Supporting Information for

Controlling Vibrational Energy Flow in Liquid Alkylbenzenes

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Contents:

Normal Modes and Mode Classification

We computed the normal modes using MP2 perturbation theory with 6-31G as the basis, using the Gaussian 09 computational package, and compared the results with previous assignments[S1-S5]. The results are shown in table S1, where the Raman-active transitions are assigned and the transitions too weak to observe via transient anti-Stokes spectroscopy are numbered. Figure S1 shows each of the normal modes, which were divided into three sets, substituent modes, phenyl modes or global modes. The mode classifications were made based on their Potential Energy Distributions (PED) computed using the VEDA-4 software package.[S6] The software carries out Vibrational Energy Distribution Analysis (VEDA) to determine PED's for the computed normal mode vectors. A wonderful review of this method can be found online.[S7] As a summary, the VEDA method transforms the Cartesian normal mode vectors into a new basis of internal 2,3 and 4 body coordinates. The contribution of each internal coordinate basis to the total potential

energy of each mode is decomposed to give their PED distribution. Modes with 80% or more of their potential energy contributed by phenyl or substituent localized were coordinates classified as phenyl or substituent. If there was less than 80% in either phenyl or substituent localized coordinates or if there was 80% or more in global coordinates the mode was classified as global. Note that the PED for a given mode doesn't add up to 100 since there are small <1% contributions from some coordinates that are not considered.

Figures S2 and S3 show IR-Raman spectra with substituent and phenyl pumping for IPB and TBB.

Literature cited

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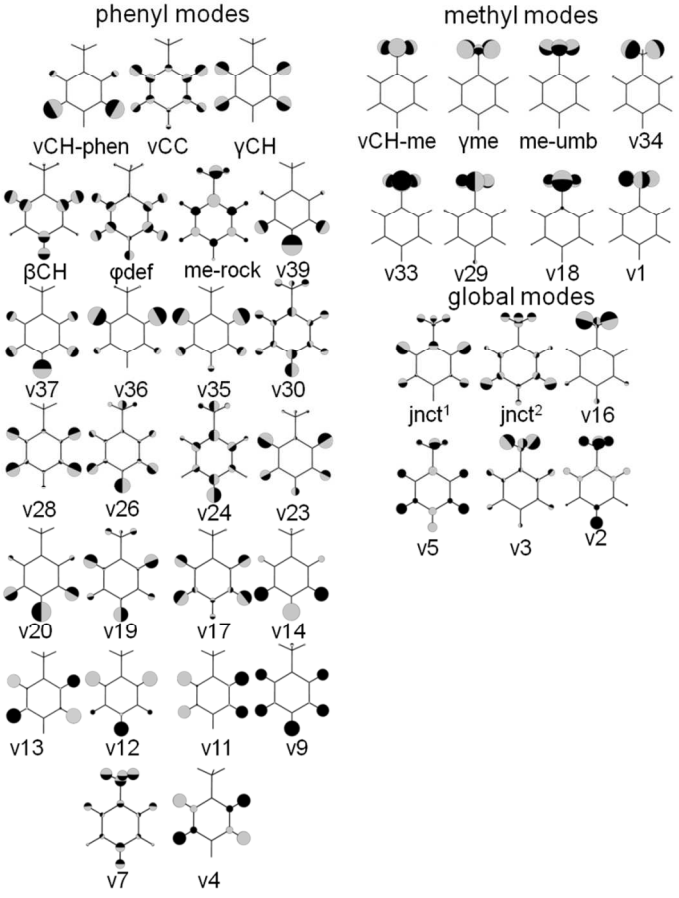
(S6) Jamroz, M. H., Vibrational Energy Distribution Analysis VEDA 4, *Warsaw* **2004-2010**

(S7) Jamroz, M. H., Vibrational energy distribution analysis (VEDA): Scopes and limitations, *Spectrochim Acta A* **2013**, 114, 220-230.

