

Electronic Supplementary Information (ESI)

Multi-spectroscopic and theoretical analyses on the diphenyl ether–*tert*-butyl alcohol complex in the electronic ground and electronically excited state

Dominic Bernhard¹, Fabian Dietrich¹, Mariyam Fatima², Cristobal Perez², Anja Poblitzki³,
Georg Jansen*⁴, Martin A. Suhm*³, Melanie Schnell*², and Markus Gerhards^{1*}

¹*TU Kaiserslautern, Fachbereich Chemie & Research Center Optimas, Erwin-Schroedinger-Str. 52, D-67663
Kaiserslautern, Germany. E-mail: gerhards@chemie.uni-kl.de*

²*Max-Planck-Institut für Struktur und Dynamik der Materie, Luruper Chaussee 149,
D-22761 Hamburg, Germany. E-mail: melanie.schnell@mpsd.mpg.de*

³*Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6,
D-37077 Göttingen, Germany. E-mail: msuhm@gwdg.de*

⁴*Fakultät für Chemie, Universität Duisburg-Essen, Universitätsstraße 5,
D-45117 Essen, Germany. E-mail: georg.jansen@uni-due.de*

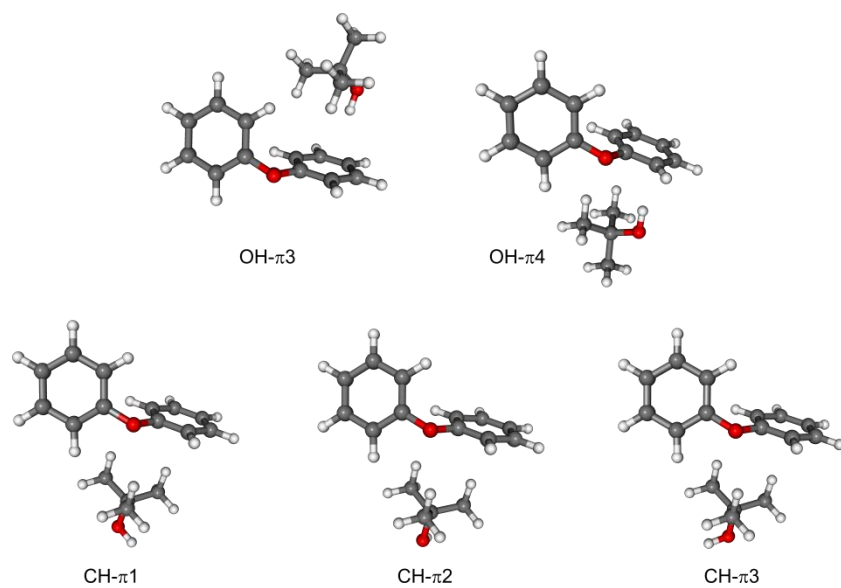


Fig. S1 Further calculated minimum structures for the electronic ground state (S_0) at the B3LYP-D3(BJ)/def2-TZVP level.

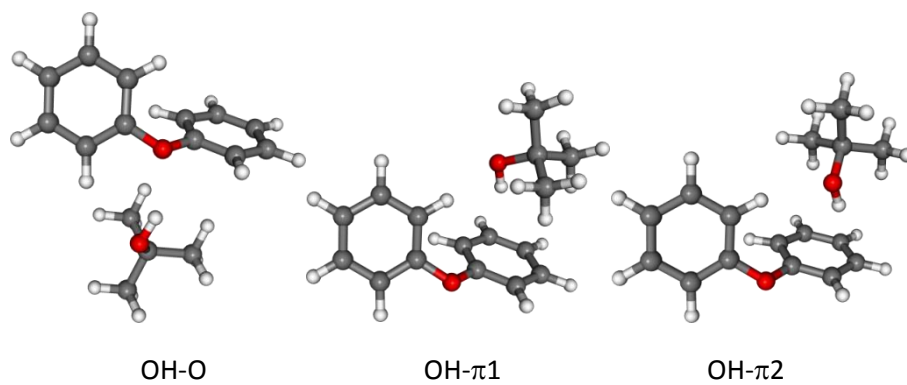


Fig. S2 Most stable calculated minimum structures for the electronically excited state (S_1); calculated at the SCS-CC2/def2-TZVP level.

