

SUPPORTING INFORMATION

To π or not to π - how does methanol dock onto anisole?

Matthias Heger, Jonas Altnöder, Anja Poblitzki, and Martin A. Suhm*

*Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, 37077 Göttingen,
Germany;*

List of Tables

S1	Anisole-methanol: electronic dissociation energies of the OH \cdots O-dimer	1
S2	Anisole-methanol: vibrational zero-point energies of the most stable dimers.	1
S3	Anisole-methanol: electronic energies of the OH \cdots O- relative to the OH \cdots π -dimer.	2
S4	Anisole-methanol: electronic energies of the OH \cdots π' relative to the OH \cdots π -dimer.	2
S5	Anisole-methanol: comparison of energies at four electronic structure levels using three different levels of structure optimization	3
S6	Anisole-methanol: formal dispersion energy gains of the dimers.	3
S7	Anisole-methanol: anharmonic wavenumber calculations in the OH stretching range.	4
S8	Anisole-methanol: anharmonic wavenumber calculations in the OH librational range.	6
S10	Anisole-water: dissociation energies	7
S12	Toluene-methanol: relative energies of the OH \cdots π' dimers	8
S13	Toluene-methanol: wavenumber calculations in the OH stretching and OH librational range	9

Note: The abbreviation D3 always implies Becke-Johnson-damping (BJ).

Tab. S1: Anisole-methanol: electronic dissociation energies of the OH \cdots O-dimer at various methods of energy calculation and structure optimization in kJ/mol. Dissociation energies including harmonic vibrational zero point energy (D_0^h) at the same level are given in parentheses.

energy \ structure	B3LYP-D3/ def2-TZVP	B3LYP-D3/ AVTZ	MP2/ AVTZ	SCS-MP2/ AVTZ	B2PLYP-D3/ def2-TZVP	B2PLYP-D3/ AVTZ
B3LYP-D3/def2-TZVP	27.3 (22.1)					
CP-B3LYP-D3/def2-TZVP (SP)	23.3					
B3LYP-D3/AVTZ		24.2 (19.4)				
SCS-MP2/AVTZ				23.8		
B2PLYP-D3/def2-TZVP					26.1	
B2PLYP-D3/AVTZ						24.3
MP2/AVTZ	27.4		28.7			27.6
CP-MP2/AVTZ (SP)	22.7		22.6			
MP2/AVQZ	25.6		25.9			25.7
CCSD(T)/AVTZ	26.8		26.7			26.9
MP2/AVQZ + Δ CCSD(T)/AVTZ	25.0		25.0			25.0

Tab. S2: Anisole-methanol: harmonic vibrational zero-point energies of the OH \cdots O- and OH $\cdots\pi$ (π')-dimers and the non-interacting monomers on B3LYP-D3-level with different basis sets.

	(G09) def-TZVP	(G09) def2-TZVP	(Tmole) def2-TZVP	AVTZ
OH \cdots O	487.30	487.61	487.26	487.19
OH $\cdots\pi$	486.14	486.96	486.50	486.23
OH $\cdots\pi'$		485.83	485.39	485.59
monomers			482.13	482.39
OH \cdots O – (monomers)			5.13	4.80
OH $\cdots\pi$ – (monomers)			4.36	3.84
OH $\cdots\pi'$ – (monomers)			3.25	3.20
(OH \cdots O) – (OH $\cdots\pi$)	1.16	0.65	0.76	0.95
(OH $\cdots\pi'$) – (OH $\cdots\pi$)		-1.13	-1.11	-0.64

Tab. S3: Anisole-methanol: electronic energies of the OH \cdots O- relative to the OH \cdots π -dimer at various methods of energy calculation and structure optimization in kJ/mol.

energy \ structure	B3LYP-D3/ def2-TZVP	B3LYP-D3/ AVTZ	MP2/ AVTZ	SCS-MP2/ AVTZ	B2PLYP-D3/ def2-TZVP	B2PLYP-D3/ AVTZ
B3LYP-D3/def2-TZVP	-1.4					
CP-B3LYP-D3/def2-TZVP (SP)	-1.6					
B3LYP-D3/AVTZ		-1.9				
SCS-MP2/AVTZ				-0.7		
B2PLYP-D3/def2-TZVP					-1.4	
B2PLYP-D3/AVTZ						-1.8
MP2/AVTZ	0.5		-0.1			0.4
CP-MP2/AVTZ (SP)	-0.4		-0.3			
MP2/AVQZ	-0.5		-0.5			-0.6
MP2/AVTZ + Δ CCSD(T)/6-311+G*	-0.4		-0.6			
CCSD(T)/AVTZ	-1.0		-0.9			-1.0
MP2/AVQZ + Δ CCSD(T)/AVTZ	-2.0		-1.3			-2.0