(a)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methyl modes
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vCC
γCH
vCH-me
γme
me-umb
ν34
βCH
φdef
me-rock
ν39
ν33
ν29
ν18
ν1
global modes
ν37
ν36
ν35
ν30
jnct1
jnct2
ν16
ν28
ν26
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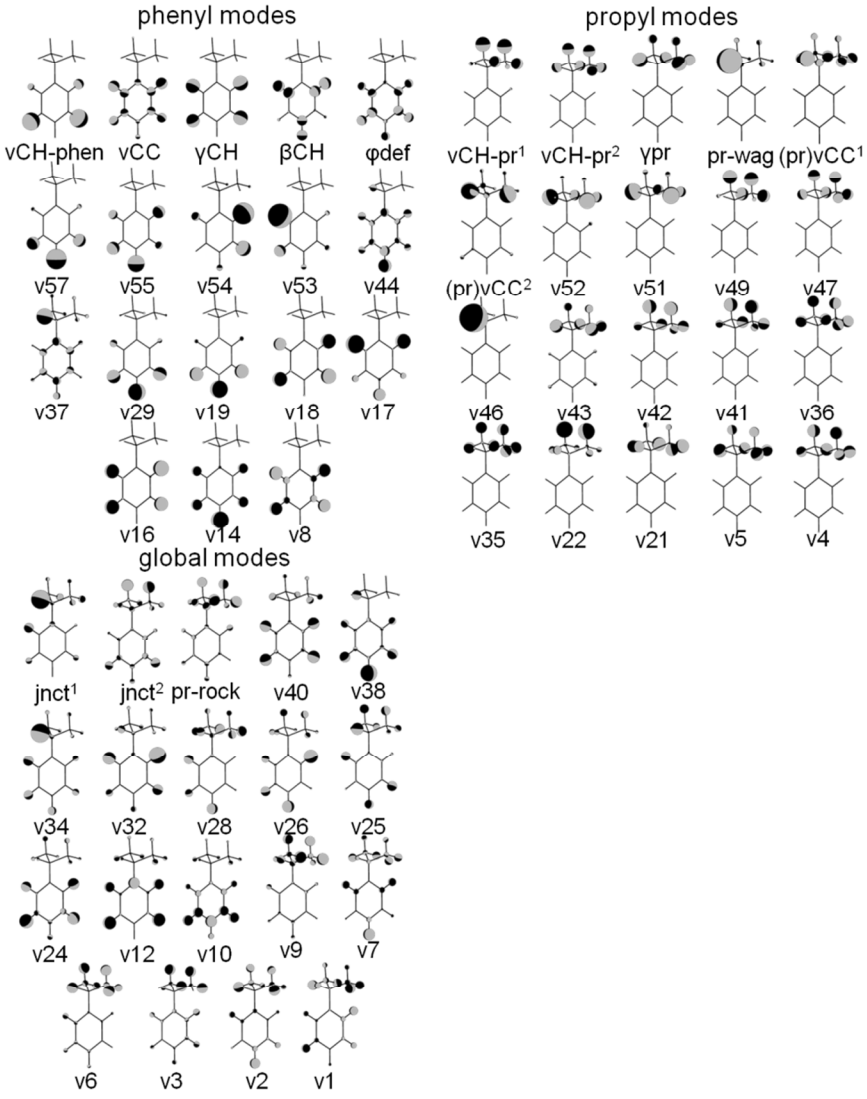
(b)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propyl modes
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vCC
γCH
βCH
φdef
