Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Alcohol dimers - how much diagonal OH anharmonicity?

Franz Kollipost, Kim Papendorf, Yu-Fang Lee, Yuan-Pern Lee and Martin A. Suhm

May 28, 2014

Supplementary Information

1 Anharmonic calculations

Anharmonic perturbation theory [1] using Gaussian 09, Revision D.01 [2] was used to predict overtone and fundamental spectra at different electronic structure levels. For MP2 the optimizations were carried out with "Tight" criteria. B2PLYP-D3 was employed with "Tight" optimization criteria and the "UltraFine" grid option. B3LYP-D3 calculations were carried out with the "VeryTight" convergence criteria and the "SuperFine" grid option. With less restricted optimization criteria and coarser grid sizes the calculations often resulted in imaginary anharmonic frequencies. For the higher derivatives, the standard step size of 0.025 Å was used. Both DFT functionals were employed with the D3 empirical dispersion [3] using Becke-Johnson damping [4]. Corrections for basis set superposition error were not applied to the harmonic and anharmonic calculations.

Table S1: Comparison of anharmonic vibrational calculations on OH stretching vibrations to experimental OH stretching transitions for methanol and ethanol (g-monomer and gg-dimer): Anharmonic wavenumber $\tilde{\nu}_{\mathrm{OH}}^{\mathrm{M}}$ of the monomer, anharmonic shift $\Delta\tilde{\nu}_{\mathrm{OH}}^{\mathrm{D_d-M}}$ of the dimer donor to the monomer, diagonal OH stretching anharmonicity constants of the monomer $x_{\mathrm{OH,OH}}^{\mathrm{M}}$ and dimer donor $x_{\mathrm{OH,OH}}^{\mathrm{D_d}}$ (all in cm^{-1}) and anharmonic fundamental/overtone intensity ratio of the monomer $\frac{\int_{\nu_{01}} \ln\left(\frac{I_0}{I_{\mathrm{M}}}\right)\mathrm{d}\tilde{\nu}}{\int_{\nu_{02}} \ln\left(\frac{I_0}{I_{\mathrm{M}}}\right)\mathrm{d}\tilde{\nu}}$ and dimer donor $\frac{\int_{\nu_{01}} \ln\left(\frac{I_0}{I_{\mathrm{D_d}}}\right)\mathrm{d}\tilde{\nu}}{\int_{\nu_{02}} \ln\left(\frac{I_0}{I_{\mathrm{D_d}}}\right)\mathrm{d}\tilde{\nu}}$.

	$\tilde{\nu}_{\mathrm{OH}}^{\mathrm{M}}$	$\Delta\tilde{\nu}_{\mathrm{OH}}^{\mathrm{D_d-M}}$	$x_{\mathrm{OH,OH}}^{\mathrm{M}}$	$x_{\mathrm{OH,OH}}^{\mathrm{D_d}}$	$\frac{\int_{\nu_{01}} \ln\left(\frac{I_0}{I_{\mathrm{M}}}\right)\mathrm{d}\tilde{\nu}}{\int_{\nu_{02}} \ln\left(\frac{I_0}{I_{\mathrm{M}}}\right)\mathrm{d}\tilde{\nu}}$	$\frac{\int_{\nu_{01}} \ln\left(\frac{I_0}{I_{\mathrm{D_d}}}\right)\mathrm{d}\tilde{\nu}}{\int_{\nu_{02}} \ln\left(\frac{I_0}{I_{\mathrm{D_d}}}\right)\mathrm{d}\tilde{\nu}}$
Methanol						
experimental	**3686(1)**	**−112(1)**	**−86(1)**	**−99.2(4)**	**12.1(9)**[a]	**320(90)**
MP2/cc-pVTZ	3706.0	−134.5	−82.9	−101.5	10.3	420
MP2/6-311+G(2d,p)	3685.9	−132.7	−83.1	−102.9	11.8	702
MP2/TZVP	3703.1	−125.6	−84.5	−101.8	7.9	536
B2PLYP-D3/cc-pVTZ	3673.9	−123.7	−86.1	−102.9	6.4	362
B2PLYP-D3/6-311+G(2d,p)	3674.2	−131.8	−86.1	−103.3	7.6	623
B3LYP-D3/6-311+G(2d,p)	3660.6	−152.1	−86.5	−106.9	6.4	599
Ethanol						
experimental	**3659.3(4)**	**−127.8(4)**	**−88(1)**	**−101.1(4)**	**7.5(4)**[a]	**400(100)**
MP2/6-311+G(2d,p)	3659.2	−148.1	−83.6	−104.5	10.3	843
MP2/TZVP	3675.1	−141.3	−84.9	−103.4	7.1	784
B2PLYP-D3/6-311+G(2d,p)	3660.9	−151.3	−85.2	−104.6	4.7	681
B3LYP-D3/6-311+G(2d,p)	3638.7	−161.7	−87.2	−109.1	5.0	656

