M | \boldsymbol{\mu}^I | 0 \rangle = 0 \quad \text{if } (I \neq M), \quad \langle \hat{T}_k^K | \boldsymbol{\mu}^I | \hat{T}_m^M \rangle = 0 \quad \text{if } (K \neq M \text{ or } K = M \neq I)$$

$$\langle \hat{T}_k^K | \boldsymbol{\mu}^I | \hat{T}_m^M \hat{T}_n^N \rangle = 0$$

- 1) if $(K \neq M \text{ and } K \neq N)$
- 2) if $(K = M \text{ and } I \neq N)$
- 3) if $(K = N \text{ and } I \neq M)$
- 4) if $(K = M \text{ and } I = N \text{ and } k \neq m)$
- 5) if $(K = N \text{ and } I = M \text{ and } k \neq n)$

3). Bra is a double unit excited basis:

$$\langle \hat{T}_k^K \hat{T}_l^L | \boldsymbol{\mu}^I | 0 \rangle = 0 \quad (\forall K, L)$$

$$\langle \hat{T}_k^K \hat{T}_l^L | \boldsymbol{\mu}^I | \hat{T}_m^M \rangle = 0$$

- 1) if $(K \neq M \text{ and } L \neq M)$

- 2) $if(K = M \text{ and } I \neq L)$
- 3) $if(L = M \text{ and } I \neq K)$
- 4) $if(K = M \text{ and } I = L \text{ and } k \neq m)$
- 5) $if(L = M \text{ and } I = K \text{ and } l \neq m)$

$$\langle \hat{T}_k^K \hat{T}_l^L | \boldsymbol{\mu}^I | \hat{T}_m^M \hat{T}_n^N \rangle = 0$$

- 1) $if(K \neq M)$
- 2) $if(K = M \text{ and } L \neq N)$
- 3) $if\{K = M \text{ and } L = N \text{ and } (k \neq m \text{ and } l \neq n)\}$
- 4) $if(K = M \text{ and } L = N \text{ and } k \neq m \text{ and } l = n \text{ and } I \neq K)$
- 5) $if(K = M \text{ and } L = N \text{ and } k = m \text{ and } l \neq n \text{ and } I \neq L)$.

All the transition moment values are obtained by using DIPJ0DVR program (J. R. Henderson, C. R. Le Sueur and J. Tennyson, *Comput. Phys. Commun.*, 1993, **75**, 379) and the finite difference method, with local unit wavefunctions and dipole moment functions.

Vibrational spectra

We will use the notation dwat4 for the deprotonated 4 waters cluster, namely OH(H₂O)₃, and dwat5 for OH⁻(H₂O)₄ as used in the text.

Lists of the excitation energies (cm⁻¹) and intensities (km/mol) of vibrational spectra calculated with local monomer unit model (LU) and LU plus inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC). The potential energy surface (PES) and dipole moment function (DMF) for each monomer unit were calculated by B3LYP/6-31+G(d,p). Figures of corresponding stick spectra were also shown.

As described in the text eq. (6), the wavefunctions with LU+LLC are written by the linear expansion of the direct product basis functions as follows,

$$\Psi = c_0 |0\rangle + \sum_I \sum_k^{N_{\text{unit}} \text{ Istate}} c_k^I \hat{T}_k^I |0\rangle + \sum_I \sum_{J>I}^{N_{\text{unit}} \text{ Nunit}} \sum_k \sum_l^{I\text{state} \text{ Jstate}} c_{k,l}^{I,J} \hat{T}_k^I \hat{T}_l^J |0\rangle,$$

Assignment of the spectra was performed by using the absolute values of the expansion coefficients {c} in each excited state Ψ . If the absolute value of the expansion coefficient of the direct product basis function $\hat{T}_m^M |0\rangle$ is largest within a certain excited state Ψ , we assigned by using the LU result of the m -th state in the M -th unit. In some cases, Ψ includes various comparable contributions from various direct product basis functions. For the fundamental transitions, we just mention the mode. For the $\Delta v=2$ overtone transitions, we write “over”, and for

combination bands we write two vibrational modes with a hyphen. For double unit excited modes, we write vibrational modes of two units in parentheses as “2units(mode,mode)”. In many cases intensities to double units excited modes are small. But these modes have the possibility to interact with the fundamental OH motions through the inter unit coupling terms. For the clusters having second shell waters as dwat4-2,5-1, 5-3 and 5-4 , some of double units excited states, i.e. one unit is excited to IHB and one of the others is excited to the bending fundamental, emerges near the energy region where the fundamental Free OH and OH⁻ stretching motions are observed. On the other hand, for dwat4-1 and dwat5-2, there does not exist the double-units excited state in such energy range.

Note that LU results in the following tables are not necessarily written by the energy level order.

[dwat4-1]

TableS1: Peak positions and intensities for dwat4-1 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1643	134.6	bend	1642	202.8	bend
1644	134.6	bend	1643	200.9	bend
1644	132.6	bend	1648	9.0	bend
2324	1965.7	IHB OH	2319	2551.1	IHB OH
2324	1979.2	IHB OH	2331	2490.4	IHB OH
2342	1950.9	IHB OH	2412	800.1	IHB OH
3249	0.5	bend over	3249	0.4	bend over
3249	0.5	bend over	3250	0.4	bend over
3251	0.5	bend over	3251	0.4	bend over
			3287	0.1	2units (bend, bend)
			3289	0.2	2units (bend, bend)
			3294	0.1	2units (bend, bend)
3687	2.2	Free OH	3687	2.2	Free OH
3687	2.2	Free OH	3687	3.1	Free OH
3687	2.6	Free OH	3687	2.5	Free OH
3695	0.5	OH-	3695	0.4	OH-
3919	47.3	bend-IHB OH	3929	45.1	bend-IHB OH
3919	47.4	bend-IHB OH	3940	21.9	bend-IHB OH
3941	41.2	bend-IHB OH	3944	25.8	bend-IHB OH
			3970	7.0	2units (bend, IHB OH)
			3983	5.3	2units (bend, IHB OH)
			3993	12.0	2units (bend, IHB OH)

