Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

On the weakly C-H···π hydrogen bonded complexes of sevoflurane and benzene

J.J. Dom, B.J. van der Veken, B. Michielsen, S. Jacobs, Zhifeng Xue, S. Hesse, H.-M. Loritz, M.A. Suhm and W.A. Herrebout

Supplementary Information

Figure S1 Van 't Hoff plot for the isopropyl-bonded complex of sevoflurane and benzene, observed in liquid xenon, obtained by using the band areas of the 682 cm^{-1}, 1497 cm^{-1} and 1520 cm^{-1} bands as a measurement for I_{compl} , I_{sevo} and I_{benz}. for a solution in liquid xenon with mole fractions 2.5×10^{-2} for sevoflurane and 5.0×10^{-3} for benzene (*a*), 9.0×10^{-4} for benzene (*b*).

Figure S2 Scatter plots of the intensity of the isopropyl-bonded complex in liquid xenon of sevoflurane and benzene, I_{compl} , of a typical complex band versus the product of the monomers sevoflurane and benzene, $(I_{sevo})^n \times (I_{benz})^m$ of appropriate powers of the intensities of monomer sevoflurane and monomer benzene : (top-left) n=1, m=1; (top-right) n=1, m=3; (bottom-left) n=1, m=2 , and (bottom-right) n=2, m=1.

