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Supporting Information

Understanding the influence of low-frequency vibrations on the hydrogen bonds of acetic acid and acetamide dimers

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Complete reference of Gaussian 09 code:

J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 09*, Revision **C. 01**, Gaussian, Inc., Wallingford CT, 2009.

Complete reference of Gaussian 16 code:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J.

M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

Table 1s Hydrogen bond distances in the acetic acid (AA-1 to AA-6) and acetamide (AMD-1 to AMD-4) dimers in their optimized geometries at the MP2 DFT/B3LYP, G4 and CBS-QB3 levels.

Isomers	Hydrogen bond distances[a,b]			
	MP2	DFT/B3LYP	G4	CBS-QB3
AA-1	1.670, 1.670	1.649, 1.649	1.634, 1.634	1.668, 1.668
AA-2	1.794, 2.274	1.786, 2.308	1.781, 2.257	1.794, 2.285
AA-3	1.878, 1.939	1.881, 1.982	1.851, 1.928	1.898, 1.946
AA-4	1.883, 2.323	1.920, 2.389	1.905, 2.315	1.899, 2.342
AA-5	2.334, 2.335	2.415, 2.416	2.367, 2.367	2.393, 2.393
AA-6	1.822, 2.559	1.831, 2.773	–	–
AMD-1	1.824, 1.824	1.832, 1.832	1.840, 1.840	1.859, 1.859
AMD-2	1.884, 2.237	1.904, 2.285	1.907, 2.240	1.919, 2.265
AMD-3	1.948, –	1.969, –	1.969, –	1.973, –
AMD-4	3.210, 3.210	2.359, 2.364	2.296, 2.296	2.327, 2.327

[a] Refer to Figure. 1 and 2 for the definition of the dimers and their hydrogen bond distances.

Table 2s Characteristic computed frequencies (in cm^{-1}) of acetic acid (*trans*-) and acetamide (AM) at the MP2/aug-cc-pVDZ and DFT/B3LYP/aug-cc-pVDZ levels after anharmonicity corrections.[a] The results are compared with the available experiments.

Monomer	Computed parameters	MP2	DFT/B3LYP	Expt.[b,c]
trans-	ν(OH)	3543	3528	3568
acetic	$\nu_{as}(CH_3)$	3073	3061	3057
	$\nu_s(CH_3)$	2970	2929	2953
acid	ν(CO)	1764	1725	1780
	νCO+δCOH	1364	1374	1325
	τ(COH)	633	634	635
	2τ(COH)	1238	1246	1259
	ν(C-C)	840	857	849
	νCO+δCOH	1137	1246	1180
AM	$\nu_{as}(NH_2)$	3585	3529	3568
	$\nu_s(NH_2)$	3439	3408	3448
	$\nu_{as}(CH_3)$	3061	3061	3049[e]
	$\nu_{as}(CH_3)$	2956	2929	2936[e]
	ν(CO)	1721	1725	1746
	$\delta(NH_2)$	1580	1570	1593
	$\tau(NH_2)$	519	507	462[e]

[a] See the manuscript for the details of such corrections.

[b] References 8, 23 (acetic acid trans), and 18 (actamide) of the manuscript.

[e] Ref. 45 of the manuscript.

Table 3s Assignments of the NIR bands of acetic acid cyclic dimer with respect to the vibrational data computed at the MP2 and DFT/B3LYP (using aug-cc-pVDZ basis sets) levels.