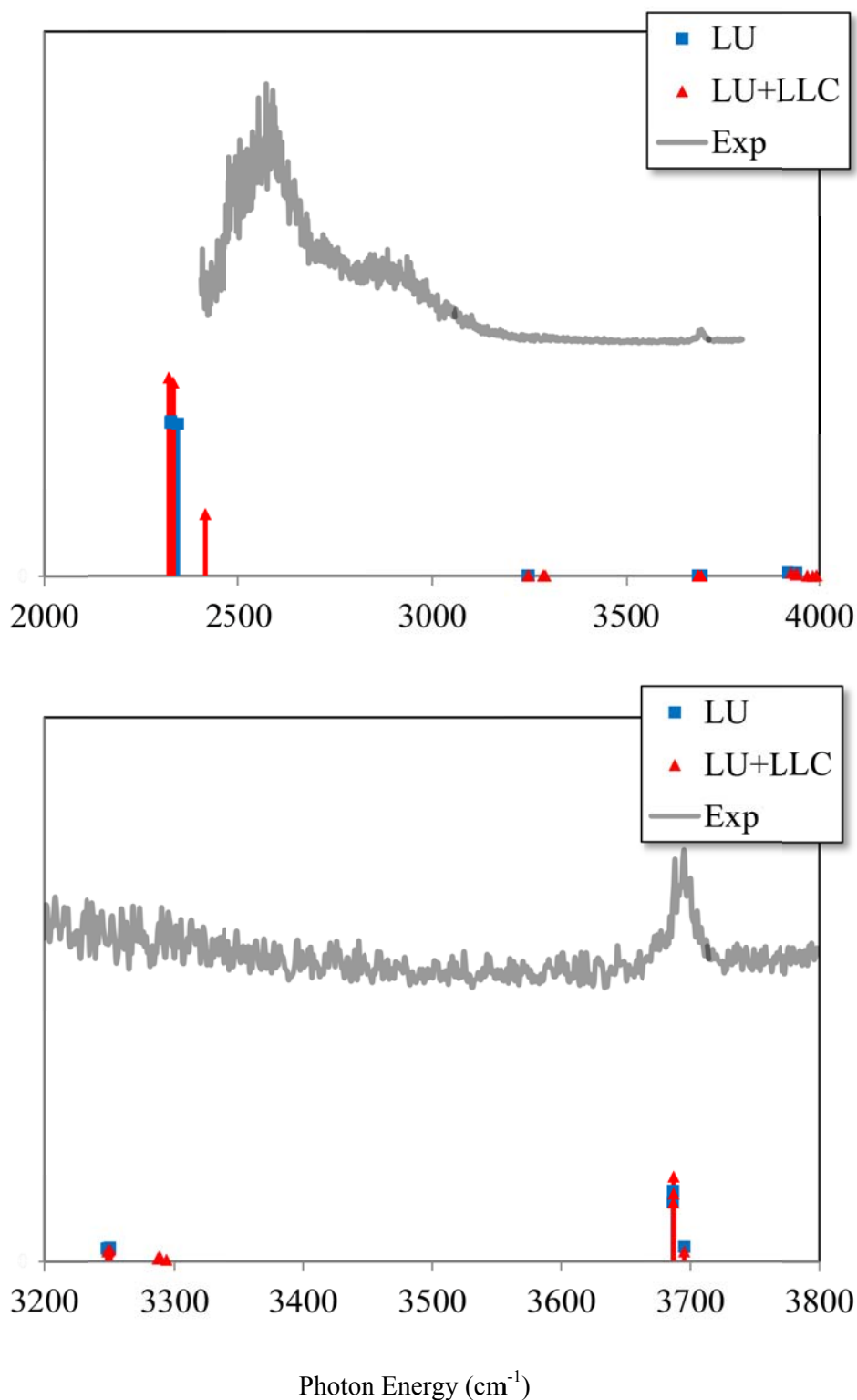


Figure S1. Line spectrum for dwat4-1 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

[dwat4-2]

TableS2: Peak positions and intensities for dwat4-2 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1502	2581.6	IHB OH	1427	1894.3	IHB OH
1503	2581.2	IHB OH	1479	2528.2	IHB OH
1626	28.1	bend	1635	44.6	bend
1626	28.1	bend	1649	64.9	bend
1689	155.4	bend(DD water)	1812	357.0	bend(DD water)
2929	254.3	IHB OH over	2813	293.2	IHB OH over
			2933	2.5	2units (IHB OH, bend)
2929	254.4	IHB OH over	2962	203.1	IHB OH over
3064	4.5	IHB OH - bend	3036	5.3	IHB OH - bend
3065	4.5	IHB OH - bend	3101	14.6	IHB OH - bend
			3121	7.0	2units (IHB OH, bend)
			3141	4.7	2units (IHB OH, bend)
			3199	5.3	2units (IHB OH, bend)
3227	3.0	bend over	3234	3.9	bend over
3227	3.0	bend over	3251	14.0	bend over
3294	230.6	bend over(DD water)	3281	209.7	bend over(DD water)
			3295	39.3	2units (bend, bend)
3366	482.2	DD water OH	3364	642.6	DD water OH
3397	203.4	DD water OH	3375	480.5	DD water OH
			3433	0.4	2units (bend, bend)
			3490	14.6	2units (bend, bend)
			3597	10.4	2units (IHB OH, bend)
3692	2.9	Free OH	3702	4.6	Free OH
3692	2.9	Free OH	3713	15.9	Free OH
3694	3.97	OH-	3714	2.8	OH-