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vCH-pr2
γpr
pr-wag
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v55
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v53
v44
(pr)vCC2
v52
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v49
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v37
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v14
v8
v35
v22
v21
v5
v4
global modes
jnct1
jnct2
pr-rock
v40
v38
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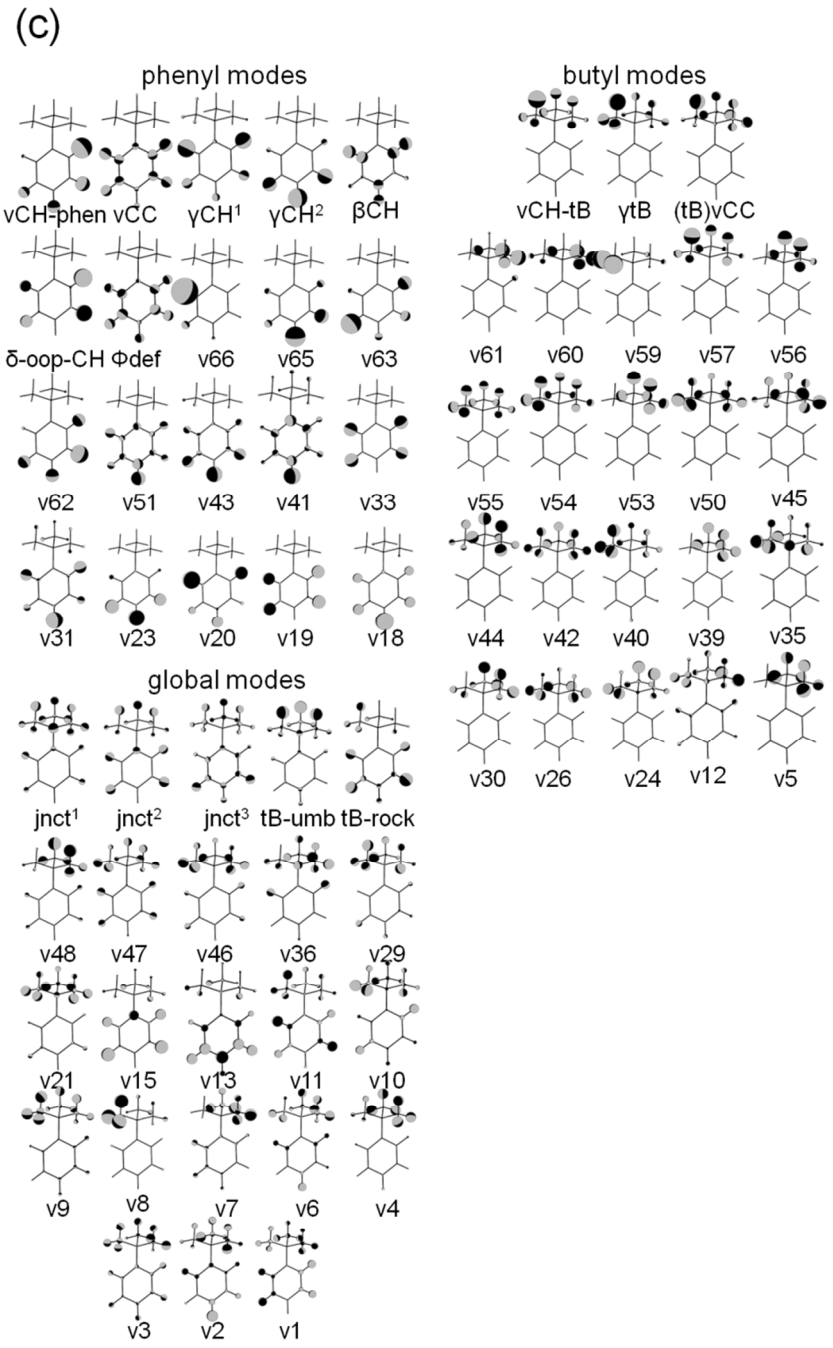