Tab. S4: Anisole-methanol: electronic energies of the OH \cdots π' relative to the OH \cdots π -dimer at various methods of energy calculation and structure optimization in kJ/mol. Dissociation energies including harmonic vibrational zero point energy (D_0^h) at the same level are given in parentheses.

energy \ structure	B3LYP-D3/ def2-TZVP	B3LYP-D3/ AVTZ	B2PLYP-D3/ AVTZ
B3LYP-D3/def2-TZVP	2.4 (1.3)		
B3LYP-D3/AVTZ		1.3 (0.7)	
B2PLYP-D3/AVTZ			1.4
MP2/AVTZ			0.5
MP2/AVQZ			0.7
CCSD(T)/AVTZ			1.2
MP2/AVQZ + Δ CCSD(T)/AVTZ			1.3

Tab. S5: Anisole-methanol: comparison of energies at four electronic structure levels using three different levels of structure optimization. In each row the energy at the B2PLYP-D3/AVTZ optimized geometry is used as reference. Note that only at the highest level (MP2/AVQZ + Δ CCSD(T)/AVTZ) the B2PLYP-D3/AVTZ geometry leads to the lowest single point energy in both dimers.

dimer	energy \ structure	B3LYP-D3/ def2-TZVP	MP2/ AVTZ	B2PLYP-D3/ AVTZ
OH \cdots O	MP2/AVTZ	0.7	-1.5	0.0
	MP2/AVQZ	0.7	-0.3	0.0
	CCSD(T)/AVTZ	0.4	-0.2	0.0
	MP2/AVQZ + Δ CCSD(T)/AVTZ	0.4	0.9	0.0
OH $\cdots\pi$	MP2/AVTZ	0.5	-0.9	0.0
	MP2/AVQZ	0.5	-0.4	0.0
	CCSD(T)/AVTZ	0.3	-0.4	0.0
	MP2/AVQZ + Δ CCSD(T)/AVTZ	0.3	0.1	0.0

Tab. S6: Anisole-methanol: formal dispersion energy gains ΔE_{D3} of the complex relative to relaxed monomers of anisole and methanol in kJ/mol. The given methods are used for geometry optimization and energy calculation, from which the absolute dispersion corrections are extracted and subtracted from each other. The values for B2PLYP-D3 are lower because dispersion is partially accounted for by the perturbation treatment.

	B3LYP-D3/ def2-TZVP	B3LYP-D3/ AVTZ	B2PLYP-D3/ AVTZ
OH \cdots O	-12	-12	-6.1
OH $\cdots\pi$	-17	-17	-8.5
OH $\cdots\pi'$	-18	-18	-9.1

Tab. S7: Anisole-methanol: fundamental and overtone OH stretching wavenumbers of the hydrogen bonded OH group in the most stable dimers at B3LYP-D3 level with three basis sets. Diagonal anharmonicity constants of the same OH stretching mode $x_{\text{OH,OH}}$ are also given. Methanol monomer and dimer are included for comparison. Harmonic (ω_{h}) and anharmonic wavenumbers ($\tilde{\nu}_{\text{anh}}$) and diagonal anharmonicity constants ($x_{\text{OH,OH}}$) in cm^{-1} , harmonic and anharmonic band strengths ($I_{\text{h/anh}}$) in km/mol .

	im. fr.		ω_{h}	I_{h}	$\tilde{\nu}_{\text{anh}}$	I_{anh}
	harm / anh					
6-311+G(2d,p) (G09)						
MeOH	0 / 0	fund.	3842	31	3662	27
		overt.	7683		7150	4.1
		$x_{\text{OH,OH}}$			-86.4	
(MeOH) ₂	0 / 0	fund.	3671	545	3509	430
		overt.	7341		6803	0.7
		$x_{\text{OH,OH}}$			-106.9	
OH...O	1 (11i) / 1 (56i)	fund.	3733	370	3555	
		overt.	7466		6909	
		$x_{\text{OH,OH}}$			-100.7	
OH... π	0 / 0	fund.	3785	140	3597	133
		overt.	7569		7004	1.5
		$x_{\text{OH,OH}}$			-94.7	
def-TZVP (G09)						
MeOH	0 / 0	fund.	3821	23	3640	20
		overt.	7642		7105	4.3
		$x_{\text{OH,OH}}$			-87.3	
(MeOH) ₂	0 / 0	fund.	3655	468	3488	359
		overt.	7309		6758	0.9
		$x_{\text{OH,OH}}$			-108.5	
OH...O	0 / 1 (12i)	fund.	3712	358	3533	278
		overt.	7425		6864	1.0
		$x_{\text{OH,OH}}$			-100.9	
OH... π	0 / 0	fund.	3770	123	3581	117
		overt.	7540		6971	1.6
		$x_{\text{OH,OH}}$			-94.8	

