Conformational Equilibria in Vanillin and Ethylvanillin
SUPPLEMENTARY INFORMATION

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Table S1. Measured rotational transitions of vanillin s-cis (obs.) and residuals (obs.-calc.) for the fit of Table 1 (frequencies in MHz).

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.	J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.
3	0	3	2	0	2	4087.9657	-0.0009	8	3	5	7	3	4	12788.3561	0.0000
3	1	2	2	1	1	4750.1114	0.0005	8	3	6	7	3	5	11659.9421	0.0002
4	0	4	3	0	3	5245.5791	0.0000	8	4	4	7	4	3	12308.0293	0.0001
4	1	3	3	1	2	6222.7482	-0.0009	8	4	5	7	4	4	11968.5793	0.0002
4	1	4	3	1	3	5083.929	0.0012	8	5	3	7	5	2	11981.3326	0.0000
4	2	2	3	2	1	6298.5448	-0.0003	8	5	4	7	5	3	11949.6564	0.0003
4	2	3	3	2	2	5744.5716	0.0004	8	6	2	7	6	1	11879.9061	-0.0005
4	2	3	3	1	2	7683.9528	0.0002	8	6	3	7	6	2	11878.6236	0.0011
5	0	5	4	0	4	6367.0203	-0.0002	9	0	9	8	0	8	10919.7867	0.0000
5	0	5	4	1	4	6206.6113	0.0005	9	1	8	8	1	7	12114.4712	0.0001
5	1	4	4	1	3	7578.1174	0.0000	9	1	9	8	1	8	10916.9976	0.0000
5	1	5	4	1	4	6278.0013	-0.0001	9	2	7	8	2	6	13514.9944	-0.0006
5	1	5	4	0	4	6438.4108	-0.0005	9	2	8	8	2	7	12036.5403	-0.0002
5	2	3	4	2	2	7966.4092	0.0000	9	3	6	8	3	5	14385.7523	0.0000
5	2	4	4	2	3	7093.1264	0.0000	9	3	7	8	3	6	12973.6272	-0.0002
5	3	2	4	3	1	7606.7321	0.0000	9	4	5	8	4	4	14099.6859	-0.0002
5	3	3	4	3	2	7404.3299	0.0001	9	4	6	8	4	5	13451.6312	0.0000
6	0	6	5	0	5	7492.7243	0.0001	9	5	4	8	5	3	13595.2455	0.0000
6	0	6	5	1	5	7421.3332	-0.0002	9	5	5	8	5	4	13500.2411	-0.0002
6	1	5	5	1	4	8797.0228	0.0002	9	6	3	8	6	2	13422.3171	-0.0017
6	1	6	5	1	5	7450.8758	0.0000	9	6	4	8	6	3	13416.5466	0.0010
6	1	6	5	0	5	7522.2664	-0.0001	10	0	10	9	0	9	12068.2864	0.0000
6	2	4	5	2	3	9553.7914	0.0001	10	1	9	9	1	8	13237.8855	0.0003
6	2	5	5	2	4	8391.7662	0.0000	10	1	10	9	1	9	12067.2387	-0.0001
6	3	3	5	3	2	9323.0135	-0.0002	10	2	8	9	2	7	14596.4663	0.0002
6	3	4	5	3	3	8867.5186	-0.0001	10	2	9	9	2	8	13202.1695	-0.0002
6	4	2	5	4	1	8977.0257	-0.0003	10	3	7	9	3	6	15833.0091	0.0001
6	4	3	5	4	2	8930.3836	0.0003	10	3	8	9	3	7	14234.3279	0.0000
6	5	1	5	5	0	8885.797	-0.0003	10	4	6	9	4	5	15907.2471	0.0006
6	5	2	5	5	1	8884.2328	0.0019	10	4	7	9	4	6	14888.0865	-0.0001
7	0	7	6	0	6	8629.2625	0.0001	10	5	5	9	5	4	15284.4758	0.0000
7	0	7	6	1	6	8599.7191	-0.0009	10	5	6	9	5	5	15049.4313	-0.0001
7	1	6	6	1	5	9917.6428	-0.0002	10	6	4	9	6	3	14991.4982	-0.0007
7	1	7	6	1	6	8611.3666	0.0002	10	6	5	9	6	4	14970.9821	0.0002
7	1	7	6	0	6	8640.9091	0.0003	11	0	11	10	0	10	13217.4275	-0.0002
7	2	5	6	2	4	11021.9467	0.0000	11	1	10	10	1	9	14373.9292	-0.0005
7	2	6	6	2	5	9642.5035	0.0003	11	1	11	10	1	10	13217.0431	0.0001
7	3	4	6	3	3	11078.9646	-0.0002	11	2	9	10	2	8	15660.1661	0.0001
7	3	5	6	3	4	10289.8469	-0.0001	11	2	10	10	2	9	14358.487	0.0000
7	4	3	6	4	2	10598.0959	0.0000	11	3	9	10	3	8	15451.5747	0.0000
7	4	4	6	4	3	10455.3695	0.0000	11	4	8	10	4	7	16267.2208	0.0001
7	5	2	6	5	1	10417.4731	-0.0008	11	5	7	10	5	6	16580.7106	0.0001
7	5	3	6	5	2	10409.1345	0.0004	11	6	5	10	6	4	16599.9643	0.0001
7	6	1	6	6	0	10357.2343	-0.0027	11	6	6	10	6	5	16539.1393	-0.0001
7	6	2	6	6	1	10357.0372	0.0027	12	0	12	11	0	11	14366.8386	-0.0005
8	0	8	7	0	7	9772.8047	-0.0001	12	1	11	11	1	10	15516.7621	0.0003
8	1	7	7	1	6	11009.7406	0.0004	12	1	12	11	1	11	14366.7007	0.0004
8	1	8	7	1	7	9765.5952	0.0004	12	2	11	11	2	10	15510.3599	0.0000
8	2	6	7	2	5	12341.9225	-0.0004	12	3	10	11	3	9	16637.7319	0.0001
8	2	7	7	2	6	10853.6062	0.0000	13	0	13	12	0	12	15516.3675	-0.0001
								13	1	13	12	1	12	15516.3185	0.0002