ν (cm^{-1})			Major contribution[a]
Expt.[a]	MP2	DFT/B3LYP	
5996	6130	5992	$\nu_{as}'\mathrm{CH_3} + \nu_{as}\mathrm{CH_3}$
5949	6030	5946	$\nu_{as}\mathrm{CH_3(1)} + \nu_{as}\mathrm{CH_3(2)}$
5808	5934	5907	$\nu_{as}'\mathrm{CH_3(1)} + \nu_{as}'\mathrm{CH_3(2)}$
5690	5908	5832	$\nu_{s}\mathrm{CH_3(1)} + \nu_{s}\mathrm{CH_3(2)}$
5658	5687	5675	$\nu_{s}\mathrm{HB(bridge)} + \nu_{s}\mathrm{CH_3}$
4691	4703	4712	$\nu\mathrm{C{=}O} + \nu_{as}\mathrm{CH_3}$
4654	4633	4670	$\delta\mathrm{CHO} + \nu_{as}\mathrm{CH_3}$, $\nu\mathrm{C{=}O} + \nu_{s}\mathrm{CH_3}$
4433	4446	4485	$\delta_{as}\mathrm{CH_3} + \nu_{as}\mathrm{CH_3}$
4376	4405	4411	$\delta_{as}'\mathrm{CH_3} + \nu_{as}'\mathrm{CH_3}$
4336	4380	4351	$\nu\mathrm{C{=}O} + \nu_{s}\mathrm{HB(bridge)}$, $(\nu\mathrm{C}\text{‾}\mathrm{O}, \delta_{\mathrm{ip}}\mathrm{OH}) + \nu_{as}'\mathrm{CH_3}$
4275	4281	4261	$(\nu\mathrm{C}\text{‾}\mathrm{O}, \delta_{\mathrm{ip}}\mathrm{OH}) + \nu_{as}'\mathrm{CH_3}$, $\nu\mathrm{C}\text{‾}\mathrm{O} + \nu_{as}'\mathrm{CH_3}$
4224	4225	4229	$(\nu\mathrm{C}\text{‾}\mathrm{O}, \delta_{\mathrm{ip}}\mathrm{OH}) + \nu_{s}\mathrm{CH_3}$, $\nu\mathrm{C}\text{‾}\mathrm{O} + \nu_{s}\mathrm{CH_3}$
4070	4114	4159	$\nu\mathrm{C{-}O} + \nu_{s}\mathrm{HB(bridge)}$
4035	4072	4071	$\delta_{\mathrm{ip}}\mathrm{OH} + \nu_{as}\mathrm{HB(bridge)}$
3978	4005	4027	$\delta_{\mathrm{ip}}\mathrm{OH} + \delta_{s}\mathrm{CH_3}$
3888	3966	3998	$\delta_{\mathrm{rock}}'\mathrm{CH_3} + \nu_{s}\mathrm{CH_3}$
3836	3864	3829	$\delta_{\mathrm{oop}}\mathrm{OH} + \nu_{s}\mathrm{HB(bridge)}$

[a] Assignments of the experimental NIR bands are from ref. 24.

Table 4s Computed binding (ΔE^B) energies (including enthalpy (ΔH^B_{298}) and Gibbs free energies (ΔG^B_{298}) of binding) (in kcal/mol, *aug*-cc-PVTZ)[a], hydrogen bond distance (r_{HB}, Å) in the optimized structure (*aug*-cc-PVDZ basis sets, see Figure 1 in the main text), and important vibrational frequencies (in cm^{-1}) of the most stable AA-1 dimer of acetic acid using various density functional techniques with dispersion corrections.

Parameters	Functionals			
	B3LYP-GD3	B2PLYPD3	M06	M06-GD3
ΔE^B	-16.9	-15.9	-16.1	-16.5
ΔH^B_{298}	-17.0	-15.9	-15.9	-16.4
ΔG^B_{298}	-5.5	-4.6	-5.4	-5.8
r_{HB}	1.65	1.65	1.69	1.69
ν(OH)	2914, 2753	2853, 2724	3053, 2939	3052, 2939
ν(CH$_3$)	3008	3038	2840	2840
ν(C=O)	1702	1698	1767	1767
δCOH+δCH$_3$	1349	1358	1304	1305
νCO-δCOH	1303	1284	1232	1232
τ(COH)	990	986	960	961
Low-Frequencies[b]	44(-),[c] 57(-),[c] 74 (111), 78(67), 127(112), 165 (160), 185(181), 187(177)	42(-),[c] 51(-),[c] 70 (75), 76(63), 126(109), 163 (156), 185(186), 188(176)	44(356*i*), 55 (601*i*), 59(194*i*), 74(59), 119(151), 119(151), 159 (142), 186(222)	43(343), 54 (595*i*), 59(200*i*), 74(62), 118(152), 118(152), 159 (143), 180!194), 186(223)

[a] All the binding energies (ΔE^B, ΔH^B_{298}, and ΔG^B_{298}) are after counterpoise corrections CP) and inclusion of zero-point energies (ZPE) with anharmonicity corrections (*aug*-cc-pVTZ level, as discussed in the method section and Table 1).

[b] Anharmonicity corrected frequencies are within parentheses.

[c] These values are not imaginary, but too large to cause some uncertainty in the zero-point energy with anharmonicity effect.