[a] from Lange *et al.*[5]. The ethanol intensity ratio is the room temperature average of both conformers.

Table S1 compares the results of exploratory anharmonic vibrational calculations, coupling the VPT2/intensity approach [6,7] with electronic structure methods including dispersion (MP2/B3LYP-D3/B2PLYP-D3) and different triple zeta quality basis sets. Even within the class of triple-zeta basis sets used here, there is

a sizeable and not always systematic variation for some sensitive properties. While the cc-pVTZ basis appears to be the best overall choice, its use had to be restricted to methanol dimer. *t*-Butyl alcohol dimers were not explored at any of the present levels. Within the cc-pVTZ results, the MP2 and B2PLYP-D3 calculations provide the best fundamental/overtone ratios and B2PLYP-D3 also captures the OH anharmonicity trend very satisfactorily. Future work will have to show to which extent the residual compromises made in the vibrational treatment, in the electron correlation and in the basis set add to or cancel each other for the demanding spectroscopic parameters of the medium sized systems studied in this work. In any event, an adequate treatment has to capture the mechanical and electronic properties of the OH group, the interaction energy in the hydrogen bond, the curvature of the dipole moment hypersurfaces and the coupling among the normal modes, including the large amplitude torsions and librations.

A brief discussion of the results in Table S1 should start with the anharmonic wavenumbers for monomers. The perfect match for MP2/6-311+G(2d,p) is clearly coincidental, as variation with the basis set shows. B2PLYP-D3 performs similarly, but with less basis set dependence, whereas B3LYP-D3 shows the well-known underestimation of bond strengths. This is amplified for the dimerization shift, which is always predicted too high, but much more so for B3LYP-D3. Even the best calculations overshoot by 10% and we will come back to this point later. However, the 25-35% overshooting by B3LYP-D3 points at substantial electronic structure deficiencies in the OH group description, which may again be related to the excessive softness of the OH oscillator. This is also reflected by the diagonal anharmonicity constant of the dimer, which becomes too large for B3LYP-D3, whereas the monomeric MP2 OH oscillator is somewhat too harmonic at least for the basis sets employed. The B2PLYP-D3 calculations achieve the best compromise, but the exaggerated hydrogen bonding of the underlying density functional still shows up in the dimer anharmonicity and dimerization red-shift. No method can achieve a simultaneous accuracy of better than 2% for the monomer and dimer anharmonicities, but maybe one should not expect more from the vibrational perturbation theory. The trend from methanol to ethanol is qualitatively captured by almost all methods. Only B2PLYP-D3 predicts slightly smaller anharmonic constants for ethanol monomer. The same is true for B2PLYP-D3/TZVP and B3LYP-D3/cc-pVTZ (see Table S2) in case of the dimer donors.