Table S2. Measured rotational transitions of vanillin *s-trans* (obs.) and residuals (obs.-calc.) for the fit of Table 1 (frequencies in MHz).

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.	J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.
4	0	4	3	0	3	5032.9654	0.0002	9	2	7	8	2	6	12768.9962	-0.0001
4	1	3	3	1	2	5686.5882	-0.0001	9	3	6	8	3	5	12769.2943	-0.0001
4	2	3	3	1	2	8306.1006	0.0000	9	4	5	8	4	4	12313.4272	0.0000
5	0	5	4	0	4	6146.0398	-0.0005	9	4	6	8	4	5	12185.5830	-0.0001
5	1	4	4	1	3	7033.1382	-0.0003	10	0	10	9	0	9	11590.0526	0.0000
5	1	5	4	1	4	5967.8972	0.0000	10	1	9	9	1	8	12806.2996	0.0000
5	1	5	4	0	4	6426.2940	0.0005	10	1	10	9	1	9	11578.6216	0.0000
5	2	4	4	2	3	6568.2795	-0.0002	10	5	6	9	5	5	13529.3974	0.0000
6	0	6	5	0	5	7231.5985	0.0000	11	0	11	10	0	10	12690.1907	-0.0002
6	0	6	5	1	5	6951.3455	0.0001	11	1	10	10	1	9	13868.0257	-0.0002
6	1	5	5	1	4	8318.4024	-0.0008	11	1	11	10	1	10	12684.4390	-0.0004
6	1	6	5	1	5	7110.7922	-0.0005	11	3	8	10	3	7	15784.2286	0.0005
6	2	5	5	2	4	7827.7143	-0.0005	11	3	9	10	3	8	14560.6180	0.0000
6	3	4	5	3	3	8067.5901	-0.0003	11	4	7	10	4	6	15358.8195	-0.0001
6	4	2	5	4	1	8071.1238	-0.0002	11	5	7	10	5	6	14922.0500	0.0000
6	4	2	6	3	3	8306.6358	0.0000	11	6	5	10	6	4	14853.3919	-0.0009
6	4	3	5	4	2	8064.5480	0.0020	12	0	12	11	0	11	13791.8730	0.0004
7	0	7	6	0	6	8313.0162	0.0000	12	1	11	11	1	10	14940.1542	-0.0002
7	0	7	6	1	6	8153.5692	0.0003	12	1	12	11	1	11	13789.0376	0.0006
7	1	6	6	1	5	9528.3169	0.0001	12	1	12	11	0	11	13794.4911	-0.0005
7	1	7	6	1	6	8239.6602	0.0002	13	0	13	12	0	12	14894.3884	0.0001
7	2	6	6	2	5	9060.5256	-0.0004	13	0	13	12	1	12	14891.7688	-0.0004
8	0	8	7	0	7	9399.7376	0.0004	13	1	12	12	1	11	16022.9033	0.0000
8	1	7	7	1	6	10663.6291	0.0004	13	1	13	12	1	12	14893.0122	-0.0003
8	1	8	7	1	7	9358.4106	-0.0003	13	2	12	12	2	11	15980.6180	0.0005
8	5	4	7	5	3	10766.8489	0.0010	14	0	14	13	0	13	15997.3455	0.0000
9	0	9	8	0	8	10492.6533	0.0000	14	1	14	13	1	13	15996.6869	0.0002
9	1	9	8	1	8	10470.5261	0.0002								