Figure S1 Classified normal modes of (a)toluene, (b) isopropylbenzene (IPB) and (c) tertbutylbenzene (TBB) computed using MP2 perturbation theory with the 6-31G basis set. Relatives sphere size indicates relative displacement while the grey and white fill represents the displacement direction.

toluene vibrational frequencies

mode	MP2	experimental	PED(%)	classification
v39	3059.16		phenyl(97)	phenyl
vCH-phen (v38)	3047.70	3055	phenyl(96)	phenyl
v37	3039.88		phenyl(96)	phenyl
v36	3026.63		phenyl(91)	phenyl
v35	3025.26		phenyl(97)	phenyl
v34	3011.92		subs.(98)	subs.
v33	2996.39		subs.(97)	subs.
vCH-me (v32)	2920.94	2920	subs.(97)	subs.
vCC (v31)	1588.04	1600	phenyl(96)	phenyl
v30	1567.12		phenyl(83) global(8) subs.(4)	phenyl
v29	1470.11		subs.(89)	subs.
v28	1469.46		phenyl(80) global(20)	phenyl
γme (v27)	1459.92	1440	subs.(99)	subs.
v26	1419.57		phenyl(83) subs.(7)	phenyl
me-umb (v25)	1384.31	1380	subs.(94)	subs.
v24	1379.60		phenyl(92) subs.(4)	phenyl
v23	1290.49		phenyl(92)	phenyl
jnct[1] (v22)	1192.21	1205	global(66) phenyl(26) subs.(4)	global
γCH (v21)	1164.36	1175	phenyl(97)	phenyl
v20	1145.28		phenyl(96)	phenyl
v19	1073.25		phenyl(81) subs.(11)	phenyl
v18	1021.20		subs.(94)	subs.
v17	1009.19		phenyl(93)	phenyl
v16	970.10		subs.(77) phenyl(21)	global
βCH(v15)	965.68	1005	phenyl(81) global(19)	phenyl
v14	836.85		phenyl(91) global(6)	phenyl
v13	833.41		phenyl(95)	phenyl
v12	810.75		phenyl(94)	phenyl
v11	787.48		phenyl(99)	phenyl
jnct[2] (v10)	763.72	795	global(65) phenyl(26)	global
v9	682.18		phenyl(92)	phenyl
φdef (v8)	599.74	608	phenyl(92)	phenyl
v7	498.57		phenyl(82) global(18)	phenyl
me-rock (v6)	474.95	510	phenyl(82) global(13)	phenyl
v5	425.74		global(82) phenyl(15)	global
v4	375.75		phenyl(90) global(7)	phenyl
v3	324.79		global(88) phenyl(4)	global
v2	195.11		global(75) phenyl(16)	global
v1	56.6		subs.(99)	subs.

isopropylbenzene (IPB) vibrational frequencies

mode	MP2	experimental	PED(%)	classification
v57	3071.97		phenyl(95)	phenyl
vCH-phen (v56)	3060.52	3060	phenyl(100)	phenyl
v55	3053.25		phenyl(100)	phenyl
v54	3042.81		phenyl(99)	phenyl
v53	3037.59		phenyl(100)	phenyl
v52	3025.02		subs.(96)	subs.
v51	3023.93		subs.(99)	subs.
vCH-pr^{1} (v50)	3016.39	3000	subs.(99)	subs.
v49	3013.09		subs.(99)	subs.
vCH-pr^{2} (v48)	2933.1	2930	subs.(99)	subs.
v47	2931.38		subs.(99)	subs.
v46	2919.41		subs.(99)	subs.
vCC (v45)	1590.16	1620	phenyl(83) global(9)	phenyl
v44	1570.78		phenyl(87) global(9)	phenyl
v43	1487.58		subs.(82) global(11)	subs.
v42	1482.32		subs.(87) global(4)	subs.
v41	1471.86		subs.(91) global(4)	subs.
v40	1470.66		global(76) phenyl(19)	global
γpr (v39)	1466.01	1480	subs.(92) global(2)	subs.
v38	1431.36		global(47) phenyl(44)	global
v37	1395.51		phenyl(80) global(8) subs.(2)	phenyl
v36	1393.75		subs.(95)	subs.
v35	1374.92		subs.(93) global(2)	subs.
v34	1333.27		global(75) phenyl(14) subs.(4)	global
pr-wag (v33)	1316.56	1330	subs.(90)	subs.
v32	1282.84		phenyl(70) global(21) subs.(2)	global
jnct^{1} (v31)	1205.33	1225	global(64) subs.(15) phenyl(13)	global
γCH (v30)	1170.37	1170	phenyl(95)	phenyl
v29	1150.91		phenyl(87) global(3)	phenyl

isopropylbenzene (IPB) vibrational frequencies (cont.)

mode	MP2	experimental	PED(%)	classification
v28	1145.42		global(71) phenyl(12) subs.(7)	global
(pr)vCC[1] (v27)	1109.95	1110	subs.(81) global(10)	subs.
v26	1074.92		global(58) phenyl(30) subs.(3)	global
v25	1039.03		global(69) phenyl(19) subs.(5)	global
v24	1010.31		phenyl(64) global(26) subs.(4)	global
βCH (v23)	968.73	1025	phenyl(85) global(10)	phenyl
v22	947.37		subs.(95)	subs.
v21	905.97		subs.(83) global(9)	subs.
(pr)vCC[2] (v20)	884.82	920	subs.(81) global(19)	subs.
v19	843.45		phenyl(93)	phenyl
v18	838.16		phenyl(97)	phenyl
v17	821.61		phenyl(94)	phenyl
v16	790.69		phenyl(95)	phenyl
jnct[2] (v15)	725.07	776	global(78) phenyl(14)	global
v14	703.22		phenyl(88) global(3)	phenyl
φdef (v13)	600.48	660	phenyl(92)	phenyl
v12	569.73		phenyl(51) global(33) subs.(7)	global
pr-rock(v11)	541.63	590	global(84) phenyl(7)	global
v10	459.57		global(94)	global
v9	447.16		global(86) subs.(5)	global
v8	377.42		phenyl(97)	phenyl
v7	299.09		global(45) phenyl(43) subs.(4)	global
v6	294.62		global(85) phenyl(2)	global
v5	264.1		subs.(94)	subs.
v4	237.91		global(96)	subs.
v3	207.22		global(89) phenyl(5)	global
v2	120.51		global(93)	global
v1	41.33		global(93)	global

