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

Electronic Supporting Information

Rovibronic Signatures of Molecular Aggregation in the Gas Phase: Subtle Homochirality Trends in the Dimer, Trimer and Tetramer of Benzyl Alcohol

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COMPUTATIONAL METHODS

Gaussian16[1] keywords for the B3LYP-D3(BJ)/may-cc-pVTZ calculation

```
# B3LYP EmpiricalDispersion=GD3BJ may-cc-pVTZ Integral(Grid=UltraFineGrid)
opt=tight freq=(vibrot,raman) output=pickett prop=EFG
```

Calculation of Raman cross sections for spectral simulation

In a first step, the Raman activities *A* and depolarization ratios *P* from the Gaussian16 calculation output are converted into the derivatives of the isotropic and anisotropic polarizability α' and γ' according to:

$$\alpha'^2 = \frac{A}{45}\left(1 - \frac{7P}{3P+3}\right)$$

$$\gamma'^2 = \frac{A \cdot P}{3P+3}$$

Detection sensitivity of our setup for differently polarized light is accounted for by an empirically determined polynomial.[2] For $\tilde{\nu}$ shifted harmonic values are used.

$$\begin{aligned} f(\tilde{\nu}) = {} & 1.7654 \\ & +0.4316 \cdot 10^{-13}\,\mathrm{cm}^4 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^4 \\ & -1.1285 \cdot 10^{-16}\,\mathrm{cm}^5 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^5 \\ & -0.1278 \cdot 10^{-19}\,\mathrm{cm}^6 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^6 \\ & +0.1926 \cdot 10^{-22}\,\mathrm{cm}^7 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^7 \\ & +0.1029 \cdot 10^{-26}\,\mathrm{cm}^8 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^8 \\ & -1.1527 \cdot 10^{-30}\,\mathrm{cm}^9 \cdot \left(\tilde{\nu} - 2000\,\mathrm{cm}^{-1}\right)^9 \end{aligned}$$

Raman cross sections $\sigma(\tilde{\nu})$ are finally obtained using the laser wavelength λ_{Laser} = 532.27 nm.

$$\sigma(\tilde{\nu}) = \frac{2\pi^2 h \lambda_{\mathrm{Laser}}^{-1}}{45c} \cdot \frac{\left(\lambda_{\mathrm{Laser}}^{-1} - \tilde{\nu}\right)^3}{\tilde{\nu}} \cdot \left(45\alpha'^2 + 4\gamma'^2 + \frac{3\gamma'^2}{f(\tilde{\nu})}\right)$$

Simulation of IR/UV spectra

Harmonic wavenumber values were extracted from the Gaussian16 output calculations. A correction factor of 0.957 was used to account for anharmonicity of wavenumber values computed at B3LYP-D3(BJ)/may-cc-pVTZ level. To reproduce the experimental spectrum bandwidth, first, each mode was represented by a Lorentzian function, with a FWMH of 5 cm^{-1}. Then, to include the experimental band broadening due to the laser (Gaussian profile of ~6 cm^{-1} FWHM), the theoretical spectrum was convoluted with a Gaussian function of 6 cm^{-1}. Finally, the band broadening due to hydrogen bond formation or to inefficient cooling of the low vibrational energy modes was simulated using a Gaussian function with a FWHM of 10 cm^{-1} for those OH vibrational modes down to 3550 cm^{-1}, of 15 cm^{-1} for those modes between 3400–3550 cm^{-1} and of 30 cm^{-1} for OH wavenumbers below 3400 cm^{-1}.

Figure S1. Experimental IR/UV spectrum of BnOH, compared to the computed predictions for the *gauche* and *trans* conformations, at B3LYP-ED=GD3BJ/6-311++G(d,p) level. For harmonic approximation, a scaling factor of 0.954 was used to account for anharmonicity. The anharmonic frequencies were computed using the Gaussian Freq=anharm keyword.

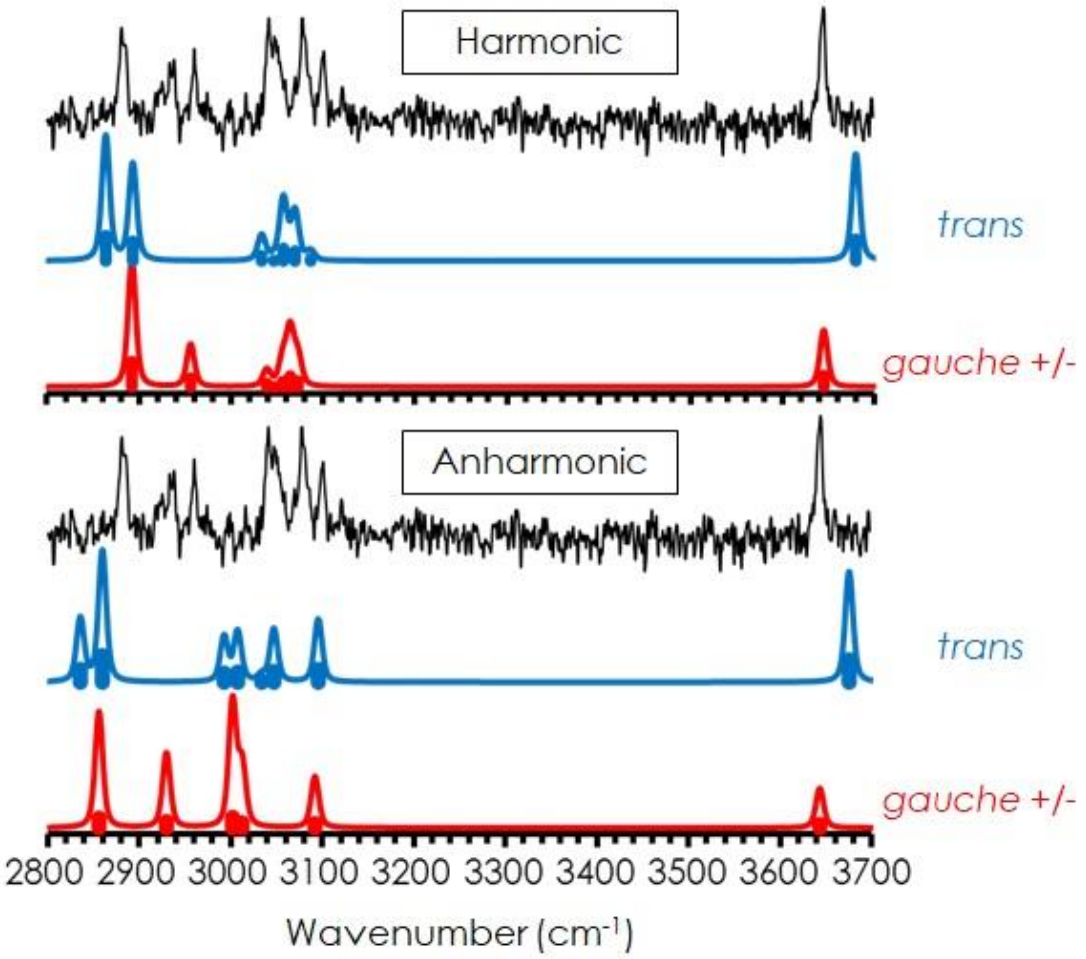


Figure S2. FTIR and Raman of BnOH in the OH stretching range with band positions and cluster size assignments (M: monomer, D: dimer, Tr: trimer, Te: tetramer, >Te: larger than tetramer).