Table S3. Measured rotational transitions of vanillin *s-cis-cis* (obs.) and residuals (obs.-calc.) for the fit of Table 2 (frequencies in MHz).

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.	J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.
3	0	3	2	0	2	4087.9657	-0.0009	8	3	5	7	3	4	12788.3561	0.0000
3	1	2	2	1	1	4750.1114	0.0005	8	3	6	7	3	5	11659.9421	0.0002
4	0	4	3	0	3	5245.5791	0.0000	8	4	4	7	4	3	12308.0293	0.0001
4	1	3	3	1	2	6222.7482	-0.0009	8	4	5	7	4	4	11968.5793	0.0002
4	1	4	3	1	3	5083.929	0.0012	8	5	3	7	5	2	11981.3326	0.0000
4	2	2	3	2	1	6298.5448	-0.0003	8	5	4	7	5	3	11949.6564	0.0003
4	2	3	3	2	2	5744.5716	0.0004	8	6	2	7	6	1	11879.9061	-0.0005
4	2	3	3	1	2	7683.9528	0.0002	8	6	3	7	6	2	11878.6236	0.0011
5	0	5	4	0	4	6367.0203	-0.0002	9	0	9	8	0	8	10919.7867	0.0000
5	0	5	4	1	4	6206.6113	0.0005	9	1	8	8	1	7	12114.4712	0.0001
5	1	4	4	1	3	7578.1174	0.0000	9	1	9	8	1	8	10916.9976	0.0000
5	1	5	4	1	4	6278.0013	-0.0001	9	2	7	8	2	6	13514.9944	-0.0006
5	1	5	4	0	4	6438.4108	-0.0005	9	2	8	8	2	7	12036.5403	-0.0002
5	2	3	4	2	2	7966.4092	0.0000	9	3	6	8	3	5	14385.7523	0.0000
5	2	4	4	2	3	7093.1264	0.0000	9	3	7	8	3	6	12973.6272	-0.0002
5	3	2	4	3	1	7606.7321	0.0000	9	4	5	8	4	4	14099.6859	-0.0002
5	3	3	4	3	2	7404.3299	0.0001	9	4	6	8	4	5	13451.6312	0.0000
6	0	6	5	0	5	7492.7243	0.0001	9	5	4	8	5	3	13595.2455	0.0000
6	0	6	5	1	5	7421.3332	-0.0002	9	5	5	8	5	4	13500.2411	-0.0002
6	1	5	5	1	4	8797.0228	0.0002	9	6	3	8	6	2	13422.3171	-0.0017
6	1	6	5	1	5	7450.8758	0.0000	9	6	4	8	6	3	13416.5466	0.0010
6	1	6	5	0	5	7522.2664	-0.0001	10	0	10	9	0	9	12068.2864	0.0000
6	2	4	5	2	3	9553.7914	0.0001	10	1	9	9	1	8	13237.8855	0.0003
6	2	5	5	2	4	8391.7662	0.0000	10	1	10	9	1	9	12067.2387	-0.0001
6	3	3	5	3	2	9323.0135	-0.0002	10	2	8	9	2	7	14596.4663	0.0002
6	3	4	5	3	3	8867.5186	-0.0001	10	2	9	9	2	8	13202.1695	-0.0002
6	4	2	5	4	1	8977.0257	-0.0003	10	3	7	9	3	6	15833.0091	0.0001
6	4	3	5	4	2	8930.3836	0.0003	10	3	8	9	3	7	14234.3279	0.0000
6	5	1	5	5	0	8885.797	-0.0003	10	4	6	9	4	5	15907.2471	0.0006
6	5	2	5	5	1	8884.2328	0.0019	10	4	7	9	4	6	14888.0865	-0.0001
7	0	7	6	0	6	8629.2625	0.0001	10	5	5	9	5	4	15284.4758	0.0000
7	0	7	6	1	6	8599.7191	-0.0009	10	5	6	9	5	5	15049.4313	-0.0001
7	1	6	6	1	5	9917.6428	-0.0002	10	6	4	9	6	3	14991.4982	-0.0007
7	1	7	6	1	6	8611.3666	0.0002	10	6	5	9	6	4	14970.9821	0.0002
7	1	7	6	0	6	8640.9091	0.0003	11	0	11	10	0	10	13217.4275	-0.0002
7	2	5	6	2	4	11021.9467	0.0000	11	1	10	10	1	9	14373.9292	-0.0005
7	2	6	6	2	5	9642.5035	0.0003	11	1	11	10	1	10	13217.0431	0.0001
7	3	4	6	3	3	11078.9646	-0.0002	11	2	9	10	2	8	15660.1661	0.0001
7	3	5	6	3	4	10289.8469	-0.0001	11	2	10	10	2	9	14358.487	0.0000
7	4	3	6	4	2	10598.0959	0.0000	11	3	9	10	3	8	15451.5747	0.0000
7	4	4	6	4	3	10455.3695	0.0000	11	4	8	10	4	7	16267.2208	0.0001
7	5	2	6	5	1	10417.4731	-0.0008	11	5	7	10	5	6	16580.7106	0.0001
7	5	3	6	5	2	10409.1345	0.0004	11	6	5	10	6	4	16599.9643	0.0001
7	6	1	6	6	0	10357.2343	-0.0027	11	6	6	10	6	5	16539.1393	-0.0001
7	6	2	6	6	1	10357.0372	0.0027	12	0	12	11	0	11	14366.8386	-0.0005
8	0	8	7	0	7	9772.8047	-0.0001	12	1	11	11	1	10	15516.7621	0.0003
8	1	7	7	1	6	11009.7406	0.0004	12	1	12	11	1	11	14366.7007	0.0004
8	1	8	7	1	7	9765.5952	0.0004	12	2	11	11	2	10	15510.3599	0.0000
8	2	6	7	2	5	12341.9225	-0.0004	12	3	10	11	3	9	16637.7319	0.0001
8	2	7	7	2	6	10853.6062	0.0000	13	0	13	12	0	12	15516.3675	-0.0001
								13	1	13	12	1	12	15516.3185	0.0002