tertbutylbenzene (TBB) vibrational frequencies

mode	MP2	experimental	PED(%)	classification
v66	3081.08		phenyl(98)	phenyl
v65	3067.96		phenyl(99)	phenyl
vCH-phen(v64)	3057.83	3080	phenyl(99)	phenyl
v63	3048.49		phenyl(99)	phenyl
v62	3041.67		phenyl(99)	phenyl
v61	3021.31		subs.(96)	subs.
v60	3020.41		subs.(100)	subs.
v59	3015.63		subs.(100)	subs.
vCH-tB(v58)	3011.91	2980	subs.(100)	subs.
v57	3006.06		subs.(100)	subs.
v56	3005.94		subs.(100)	subs.
v55	2928.45		subs.(100)	subs.
v54	2924.12		subs.(100)	subs.
v53	2924.06		subs.(100)	subs.
vCC(v52)	1586.48	1602	phenyl(96)	phenyl
v51	1565.31		phenyl(92) subs.(2)	phenyl
v50	1495.93		subs.(100)	subs.
γtB(v49)	1483.84	1465	subs.(96)	subs.
v48	1482.44		subs. (76) phenyl(12) global(6)	global
v47	1473.14		subs.(52) phenyl(43) global(2)	global
v46	1464.36		subs.(72) phenyl(24) global(1)	global
v45	1463.18		subs.(90)	subs.
v44	1460.2		subs.(97)	subs.
v43	1422.99		phenyl(93) subs.(7)	phenyl
v42	1400.88		subs.(98)	subs.
v41	1386.46		phenyl(93) subs.(6)	phenyl
v40	1371.13		subs.(91) phenyl(7)	subs.
v39	1370.85		subs.(99)	subs.
γCH[1] (v38)	1298.53	1274	phenyl(90) subs.(8)	phenyl
jnct[1] (v37)	1269.2	1204	subs.(69) global(22) phenyl(7)	global
v36	1214.78		subs.(77) phenyl(19) global(1)	global
v35	1213.4		subs.(95) phenyl(3)	subs.
γCH[2] (v34)	1179.57	1180	phenyl(96)	phenyl

tertbutylbenzene (TBB) vibrational frequencies (cont.)

mode	MP2	experimental	PED(%)	classification
v33	1150.75		phenyl(99)	phenyl
jnct^2 (v32)	1099.55	1122	phenyl(45) subs.(44) global(14)	global
v31	1073.92		phenyl(88) subs.(9)	phenyl
v30	1023.28		subs.(98)	subs.
v29	1016.09		subs.(78) phenyl(21)	global
tB-rock(v28)	1013.17	1040	phenyl(78) subs.(17) global(4)	global
βCH(v27)	966.72	1010	phenyl(95)	phenyl
v26	935.2		subs.(93)	subs.
(tB)vCC (v25)	928.31	935	subs.(93)	subs.
v24	918.98		subs.(98)	subs.
v23	842.5		phenyl(95)	phenyl
δ-oop-CH (v22)	841.13	850	phenyl(97)	phenyl
v21	828.67		subs.(62) phenyl(24) global(8)	global
v20	825.69		phenyl(96) global(2)	phenyl
v19	789.98		phenyl(96)	phenyl
v18	705.43		phenyl(91)	phenyl
jnct^3 (v17)	685.41	720	phenyl(43) subs.(31) global(21)	global
Φdef(v16)	599.85	630	phenyl(94) subs.(3)	phenyl
v15	578.75		subs.(52) phenyl(32) global(13)	global
tB-umb(v14)	514.77	546	subs.(74) phenyl(16) global(7)	global
v13	461.06		phenyl(54) subs.(26) global(17)	global
v12	445.54		subs.(94) phenyl(3)	subs.
v11	379.27		subs.(48) phenyl(45)	global
v10	374.91		subs.(77) phenyl(14)	global
v9	339.53		phenyl(35) subs.(53) global(8)	global
v8	334.09		subs.(53) phenyl(43)	global
v7	306.66		phenyl(46) subs.(46) global(3)	global
v6	306.51		phenyl(71) subs.(26) global(1)	global
v5	274.5		subs.(92) phenyl(5) global(4)	subs.
v4	235.56		subs.(77) phenyl(22) global(1)	global
v3	222.58		subs.(78) phenyl(21)	global
v2	119.93		global(57) subs.(32) phenyl(6)	global
v1	50.17		global(96)	global