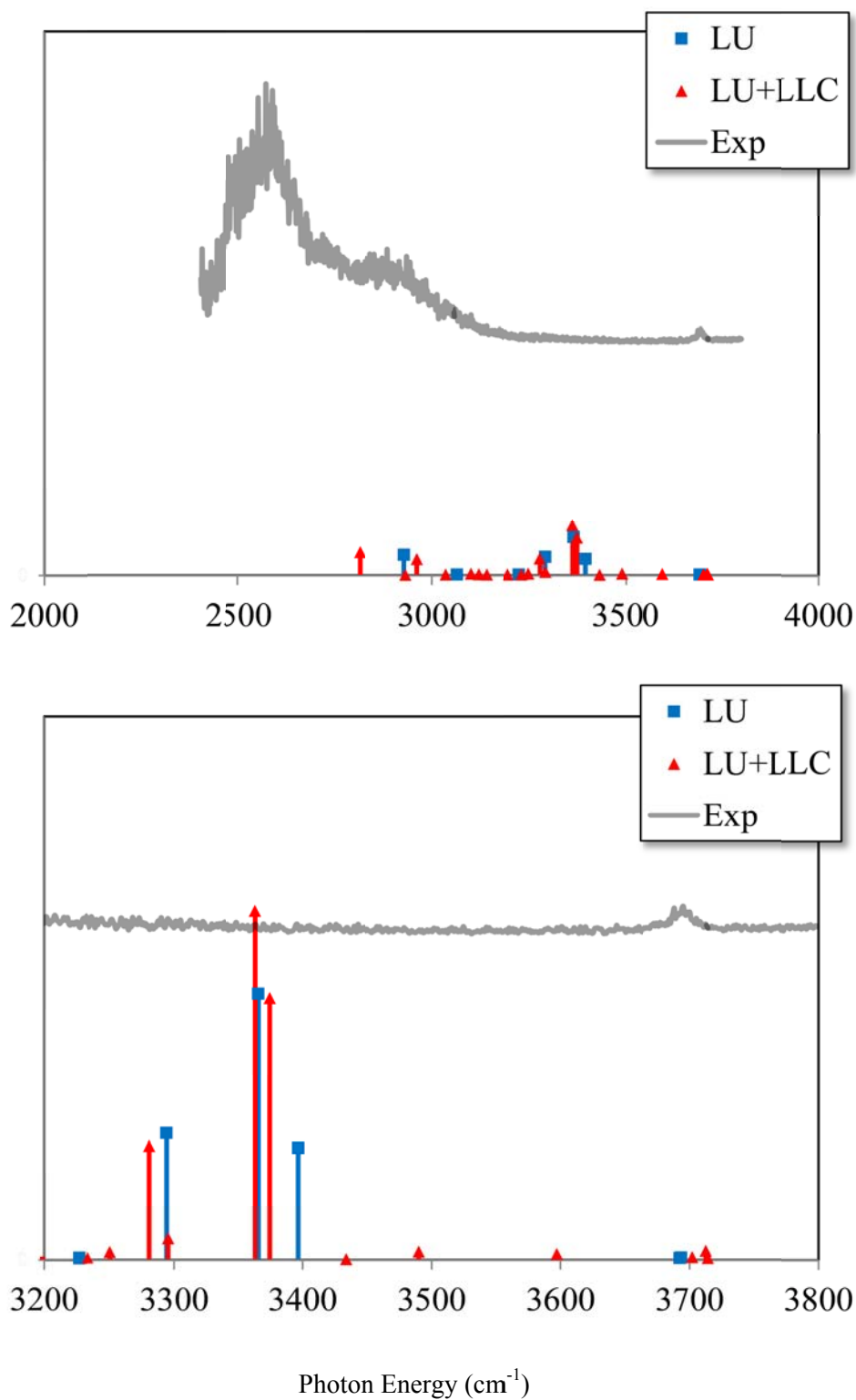


Figure S2. Line spectrum for dwat4-2 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

[dwat5-1]

TableS3: Peak positions and intensities for dwat5-1 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1681	100.3	bend (DDA water)	1565	395.0	bend (DDA water)
1628	144.9	bend	1633	118.3	bend
1628	150.3	bend	1657	183.3	bend
1682	164.2	bend (DD water)	1702	171.0	bend (DD water)
2018	1852.1	IHB OH	2052	1255.0	IHB OH
2019	1850.2	IHB OH	2165	2160.8	IHB OH
3031	788.3	IHB OH (DD water)	3061	482.3	IHB OH (DD water)
3277	187.2	bend over (DDA water)	3084	148.2	bend over (DDA water)
3214	2.0	bend over	3215	4.2	bend over
3228	2.0	bend over	3223	16.4	bend over
			3250	5.9	2units (bend, bend)
			3271	15.2	2units (bend, bend)
			3277	23.0	2units (bend, bend)
3464	144.9	IHB over	3308	5.7	IHB over
			3320	24.8	2units (bend, bend)
			3353	2.6	2units (bend, bend)
			3365	27.0	2units (bend, bend)
3363	509.7	DDA water OH	3387	286.5	DDA water OH
3326	11.9	bend over (DD water)	3402	428.5	bend over (DD water)
3384	172.6	DDA water OH	3413	482.4	DDA water OH
3466	144.3	IHB over	3530	160.5	IHB over
		Inter water OH			Inter water OH
3540	133.2	(DD water)	3601	80.4	(DD water)
3618	2.4	IHB OH - bend	3654	0.5	IHB OH - bend
3620	2.6	IHB OH - bend	3687	6.0	IHB OH - bend
3693	11.4	Free OH	3709	12.8	Free OH
3694	11.4	Free OH	3729	2.6	Free OH
3716	2.4	OH-	3741	2.9	OH-
			3763	2.4	2units (bend, IHB OH)
			3796	1.0	2units (bend, IHB OH)
			3824	7.3	2units (bend, IHB OH)
			3833	7.6	2units (bend, IHB OH)
			3863	7.6	2units (bend, IHB OH)
			3919	8.4	2units (bend, IHB OH)