Concerning the experimentally more difficult fundamental/overtone dimer intensity ratio, the large basis set dependence for MP2 and B2PLYP-D3 results should be noted. cc-pVTZ ratios are significantly smaller and closer to experiment than those for Pople or Ahlrichs basis sets. This may however also be connected to the lack of diffuse functions in the former. Like for the dimer anharmonicities and red-shifts, all levels overshoot for the dimer intensity ratio, but the methanol-to-ethanol trend is qualitatively reproduced. We refrain from a detailed discussion of monomer intensity ratios, noting only the large scatter in the theoretical results and our inability to improve the experimental values reliably.

In conclusion, the lower computational cost of B3LYP-D3 comes with a significant loss in accuracy relative to B2PLYP-D3 and MP2. It may be the preferred option for larger systems, but should then be calibrated for the model systems presented in this work. We finally come back to the experimentally well characterized dimerization shift in the fundamental region. Accurately known for more than a

decade at least in the case of methanol[8–10], it has been the prime spectroscopic indicator for hydrogen bonding for more than 80 years[11]. Therefore, it is not fully satisfactory that even the best vibrational perturbation theory results for the simplest prototype system still overestimate this shift by at least 10%. For the traditional harmonic approximation, the discrepancy is even larger. E.g., the harmonic shift at B2PLYP-D3/cc-pVTZ level is $-140\,\mathrm{cm}^{-1}$ and at MP2/cc-pVTZ level it is $-143\,\mathrm{cm}^{-1}$, to be compared with the experimental anharmonic value of $-112(1)\,\mathrm{cm}^{-1}$. One might be tempted to improve these harmonic predictions by adding twice the difference of diagonal anharmonic constants between the dimer and the monomer OH stretching modes, which have been experimentally verified in the present work at high accuracy. However, this diatomic anharmonic correction obviously increases the dimerization shifts to $-174\,\mathrm{cm}^{-1}$ (B2PLYP-D3) and $-180\,\mathrm{cm}^{-1}$ (MP2), still further away from the experimental value of $-112(1)\,\mathrm{cm}^{-1}$. We note that this is qualitatively opposite to what the popular linear 0.9xy scaling of computed harmonic wavenumbers (and shifts) to estimate anharmonic wavenumbers (and shifts) would achieve. Clearly, off-diagonal corrections play a major corrective role, and among those, the couplings between large amplitude hydrogen bond librations and OH stretching motion are most prominent.

[1] G. Amat, H. Nielsen and G. Tarrago, *Rotation-Vibration Spectra of Molecules*, M. Dekker, New York, 1971.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, 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, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, `Gaussian09, Revision D.01`, Gaussian Inc., Wallingford CT, 2013.

[3] S. Grimme, *The Journal of Chemical Physics*, 2006, **124**, 034108.

[4] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104.

[5] K. R. Lange, N. P. Wells, K. S. Plegge and J. A. Phillips, *The Journal of Physical Chemistry A*, 2001, **105**, 3481–3486.

[6] V. Barone, *The Journal of Chemical Physics*, 2005, **122**, 014108.

[7] J. Bloino and V. Barone, *The Journal of Chemical Physics*, 2012, **136**, 124108.

[8] F. Huisken, A. Kulcke, C. Laush and J. M. Lisy, *The Journal of Chemical Physics*, 1991, **95**, 3924–3929.

[9] R. A. Provencal, J. B. Paul, K. Roth, C. Chapo, R. N. Casaes, R. J. Saykally, G. S. Tschumper and H. F. Schaefer III, *The Journal of Chemical Physics*, 1999, **110**, 4258–4267.

[10] R. Wugt Larsen, P. Zielke and M. A. Suhm, *The Journal of Chemical Physics*, 2007, **126**, 194307.

[11] G. Pimentel and A. McClellan, *The hydrogen bond*, W.H. Freeman, 1960.

Table S2: Computational results on methanol and ethanol (g-monomer and homochiral gg-dimer): electronic energies E without zero point correction for the monomer and dimer and spectroscopic constants of the monomer OH stretching vibration and the dimer donor OH stretching vibration: fundamental wavenumbers $\tilde{\nu}_{\mathrm{OH}}$, diagonal anharmonicity constants $x_{\mathrm{OH,OH}}$, fundamental band strengths S_{01} and overtone band strengths S_{02}.