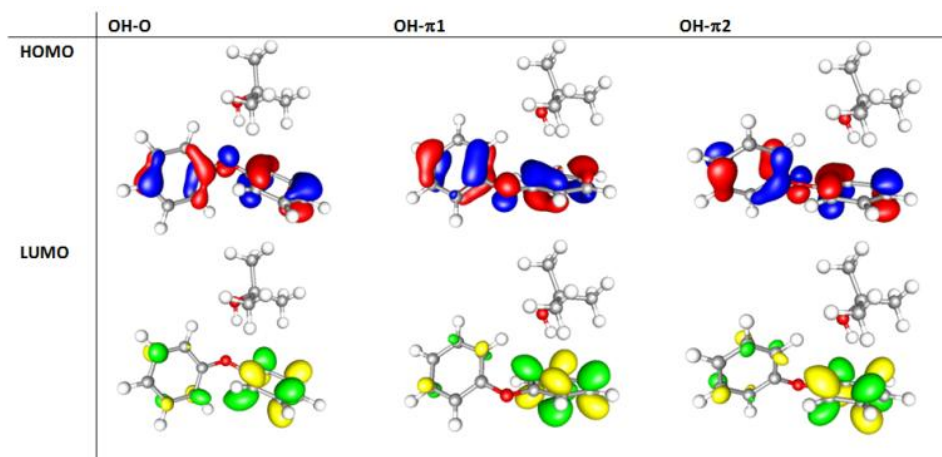


Fig. S3 Visualization of the HOMOs and LUMOs for the three lowest calculated minimum structures

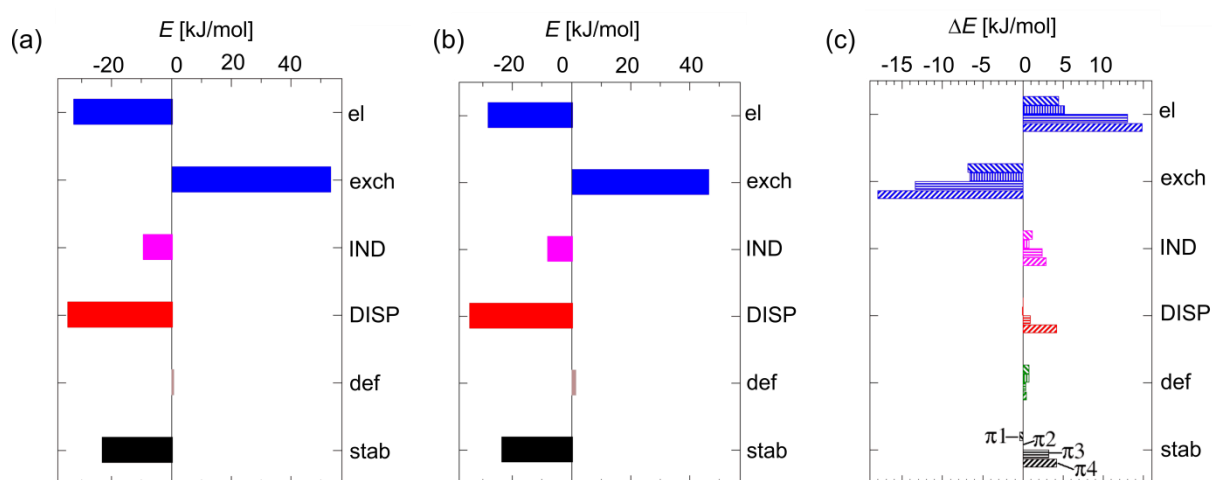


Fig. S4 DFT-SAPT energy contributions to the total stabilization energy of (a) the OH-O and (b) the OH- π 1 isomer and (c) the differences in these contributions for the various OH- π isomers as obtained for the B3LYP-D3(BJ) geometries.

Table S1 Relative electronic energies ΔE for calculated minimum structures at the B3LYP-D3(BJ)/def2-TZVP level; relative energies ΔE_0 include ZPE; scaled OH-stretching vibration $\tilde{\nu}$ (scaling factor = 0.9622), calculated IR intensity I , rotational constants A , B , C and components of the dipole moment μ_a, μ_b, μ_c for isomers OH-O and OH- π 1-4.

	$\Delta E/\text{kJ/mol}$	$\Delta E_0/\text{kJ/mol}$	$\tilde{\nu}/\text{cm}^{-1}$	$I/\text{km/mol}$	A/MHz	B/MHz	C/MHz	$\mu_a \mu_b \mu_c/\text{D}$
OH-O	-0.77	0.08	3580	251	435.1775	342.1914	217.2769	0.8 2.2 1.6
OH- π 1	0.00	0.00	3613	109	537.9754	294.5549	220.5395	0.7 0.6 0.1
OH- π 2	0.39	0.11	3606	118	535.0402	300.5749	221.7424	1.1 0.04 1.7
OH- π 3	4.91	4.58	3601	151	543.2928	282.2642	211.3234	1.8 0.3 0.2
OH- π 4	6.30	5.44	3606	152	586.0810	256.3124	203.6024	2.1 0.5 2.0
CH- π 1	10.5	9.4	3642	13	480.0505	304.7883	241.9050	
CH- π 2	10.6	9.5	3642	12	478.8069	305.7216	215.1915	
CH- π 3	11.1	9.8	3641	11	483.2966	301.5195	213.6017	

Table S2 Relative electronic energies ΔE for calculated minimum structures at the SCS-CC2/def2-TZVP level; relative energies ΔE_0 include ZPE; scaled OH-stretching vibration $\tilde{\nu}$ (scaling factor = 0.9686), calculated IR intensity I , rotational constants A, B, C and components of the dipole moment μ_a, μ_b, μ_c .