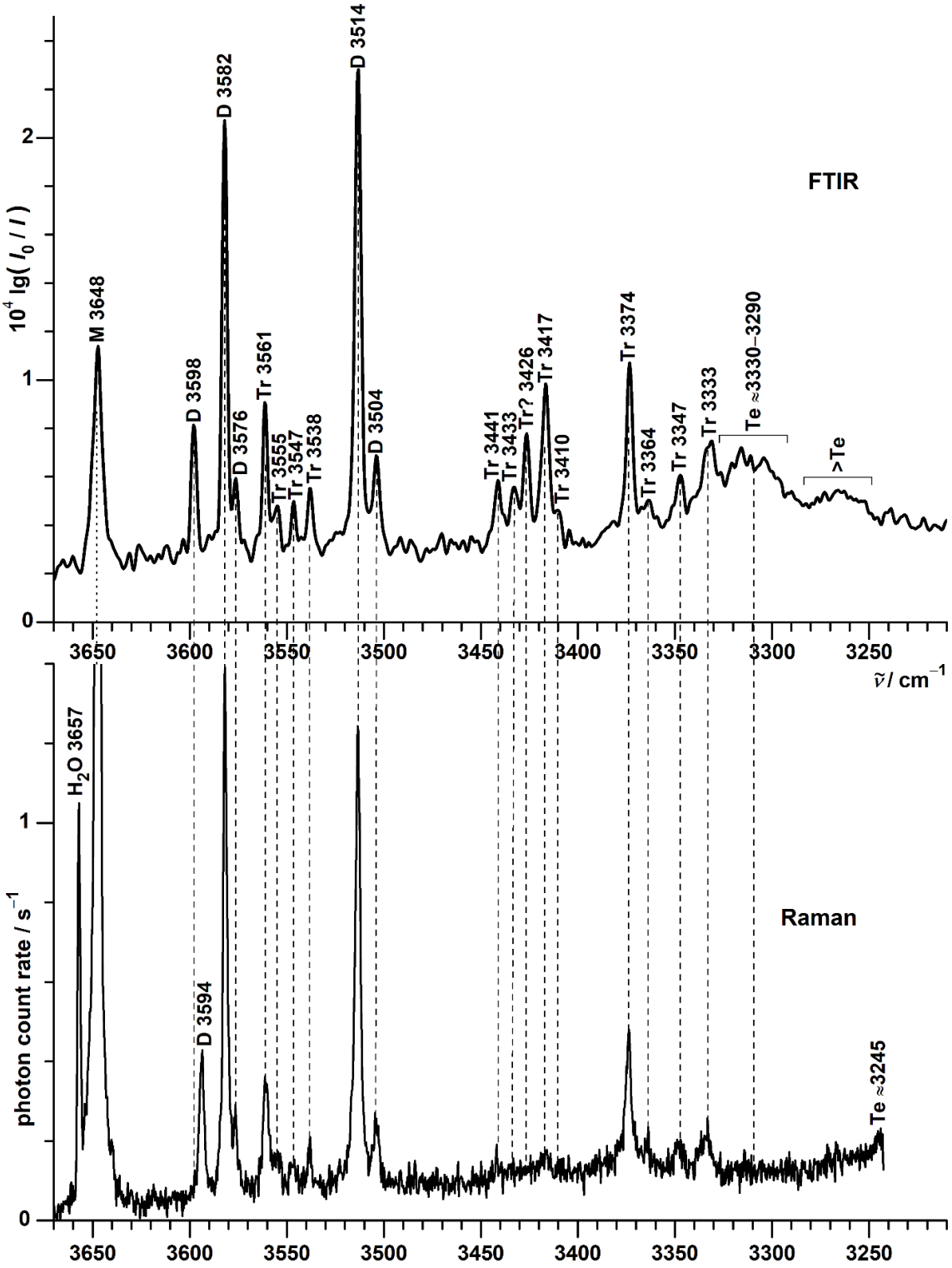


Figure S3. 3D NCI plots of the most relevant $(BnOH)_n$, n = 1–2 species.