Table 5s Computed binding (ΔE^B) energies (including enthalpy (ΔH^B_{298}) and Gibbs free energies (ΔG^B_{298}) of binding) (in kcal/mol, *aug*-cc-PVTZ)[a], hydrogen bond distance (r_{HB}, Å) in the optimized structure (*aug*-cc-PVDZ basis sets, see Figure 1 in the main text), and important vibrational frequencies (in *cm^{-1}*) of the most stable AMD-1 dimer of acetamide using various density functional techniques with dispersion corrections.

Parameters	Functionals			
	B3LYP-GD3	B2PLYPD3	M06	M06-GD3
ΔE^B	-14.5	-13.7	-14.3	-14.6
ΔH^B_{298}	-14.8	-13.6	-14.6	-14.8
ΔG^B_{298}	-3.6	-2.4	-3.4	-3.5
r_{HB}	1.83	1.82	1.83	1.83
$\nu_{as}(NH_2)$	3490	3514	3513	3513
$\nu_s(NH_2)$	3048	3086	2971	2970
$\nu_{as}(CH_3)$	2980	2996	2891	2890
$\nu_s(CH_3)$	2913	2944	2927	2926
$\nu(C=O)$	1691	1681	1737	1736
$\delta(NH_2)$	1595	1614	1600	1596
τNH_2-inp	857	862	865	866
Low-Frequencies[b]	17(-),[c] 24(-),[c] 42 (143), 82(155), 99(152), 143 (142), 159(168), 165(150)	27(-),[c] 32(-),[c] 42 (86), 82(111), 98(104), 136 (127), 158(151) 162(149)	39(-),[c] 57(-),[c] 74 (9*i*), 89(8*i*), 107(39*i*), 125 (59), 162(153), 170(155)	38(-),[c] 57 (-),[c] 59(15*i*), 89(11*i*), 106(42*i*), 124(59), 162 (133), 170(156)

[a] All the binding energies (ΔE^B, ΔH^B_{298}, and ΔG^B_{298}) are after counterpoise corrections CP) and inclusion of zero-point energies (ZPE) with anharmonicity corrections (*aug*-cc-pVTZ level, as discussed in the method section and Table 3).

[b] Anharmonicity-corrected frequencies are within parentheses.

[c] These values are not imaginary, but too large to cause some uncertainty in the zero-point energy with anharmonicity effect.

Table 6s The vibrational frequencies (cm^{-1}) and their corresponding intensities (KM/Mole) of the OH (ν_{OH}) and NH (ν_{sNH}) stretching modes of acetic acid (AA-1 to AA-6) and acetamide (AMD-1 to AMD-4) dimers at the MP2, and DFT/B3LYP levels. The frequencies are anharmonicity corrected and the intensities are considered to remain unchanged with respect to the harmonic counterpart.

Dimer	ν_{OH}		I		Dimer	ν_{sNH}		I	
	MP2	DFT	MP2	DFT		MP2	DFT	MP2	DFT
AA-1	2950	2788	2919	3442	AMD-1	3104	3062	1789	1887
AA-2	3248	3186	1025	1118	AMD-2	3414	3412	662	709
AA-3	3384	3401	660	569	AMD-3	3433	3410	412	487
AA-4	3362	3358	642	631	AMD-4	3429	3412	25	24
AA-5	3545	3551	138	118					
AA-6	3267	3240	886	934					

Table 7s The low-frequency vibrational modes (cm^{-1}) and their corresponding intensities (KM/Mole) for the acetic acid (AA-1 to AA-6) and acetamide (AMD-1 to AMD-4) dimers at the MP2, DFT/B3LYP, G4, CBS-QB3, and G2MP2 levels. The frequencies are anharmonicity corrected (for MP2 and DFT/B3LYP) and the intensities are considered to remain unchanged with respect to the harmonic counterpart.

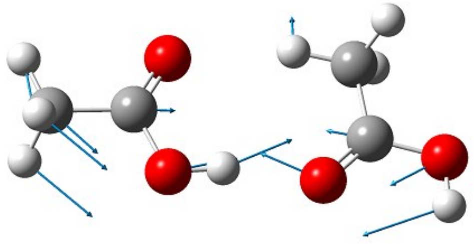
Dimer	ν_7, I				
	MP2	DFT	G4	CBS-QB3	G2MP2
AA-1	173, 30	176, 33	185, 32	179, 31	158, 21
AA-2	129, 13	132, 15	147, 14.5	146, 13.2	137, 8.8
AA-3	428, 9.2	430, 15	429, 8.2	433, 10.2	460, 13.5
AA-4	126, 9.3	111, 7.9	133, 8.2	135, 7.5	118, 4.4
AA-5	92, 0.8	80, 0.6	149, 1.1	130, 1.2	139, 0.2
AA-6	429, 6.3	429, 6.6	—	—	—
AMD-1	155, 45	147, 46	154, 42	151, 41	136, 36
AMD-2	136, 37	99, 28	144, 26	143, 25	130, 25
AMD-3	142, 13	102, 9	141, 11	141, 9.6	123, 7.6
AMD-4	113, 0.6	63, 0.4	113, 0.004	165, 4.2	141, 0.3