Table S1 Vibrational frequencies and mode classifications of toluene, isopropylbenzene (IPB) and *t*-butylbenzene (TBB). The named modes are those that are visible in the experiment while others are only numbered.

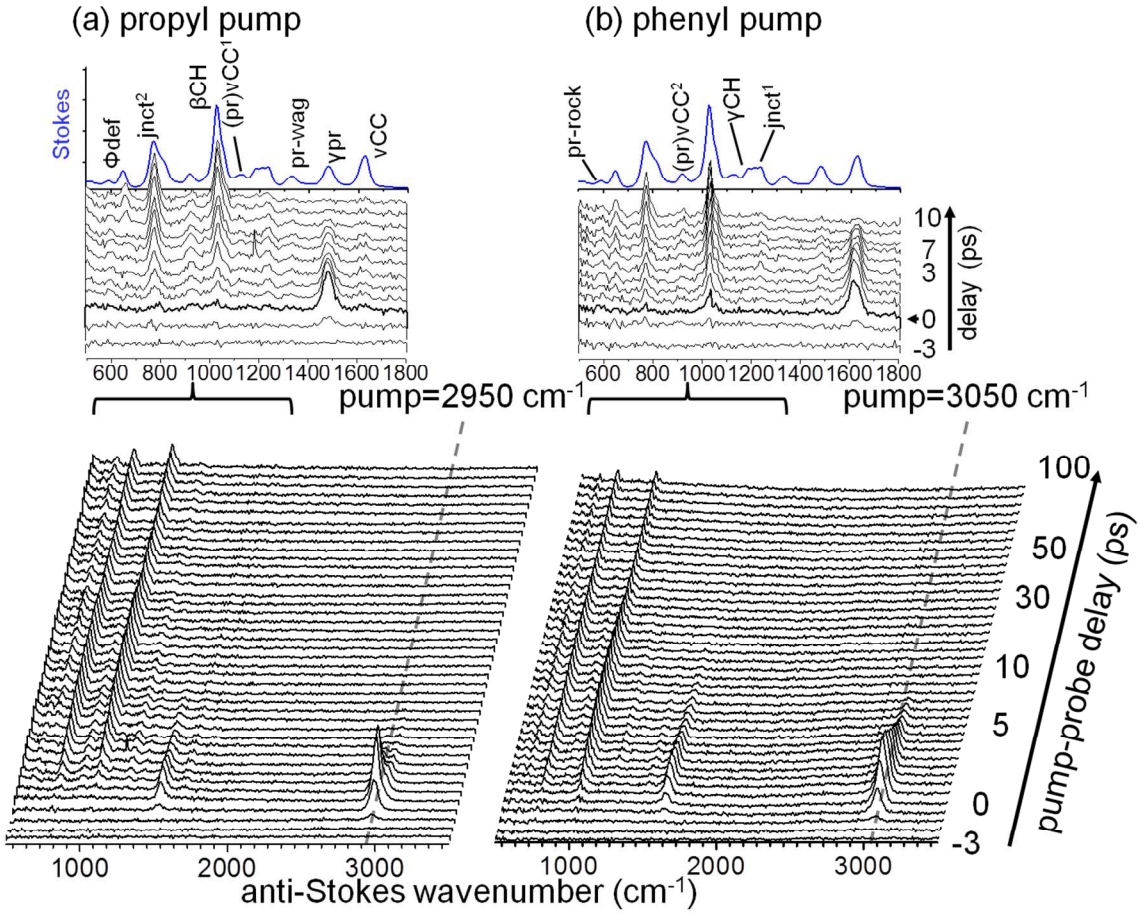

Figure S2 Time dependent IR-Raman spectra of isopropylbenzene (IPB) using (a) propyl pump and (b) phenyl pump. The insets show the daughter excitations created during first 10 ps. The Stokes-Raman spectra are shown as a reference to see the Raman cross-sections of each transition.