	$\Delta E/\text{kJ/mol}$	$\Delta E_0/\text{kJ/mol}$	$\tilde{\nu}/\text{cm}^{-1}$	$I/\text{km/mol}$	A/MHz	B/MHz	C/MHz	$\mu_a \mu_b \mu_c/\text{D}$
OH-O	-0.2	0.72	3588	195	433.4743	340.2644	216.4502	0.6 2.2 1.7
OH- π 1	0.00	0.00	3613	78	541.7249	288.7001	219.1483	0.8 0.3 0.006
OH- π 2	0.39	0.01	3603	90	533.9304	297.0943	220.0477	0.8 0.2 1.9
OH- π 3	4.95	4.32	3605	114	539.6264	281.2053	210.4543	1.9 0.3 0.3
OH- π 4	5.64	4.62	3607	115	581.8972	256.3226	203.5591	2.1 0.5 2.1

Table S3 Energy decompositions (kJ/mol) from a SAPT(0)/jun-cc-pVDZ analysis for the B3LYP-D3(BJ) geometries, in comparison for both DPE-*t*-BuOH and DPE-MeOH¹. E_{IND} and E_{DISP} are the sums of the individual contributions as defined in Section 3, which are given here also for better comparison with the results for the DPE-MeOH complex¹.

species	isomer	E_{int}	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-exch}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-exch}}^{(2)}$	$\delta(\text{HF})$
DPE- <i>t</i> -BuOH	OH-O	-29.36	-34.08	44.70	-9.53	-15.70	10.64	-30.46	-34.40	3.94	-4.46
	OH- π 1	-26.85	-29.39	41.89	-8.31	-14.07	9.72	-31.05	-35.05	4.00	-3.96
	OH- π 2	-26.16	-28.49	42.25	-8.85	-14.70	10.00	-31.06	-35.10	4.04	-4.15
DPE-MeOH	OH-O	-23.9	-30.5	34.5	-8.0			-19.8			
	OH- π	-22.8	-25.9	32.4	-7.3			-22.0			

Table S4 Stabilization energies E_{stab} for the SCS-CC2 geometries, all results in kJ/mol with MP2-F12 / SCS-MP2-F12 (aVTZ,CPC), and SAPT with aVDZ/aVTZ extrapolation of dispersion contributions.

	MP2	SCS-MP2	DFT-SAPT	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-excl}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-excl}}^{(2)}$	$\delta(\text{HF})$	E_{def}
OH-O	-32.32	-24.51	-23.51	-30.07	47.60	-8.37	-18.57	14.40	-33.11	-38.74	5.63	-4.20	0.44
OH- π 1	-31.48	-23.57	-24.93	-24.98	39.53	-7.03	-13.99	10.40	-32.26	-37.57	5.31	-3.44	0.82
OH- π 2	-31.41	-23.35	-23.99	-25.08	40.56	-7.61	-14.60	10.81	-32.53	-37.91	5.38	-3.82	0.67
OH- π 3	-27.68	-19.60	-20.58	-18.58	36.25	-6.44	-12.55	9.68	-32.31	-37.31	5.00	-3.57	0.51
OH- π 4	-26.05	-18.65	-19.51	-17.00	32.21	-5.99	-12.15	9.40	-29.23	-33.72	4.49	-3.24	0.49

Table S5 Stabilization energies E_{stab} for the B3LYP-D3(BJ) geometries, all results in kJ/mol with MP2-F12 / SCS-MP2-F12 (aVTZ,CPC), and SAPT with aVDZ/aVTZ extrapolation of dispersion contributions.

	MP2	SCS-MP2	DFT-SAPT	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-excl}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-excl}}^{(2)}$	$\delta(\text{HF})$	E_{def}
OH-O	-32.38	-24.27	-23.20	-32.80	53.12	-9.34	-21.02	16.39	-34.63	-40.75	6.12	-4.71	0.45
OH- π 1	-31.50	-22.99	-23.58	-28.33	46.28	-8.13	-16.36	12.46	-34.58	-40.55	5.97	-4.23	1.18
OH- π 2	-30.96	-22.41	-23.17	-27.59	46.52	-8.56	-16.74	12.60	-34.70	-40.70	6.00	-4.42	1.17
OH- π 3	-28.09	-18.93	-20.01	-19.82	39.75	-6.98	-13.89	10.81	-33.72	-39.10	5.38	-3.90	0.77
OH- π 4	-25.72	-18.05	-18.98	-18.02	35.11	-6.46	-13.34	10.40	-30.49	-35.30	4.81	-3.52	0.85

Table S6 Relative energy contributions compared to the OH-O isomer (kJ/mol) from a SAPT(0)/jun-cc-pVDZ analysis for the B3LYP-D3(BJ) geometries, in comparison for both DPE-*t*-BuOH and DPE-MeOH¹. E_{IND} and E_{DISP} are the sums of the individual contributions as defined in Section 3, which are given here also for better comparison with the results for the DPE-MeOH complex¹.