		E/Hartree	$\tilde{\nu}_{\mathrm{OH}}/\mathrm{cm}^{-1}$ (harm./anharm)	$x_{\mathrm{OH,OH}}/\mathrm{cm}^{-1}$	$S_{01}/\frac{\mathrm{km}}{\mathrm{mol}}$ (harm./anh.)	$S_{02}/\frac{\mathrm{km}}{\mathrm{mol}}$ (anh.)
Methanol						
MP2/cc-pVTZ	monomer	−115.5174752	3882.5/3706.0	−82.9	35.6/31.8	3.08
	dimer	−231.0463238	3740.0/3571.5	−101.5	403/321	0.762
MP2/6-311+G(2d,p)	monomer	−115.4691856	3863.5/3685.9	−83.1	40.7/36.7	3.12
	dimer	−230.9485280	3711.9/3553.2	−102.9	480/365	0.520
MP2/TZVP	monomer	−115.4499621	3883.2/3703.1	−84.5	29.0/25.7	3.26
	dimer	−230.9106606	3737.5/3577.5	−101.8	415/326	0.608
B2PLYPD3/cc-pVTZ	monomer	−115.6780898	3858.4/3673.9	−86.1	28.3/24.2	3.78
	dimer	−231.3677987	3718.4/3550.2	−102.9	408/337	0.931
B2PLYPD3/6-311+G(2d,p)	monomer	−115.6607782	3859.2/3674.2	−86.1	33.6/29.1	3.81
	dimer	−231.3317528	3702.4/3542.4	−103.3	509/398	0.639
B2PLYPD3/TZVP	monomer	−115.6570169	3852.9/3665.5	−87.3	25.3/21.4	3.98
	dimer	−231.3253679	3700.1/3538.0	−104.2	438/340	0.804
B3LYPD3/cc-pVTZ	monomer	−115.7753532	3830.5/3648.9	−86.6	25.3/21.1	4.10
	dimer	−231.5626231	3680.1/3500.7	−108.1	433/336	1.02
B3LYPD3/6-311+G(2d,p)	monomer	−115.7707194	3841.7/3660.6	−86.5	31.0/26.6	4.13
	dimer	−231.5518179	3670.6/3508.5	−106.9	545/430	0.718
B3LYPD3/TZVP	monomer	−115.7740930	3821.0/3638.5	−87.4	23.3/19.5	4.30
	dimer	−231.5599516	3654.7/3487.2	−108.5	468/357	0.905
Ethanol						
MP2/6-311+G(2d,p)	monomer	−154.6757691	3839.5/3659.2	−83.6	30.2/26.3	2.55
	dimer	−309.3633385	3679.3/3511.1	−104.5	402/344	0.408
MP2/TZVP	monomer	−154.6519647	3858.7/3675.1	−84.9	22.4/19.0	2.68
	dimer	−309.3159448	3702.1/3533.8	−103.4	366/321	0.409
B2PLYPD3/6-311+G(2d,p)	monomer	−154.9479381	3837.9/3660.9	−85.2	24.3/14.8	3.18
	dimer	−309.9073195	3676.8/3509.6	−104.6	419/347	0.509
B2PLYPD3/TZVP	monomer	−154.9443609	3832.0/3653.2	−85.8	19.5/15.5	3.36
	dimer	−309.9011272	3668.5/3498.5	−104.1	396/342	0.564
B3LYPD3/cc-pVTZ	monomer	−155.1131167	3812.3/3630.3	−86.6	18.8/15.2	3.61
	dimer	−310.2398191	3638.8/3455.4	−108.1	423/323	0.642
B3LYPD3/6-311+G(2d,p)	monomer	−155.1054374	3822.8/3638.7	−87.2	21.9/17.1	3.45
	dimer	−310.2225399	3649.9/3476.9	−109.1	441/376	0.573
B3LYPD3/TZVP	monomer	−155.1112720	3803.7/3617.8	−87.9	17.7/13.2	3.66
	dimer	−310.2355027	3628.4/3452.0	−108.6	422/369	0.661