FIGURE CAPTIONS

Figure 1s. IR-active low-frequency modes (cm^{-1}) of various acetic acid (AA2 – AA6) and acetamide (AMD-2 – AMD-4) dimers are presented along with their nuclear displacements. The corresponding intensities (I, KM/Mole) of such modes are used in correlation in FIG. 5(C), 5(D) 6 (main manuscript). The details of these modes are available in Table 5s.

Figure 2s. Correlations of IR-intensities (I) of $\nu_{OH}/\ \nu_{NH}$ modes of various acetic acid, formic acid, acetamide and formamide dimers against their binding energies (ΔE^B) are presented using results of MP2 and G4 calculations. Panel (a): correlation of IR-intensities of ν(OH) of various acetic acid (AA-1 –AA-6) and formic acid (TT-1 – TT-5) dimers against their ΔE^B (MP2 (red): $I = -212\Delta E^B - 550$, R = 0.97; panel (b): correlation of IR-intensities of ν_s(NH) of various acetamide (AMD-1 to AMD-4) and formamide (FMAD-A – FMAD-E) against their ΔE^B (MP2 (red): $I = -169\Delta E^B – 723$, R = 0.97). Panel (c) and (d) are similar to (a) and (b) respectively using G4 level of calculations. Panel (c): (blue) $I = -229.4\Delta E^B – 530.2$, R = 0.96; panel (d) (blue); $I = -165.4\Delta E^B – 536.8$, R = 0.97. The IR-intensities acetic acid and acetamide dimers are available in Table 4s, and the data for formic acid and formamide dimers are taken from ref. 27 of manuscript.

Figure 3s. Correlations of the IR intensities of the ν(OH)/ ν_s(NH) modes of different acetic acid and acetamide dimers are presented against their ΔE^B values at the G4MP2, CBS-QB3, and G2MP2 level of theories. Panel (a): correlations for acetic acid dimers (G4 (blue): $I = -274.4\Delta E^B -706.9$, R = 0.99; CBS-QB3 (red): $I = -246.5\Delta E^B -714.3$, R = 0.99; G2MP2 (green): $I = -159.3\Delta E^B – 255.1$, R = 0.99). Panel (b): correlations for acetamide dimers (G4 (red): $I = -205.9\Delta E^B -907.0$, R = 1.00; CBS-QB3 (green): $I = -180.5\Delta E^B -842.8$, R = 1.00; G2MP2 (blue): $I = -123.6\Delta E^B -572.1$, R = 1.00).



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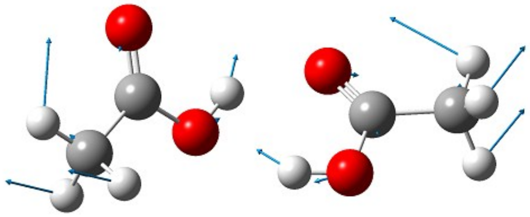

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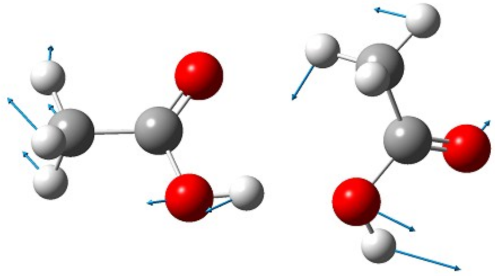

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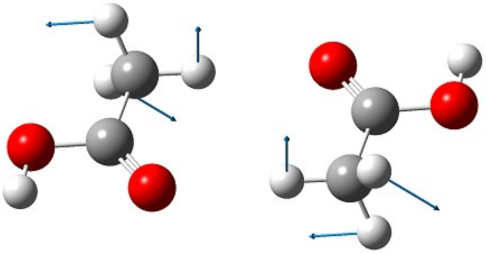