species	isomer	E_{int}	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-exch}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-exch}}^{(2)}$	$\delta(\text{HF})$
DPE- <i>t</i> -BuOH	OH-O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OH- π 1	2.51	4.69	-2.81	1.22	1.63	-0.92	-0.59	-0.65	0.06	0.50
	OH- π 2	3.20	5.59	-2.45	0.68	1.00	-0.64	-0.60	-0.70	0.10	0.31
DPE-MeOH	OH-O	0.00	0.00	0.00	0.00			0.00			
	OH- π	1.10	4.60	-2.10	0.70			-2.20			

Table S7 Relative energy contributions compared to the OH-O isomer for the SCS-CC2 geometries, all results in kJ/mol with MP2-F12 / SCS-MP2-F12 (aVTZ,CPC), and SAPT with aVDZ/aVTZ extrapolation of dispersion contributions.

	MP2	SCS-MP2	DFT-SAPT	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-excl}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-ex}}^{(2)}$	$\delta(\text{HF})$	E_{def}
OH-O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OH- π 1	0.84	0.94	-1.42	5.09	-8.07	1.34	4.58	-4.00	0.85	1.17	-0.32	0.76	0.38
OH- π 2	0.91	1.16	-0.48	4.99	-7.04	0.76	3.97	-3.59	0.58	0.83	-0.25	0.38	0.23
OH- π 3	4.64	4.91	2.93	11.49	-11.35	1.93	6.02	-4.72	0.80	1.43	-0.63	0.63	0.07
OH- π 4	6.27	5.86	4.00	13.07	-15.39	2.38	6.42	-5.00	3.88	5.02	-1.14	0.96	0.05

Table S8 Relative energy contributions compared to the OH-O isomer for the B3LYP-D3 geometries, all results in kJ/mol with MP2-F12 / SCS-MP2-F12 (aVTZ,CPC), and SAPT with aVDZ/aVTZ extrapolation of dispersion contributions.

	MP2	SCS-MP2	DFT-SAPT	$E_{\text{el}}^{(1)}$	$E_{\text{exch}}^{(1)}$	E_{IND}	$E_{\text{ind}}^{(2)}$	$E_{\text{ind-excl}}^{(2)}$	E_{DISP}	$E_{\text{disp}}^{(2)}$	$E_{\text{disp-ex}}^{(2)}$	$\delta(\text{HF})$	E_{def}
OH-O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OH- π 1	0.88	1.28	-0.38	4.47	-6.84	1.21	4.66	-3.93	0.05	0.20	-0.15	0.48	0.73
OH- π 2	1.42	1.86	0.03	5.21	-6.60	0.78	4.28	-3.79	-0.07	0.05	-0.12	0.29	0.72
OH- π 3	4.29	5.34	3.19	12.98	-13.37	2.36	7.13	-5.58	0.91	1.65	-0.74	0.81	0.32
OH- π 4	6.66	6.22	4.22	14.78	-18.01	2.88	7.68	-5.99	4.14	5.45	-1.31	1.19	0.40

Table S9 Relative electronic energies ΔE for calculated minimum structures at the SCS-CC2/def2-TZVP level in the first excited state; relative energies ΔE_0 include ZPE; scaled OH-stretching vibration $\tilde{\nu}$ (scaling factor = 0.9686), calculated IR intensity I , adiabatic excitation energy $E_{S_1 \leftarrow S_0, \text{adiab.}}$

	$\Delta E/\text{kJ/mol}$	$\Delta E_0/\text{kJ/mol}$	$\tilde{\nu}/\text{cm}^{-1}$	$I/\text{km/mol}$	$E_{S_1 \leftarrow S_0, \text{adiab.}}/\text{cm}^{-1}$
OH-O	4.13	4.32	3617	107	37616
OH- π 1	0.00	0.00	3583	110	37259
OH- π 2	1.78	1.43	3601	89	37360
OH- π 3	5.87	6.22	3568	144	37314
OH- π 4	6.58	5.53	3573	164	37328

Table S10 Calculated dissociation energies for different minimum structures obtained at the SCS-CC2/def2-TZVP level in the ground and first excited state; energies are given in kJ/mol.

	$D(S_0)$	$D(S_1)$	$D_0(S_0)$	$D_0(S_1)$
OH-O	28.22	27.46	24.58	24.42
OH- π 1	28.03	31.60	25.30	28.74
OH- π 2	27.65	29.82	25.29	27.31
OH- π 3	23.08	25.73	20.98	22.52
OH- π 4	22.39	25.02	20.68	23.21