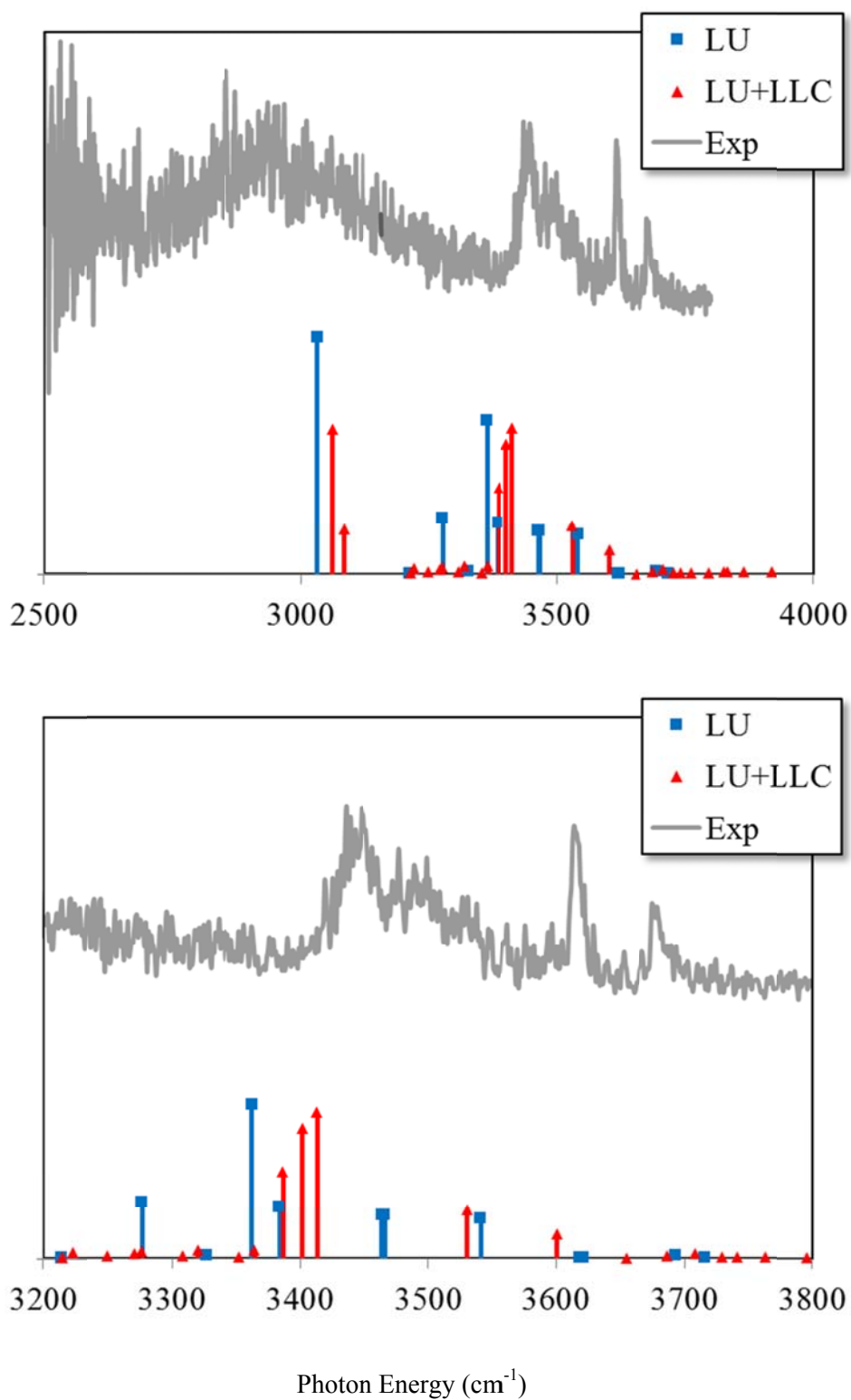


Figure S3. Line spectrum for dwat5-1 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

[dwat5-2]

TableS4: Peak positions and intensities for dwat5-2 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1658	168.2	bend	1654	10.1	bend
1658	168.2	bend	1655	293.9	bend
1658	168.2	bend	1656	305.1	bend
1658	168.2	bend	1667	64.4	bend
2863	1058.3	IHB OH	2855	1543.9	IHB OH
2862	1058.6	IHB OH	2856	1534.8	IHB OH
2863	1058.2	IHB OH	2865	8.4	IHB OH
2862	1058.6	IHB OH	2918	1097.1	IHB OH
3281	3.6	bend over	3279	5.6	bend over
3281	3.6	bend over	3279	4.4	bend over
3281	3.6	bend over	3280	4.2	bend over
3281	3.6	bend over	3281	1.9	bend over
			3309	0.1	2units (bend, bend)
			3311	0.0	2units (bend, bend)
			3316	0.1	2units (bend, bend)
			3317	0.2	2units (bend, bend)
			3318	0.2	2units (bend, bend)
			3331	0.5	2units (bend, bend)
3651	25.0	Free OH	3648	31.4	Free OH
3651	25.0	Free OH	3650	41.9	Free OH
3651	25.0	Free OH	3651	41.2	Free OH
3651	25.0	Free OH	3652	0.4	Free OH
3711	0.3	OH-	3708	1.0	OH-