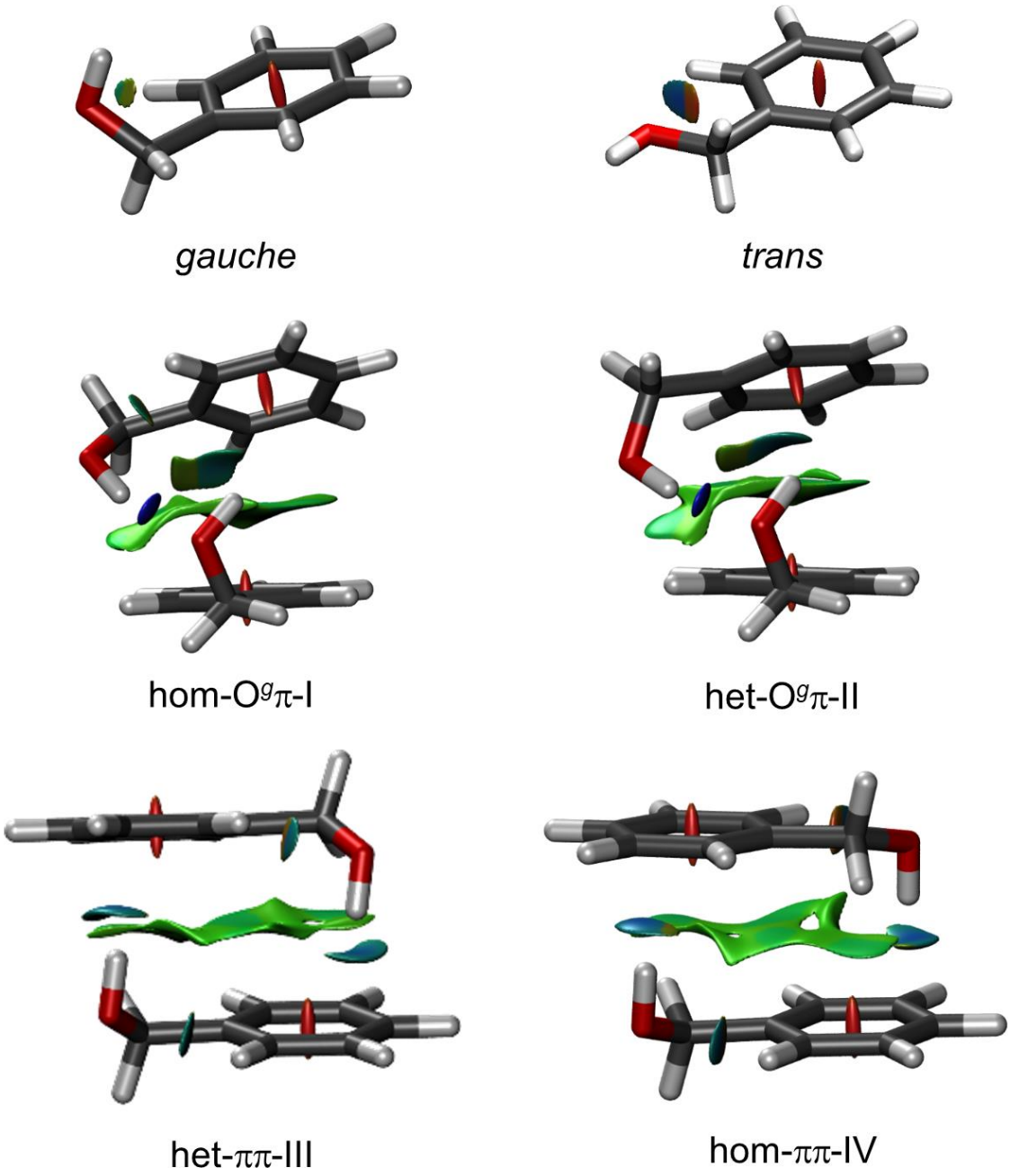
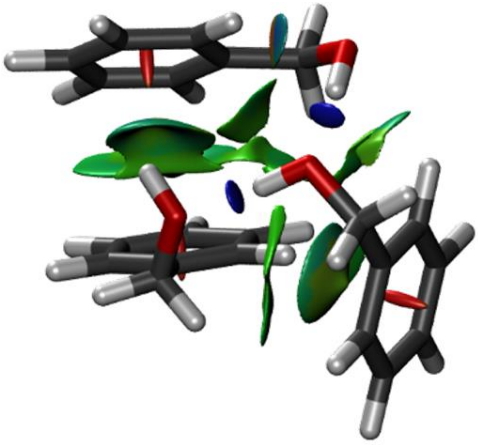
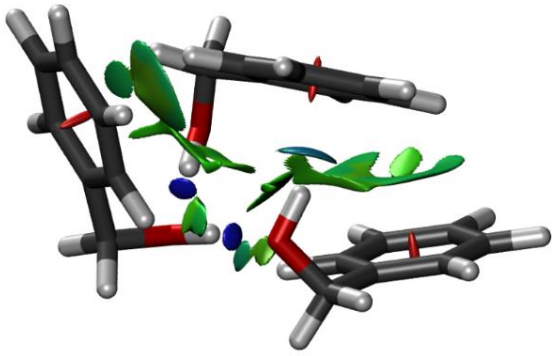


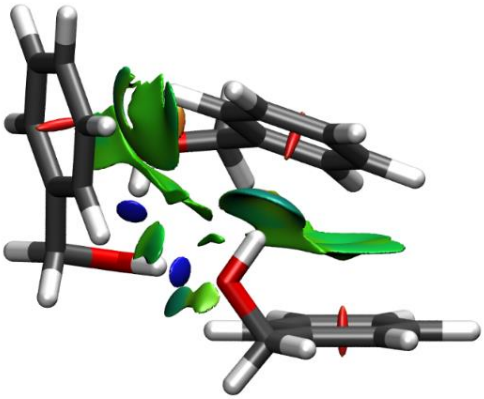
Figure S4. 3D NCI plots of the most relevant $(BnOH)_n$, n = 3–4 species.



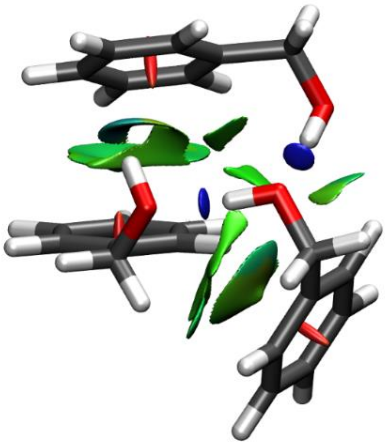
homhom-$O^gO^g\pi$-I



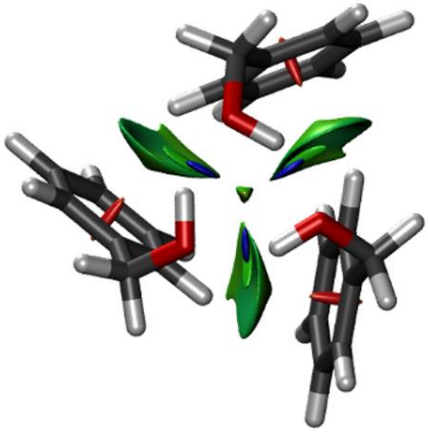
homhet-$O^gO^g\pi$-II



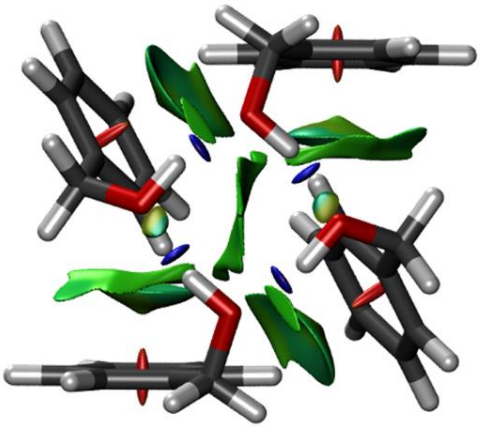
hethet-$O^gO^g\pi$-III



hethom-$O^gO^g\pi$-IV



homhom-$O^gO^gO^g$-XI



homhomhom-$O^gO^gO^gO^g$-I

Figure S5. Comparison between RDG vs sign (λ_2)ρ diagrams of the two BnOH monomers (upper diagram) and of the two most stable BnOH dimers (center diagram), as well as between hom-O$^g\pi$-I and het-$\pi\pi$-III isomers (lower diagram).