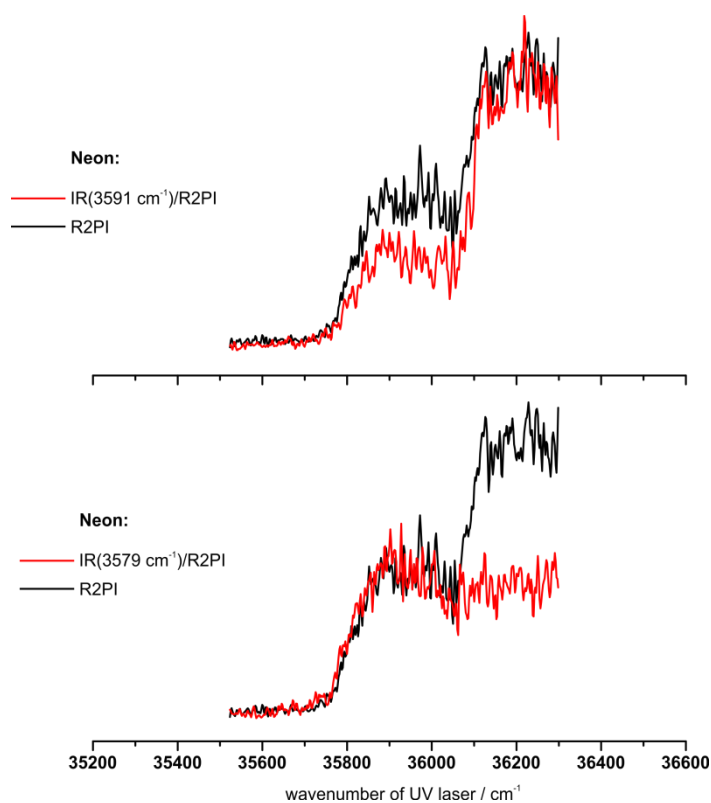


Fig. S5 IR_{fixed}/R2PI spectra (red) as well as the one color R2PI spectrum (black), carrier gas neon.

Table S11 Rotational transitions observed for the OH-O isomer of DPE-*t*-BuOH using broadband rotational spectroscopy.

J'	K _a '	K _c '	J''	K _a ''	K _c ''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}}-\nu_{\text{calc}}/\text{MHz}$	
3	1	2	←	2	0	2	2179.0803	-0.0062
3	2	1	←	2	1	1	2190.0926	0.0010
5	0	5	←	4	1	4	2300.0086	-0.0042
5	1	5	←	4	1	4	2300.4668	-0.0022
3	2	2	←	2	1	2	2301.6471	0.0011
5	1	5	←	4	0	4	2302.7382	-0.0043
4	2	3	←	3	1	2	2305.8414	-0.0051
3	3	1	←	2	2	0	2398.4353	0.0014
9	2	7	←	9	1	8	2401.9592	0.0023
9	3	7	←	9	2	8	2403.5786	-0.0064
4	3	1	←	3	3	0	2403.7120	0.0094
3	3	0	←	2	2	0	2424.2002	0.0002
4	2	2	←	3	2	1	2459.8093	0.0029
3	3	1	←	2	2	1	2463.7815	0.0004
3	3	0	←	2	2	1	2489.5457	-0.0014
5	1	4	←	4	2	3	2589.9479	-0.0039
5	2	4	←	4	2	3	2608.9706	-0.0012
5	2	3	←	4	3	2	2618.1395	-0.0049
6	0	6	←	5	1	5	2728.5619	-0.0112
6	1	6	←	5	0	5	2729.1060	-0.0091
4	3	2	←	3	2	1	2843.2412	0.0094
4	2	2	←	3	1	2	2875.7788	0.0027
4	1	3	←	3	0	3	2961.4037	-0.0004
4	3	1	←	3	2	1	2987.0488	0.0045
5	2	3	←	4	2	2	3001.5741	0.0042
6	3	3	←	5	4	2	3010.1795	0.0162
4	2	3	←	3	1	3	3015.0497	0.0055
6	1	5	←	5	2	4	3045.8398	0.0014
6	2	5	←	5	2	4	3050.5810	-0.0039
6	1	5	←	5	1	4	3064.8596	0.0011
6	2	5	←	5	1	4	3069.6046	-0.0003
4	3	2	←	3	2	2	3099.1665	0.0065
7	0	7	←	6	1	6	3156.3147	-0.0075
7	1	7	←	6	0	6	3156.4336	0.0102
5	3	3	←	4	2	2	3208.1640	-0.0020
6	2	4	←	5	3	3	3242.7265	-0.0124
4	3	1	←	3	2	2	3242.9693	-0.0031
4	4	1	←	3	3	0	3286.1381	-0.0020
4	4	0	←	3	3	0	3294.4956	-0.0024
4	4	1	←	3	3	1	3311.9261	0.0197
4	4	0	←	3	3	1	3320.2594	-0.0047