continued on next page

Tab. S7 – Anisole-methanol: wavenumber calculations in the OH stretching range.

	im. fr.		ω_h	I_h	$\tilde{\nu}_{\text{anh}}$	I_{anh}
	harm / anh					
def2-TZVP (G09)						
MeOH	0 / 0	fund.	3813.0	25.2	3636.8	22.1
		overt.	7626.0		7103.7	4.3
		$x_{\text{OH,OH}}$				-85.0
(MeOH) ₂	0 / 0	fund.	3648.1	482.5	3485.9	382.8
		overt.	7296.3		6761.0	0.8
		$x_{\text{OH,OH}}$				-105.4
OH...O	0 / 1 (82i)	fund.	3710.7	356.5	3530.3	264.9
		overt.	7421.4		6861.6	0.9
		$x_{\text{OH,OH}}$				-99.5
OH... π	0 / 0	fund.	3760.5	131.2	3574.6	119.6
		overt.	7521.1		6963.2	1.5
		$x_{\text{OH,OH}}$				-93.0
OH... π'	0 / 2 (46i, 12i)	fund.	3777.8	142.4	3590.5	121.9
		overt.	7555.6		7000.9	1.4
		$x_{\text{OH,OH}}$				-90.1
AVTZ (Tmole)						
MeOH	0 /	fund.	3826.2	30.8		
OH...O	0 /	fund.	3711.5	377.6		
OH... π	0 /	fund.	3766.7	148.7		
OH... π'	0 /	fund.	3782.9	150.8		

Tab. S8: Anisole-methanol: harmonic (ω_h) and anharmonic ($\tilde{\nu}_{\text{anh}}$) wavenumbers of libration modes in most stable anisole-methanol dimers and the methanol dimer at B3LYP-D3 level using three basis sets. $x_{i,j}$ are anharmonicity constants of the OH libration ($_{\text{lib}}$) and the stretching mode ($_{\text{OH}}$). All wavenumbers in cm^{-1} . Listed are the two modes with highest librational character, because there is mode mixing in some cases.

		$\omega_{h,1}$	$\tilde{\nu}_{\text{anh},1}$	$\omega_{h,1}$	$\tilde{\nu}_{\text{anh},1}$
6-311+G(2d,p)					
(MeOH) ₂	(modes 23, 24)	707.9	595.2	355.3	285.3
	$x_{\text{OH,lib}}$		59.1		14.4
	$x_{\text{lib,lib}}$		-45.7		-30.3
OH...O	(modes 45, 46)	636.4	606.6	622.8	549.1
	$x_{\text{OH,lib}}$		13.4		36.0
	$x_{\text{lib,lib}}$		-2.3		-22.8
OH... π	(modes 49, 50)	427.4	413.6	414.7	366.2
	$x_{\text{OH,lib}}$		0.9		11.3
	$x_{\text{lib,lib}}$		-0.2		-17.8
def-TZVP					
(MeOH) ₂	(modes 23, 24)	722.9	618.8	353.2	269.1
	$x_{\text{OH,lib}}$		55.1		21.0
	$x_{\text{lib,lib}}$		-40.0		-43.0
OH...O	(modes 44, 46)	663.4	550.1	632.9	624.6
	$x_{\text{OH,lib}}$		43.9		1.7
	$x_{\text{lib,lib}}$		-40.1		0.1
OH... π	(modes 48, 49)	453.6	441.1	439.5	380.5
	$x_{\text{OH,lib}}$		0.8		10.4
	$x_{\text{lib,lib}}$		-0.2		-19.0
def2-TZVP					
(MeOH) ₂	(modes 23, 24)	701.7	590.2	358.0	292.8
	$x_{\text{OH,lib}}$		53.7		16.9
	$x_{\text{lib,lib}}$		-41.6		-33.6
OH...O	(modes 45, 46)	638.6	558.8	626.8	556.4
	$x_{\text{OH,lib}}$		24.9		21.6
	$x_{\text{lib,lib}}$		-15.7		-12.3
OH... π	(modes 49, 50)	433.1	379.3	423.9	396.4
	$x_{\text{OH,lib}}$		8.0		4.0
	$x_{\text{lib,lib}}$		-11.9		-2.6
OH... π'	(modes 43, 50)	773.0	788.1	336.6	274.1
	$x_{\text{OH,lib}}$		0.7		5.7
	$x_{\text{lib,lib}}$		2.1		-19.7