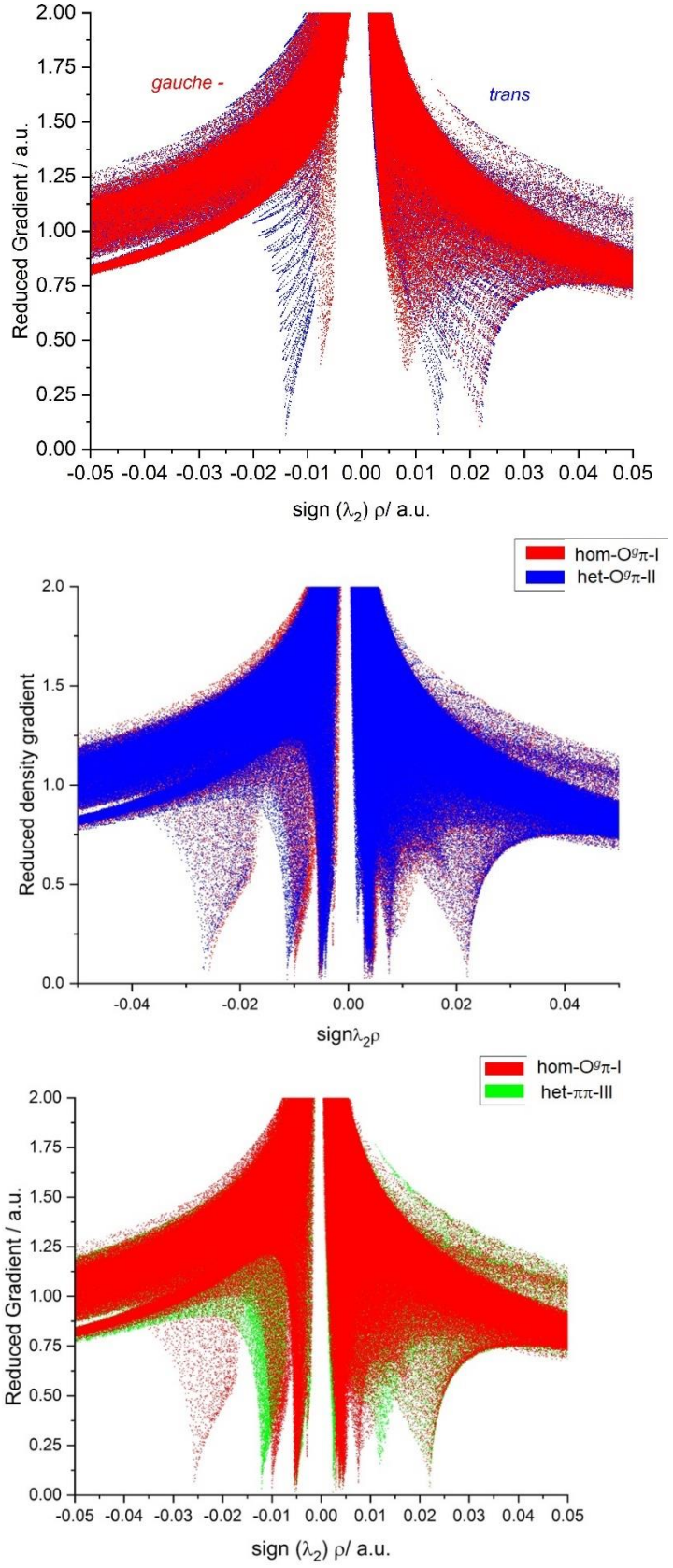


Table S1. Observed rotational transitions of the benzyl alcohol dimer (quantum numbers: $J_{K-1,K+1}$), together with the (observed-calculated, O.-C.) residuals for the fit of Table 1 and frequency uncertainties (Unc.).

J	K_{-1}	K_{+1}	*J*	K_{-1}	K_{+1}	*Freq.*	*O.-C.*	Unc.
3	0	3	2	1	2	2077.4454	-0.0001	0.020
8	4	4	8	3	5	2088.0355	-0.0002	0.020
9	2	8	9	1	9	2121.6743	-0.0005	0.020
10	3	8	10	2	9	2131.0862	0.0000	0.020
7	4	3	7	3	4	2154.6743	-0.0009	0.020
6	4	2	6	3	3	2196.3684	0.0007	0.020
5	4	1	5	3	2	2219.4473	0.0018	0.020
6	4	3	6	3	4	2228.7067	-0.0002	0.020
7	4	4	7	3	5	2230.5732	-0.0081	0.020
5	4	2	5	3	3	2230.6863	0.0038	0.020
4	4	0	4	3	1	2230.8000	0.0373	0.020
4	4	1	4	3	2	2233.6391	-0.0083	0.020
8	4	5	8	3	6	2240.3261	0.0000	0.020
10	1	9	10	0	10	2243.9213	-0.0026	0.020
15	3	12	15	2	13	2255.2618	-0.0026	0.020
9	4	6	9	3	7	2262.7144	0.0000	0.020
3	1	3	2	1	2	2273.7259	-0.0008	0.020
5	2	4	4	3	1	2283.3301	-0.0007	0.020
10	4	7	10	3	8	2302.6847	0.0004	0.020
11	3	9	11	2	10	2306.1608	0.0050	0.020
3	0	3	2	0	2	2329.1252	-0.0002	0.020
14	5	9	14	4	10	2339.7947	-0.0124	0.020
3	2	2	2	2	1	2351.6227	-0.0002	0.020
10	2	9	10	1	10	2358.0851	0.0041	0.020
11	4	8	11	3	9	2364.7086	-0.0013	0.020
3	2	1	2	2	0	2374.1137	-0.0002	0.020
4	1	3	3	2	2	2405.8440	0.0022	0.020
3	1	2	2	1	1	2422.2813	0.0007	0.020
12	4	9	12	3	10	2452.2620	0.0038	0.020
13	2	11	13	1	12	2462.8676	0.0108	0.020
5	2	3	4	3	2	2464.8206	-0.0006	0.020
5	1	5	4	2	2	2473.6344	-0.0031	0.020
13	5	8	13	4	9	2483.9586	-0.0039	0.020
6	3	4	5	4	1	2493.5120	-0.0008	0.020
2	2	1	1	1	0	2504.1817	0.0003	0.020
12	3	10	12	2	11	2504.4011	0.0037	0.020
3	1	3	2	0	2	2525.4072	0.0005	0.020
11	1	10	11	0	11	2534.2355	-0.0006	0.020
2	2	0	1	1	1	2559.5871	0.0007	0.020
13	4	10	13	3	11	2567.3970	-0.0023	0.020
11	2	10	11	1	11	2604.4806	-0.0032	0.020
12	5	7	12	4	8	2607.5465	0.0007	0.020
11	5	6	11	4	7	2702.3391	-0.0001	0.020
14	4	11	14	3	12	2710.6143	0.0040	0.020
13	3	11	13	2	12	2722.2274	-0.0015	0.020
10	5	5	10	4	6	2768.7906	0.0012	0.020
9	5	4	9	4	5	2812.3447	0.0017	0.020
12	1	11	12	0	12	2816.1188	-0.0017	0.020
3	1	2	2	0	2	2822.9401	0.0041	0.020
11	5	7	11	4	8	2826.1948	0.0020	0.020
12	5	8	12	4	9	2828.7241	-0.0001	0.020
10	5	6	10	4	7	2831.6576	0.0012	0.020