6	2	4	←	5	2	3	3449.3429	0.0076
7	1	6	←	6	2	5	3481.2040	-0.0108
7	2	6	←	6	2	5	3482.2662	-0.0128
7	2	6	←	6	1	5	3487.0233	-0.0021
6	3	4	←	5	2	3	3532.1080	-0.0005
8	0	8	←	7	1	7	3583.9201	0.0032
5	3	2	←	4	2	2	3608.6941	-0.0037
5	2	3	←	4	1	3	3635.3292	-0.0021
6	4	2	←	5	4	1	3640.0473	-0.0018
6	3	3	←	5	3	2	3703.0585	-0.0086
5	1	4	←	4	0	4	3737.1862	0.0052
5	2	4	←	4	1	4	3753.9331	0.0055
7	2	5	←	6	3	4	3765.3011	0.0167
5	4	2	←	4	3	1	3774.3623	-0.0016
5	3	3	←	4	2	3	3778.0927	-0.0028
5	4	1	←	4	3	1	3838.2841	-0.0048
7	2	5	←	6	2	4	3848.0488	-0.0089
7	3	5	←	6	2	4	3873.9931	0.0187
8	1	7	←	7	2	6	3910.4608	0.0027
8	2	7	←	7	2	6	3910.6835	0.0034
8	1	7	←	7	1	6	3911.5251	0.0029
8	2	7	←	7	1	6	3911.7495	0.0052
5	4	2	←	4	3	2	3918.1811	0.0047
5	4	1	←	4	3	2	3982.1004	-0.0009
9	0	9	←	8	1	8	4011.4836	-0.004
5	5	1	←	4	4	0	4159.8215	-0.0055
6	4	3	←	5	3	2	4160.8642	0.0042
5	5	0	←	4	4	0	4162.2513	-0.0032
5	5	1	←	4	4	1	4168.1766	-0.0082
5	5	0	←	4	4	1	4170.6057	-0.0066
5	3	2	←	4	2	3	4178.6317	0.0044
8	2	6	←	7	3	5	4226.9448	0.0116
7	3	4	←	6	3	3	4228.7942	0.0003
8	3	6	←	7	3	5	4233.8719	0.0109
8	3	6	←	7	2	5	4259.7807	0.0030
6	3	3	←	5	2	3	4310.1912	-0.0040
9	1	8	←	8	2	7	4338.2209	0.0020
9	2	8	←	8	1	7	4338.4795	-0.0055
6	4	2	←	5	3	2	4396.8769	-0.0011
6	2	4	←	5	1	4	4430.8779	-0.0048
10	0	10	←	9	1	9	4439.0545	-0.0014
7	4	4	←	6	3	3	4468.3673	0.0118
6	3	4	←	5	2	4	4494.6358	-0.0002
6	1	5	←	5	0	5	4499.7537	0.0006
6	2	5	←	5	1	5	4504.0479	0.0045