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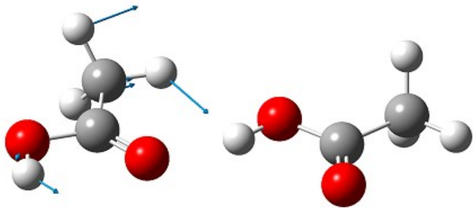

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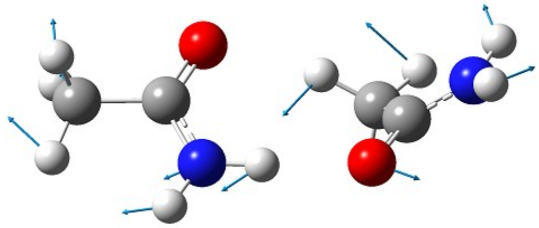

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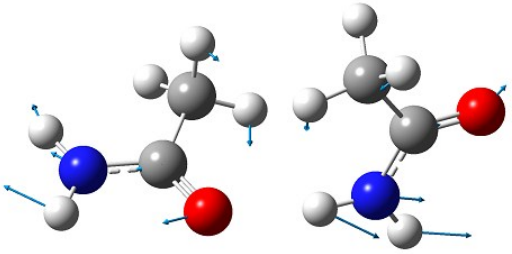
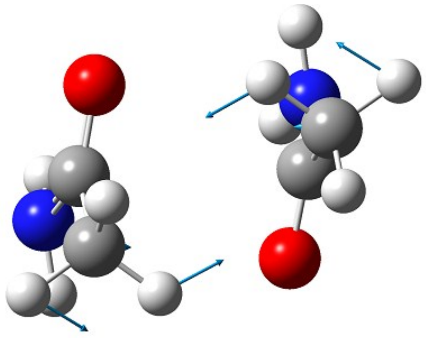
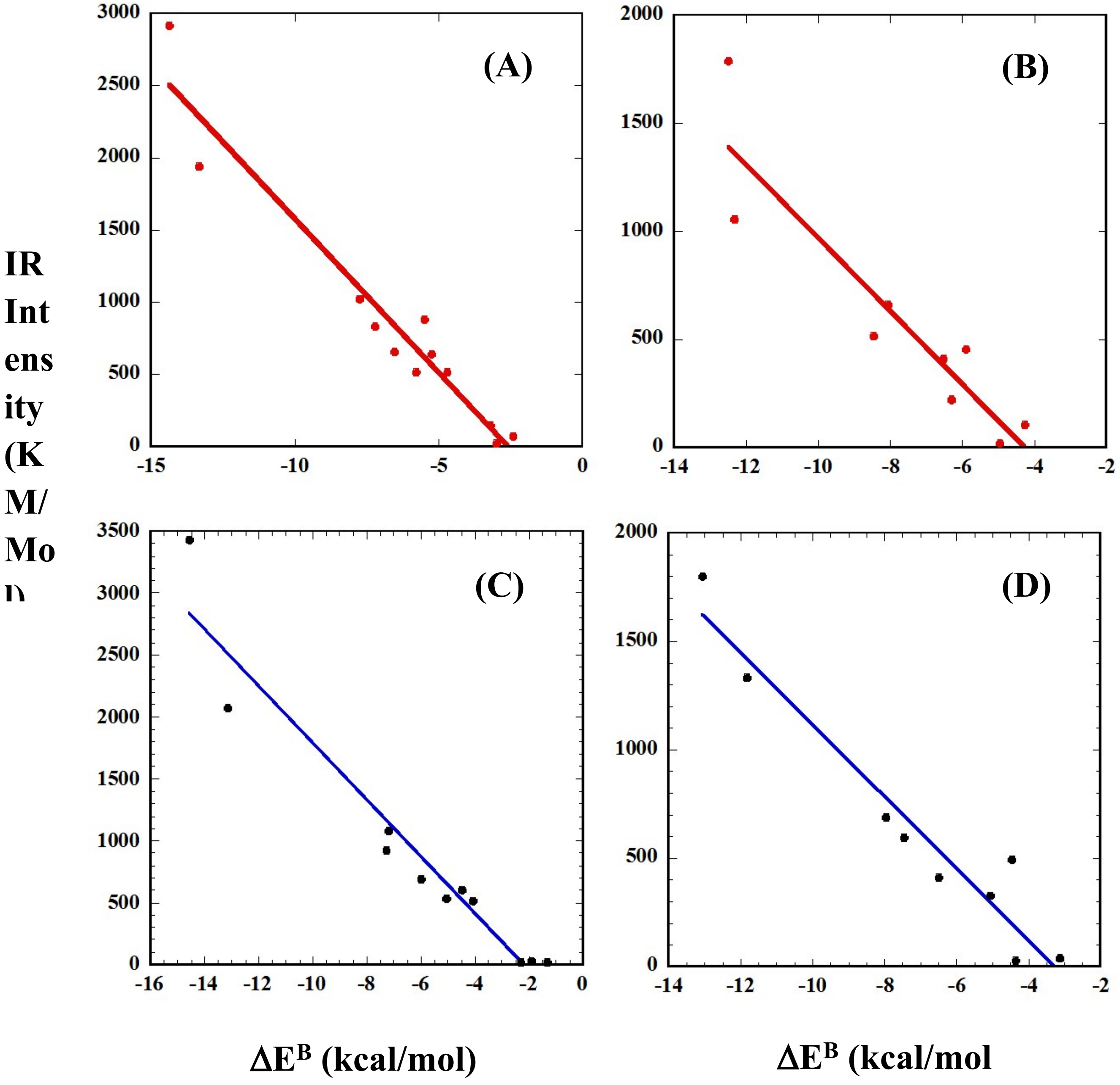