2 Spectroscopic data

Table S3: Measured bands of methanol in p-H_2 and Ne matrices: main peaks of monomer (M) and dimer donor (D_d) OH stretching vibrations in cm^{-1}, integrated absorbances $\int \ln\left(\frac{I_0}{I}\right) d\tilde{\nu}$ in cm^{-1} of the whole bands are given in italics.

	M	D_d
methanol/p-H_2		
ν_{OH}	3671.2	3538.5
	5.4(4)	*8.7(6)*
$2\nu_{OH}$	7171.4	6873.9
	0.6(2)	*0.03(2)*
methanol/Ne		
ν_{OH}	3689.3	3567.5 ; 3560.0
	8.0(3)	*16.6(3)*
$2\nu_{OH}$	7206.7	6943 ; 6924
	0.7(2)	*0.05(2)*

Table S4: Measured bands of methanol and t-butyl alcohol: band centres of monomer (M), dimer acceptor (D_a) and donor (D_d) OH stretching vibrations in cm^{-1}, integrated absorbances $\int 10^3 \ln\left(\frac{I_0}{I}\right) d\tilde{\nu}$ in cm^{-1} of the bands are given in italics. In order to derive the fundamental/overtone intensity ratios the fundamental intensity has to be corrected by a factor of 0.78(15) to account for the different detector sensitivities.

	M	D_a	D_d
methanol			
ν_{OH}	3686		3574.5(3)
	25(1)		*14.5(8)*
$2\nu_{OH}$	7198		6950.6(6)
	3.5(1)		*0.035(6)*
t-butyl alcohol			
ν_{OH}	3642.3(2)	3630.4(2)	3497.1(3)
	4.15(9)	*1.3(1)*	*16.9(6)*
$2\nu_{OH}$	7110.6(2)	7085.1(4)	6789.1(4)
	0.9(2)	*0.11(2)*	*0.013(4)*

Table S5: Measured bands of ethanol: band centres of g- and t- monomer (M), dimer acceptor (D_a) and donor (D_d) OH stretching vibrations in cm^{-1} of the most stable gg-dimer and the second most stable gt-dimer, integrated absorbances $\int 10^3 \ln\left(\frac{I_0}{I}\right) d\tilde{\nu}$ in cm^{-1} of the bands are given in italics. In order to derive the fundamental/overtone intensity ratios the fundamental intensity has to be corrected by a factor of 0.78(15) to account for the different detector sensitivities.

medium	transition	M_t	M_g	D_a^{gt}	D_a^{gg}	D_d^{gt}	D_d^{gg}
gas phase	ν_{OH}	3676.3(2)	3662.0(1)				
			3658.7(1)				
			3655.9(1)				
	$2\nu_{OH}$	7180.5(2)	7146.2(2)				
			7143.1(1)				
			7141.5(3)				
			7139.0(4)				
He expansion	ν_{OH}	3676.6(2)		3670.4(4)		3547.1(3)	3531.2(3)
		8(1)		*2.4(5)*		*4.4(3)*	*4.2(3)*
	$2\nu_{OH}$	7180.6(2)		7170(2)		(6894(1))	(6861.2(9))
		1.3(3)		*0.24(9)*		(*0.008(3)*)	(*0.008(3)*)
He+Ar expansion	ν_{OH}	3676.3(3)			3653.3(5)	3546.9(2)	3531.5(2)
		6.9(7)			*1.8(3)*	*2.4(2)*	*8.5(4)*
	$2\nu_{OH}$	7180.4(3)			7130.3(7)		6860.9(7)
		1.2(2)			*0.17(6)*		*0.016(3)*