6	4	3	←	5	3	3	4561.3977	0.0059	8	5	4	←	7	4	4	6018.6262	-0.0022
9	2	7	←	8	3	6	4664.0167	-0.0049	13	1	12	←	12	2	11	6048.1416	-0.0035
9	3	7	←	8	3	6	4665.6947	0.0008	8	6	2	←	7	5	2	6130.6825	-0.0043
9	2	7	←	8	2	6	4670.9479	-0.0016	11	4	7	←	10	5	6	6132.0736	0.0358
9	3	7	←	8	2	6	4672.6228	0.0010	8	6	3	←	7	5	3	6198.4000	-0.0091
6	5	1	←	5	4	1	4715.9003	0.0043	8	6	2	←	7	5	3	6244.3688	0.0162
8	4	5	←	7	3	4	4751.6506	0.0062	11	5	7	←	10	4	6	6271.4336	0.0071
6	5	2	←	5	4	2	4756.2069	0.0074	12	3	9	←	11	4	8	6277.6374	-0.0096
6	5	1	←	5	4	2	4779.8226	0.0017	12	4	9	←	11	4	8	6278.1673	-0.0048
6	4	2	←	5	3	3	4797.4077	-0.0021	12	4	9	←	11	3	8	6280.3831	-0.0015
11	0	11	←	10	1	10	4866.6121	-0.0115	8	7	2	←	7	6	1	6457.1603	-0.0036
9	3	6	←	8	4	5	4946.4439	0.0130	8	7	1	←	7	6	1	6459.5068	-0.0047
6	6	1	←	5	5	0	5025.7072	0.0022	8	7	2	←	7	6	2	6464.8974	-0.0099
6	6	0	←	5	5	0	5026.3608	-0.0033	8	7	1	←	7	6	2	6467.2477	-0.0072
6	6	1	←	5	5	1	5028.1329	0.0004	9	6	4	←	8	5	3	6474.1454	0.0054
6	6	0	←	5	5	1	5028.7969	0.0053	14	1	13	←	13	1	12	6475.6501	-0.0044
10	2	8	←	9	3	7	5093.4367	-0.0059	15	0	15	←	14	0	14	6576.8797	0.0121
10	3	8	←	9	2	7	5095.4828	-0.0076	12	5	8	←	11	4	7	6641.7812	0.0005
7	5	3	←	6	4	2	5132.7190	-0.0005	9	6	3	←	8	5	3	6649.2970	-0.0071
11	1	10	←	10	2	9	5193.1669	0.0017	13	3	10	←	12	4	9	6704.6772	-0.0036
7	2	5	←	6	1	5	5214.0783	-0.0038	13	4	10	←	12	4	9	6704.8016	0.0026
7	3	5	←	6	2	5	5235.2524	0.0002	13	3	10	←	12	3	9	6705.1969	-0.0091
7	1	6	←	6	0	6	5256.6890	0.0039	13	4	10	←	12	3	9	6705.3186	-0.0054
7	2	6	←	6	1	6	5257.6683	0.0048	9	5	5	←	8	4	5	6709.8369	-0.0069
7	5	3	←	6	4	3	5368.7432	0.0054	9	4	6	←	8	3	6	6710.9020	-0.0099
10	4	7	←	9	3	6	5450.5682	0.0026	9	2	7	←	8	1	7	6740.3934	-0.0044
8	5	4	←	7	4	3	5461.2808	0.0071	9	3	7	←	8	2	7	6741.8430	-0.0050
7	5	2	←	6	4	3	5482.4110	0.0076	14	2	12	←	13	3	11	6802.6806	0.0004
11	2	9	←	10	3	8	5520.9620	-0.0002	9	6	4	←	8	5	4	6816.1793	-0.0045
11	3	9	←	10	3	8	5521.0431	0.0008	9	7	3	←	8	6	2	6998.5350	0.0004
11	2	9	←	10	2	8	5521.3315	-0.0064	9	7	2	←	8	6	2	7014.9588	0.0009
11	3	9	←	10	2	8	5521.4184	0.0005	13	4	9	←	12	5	8	7034.5275	-0.0081
7	6	2	←	6	5	1	5583.5282	-0.0042	9	7	3	←	8	6	3	7044.4788	0.0008
7	6	1	←	6	5	1	5591.2787	0.0029	13	5	9	←	12	4	8	7047.2184	-0.0042
7	6	2	←	6	5	2	5607.1444	-0.0093	9	7	2	←	8	6	3	7060.8968	-0.0044
7	6	1	←	6	5	2	5614.8958	-0.0013	14	4	11	←	13	3	10	7131.5712	0.0014
12	1	11	←	11	2	10	5620.6414	-0.0052	15	2	13	←	14	3	12	7230.0336	0.0030
13	0	13	←	12	1	12	5721.7534	0.0005	9	8	2	←	8	7	1	7323.1492	0.0062
11	4	8	←	10	3	7	5859.4129	-0.0002	9	8	1	←	8	7	1	7323.8236	0.0069
7	7	1	←	6	6	0	5888.7241	-0.0009	9	8	2	←	8	7	2	7325.4895	-0.0010
7	7	1	←	6	6	1	5889.3821	-0.0020	9	8	1	←	8	7	2	7326.1609	-0.0033
7	7	0	←	6	6	1	5889.5558	0.0005	16	1	15	←	15	2	14	7330.6840	-0.0026
12	3	10	←	11	2	9	5948.2586	0.0006	10	6	5	←	9	5	5	7472.4723	-0.0124
8	2	6	←	7	1	6	5980.9629	-0.0076	10	2	8	←	9	1	8	7497.0662	-0.0055
8	3	6	←	7	2	6	5986.8319	-0.0022	10	3	8	←	9	2	8	7497.4013	-0.0020
8	1	7	←	7	0	7	6011.7993	0.0000	10	1	9	←	9	0	9	7520.5694	0.0053
8	2	7	←	7	1	7	6012.0110	0.0049	10	7	3	←	9	6	3	7539.1102	0.0046

10	7	4	←	9	6	4	7638.4041	0.0058
16	2	14	←	15	3	13	7657.4254	0.0052
10	8	2	←	9	7	2	7889.0416	0.0038
15	4	11	←	14	5	10	7889.3683	-0.0006

15	5	11	←	14	4	10	7890.1883	0.0057
10	8	3	←	9	7	3	7900.0637	0.0046
10	8	2	←	9	7	3	7905.4645	0.0033
RMS								6.600kHz

Table S12 Rotational transitions observed for the OH- π 1 isomer of DPE-*t*-BuOH using broadband rotational spectroscopy.

J'	K _a '	K _c '		J''	K _a ''	K _c ''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}}-\nu_{\text{calc}}/\text{MHz}$
4	3	2	←	3	3	1	2037.0887	-0.0047
4	3	1	←	3	3	0	2045.9123	0.0041
4	2	2	←	3	2	1	2114.2635	0.0026
9	4	5	←	8	5	4	2249.9962	0.0107
5	1	5	←	4	1	4	2299.2081	0.0060
5	2	4	←	4	2	3	2490.3503	-0.0060
5	3	3	←	4	3	2	2549.8483	-0.0087
5	3	2	←	4	3	1	2579.1855	0.0048
5	2	3	←	4	2	2	2673.1364	0.0097
6	0	6	←	5	0	5	2761.2173	-0.0167
6	2	5	←	5	2	4	2965.9580	-0.0045
5	3	2	←	5	0	5	3036.2823	0.0085
6	3	4	←	5	3	3	3059.9410	-0.0008
6	4	3	←	5	4	2	3065.0883	0.0040
6	4	2	←	5	4	1	3070.0916	0.0054
6	3	3	←	5	3	2	3130.9009	0.0060
7	1	7	←	6	1	6	3178.8126	0.0065
7	0	7	←	6	0	6	3189.1725	-0.0086
8	2	6	←	7	3	5	3429.7884	-0.0110
7	2	6	←	6	2	5	3431.4048	-0.0010
7	6	2	←	6	6	1	3563.2552	0.0103
7	3	5	←	6	3	4	3564.1269	-0.0022
7	5	3	←	6	5	2	3572.8207	0.0056
7	5	2	←	6	5	1	3573.4954	0.0071
7	4	4	←	6	4	3	3584.8800	0.0062
7	4	3	←	6	4	2	3600.7923	0.0027
8	1	8	←	7	1	7	3614.3752	0.0071
8	0	8	←	7	0	7	3619.3181	-0.0054
8	2	7	←	7	2	6	3887.2833	-0.0011
9	1	9	←	8	1	8	4048.6551	0.0056
9	0	9	←	8	0	8	4050.9157	0.0029
8	3	6	←	7	3	5	4059.6019	-0.0058
8	5	4	←	7	5	3	4093.5151	0.0082