8	5	3	8	4	4	2839.6119	0.0025	0.020
9	5	5	9	4	6	2840.9960	0.0006	0.020
13	5	9	13	4	10	2844.0740	0.0017	0.020
8	5	4	8	4	5	2851.1330	-0.0009	0.020
7	5	2	7	4	3	2856.1776	0.0042	0.020
12	2	11	12	1	12	2857.7416	0.0057	0.020
7	5	3	7	4	4	2860.1339	-0.0073	0.020
6	5	1	6	4	2	2866.0112	0.0093	0.020
6	5	2	6	4	3	2867.0904	-0.0189	0.020
5	5	0	5	4	1	2871.6640	0.0008	0.020
5	5	1	5	4	2	2871.8563	-0.0320	0.020
14	5	10	14	4	11	2877.2301	-0.0078	0.020
15	4	12	15	3	13	2880.7661	-0.0149	0.020
4	0	4	3	1	3	2885.8366	0.0002	0.020
15	5	11	15	4	12	2932.8071	-0.0016	0.020
14	3	12	14	2	13	2955.6601	-0.0041	0.020
6	1	6	5	2	3	2988.5268	-0.0070	0.020
6	2	5	5	3	2	3017.2411	0.0000	0.020
4	1	4	3	1	3	3025.8217	0.0006	0.020
4	0	4	3	0	3	3082.1181	0.0005	0.020
15	2	13	15	1	14	3090.6011	-0.0044	0.020
4	2	3	3	2	2	3130.9990	0.0017	0.020
4	3	2	3	3	1	3145.8353	0.0028	0.020
4	3	1	3	3	0	3148.3228	-0.0007	0.020
4	2	2	3	2	1	3184.3284	0.0014	0.020
4	1	3	3	1	2	3221.9570	0.0010	0.020
4	1	4	3	0	3	3222.1028	0.0004	0.020
15	6	9	15	5	10	3228.3385	-0.0070	0.020
3	2	2	2	1	1	3238.3962	0.0014	0.020
3	2	1	2	1	1	3266.6366	0.0045	0.020
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5	1	4	4	2	3	3288.5906	0.0012	0.020
6	3	3	6	0	6	3295.9469	-0.0077	0.020
14	6	8	14	5	9	3317.9247	0.0001	0.020
6	2	4	5	3	3	3355.4890	0.0020	0.020
7	3	4	6	4	3	3363.8853	0.0011	0.020
13	6	7	13	5	8	3381.3767	-0.0008	0.020
3	2	2	2	1	2	3387.3740	0.0037	0.020
15	6	10	15	5	11	3398.7866	-0.0007	0.020
14	6	9	14	5	10	3412.0603	0.0000	0.020
3	2	1	2	1	2	3415.6082	0.0006	0.020
7	1	7	6	2	4	3422.5127	0.0019	0.020
12	6	6	12	5	7	3425.2225	0.0003	0.020
13	6	8	13	5	9	3429.5251	-0.0019	0.020
8	4	5	7	5	2	3447.7958	0.0005	0.020
12	6	7	12	5	8	3447.9372	0.0055	0.020
11	6	5	11	5	6	3455.2929	0.0037	0.020
8	4	4	7	5	3	3459.7967	-0.0001	0.020
11	6	6	11	5	7	3465.0810	-0.0003	0.020
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9	6	4	9	5	5	3491.4901	-0.0093	0.020
7	6	2	7	5	3	3506.6947	-0.0061	0.020
6	6	0	6	5	1	3510.9635	0.0085	0.020
6	6	1	6	5	2	3510.9635	-0.0065	0.020
7	3	4	7	0	7	3571.8034	-0.0030	0.020