Table S4. Measured rotational transitions of vanillin *s-cis-trans* (obs.) and residuals (obs.-calc.) for the fit of Table 2 (frequencies in MHz).

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.	J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	obs.	obs.-calc.
4	1	3	3	1	2	4774.2999	0.0002	8	6	3	7	6	2	9128.3065	0.0017
5	0	5	4	0	4	4873.7400	0.0001	9	3	7	8	3	6	9945.2934	0.0000
5	1	5	4	1	4	4809.8457	-0.0001	10	4	7	9	4	6	11425.9096	-0.0002
5	3	2	4	3	1	5852.9496	-0.0011	11	3	9	10	3	8	11834.6616	0.0001
6	1	6	5	1	5	5707.4332	0.0000	12	1	11	11	1	10	11880.9654	0.0006
6	4	3	5	4	2	6862.3482	0.0006	12	2	10	11	2	9	12811.2728	0.0005
7	0	7	6	0	6	6608.0945	0.0000	12	3	9	11	3	8	13941.2781	-0.0004
7	1	6	6	1	5	7586.4436	-0.0007	13	0	13	12	0	12	11885.0223	-0.0006
7	1	7	6	1	6	6595.8446	-0.0004	13	1	13	12	1	12	11884.9938	0.0005
7	2	5	6	2	4	8453.2980	0.0002	13	4	10	12	4	9	14440.7457	0.0009
7	2	6	6	2	5	7388.7299	0.0000	13	5	9	12	5	8	14979.2891	-0.0004
7	3	4	6	3	3	8527.0542	0.0012	14	1	13	13	1	12	13638.7742	0.0004
7	3	5	6	3	4	7896.9475	0.0005	14	2	13	13	2	12	13638.1641	0.0001
7	4	3	6	4	2	8154.3118	-0.0004	14	3	12	13	3	11	14516.5212	-0.0003
7	4	4	6	4	3	8033.7395	-0.0002	15	0	15	14	0	14	13646.4124	0.0005
7	5	2	6	5	1	8006.6442	-0.0021	15	1	15	14	1	14	13646.4083	0.0000
7	5	3	6	5	2	7999.2963	-0.0004	16	1	15	15	1	14	15398.9229	0.0007
8	0	8	7	0	7	7484.5601	-0.0002	16	2	15	15	2	14	15398.8362	-0.0016
8	1	8	7	1	7	7479.7345	0.0002	17	0	17	16	0	16	15407.8476	0.0000

Table S5. *Ab initio* structure for *s-cis* vanillin (MP2-6-311++G(d,p), principal axes system).