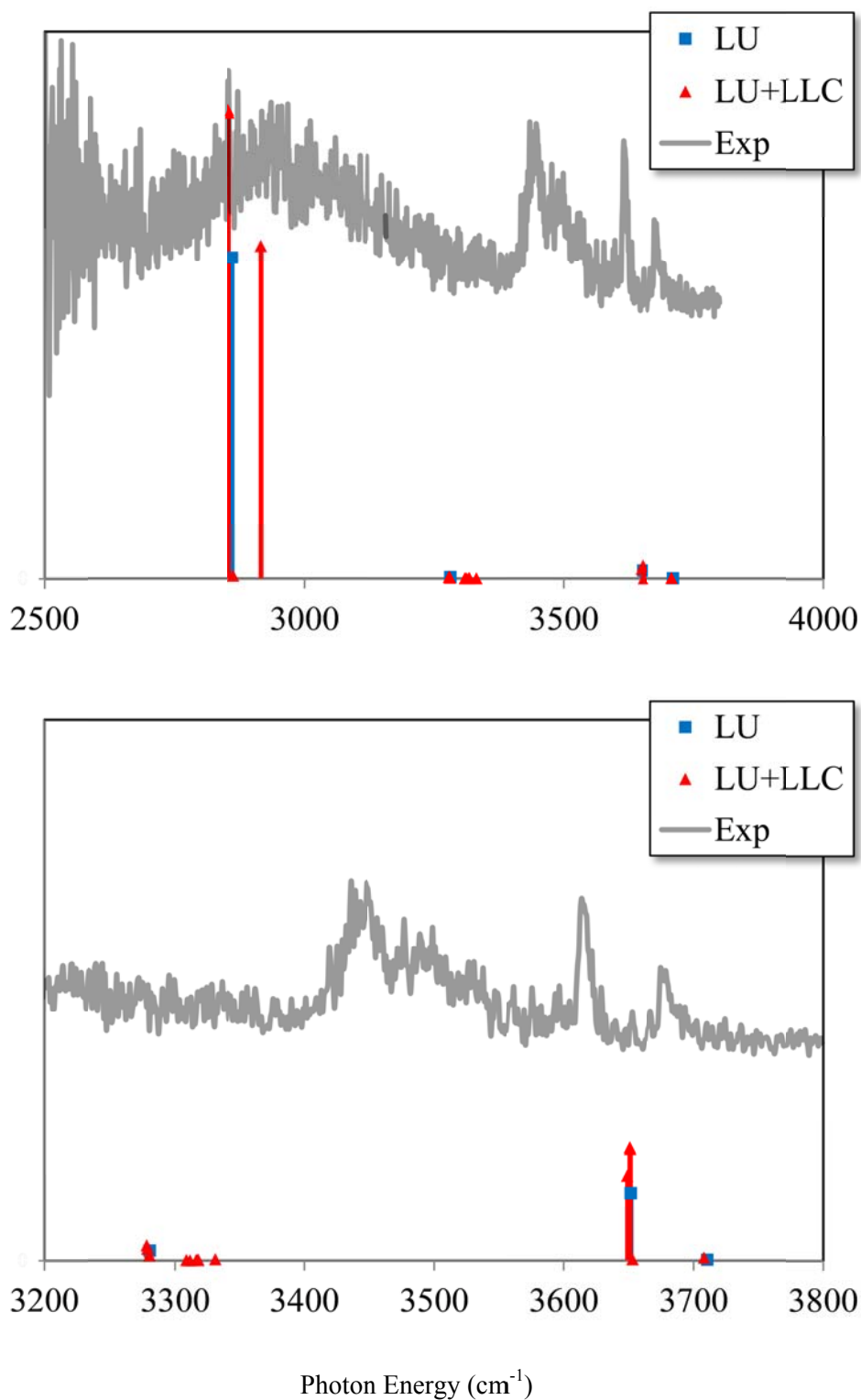


Figure S4. Line spectrum for dwat5-2 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

[dwat5-3]

TableS5: Peak positions and intensities for dwat5-3 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1683	170.6	bend(DD water)	1619	669.8	bend (DD water)
1629	110.8	bend	1643	90.7	bend
1647	71.1	bend	1649	83.2	bend
1650	75.9	bend	1672	55.1	bend
2104	2071.0	IHB OH	2135	1947.5	IHB OH
2163	2093.8	IHB OH	2246	1714.2	IHB OH
2439	1944.7	IHB OH	2485	1651.7	IHB OH
3300	124.2	bend over (DD water)	3164	31.3	bend over (DD water)
3221	1.2	bend over	3234	1.1	bend over
3257	0.6	bend over	3257	0.8	bend over
3263	0.6	bend over	3276	3.6	bend over
			3285	0.3	2units (bend, bend)
			3296	1.5	2units (bend, bend)
			3309	0.1	2units (bend, bend)
			3319	7.4	2units (bend, bend)
			3322	3.7	2units (bend, bend)
			3333	50.3	2units (bend, bend)
3404	378.7	DD water OH	3411	430.5	DD water OH
3418	322.9	DD water OH	3416	507.5	DD water OH
3641	111.5	IHB OH over	3604	182.9	IHB OH over
3768	124.9	IHB OH over	3695	90.1	IHB OH over
3690	2.6	Free OH	3703	19.4	Free OH
3691	4.2	Free OH	3705	4.2	Free OH
3696	0.1	OH-	3709	0.8	OH-
3691	25.4	bend - IHB OH	3723	132.1	bend - IHB OH
3800	0.9	bend - IHB OH	3780	2.8	bend - IHB OH
			3801	5.0	2units (bend, IHB OH)
3751	5.3	Free OH	3817	5.8	Free OH
			3849	2.6	2units (bend, IHB OH)
			3898	3.7	2units (bend, IHB OH)
			3914	1.6	2units (bend, IHB OH)
			3937	4.7	2units (bend, IHB OH)
			3982	15.7	2units (bend, IHB OH)