5	0	5	4	1	4	3682.1156	0.0003	0.020
7	2	6	6	3	3	3714.0986	0.0009	0.020
4	1	3	3	0	3	3715.7647	-0.0017	0.020
5	1	5	4	1	4	3774.0239	-0.0002	0.020
8	1	8	7	2	5	3776.9481	0.0013	0.020
5	0	5	4	0	4	3822.1002	0.0002	0.020
5	2	4	4	2	3	3906.5723	0.0000	0.020
5	1	5	4	0	4	3914.0092	0.0003	0.020
5	4	2	4	4	1	3932.1189	0.0080	0.020
5	4	1	4	4	0	3932.3004	-0.0117	0.020
5	3	3	4	3	2	3935.0775	0.0016	0.020
5	3	2	4	3	1	3943.6295	0.0002	0.020
4	2	3	3	1	2	3947.1122	0.0006	0.020
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3	3	0	2	2	0	3951.7936	0.0016	0.020
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8	7	2	8	6	3	4146.2100	0.0016	0.020
8	7	1	8	6	3	4146.2100	0.0015	0.020
7	7	0	7	6	1	4149.9622	-0.0145	0.020
7	7	1	7	6	2	4149.9622	-0.0154	0.020
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7	2	5	6	3	4	4275.0717	-0.0005	0.020
4	2	2	3	1	3	4326.2044	-0.0033	0.020
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6	0	6	5	0	5	4554.0388	-0.0024	0.020
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6	2	5	5	2	4	4677.5368	-0.0026	0.020
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6	4	3	5	4	2	4722.4504	0.0039	0.020
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6	4	2	5	4	1	4723.3425	0.0000	0.020
6	3	4	5	3	3	4724.4177	-0.0042	0.020
4	3	1	3	2	1	4726.0094	0.0078	0.020
6	3	3	5	3	2	4746.4251	0.0046	0.020
4	3	2	3	2	2	4751.3407	0.0119	0.020
4	3	1	3	2	2	4754.2434	0.0045	0.020
12	8	5	12	7	5	4766.1392	0.0037	0.020
12	8	4	12	7	5	4766.1392	0.0029	0.020
12	8	5	12	7	6	4766.1392	-0.0352	0.020
12	8	4	12	7	6	4766.1392	-0.0360	0.020
11	8	4	11	7	4	4774.4289	0.0089	0.020
11	8	3	11	7	4	4774.4289	0.0087	0.020
11	8	4	11	7	5	4774.4289	-0.0014	0.020
11	8	3	11	7	5	4774.4289	-0.0016	0.020
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10	8	3	10	7	3	4780.7629	0.0162	0.020
10	8	3	10	7	4	4780.7629	0.0139	0.020
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9	8	1	9	7	2	4785.4646	-0.0018	0.020
9	8	2	9	7	2	4785.4646	-0.0018	0.020
9	8	1	9	7	3	4785.4646	-0.0022	0.020
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8	8	0	8	7	1	4788.8758	-0.0084	0.020
8	8	1	8	7	2	4788.8758	-0.0085	0.020
6	1	5	5	1	4	4794.3955	0.0050	0.020
5	2	3	4	1	3	4810.3218	0.0134	0.020
6	2	4	5	2	3	4825.7401	-0.0013	0.020
9	3	7	8	4	4	4827.7911	0.0011	0.020
9	2	8	8	3	5	4933.9701	0.0159	0.020
10	4	7	9	5	4	5054.3738	0.0138	0.020
7	1	6	6	2	5	5059.5713	0.0019	0.020
9	3	6	8	4	5	5137.7175	-0.0224	0.020
8	2	6	7	3	5	5215.8827	0.0007	0.020
7	0	7	6	1	6	5226.9302	0.0028	0.020
7	1	7	6	1	6	5259.7149	-0.0035	0.020
7	0	7	6	0	6	5283.2730	-0.0041	0.020
6	2	5	5	1	4	5295.5175	-0.0049	0.020
5	2	3	4	1	4	5303.9685	-0.0039	0.020
7	1	7	6	0	6	5316.0669	-0.0012	0.020
4	4	1	3	3	0	5379.0601	-0.0008	0.020
4	4	0	3	3	0	5379.0601	-0.0262	0.020
4	4	1	3	3	1	5379.5116	0.0317	0.020
4	4	0	3	3	1	5379.5116	0.0064	0.020
11	9	2	11	8	3	5420.3027	-0.0047	0.020
11	9	3	11	8	3	5420.3027	-0.0047	0.020
11	9	2	11	8	4	5420.3027	-0.0049	0.020
11	9	3	11	8	4	5420.3027	-0.0049	0.020
10	9	1	10	8	2	5424.5517	0.0066	0.020
10	9	1	10	8	3	5424.5517	0.0066	0.020
10	9	2	10	8	2	5424.5517	0.0066	0.020
10	9	2	10	8	3	5424.5517	0.0066	0.020
10	2	9	9	3	6	5427.6008	0.0040	0.020
7	2	6	6	2	5	5443.2820	0.0049	0.020
5	3	3	4	2	2	5473.8450	0.0046	0.020
5	3	2	4	2	2	5485.3004	-0.0035	0.020
7	6	2	6	6	1	5503.2665	0.0025	0.020
7	6	1	6	6	0	5503.2665	0.0017	0.020
7	5	3	6	5	2	5507.5152	-0.0179	0.020
7	3	5	6	3	4	5512.6122	-0.0146	0.020
7	4	4	6	4	3	5514.5034	0.0021	0.020
7	4	3	6	4	2	5517.4350	-0.0016	0.020
5	3	3	4	2	3	5555.4148	0.0075	0.020
7	3	4	6	3	3	5559.1273	-0.0017	0.020
7	1	6	6	1	5	5560.6983	-0.0030	0.020
10	3	8	9	4	5	5564.0172	-0.0014	0.020
5	3	2	4	2	3	5566.8747	0.0039	0.020
6	2	4	5	1	4	5622.2924	-0.0123	0.020
7	2	5	6	2	4	5644.0046	-0.0026	0.020
8	1	7	7	2	6	5927.3915	-0.0027	0.020
7	2	6	6	1	5	5944.4044	-0.0046	0.020
8	0	8	7	1	7	5980.0783	-0.0039	0.020
11	4	7	10	5	6	5991.9835	-0.0015	0.020

8	1	8	7	1	7	5998.4432	-0.0001	0.020
8	0	8	7	0	7	6012.8714	-0.0020	0.020
12	5	8	11	6	5	6016.6465	-0.0228	0.020
6	2	5	5	1	5	6028.9025	-0.0049	0.020
8	1	8	7	0	7	6031.2304	-0.0040	0.020
12	10	3	12	9	4	6059.6166	0.0077	0.020
4	3	2	3	0	3	6061.2506	-0.0028	0.020
11	10	1	11	9	2	6063.4910	0.0027	0.020
11	10	2	11	9	3	6063.4910	0.0027	0.020
10	3	7	9	4	6	6082.2454	-0.0016	0.020
5	4	2	4	3	1	6162.8422	-0.0059	0.020
5	4	1	4	3	1	6163.0750	0.0002	0.020
5	4	2	4	3	2	6165.7532	-0.0050	0.020
5	4	1	4	3	2	6165.9857	0.0008	0.020
9	2	7	8	3	6	6168.2941	0.0014	0.020
6	3	4	5	2	3	6194.6815	0.0049	0.020
8	2	7	7	2	6	6203.4483	0.0029	0.020
6	3	3	5	2	3	6228.1317	-0.0068	0.020
11	3	9	10	4	6	6258.0574	-0.0098	0.020
8	7	2	7	7	1	6288.9171	0.0017	0.020
8	7	1	7	7	0	6288.9171	0.0017	0.020
8	6	3	7	6	2	6292.6862	0.0015	0.020
8	6	2	7	6	1	6292.6862	-0.0039	0.020
8	3	6	7	3	5	6298.2844	0.0024	0.020
8	5	4	7	5	3	6299.0215	0.0021	0.020
8	5	3	7	5	2	6299.3130	-0.0032	0.020
8	4	5	7	4	4	6308.0276	0.0009	0.020
8	1	7	7	1	6	6311.0979	-0.0041	0.020
8	4	4	7	4	3	6315.8828	0.0027	0.020
6	2	4	5	1	5	6355.6914	0.0015	0.020
6	3	4	5	2	4	6373.2601	0.0032	0.020
8	3	5	7	3	4	6382.5164	-0.0030	0.020
6	3	3	5	2	4	6406.7224	0.0034	0.020
6	2	4	5	0	5	6447.6012	0.0024	0.020
8	2	6	7	2	5	6453.4315	-0.0051	0.020
7	2	5	6	1	5	6471.9271	0.0054	0.020
8	2	7	7	1	6	6587.1553	0.0022	0.020
7	1	6	6	0	6	6626.3394	-0.0050	0.020
12	4	9	11	5	6	6643.2268	-0.0075	0.020
9	0	9	8	1	8	6725.3778	-0.0019	0.020
9	1	9	8	1	8	6735.3728	0.0020	0.020
9	0	9	8	0	8	6743.7406	-0.0001	0.020
9	1	9	8	0	8	6753.7183	-0.0134	0.020
9	1	8	8	2	7	6771.3561	0.0035	0.020
5	5	1	4	4	0	6803.9894	0.0155	0.020
5	5	0	4	4	0	6803.9894	0.0141	0.020
5	5	1	4	4	1	6803.9894	-0.0097	0.020
5	5	0	4	4	1	6803.9894	-0.0111	0.020
7	3	5	6	2	4	6881.5646	0.0027	0.020
12	3	10	11	4	7	6893.3017	-0.0136	0.020
12	4	8	11	5	7	6898.5664	-0.0074	0.020
5	3	3	4	0	4	6914.2163	0.0045	0.020
6	4	3	5	3	2	6941.6613	-0.0040	0.020
6	4	2	5	3	2	6942.7923	0.0042	0.020
6	4	3	5	3	3	6953.1313	0.0023	0.020
7	2	6	6	1	6	6953.7058	0.0033	0.020
6	4	2	5	3	3	6954.2492	-0.0023	0.020