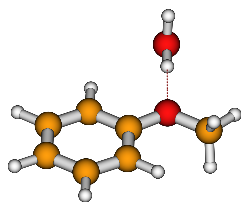


Fig. S9: Anisole-water: OH \cdots O dimer optimized on B2PLYP-D3/AVTZ level.

Tab. S10: Anisole-water: dissociation energies of the OH \cdots O anisole-water dimer (Fig. S9). Dissociation energies including harmonic vibrational zero point energy (D_0^h) at the same level are given in parentheses.

energy	structure	B3LYP-D3/ def2-TZVP	B3LYP-D3/ AVTZ	B2PLYP-D3/ AVTZ
B3LYP-D3/def2-TZVP		24.7 (17.8)		
B3LYP-D3/AVTZ			21.4 (14.7)	
B2PLYP-D3/AVTZ				21.5
MP2/AVTZ				23.0
MP2/AVQZ				21.9
CCSD(T)/AVTZ				23.0
MP2/AVQZ + Δ CCSD(T)/AVTZ				21.9

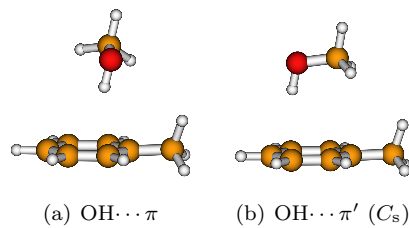


Fig. S11: Toluene-methanol: dimers optimized on B3LYP-D3/AVTZ level.

Tab. S12: Toluene-methanol: relative energies of the OH... π (') dimers with (E_0^h) and without (E_e) harmonic vibrational zero point energy at B3LYP-D3-level with basis sets def2-TZVP and aug-cc-pVTZ in kJ/mol; the number of imaginary wavenumbers in harmonic and anharmonic treatment are also included. Note that OH... π does not profit from CH...O contacts compared to anisole-methanol and is therefore energetically similar to OH... π' .

	E_e	E_0^h	im. fr. harm / anh
def2-TZVP (G09)			
OH... π	0	0	0 / 0
OH... π' (C_s)	0.4	0.1	0 / 2 (9i, 89i)
AVTZ (Tmole)			
OH... π	0	0	0 /
OH... π' (C_s)	-0.04	-0.2	0 /

Tab. S13: Toluene-methanol: harmonic and anharmonic wavenumbers (ω_h , $\tilde{\nu}_{\text{anh}}$) and infrared band strengths ($I_{\text{h/anh}}$) of the OH stretching (fundamental and first overtone) and OH librational modes along with diagonal and off-diagonal anharmonicity constants $x_{i,j}$ calculated at B3LYP-D3-level with two basis sets. All wavenumbers in cm^{-1} and band strengths in km/mol .

			ω_h	I_h	$\tilde{\nu}_{\text{anh}}$	I_{anh}
def2-TZVP (G09)						
OH $\cdots\pi$	OH stretch	fund.	3768.4	165.2	3585.1	137.0
		overt.	7536.9		6986.7	1.2
		$x_{\text{OH,OH}}$			-91.8	
	OH lib	fund.	387.7	75.6	315.6	41.0
		$x_{\text{OH,lib}}$			10.9	
		$x_{\text{lib,lib}}$			-24.4	
OH $\cdots\pi'$ (C_s)	OH stretch	fund.	3777.8	149.0	3589.9	130.8
		overt.	7555.5		7001.2	1.3
		$x_{\text{OH,OH}}$			-89.3	
	OH lib	fund.	336.1	45.3	304.0	62.1
		$x_{\text{OH,lib}}$			1.4	
		$x_{\text{lib,lib}}$			-11.3	
AVTZ (Tmole)						
OH $\cdots\pi$	OH stretch	fund.	3774.5	174.8		
OH $\cdots\pi'$ (C_s)	OH stretch	fund.	3784.3	153.3		