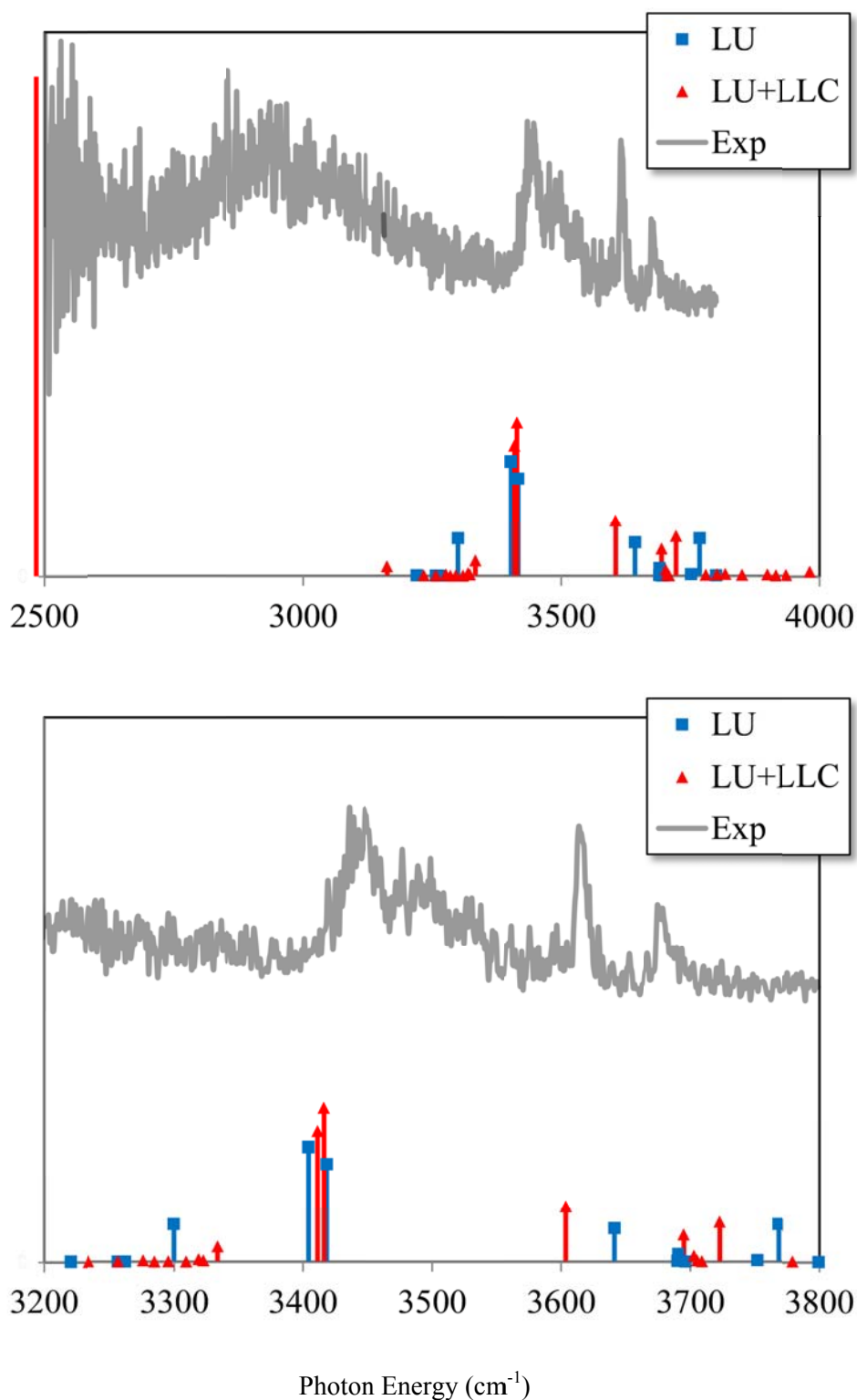


Figure S5. Line spectrum for dwat5-3 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

[dwat5-4]

TableS6: Peak positions and intensities for dwat5-4 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs.

LU			LU+LLC		
Excitation Energy	Intensity	Assignments	Excitation Energy	Intensity	Assignments
cm ⁻¹	km/mol		cm ⁻¹	km/mol	
1686	155.8	bend (DD water)	1632	431.3	bend (DD water)
1635	79.9	bend	1641	74.0	bend
1635	79.9	bend	1660	334.6	bend
1662	110.7	bend	1679	37.9	bend
2111	2054.1	IHB OH	2137	2072.8	IHB OH
2111	2054.0	IHB OH	2250	1388.3	IHB OH
2498	1782.4	IHB OH	2544	1576.5	IHB OH
3303	128.3	bend over(DD water)	3228	42.3	bend over(DD water)
3234	0.6	bend over	3233	0.6	bend over
3234	0.6	bend over	3245	0.8	bend over
			3291	0.6	2units (bend, bend)
			3300	0.7	2units (bend, bend)
3286	1.9	bend over	3302	1.8	bend over
			3312	0.7	2units (bend, bend)
			3313	0.1	2units (bend, bend)
			3319	4.4	2units (bend, bend)
			3338	1.4	2units (bend, bend)
3414	428.5	DD water OH	3430	490.4	DD water OH
3418	260.9	DD water OH	3437	575.7	DD water OH
3657	82.8	IHB OH over	3693	27.8	IHB OH over
3657	82.7	IHB OH over	3702	11.4	IHB OH over
3691	5.0	Free OH	3707	5.8	Free OH
3704	0.0	OH-	3719	0.1	OH-
3693	48.9	bend - IHB OH	3724	44.8	bend - IHB OH
3693	49.1	bend - IHB OH	3751	111.0	bend - IHB OH
3737	6.7	Free OH	3777	35.9	Free OH
3737	6.7	Free OH	3787	30.2	Free OH
			3797	35.2	2units (bend, IHB OH)
			3834	7.1	2units (bend, IHB OH)
			3865	9.0	2units (bend, IHB OH)
			3876	10.1	2units (bend, IHB OH)
			3885	14.5	2units (bend, IHB OH)
			3949	1.4	2units (bend, IHB OH)