9	2	8	8	2	7	6958.0580	-0.0016	0.020
7	3	4	6	2	4	6961.5289	0.0027	0.020
6	3	3	5	1	4	7024.7029	0.0010	0.020
9	1	8	8	1	7	7047.4071	0.0036	0.020
11	3	8	10	4	7	7060.0093	-0.0031	0.020
9	8	1	8	8	0	7074.5990	0.0001	0.020
9	8	2	8	8	1	7074.5990	0.0001	0.020
9	7	3	8	7	2	7078.0240	0.0075	0.020
9	7	2	8	7	1	7078.0240	0.0072	0.020
9	3	7	8	3	6	7080.0280	0.0004	0.020
9	6	4	8	6	3	7083.4224	0.0116	0.020
9	6	3	8	6	2	7083.4224	-0.0136	0.020
9	5	5	8	5	4	7092.2839	0.0064	0.020
9	5	4	8	5	3	7093.2292	0.0028	0.020
9	4	6	8	4	5	7102.4158	-0.0002	0.020
9	4	5	8	4	4	7120.4916	-0.0011	0.020
10	2	8	9	3	7	7121.2891	-0.0034	0.020
7	3	5	6	2	5	7208.3484	0.0041	0.020
9	3	6	8	3	5	7213.8696	0.0053	0.020
9	2	8	8	1	7	7234.1055	-0.0052	0.020
9	2	7	8	2	6	7250.6914	-0.0012	0.020
7	3	4	6	2	5	7288.3104	0.0018	0.020
8	2	6	7	1	6	7364.6590	0.0019	0.020
13	4	10	12	5	7	7412.8213	0.0073	0.020
13	3	11	12	4	8	7452.9593	-0.0009	0.020
10	0	10	9	1	9	7465.7851	0.0033	0.020
10	1	10	9	1	9	7471.0983	-0.0024	0.020
10	0	10	9	0	9	7475.7668	-0.0059	0.020
10	1	10	9	0	9	7481.0943	0.0025	0.020
8	3	6	7	2	5	7535.8372	0.0007	0.020
10	1	9	9	2	8	7588.0279	-0.0028	0.020
6	5	2	5	4	1	7589.2989	-0.0303	0.020
6	5	1	5	4	2	7589.6036	0.0327	0.020
10	2	9	9	2	8	7707.5037	-0.0031	0.020
7	4	4	6	3	3	7709.7459	-0.0002	0.020
7	4	3	6	3	3	7713.7886	-0.0156	0.020
7	4	4	6	3	4	7743.2091	0.0009	0.020
7	4	3	6	3	4	7747.2666	0.0003	0.020
14	5	9	13	6	8	7751.6666	-0.0051	0.020
10	1	9	9	1	8	7774.7367	-0.0013	0.020
15	6	9	14	7	8	7805.3001	0.0176	0.020
6	3	4	5	0	5	7816.5405	0.0066	0.020
10	3	8	9	3	7	7856.7189	-0.0024	0.020
10	8	2	9	8	1	7863.4692	0.0064	0.020
10	8	3	9	8	2	7863.4692	0.0064	0.020
10	7	4	9	7	3	7868.1967	0.0161	0.020
10	7	3	9	7	2	7868.1967	0.0141	0.020
10	6	5	9	6	4	7875.6289	0.0197	0.020
10	5	6	9	5	5	7887.3591	0.0068	0.020
10	5	5	9	5	4	7889.9513	0.0037	0.020
10	4	7	9	4	6	7896.6959	0.0047	0.020
10	4	6	9	4	5	7933.5076	0.0065	0.020

Table S2. Calculated relative zero-point corrected energies, rotational constants and absolute dipole moment components at B3LYP-D3(BJ)/may-cc-pVTZ level for isomers of benzyl alcohol monomers, dimers, trimers and tetramers up to 5 kJ mol^{-1}.

Isomer	E_0 / kJ mol^{-1}	A / MHz	B / MHz	C / MHz	$\lvert\mu_A\rvert$ / D	$\lvert\mu_B\rvert$ / D	$\lvert\mu_C\rvert$ / D
gauche	0	4784	1473	1193	1.3	0.9	0.3
trans	3.8	4974	1496	1159	1.0	1.4	0
hom-O^{g}π-I	0	697.6	441.2	383.0	1.7	3.0	0.6
het-O^{g}π-II	0.2	697.8	456.3	393.7	1.3	2.4	1.1
het-ππ-III	1.6	721.0	473.9	365.8	0	0	0
hom-ππ-IV	2.0	717.2	471.6	369.8	0	0	2.0
hom-O^{t}π-V	3.2	862.2	397.2	344.0	2.1	2.1	0.2
het-O^{t}V-VI	4.3	724.2	366.5	282.0	3.0	1.4	0.6
hom-O^{g}V-VII	4.4	774.2	357.1	318.2	1.3	1.7	1.3
het-O^{g}V-VIII	4.5	708.6	428.2	359.8	2.6	1.7	1.2
het-O^{t}π-IX	4.8	847.3	399.7	344.6	2.7	1.7	1.2
homhom-O^{g}O^{g}π-I	0	307.4	215.8	169.5	0.0	3.9	1.4
homhet-O^{g}O^{g}π-II	0.9	413.5	161.7	158.1	0.2	0.7	3.0
hethet-O^{g}O^{g}π-III	1.2	408.8	165.1	158.4	1.7	1.5	2.3
hethom-O^{g}O^{g}π-IV	1.9	290.2	221.7	167.1	0.3	2.7	1.4
hethom-O^{g}O^{g}π-V	2.5	259.8	244.4	168.0	3.6	1.5	0.6
hethom-O^{g}O^{g}π-VI	3.3	312.1	200.7	160.7	0.1	1.7	1.9
hom*trans* O^{g}O^{g}O^g-VII	3.9	265.3	221.9	190.3	0.3	0.3	3.1
homhom-O^{t}O^{g}π-VIII	4.0	309.9	185.9	155.6	1.1	3.0	2.2
homhet-O^{g}O^{g}O^t-IX	4.5	261.9	218.9	187.9	0.2	0.7	2.8
hethet-O^{g}O^{t}π-X	4.7	285.1	207.6	150.7	2.8	1.7	0.5
homhom-O^{g}O^{g}O^g-XI	4.7	234.2	234.2	197.8	0	0	2.3
het*trans* O^{g}O^{g}π-XII	4.8	333.4	176.9	158.1	1.2	2.0	2.5
homhomhom-O^{g}O^{g}O^{g}O^g-I	0	157.9	136.2	110.5	0	0	2.5
homhomhet-O^{g}O^{g}O^{g}O^t-II	1.5	162.6	127.5	102.1	0.1	0.8	2.8
homhom*trans*-O^{g}O^{g}O^{g}O^g-III	3.7	200.0	107.6	96.5	1.1	1.3	2.2
homhom*trans*-O^{g}O^{g}O^{g}O^g-IV	4.8	162.3	128.1	102.6	0.4	0.5	3.2