8	4	5	←	7	4	4	4105.0018	-0.0045
10	1	10	←	9	1	9	4482.2740	-0.0110
10	0	10	←	9	0	9	4483.2746	-0.0118
9	3	7	←	8	3	6	4544.4470	0.0036
9	6	4	←	8	6	3	4599.2536	-0.0025
9	6	3	←	8	6	2	4599.6136	-0.0010
9	5	5	←	8	5	4	4617.3143	-0.0051
9	4	6	←	8	4	5	4622.6356	0.0011
9	5	4	←	8	5	3	4625.4563	-0.0022
13	8	5	←	14	4	10	4696.6614	-0.0013
9	4	5	←	8	4	4	4708.7330	-0.0125
10	1	9	←	9	1	8	4802.4481	-0.0122
10	3	8	←	9	3	7	5017.8420	0.0142
10	6	5	←	11	1	10	5018.1737	0.0080
10	7	4	←	9	7	3	5105.2866	0.0142
10	6	5	←	9	6	4	5122.0404	-0.0009
10	4	7	←	9	4	6	5134.5069	0.0169
10	5	6	←	9	5	5	5143.2968	0.0032
12	1	12	←	11	0	11	5349.1441	0.0147
9	3	6	←	9	1	9	5359.0205	-0.0055
7	6	2	←	8	2	7	5531.7816	0.0005
9	6	3	←	9	4	6	5599.2594	0.0042
11	8	4	←	10	8	3	5611.8369	0.0113
11	7	5	←	10	7	4	5626.4034	-0.0048
11	7	4	←	10	7	3	5626.5860	-0.0030
11	4	8	←	10	4	7	5637.5344	0.0011
11	6	6	←	10	6	5	5648.1712	-0.0174
11	6	5	←	10	6	4	5652.1803	-0.0129
12	2	10	←	11	2	9	6008.2201	-0.0132
12	4	9	←	11	4	8	6129.5237	0.0160
12	7	6	←	11	7	5	6150.6262	-0.0148
9	5	5	←	9	2	8	6793.0308	-0.0124
14	5	10	←	13	5	9	7220.9031	0.0080
RMS								8.515kHz

Remark on the number and intensities of rotational transitions vs. the magnitudes of the dipole moment components

If a particular type of transition is stronger, we will “on average” most likely also detect a larger number of transitions. Note that in a chirped pulse experiment the intensity of a rotational transition scales, among other things, with the square of the dipole moment. This implies that an increase or decrease of a factor of two in the dipole moment will lead, in general, to a factor of four increase or decrease in the spectral intensity. This is also why we can relate the number of transitions of a particular type with the magnitude of the corresponding dipole moment components. Weak dipole-moment components will lead to fewer rotational transitions of the corresponding type than stronger dipole-moment components.

In addition to that, the number of rotational transitions observed for a certain spectrometer range also depends on the rotational constants. However, there are mainly two aspects why we think that the dipole-moment component effect is dominant: a) We cover a broad frequency range of 6 GHz, which for the rather small rotational constants of these complexes ($A, B, C < 500$ MHz) is quite a lot, and b) the rotational constants are very similar for the two isomers discussed here, so that the effect introduced by the rotational constants should be very comparable for both isomers. Nevertheless, we see a clear difference in the number of different types of rotational transitions, which can thus mostly be attributed to the differences in dipole moment components.

Remark on the preparation temperature vs. temperature in the supersonic jet

The preparation temperature of the compounds has no significant influence on the cluster temperatures, as there are no metastable monomer conformations and the cluster formation happens under supersonic jet conditions. Therefore calculations were performed at 0 K, which is common practice for comparison with molecular beam experiments.

Reference

- 1 C. Medcraft, S. Zinn, M. Schnell, A. Poblitzki, J. Altnöder, M. Heger, M. A. Suhm, D. Bernhard, A. Stamm, F. Dietrich, M. Gerhards, *Phys. Chem. Chem. Phys.*, 2016, **18**, 25975–25983.