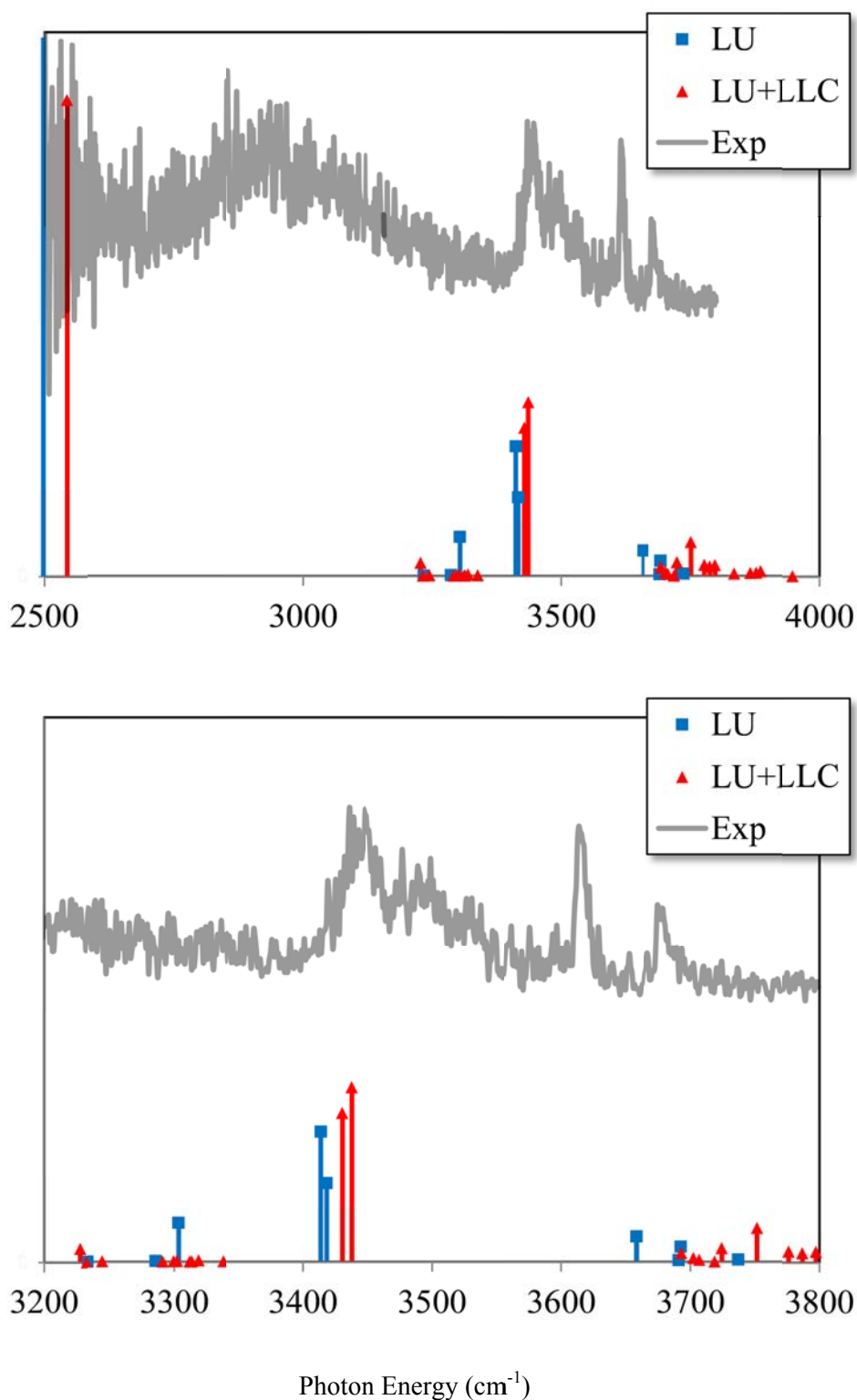


Figure S6. Line spectrum for dwat5-4 with local monomer unit model (LU), and LU including the inter unit coupling by the lowest order linear-linear coupling terms (LU+LLC) using B3LYP/6-31+G(d,p) for PESs and DMFs. Experimental spectrum is from the *Science*, 2003, **299**, 1367 by Robertson *et al.*

Optimized Geometry

B3LYP/6-31+G(d,p)

[dwat4-1]

O	0.530529	2.095628	1.028272
O	1.936973	-1.268376	-1.136469
O	-2.216966	-0.671602	-0.464436
O	0.042157	0.540975	-1.026698
H	0.300980	1.531844	0.210845
H	1.363144	1.712563	1.328329
H	1.239415	-0.525528	-1.116142
H	1.409590	-2.063922	-0.998630
H	-1.344826	-0.223408	-0.740024
H	-2.417580	-0.251754	0.380324
H	-0.017874	1.042324	-1.849143

[dwat4-2]

O	0.942858	2.024750	0.879957
O	2.057071	-1.092947	-1.177622
O	0.096194	0.489190	-0.944230
O	3.392750	0.459170	0.886443
H	0.568458	1.432149	0.093428
H	0.401367	1.785225	1.640838
H	1.235596	-0.434481	-1.138489
H	1.724140	-1.916005	-0.801778
H	-0.133682	0.946717	-1.761944
H	3.085621	-0.130513	0.166823
H	2.648968	1.091010	0.972959

[dwat5-1]

O	2.019635	0.109131	-0.826800
O	-2.021731	0.108080	-0.822845
O	0.003395	-0.544670	2.049977
O	-0.000639	1.941966	0.152978
O	-0.000484	-1.447376	-0.540210
H	1.251164	-0.576503	-0.801170
H	2.511782	-0.069936	-0.016146
H	-1.252901	-0.577299	-0.798440
H	-2.513060	-0.071617	-0.011842
H	0.002080	-1.052332	1.197811
H	0.002225	0.376605	1.739053
H	-0.769365	1.483076	-0.245814
H	0.767346	1.483587	-0.247812
H	-0.000684	-2.332629	-0.920443

[dwat5-2]

O	-1.174442	1.470520	1.361076
O	1.800356	1.467173	0.042425
O	0.348759	-0.689395	0.788122
O	-2.000680	-1.069887	-0.496150
O	0.974119	-1.073260	-1.814804
H	-0.656079	0.619807	1.299070
H	-0.562833	2.097693	0.950538
H	1.359638	0.670880	0.452213
H	1.836363	1.207847	-0.888924
H	0.653284	-1.291795	1.476644

H	0.866931	-1.035905	-0.823152
H	-2.347250	-0.196198	-0.266988
H	-1.148793	-1.086958	0.023691
H	0.051838	-1.085870	-2.106681

[dwat5-3]

O	0.050309	1.157104	0.277837
O	0.347129	-0.022460	-2.009459
O	2.310806	1.740253	1.507500
O	-1.309336	-0.745785	1.398382
O	-1.402895	-2.189792	-1.123165
H	-0.800828	0.041511	0.981676
H	1.419277	1.517529	1.077167
H	-0.695273	-1.113126	2.044630
H	-0.858741	-1.516756	-1.578143
H	-0.478324	1.961477	0.204483
H	2.905000	1.856899	0.757514
H	1.245079	-0.370901	-1.964778
H	0.222448	0.490521	-1.127901
H	-1.480870	-1.822593	-0.219573

[dwat5-4]

O	0.917217	-0.053958	1.293159
O	-0.468727	1.927890	0.380564
O	3.220933	-0.116940	-0.006100
O	-0.573317	-1.959924	0.383708
O	-2.131352	0.026122	-1.079335
H	0.017455	-1.230301	0.800906

H	2.373967	-0.093725	0.548703
H	0.031685	-2.481494	-0.156102
H	-1.675443	0.778170	-0.651493
H	1.009275	-0.055658	2.253498
H	2.900988	-0.109041	-0.915594
H	0.163437	2.415370	-0.159982
H	0.081987	1.168231	0.798967
H	-1.716521	-0.748639	-0.650222

[dwat5-5]