Table S3. Calculated harmonic OH stretching wavenumbers and associated infrared band strengths at B3LYP-D3(BJ)/may-cc-pVTZ level for isomers of benzyl alcohol monomers, dimers, trimers and tetramers up to 5 kJ mol^{-1}.

Isomer	ω_1 / cm^{-1}	ω_2 / cm^{-1}	ω_3 / cm^{-1}	ω_4 / cm^{-1}	B_1 / km mol^{-1}	B_2 / km mol^{-1}	B_3 / km mol^{-1}	B_4 / km mol^{-1}
gauche	3809				24			
trans	3847				46			
hom-O$^g\pi$-I	3756	3639			124	251		
het-O$^g\pi$-II	3741	3625			150	268		
het-$\pi\pi$-III	3751	3746			426	0		
hom-$\pi\pi$-IV	3753	3750			377	1		
hom-O$^t\pi$-V	3718	3651			203	208		
het-O^{t}V-VI	3816	3635			31	499		
hom-O^{g}V-VII	3805	3612			31	387		
het-O^{g}V-VIII	3812	3645			34	321		
het-O$^t\pi$-IX	3720	3664			200	194		
homhom-O^{g}O$^g\pi$-I	3738	3534	3483		183	659	426	
homhet-O^{g}O$^g\pi$-II	3702	3551	3448		229	460	590	
hethet-O^{g}O$^g\pi$-III	3724	3546	3466		191	479	517	
hethom-O^{g}O$^g\pi$-IV	3716	3525	3472		254	727	446	
hethom-O^{g}O$^g\pi$-V	3716	3531	3480		259	688	541	
hethom-O^{g}O$^g\pi$-VI	3729	3523	3449		206	750	425	
hom*trans* O^{g}O^{g}O^g-VII	3600	3571	3513		615	631	106	
homhom-O^{t}O$^g\pi$-VIII	3733	3577	3451		215	692	464	
homhet-O^{g}O^{g}O^t-IX	3593	3573	3511		540	452	147	
hethet-O^{g}O$^t\pi$-X	3725	3520	3469		204	707	535	
homhom-O^{g}O^{g}O^g-XI	3585	3585	3539		618	618	1	
het*trans* O^{g}O$^g\pi$-XII	3741	3521	3473		388	582	538	
homhomhom-O^{g}O^{g}O^{g}O^g-I	3464	3435	3429	3360	12	1346	1648	1
homhomhet-O^{g}O^{g}O^{g}O^t-II	3462	3426	3423	3346	175	1011	1615	80
homhom*trans*-O^{g}O^{g}O^{g}O^g-III	3488	3432	3401	3334	957	651	1331	213
homhom*trans*-O^{g}O^{g}O^{g}O^g-IV	3454	3415	3409	3327	193	1591	1415	46

Table S4. Calculated Raman activities and depolarization ratios for harmonic OH stretching wavenumbers at B3LYP-D3(BJ)/may-cc-pVTZ level for isomers of benzyl alcohol monomers, dimers, trimers and tetramers up to 5 kJ mol^{-1}.

Isomer	A_1 / Å^4 u^{-1}	A_2 / Å^4 u^{-1}	A_3 / Å^4 u^{-1}	A_4 / Å^4 u^{-1}	P_1	P_2	P_3	P_4
gauche	67				0.15			
trans	154				0.26			
hom-O$^g\pi$-I	79	79			0.24	0.17		
het-O$^g\pi$-II	87	86			0.24	0.17		
het-$\pi\pi$-III	0	280			0	0.28		
hom-$\pi\pi$-IV	1	264			0.75	0.28		
hom-O$^t\pi$-V	81	116			0.27	0.17		
het-O^{t}V-VI	61	144			0.11	0.23		
hom-O^{g}V-VII	86	104			0.17	0.19		
het-O^{g}V-VIII	61	144			0.11	0.23		
het-O$^t\pi$-IX	74	121			0.27	0.17		
homhom-O^{g}O$^g\pi$-I	89	43	144		0.26	0.69	0.11	
homhet-O^{g}O$^g\pi$-II	87	48	122		0.27	0.37	0.13	
hethet-O^{g}O$^g\pi$-III	72	45	123		0.26	0.47	0.13	
hethom-O^{g}O$^g\pi$-IV	118	53	158		0.29	0.65	0.10	
hethom-O^{g}O$^g\pi$-V	103	59	162		0.27	0.68	0.10	
hethom-O^{g}O$^g\pi$-VI	119	65	142		0.27	0.42	0.12	
hom*trans* O^{g}O^{g}O^g-VII	45	57	173		0.54	0.50	0.07	
homhom-O^{t}O$^g\pi$-VIII	128	143	119		0.28	0.29	0.15	
homhet-O^{g}O^{g}O^t-IX	43	56	155		0.53	0.32	0.08	
hethet-O^{g}O$^t\pi$-X	40	40	203		0.75	0.75	0.07	
homhom-O^{g}O^{g}O^g-XI	81	61	176		0.28	0.74	0.10	
het*trans* O^{g}O$^g\pi$-XII	217	47	156		0.33	0.72	0.11	
homhomhom-O^{g}O^{g}O^{g}O^g-I	113	1	4	296	0.75	0.75	0.75	0.09
homhomhet-O^{g}O^{g}O^{g}O^t-II	88	15	19	280	0.75	0.58	0.42	0.09
homhom*trans*-O^{g}O^{g}O^{g}O^g-III	161	25	37	265	0.45	0.61	0.43	0.09
homhom*trans*-O^{g}O^{g}O^{g}O^g-IV	107	13	18	295	0.75	0.67	0.41	0.09

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