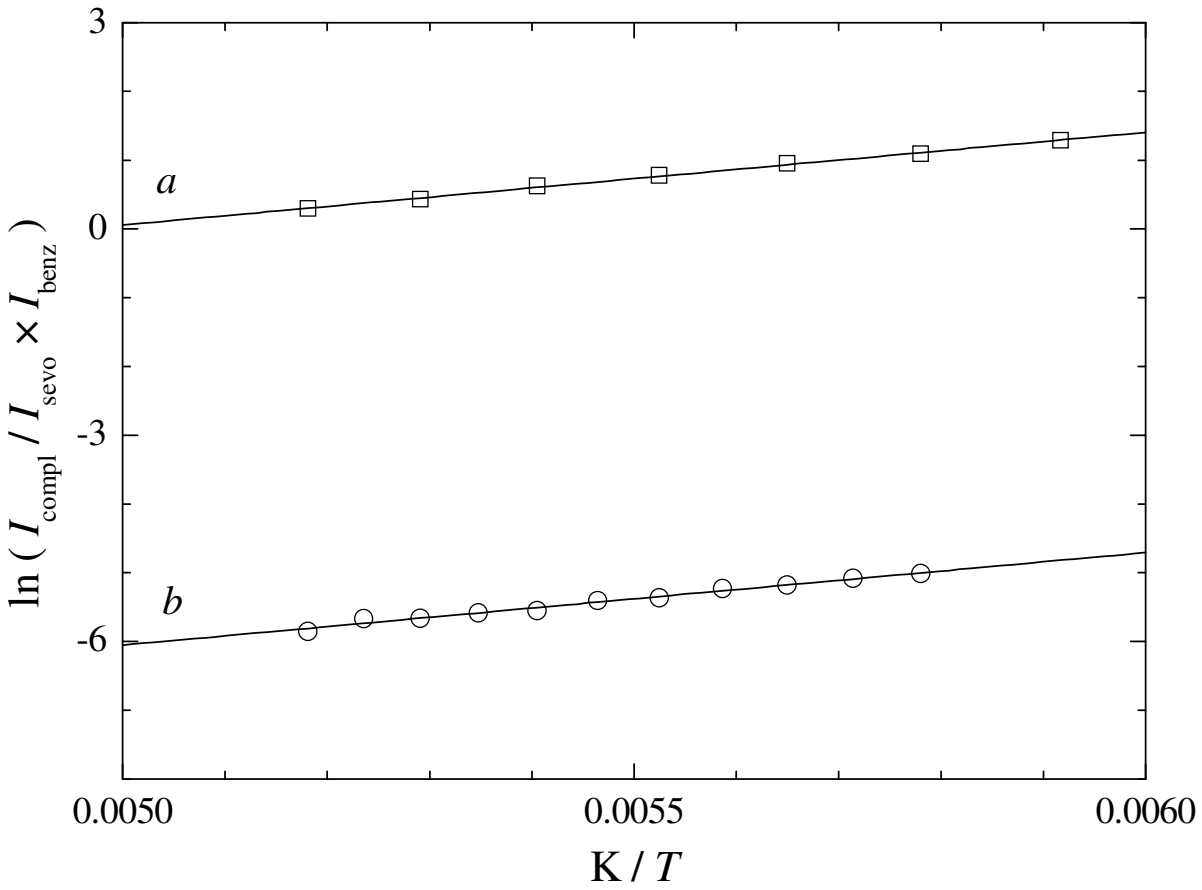

Figure S1

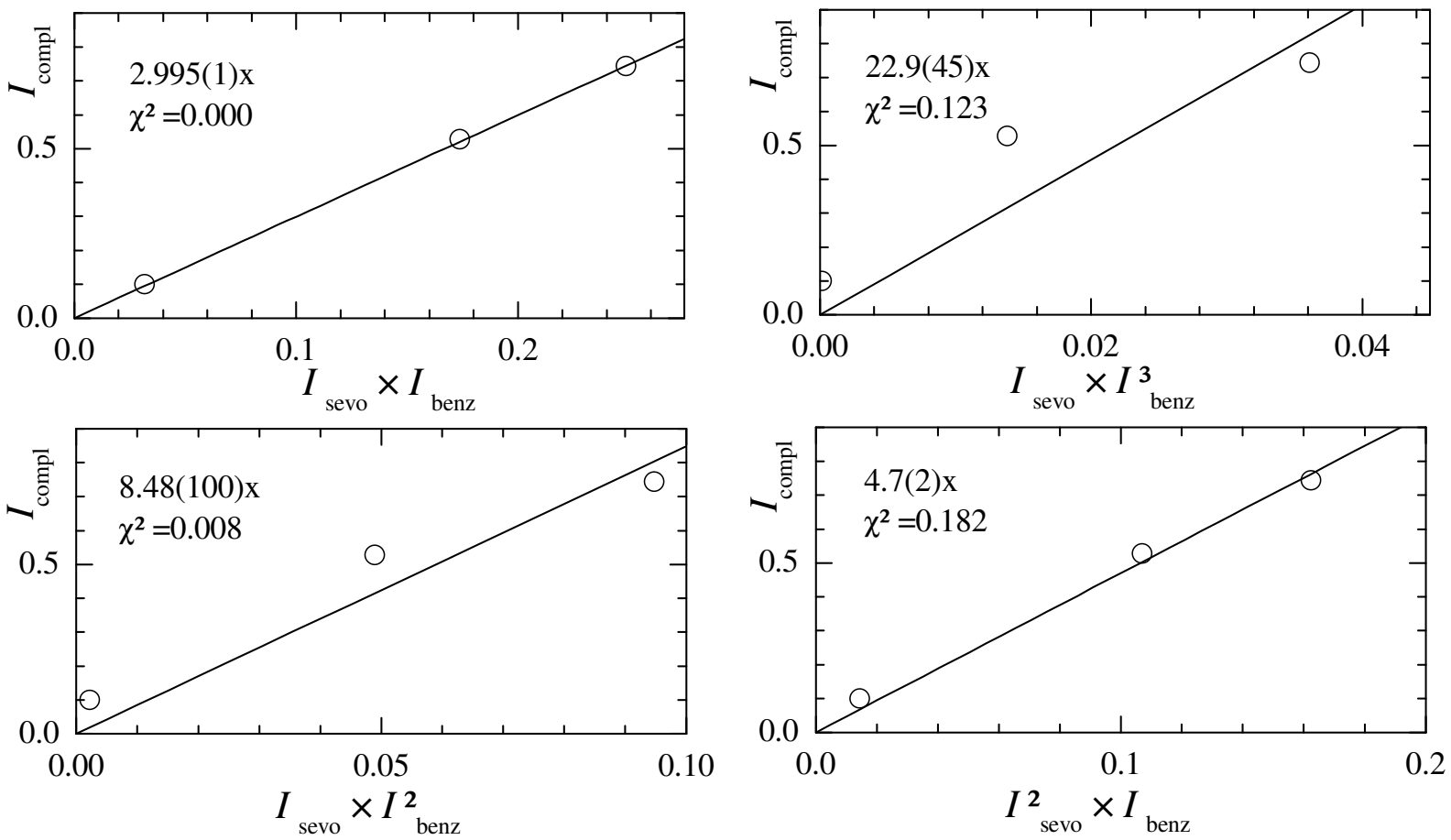

Figure S2

Table S1 Characteristic frequencies ν, in cm^{-1}, and vibrational assignments for jet expansions of sevoflurane and for solutions in liquid xenon at 173 K, in comparison with harmonic MP2/cc-pVDZ vibrational frequencies, in cm^{-1}, and infrared intensities *Int*, in km mol^{-1}, for the three conformers of sevoflurane, SEV1, SEV2 and SEV3.