AMD-3



AMD-4

Fig. 1s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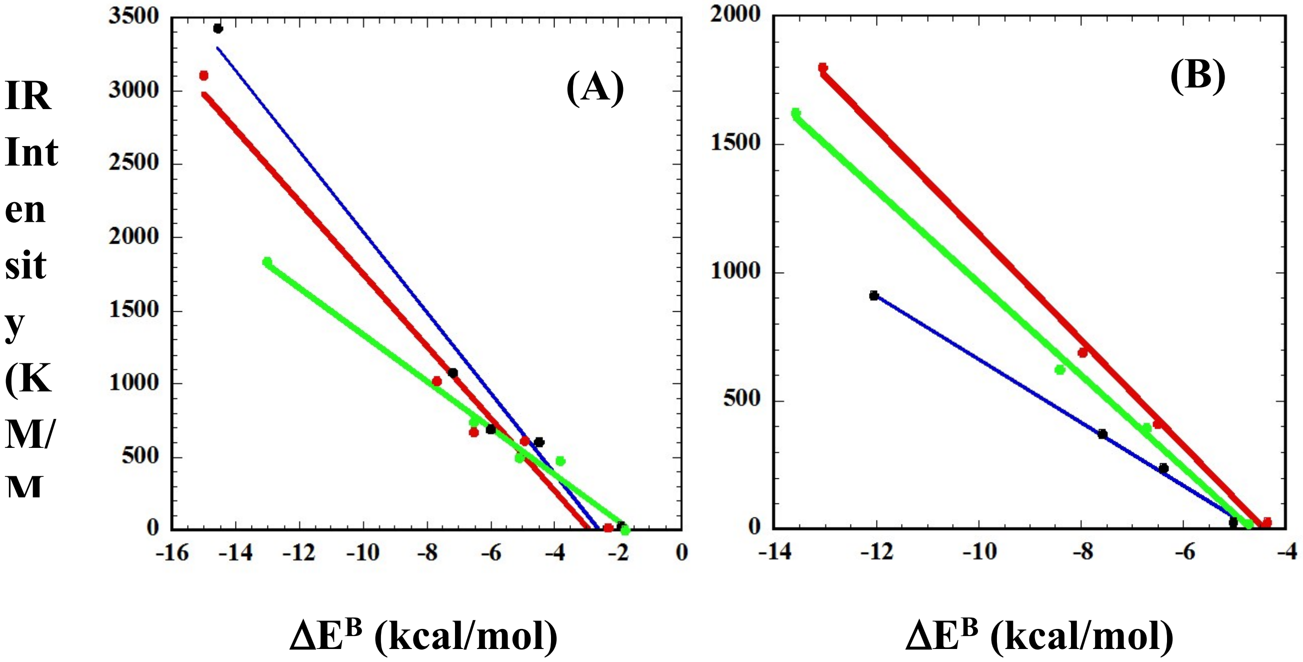
ΔE^B (kcal/mol

Fig. 2s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ΔE^B (kcal/mol)

Fig. 3s