Atom	a / Å	b / Å	c / Å
6	0.493253	0.650882	0.000233
6	1.427238	-0.403081	-0.000479
6	0.997094	-1.735466	0.000193
6	-0.369621	-2.032781	-0.000243
6	-1.300865	-0.996205	0.000222
6	-0.864669	0.351551	-0.000295
1	0.863846	1.670364	0.000107
1	1.729858	-2.539276	0.000076
1	-0.732543	-3.056235	0.000002
8	-2.627933	-1.279836	0.000136
1	-3.095036	-0.432648	0.000479
8	-1.889845	1.254045	-0.000218
6	-1.523657	2.631974	0.000144
1	-2.460455	3.187103	0.000291
1	-0.944755	2.877672	0.895898
1	-0.944742	2.878171	-0.895465
6	2.873434	-0.100187	0.000161
8	3.347417	1.02485	-0.000005
1	3.533201	-0.993376	0.000767

Table S6. *Ab initio* structure for *s-trans* vanillin (MP2-6-311++G(d,p), principal axes system).

Atom	a / Å	b / Å	c / Å
6	0.210671	-0.92256	0.000022
6	1.395993	-0.162799	-0.000322
6	1.341997	1.237725	0.000147
6	0.106019	1.885169	-0.000124
6	-1.074948	1.139757	0.000178
6	-1.02211	-0.271406	-0.000276
1	0.273949	-2.006904	-0.000173
1	2.270287	1.801256	0.000091
1	0.030988	2.968699	0.000112
8	-2.273159	1.778068	0.000145
1	-2.956272	1.093314	0.000253
8	-2.253084	-0.867396	-0.00034
6	-2.272026	-2.291158	0.000311
1	-3.32355	-2.57438	0.000452
1	-1.782561	-2.686117	-0.895872
1	-1.782518	-2.685262	0.896847
6	2.692899	-0.874539	0.000048
8	3.785549	-0.333105	0.000084
1	2.611502	-1.983492	0.000261

Table S7. *Ab initio* structure for *s-cis-trans* ethylvanillin (MP2-6-311++G(d,p), principal axes system).

Atom	a / Å	b / Å	c / Å
6	0.585232	0.205349	-0.023353
6	-0.526682	-0.629995	-0.03858
6	-1.813173	-0.060974	0.025219
6	-1.97553	1.329877	0.028829
6	-0.85581	2.1681	0.038462
6	0.421143	1.612556	-0.013958
1	-0.43948	-1.711133	-0.052086
1	-2.975403	1.756448	0.06718
1	-0.951605	3.249737	0.049427
6	-3.002728	-0.93713	0.004386
8	-2.96629	-2.157357	-0.01646
1	-3.973999	-0.398978	0.011524
8	1.51155	2.420651	-0.013298
1	2.286203	1.840972	-0.030833
8	1.892307	-0.188874	-0.060029
6	2.146665	-1.596769	0.027612
1	1.683855	-1.986293	0.942082
1	1.695566	-2.09762	-0.837039
6	3.648779	-1.782577	0.045748
1	4.095382	-1.379636	-0.866151
1	4.087167	-1.278482	0.910058
1	3.885196	-2.848633	0.107243

Table S8. *Ab initio* structure for *s-trans-trans* vanillin (MP2-6-311++G(d,p), principal axes system).

Atom	a / Å	b / Å	c / Å
6	0.68306	0.138029	-0.039929
6	-0.345265	-0.803536	-0.058751
6	-1.682975	-0.371414	0.015593
6	-1.985898	0.997079	0.034278
6	-0.954569	1.936753	0.049883
6	0.375764	1.516031	-0.011779
1	-0.130605	-1.867969	-0.085379
1	-3.025999	1.306276	0.07887
1	-1.157108	3.003575	0.074164
6	-2.756426	-1.388883	-0.013413
8	-3.950902	-1.144052	0.011959
1	-2.395629	-2.439586	-0.060022
8	1.37454	2.435846	-0.004464
1	2.206872	1.942816	-0.020796
8	2.0242	-0.125638	-0.090302
6	2.42121	-1.494951	0.040378
1	1.998368	-1.902716	0.966667
1	2.029549	-2.067272	-0.809241
6	3.93458	-1.525581	0.064269
1	4.339543	-1.105755	-0.859325
1	4.31589	-0.953062	0.912807
1	4.279635	-2.559213	0.15761