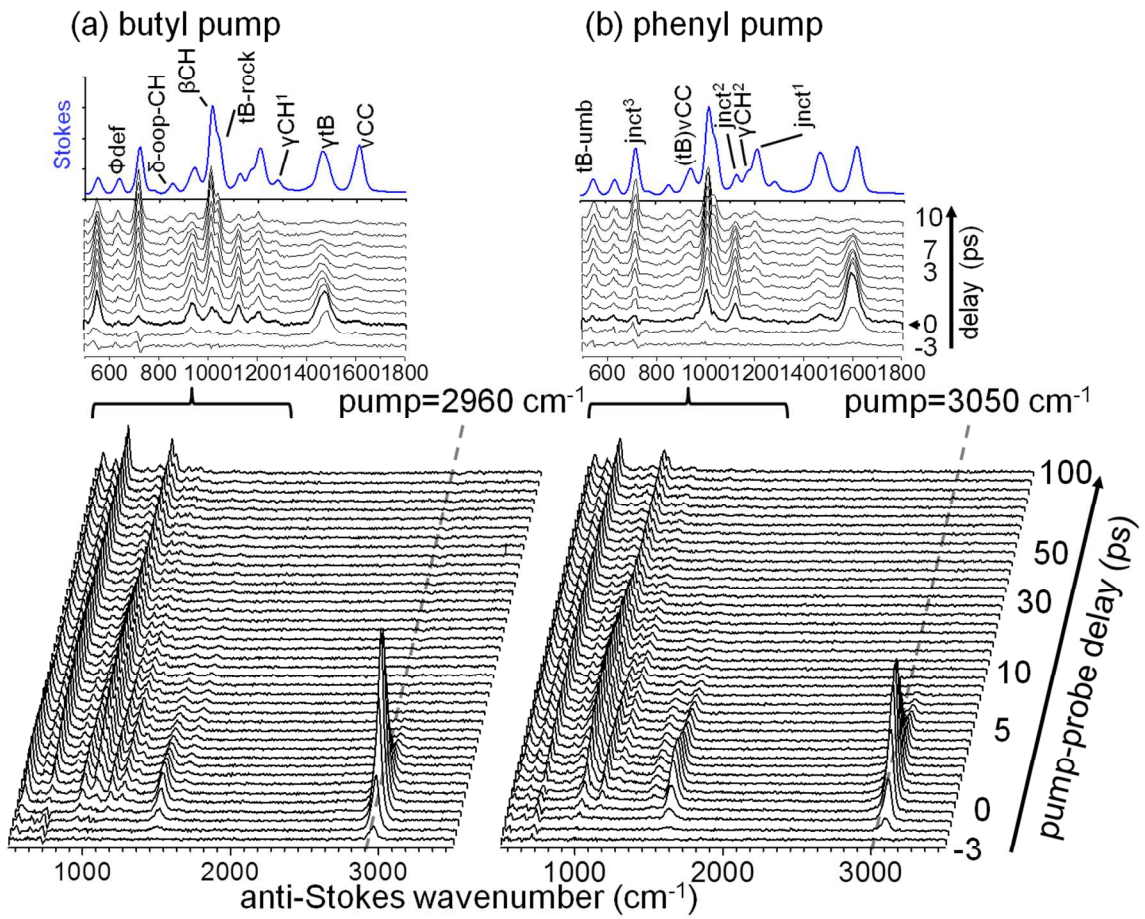

Figure S3 Time dependent IR-Raman spectra of *t*-butylbenzene (TBB) using (a) butyl pump and (b) phenyl pump. The insets show the daughter excitations created during first 10 ps. The Stokes-Raman spectra are shown as a reference to see the Raman cross-sections of each transition.