O	-1.418431	0.442447	-0.331340
O	2.517314	1.657431	0.489816
O	0.878194	-0.416302	0.292936
O	-3.577931	-0.258251	1.178005
H	1.901402	-1.744638	-1.755805
H	-0.484133	0.047078	-0.059529
H	-1.277895	1.396452	-0.347038
H	1.869928	0.881814	0.474131
H	3.126980	1.447368	-0.227389
H	1.547822	-1.257998	-0.942587
H	0.876268	-0.953561	1.094456
H	-3.147674	-0.511836	2.002541
H	-2.820753	-0.014159	0.581798
H	1.145529	-1.755106	-2.354480

[dwat5-6]

O	1.695362	-1.468344	0.119296
O	-1.953097	-1.424920	0.289486

O	-0.039471	0.041284	1.424099
O	2.398606	1.360077	1.443311
O	-2.016059	1.685948	0.370315
H	1.029197	-0.952095	0.680449
H	1.674761	-1.017340	-0.733253
H	-1.236221	-0.894608	0.763283
H	-1.456830	-2.077241	-0.218931
H	-0.125267	-0.111548	2.374108
H	-1.231127	1.275837	0.813124
H	2.850688	0.552205	1.163807
H	1.451682	1.061038	1.449560
H	-2.467313	0.902777	0.023871

[dwat5-7]

O	-0.047626	0.293142	-0.525076
O	-1.800310	-1.446995	-0.121249
O	3.676895	1.660672	1.401762
O	2.431072	0.036356	-0.379521
O	-4.340373	-0.503516	-0.283977
H	1.367150	0.142961	-0.421658
H	-1.057885	-0.704662	-0.303933
H	-1.530355	-1.873718	0.699531
H	-3.426415	-0.886415	-0.181755
H	2.993174	1.752613	2.075100
H	-0.331923	1.160795	-0.214118
H	3.259028	1.067920	0.718198
H	2.724590	0.101615	-1.295081

H	-4.221844	0.196792	-0.935863
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MP2/6-311++G(3df,3pd)

[dwat4-1]

O	1.139240	2.062688	-0.265642
O	-2.345603	-0.043530	-0.286152
O	1.218649	-2.007995	-0.267798
O	-0.001916	0.003707	0.865981
H	0.737335	1.277330	0.224707
H	0.400448	2.353961	-0.801809
H	-1.468928	0.003712	0.211774
H	-2.223217	-0.831178	-0.817910
H	0.736007	-1.269883	0.223127
H	1.844498	-1.511000	-0.796418
H	-0.007172	0.003130	1.824858

[dwat4-2]

O	-1.965074	-0.545943	0.015359
O	1.993541	-0.132215	0.045395
O	0.151848	-1.708411	0.755042
O	-0.174460	1.535642	-0.924076
H	-1.111730	-1.071320	0.302454
H	-2.333857	-0.263999	0.853440
H	1.263053	-0.823128	0.320473
H	2.283443	0.218567	0.888473
H	0.246017	-2.581420	0.368970

H	0.629779	1.058800	-0.658250
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H	-0.866628	0.902404	-0.669604
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[dwat5-1]

O	2.073427	0.132680	-0.694408
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O	-2.075439	0.131421	-0.690108
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O	0.002446	-0.459113	1.974883
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O	-0.000799	1.989075	0.096698
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O	-0.000469	-1.369599	-0.574628
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H	1.295661	-0.523795	-0.731749
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H	2.405276	-0.007748	0.195105
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H	-1.297356	-0.524622	-0.728987
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H	-2.405648	-0.009359	0.199957
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H	0.001483	-0.953318	1.120850
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H	0.001614	0.453609	1.661112
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H	-0.758978	1.489848	-0.252406
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H	0.756937	1.490355	-0.254079
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H	-0.000601	-2.249840	-0.952860
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[dwat5-2]

O	1.440048	-1.677562	-0.326995
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O	-1.677621	-1.440016	-0.326975
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O	-0.000001	-0.000009	1.206819
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O	1.677609	1.440044	-0.326945
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O	-1.440016	1.677583	-0.326990
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H	1.019491	-1.107527	0.365001
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H	0.653240	-1.968295	-0.798319
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H	-1.107553	-1.019481	0.365007
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H	-1.968351	-0.653194	-0.798280
H	-0.000007	-0.000017	2.165637
H	-1.019475	1.107529	0.365000
H	1.968280	0.653242	-0.798320
H	1.107553	1.019483	0.365033
H	-0.653205	1.968215	-0.798374

[dwat5-3]

O	0.854492	-0.234157	0.798459
O	-0.382734	1.891374	0.005420
O	2.990372	0.269032	-0.651835
O	-0.891095	-2.025407	0.176591
O	-2.716718	0.160832	-0.389238
H	-0.185194	-1.347076	0.457669
H	2.197150	0.025912	-0.084187
H	-0.531333	-2.388593	-0.633743
H	-2.042468	0.842544	-0.242982
H	1.078089	-0.266565	1.730833
H	3.015545	1.222996	-0.569384
H	-0.049398	1.942724	-0.892064
H	0.106725	1.083020	0.379353
H	-2.212858	-0.650460	-0.213612

[dwat5-5]

O	-1.563517	0.251323	-0.470513
O	2.512683	1.387685	0.274809
O	0.673207	-0.553026	0.370739
O	-3.510290	-0.093153	1.404383

H	2.236739	-1.251372	-1.606724
H	-0.661202	-0.117200	-0.107777
H	-1.382341	1.186523	-0.578890
H	1.797472	0.722425	0.448154
H	2.942423	0.976431	-0.479528
H	1.633991	-1.055867	-0.824039
H	0.631301	-1.155390	1.115408
H	-2.977648	-0.159936	2.197592
H	-2.829422	0.022271	0.700817
H	1.633225	-1.199975	-2.348917

[dwat5-6]

O	1.355528	-1.566244	0.048870
O	-1.854051	-1.495879	0.560552
O	0.021169	0.195695	1.489021
O	2.451572	1.326339	1.098895
O	-1.991828	1.648016	0.349219
H	0.870140	-0.940411	0.663727
H	1.423632	-1.047325	-0.754462
H	-1.208548	-0.863229	0.975512
H	-1.254146	-2.066037	0.073794
H	0.006700	0.114779	2.445811
H	-1.209628	1.266278	0.812466
H	2.876107	0.493892	0.881408
H	1.519261	1.024592	1.254736
H	-2.431000	0.842603	0.062980