	Experimental frequencies				SEV1		SEV2		SEV3	
	IR (LXe)	Raman (LXe)	IR jet	Raman jet	MP2/cc-pvdz		MP2/cc-pvdz		MP2/cc-pvdz	
Assignment		*v*	*v*	*v*	*v*	*Int*	*v*	*Int*	*v*	*Int*
ν_1	3021	3021	3032	3031	3220.2	25.0	3234.2	17.3	3144.9	49.4
ν_2	2956	2956	2968	2966	3143.0	2.2	3157.4	2.5	3105.3	8.8
ν_3	2929	2929	2939	2938	3119.5	42.3	3149.5	36.0	3064.6	40.2
ν_4	1497.7	1496.9	-	-	1538.2	2.7	1532.8	1.8	1553.0	2.9
ν_5	1415.9	1415.9	-	1414.3	1465.3	21.6	1475.4	40.5	1495.4	53.7
ν_6	1380.5	-	-	-	1438.3	134.8	1423.4	155.5	1429.3	146.9
ν_7	1370.0	1370.3	-	1370.9	1416.4	55.6	1407.8	34.0	1423.5	22.5
ν_8	1299.7	1297.8	-	1302.0	1348.9	329.8	1354.2	216.1	1354.4	353.6
ν_9	1291.6	-	-	1290.3	1321.5	32.4	1331.2	43.0	1325.0	43.9
ν_{10}	1280.1	1279.3	-	1278.1	1311.1	22.4	1303.3	77.1	1283.8	72.8
ν_{11}	1270.3	-	-	1270.1	1283.2	458.2	1292.8	293.6	1279.3	472.4
ν_{12}	1233.0	-	-	1234.9	1257.5	215.5	1256.8	279.6	1253.6	148.2
ν_{13}	1213.7	1212.1	-	1212.5	1215.2	50.1	1223.5	47.8	1214.1	20.6

ν_{14}	1182.9	-	-	1182.5	1211.1	101.0	1206.2	167.2	1192.1	100.2
ν_{15}	1130.4	1129.7	-	1130.2	1166.0	171.9	1166.8	142.9	1179.1	18.7
ν_{16}	1111.5	1110.7	-	1111.5	1145.3	173.4	1146.8	127.5	1173.3	268.8
ν_{17}	1032.2	1031.3	1038.5	1035.4	1091.5	128.8	1099.2	180.5	1143.2	178.0
ν_{18}	1021.6	1020.0	1027.9	1026.9	1060.8	27.0	1016.7	59.9	1103.6	74.9
ν_{19}	905.3	906.0	910.6		928.3	50.3	917.3	42.2	926.7	53.5
ν_{20}	879.1	879.9	882.8		902.1	20.2	878.5	21.0	901.0	21.5
ν_{21}	742.6	742.5	744.8	743.3	749.3	7.4	757.0	8.6	746.7	8.8
ν_{22}	690.9	690.3	692.3	690.5	697.0	49.4	697.8	49.5	696.9	46.1
ν_{23}	-	602.8	603.4	603.0	611.0	6.7	619.4	0.6	664.2	10.1
ν_{24}	567.4	566.2	-	566.2	582.9	5.8	566.3	3.7	555.4	1.6
ν_{25}	548.5	-	-	-	556.1	2.0	553.6	1.0	545.0	6.8
ν_{26}	537.2	536.6	-	536.7	542.5	3.6	540.9	5.5	542.1	3.3
ν_{27}	523.3	-	-	522.2	526.3	11.5	524.0	10.1	516.4	4.2
ν_{28}	444.1	442.9	-	443.5	452.8	2.2	479.5	4.1	358.0	0.1
ν_{29}	358.9	358.9	-	358.9	366.9	4.7	334.2	0.4	344.2	0.2
ν_{30}	329.3	328.8	-	327.1	336.2	1.3	331.6	2.3	331.8	0.4
ν_{31}	298.3	298.2	-	298.4	297.9	1.9	305.5	3.1	297.6	0.6
ν_{32}	294.4	294.6	-	293.5	295.6	1.7	293.6	0.5	292.7	1.8
ν_{33}	224.3	224.0	-	219.5	225.1	2.0	220.8	1.2	253.1	2.2
ν_{34}	193.8	193.2	-	-	191.2	0.3	216.7	7.1	161.1	1.9

ν_{35}	161.7	-	-	-	166.2	4.4	167.7	1.9	153.1	3.2
ν_{36}	106.4	-	-	-	111.4	4.5	126.7	3.4	71.4	0.2
ν_{37}	71.8	-	-	-	70.7	0.5	98.4	0.4	53.6	6.3
ν_{38}	54.7	-	-	-	54.8	1.1	81.7	2.6	45.6	1.5
ν_{39}	-	-	-	-	31.0	0.0	33.3	0.2	22.8	1.7

Table S2 MP2/cc-pvdz infrared harmonic vibrational frequencies ν, in cm^{-1}, intensities *Int*, in km mol^{-1} and complexation shifts $\Delta\nu$, in cm^{-1}, for sevoflurane, benzene and the complexes of sevoflurane with benzene

Sevoflurane		monomer		isopropyl-bonded complex			fluoromethyl-bonded complex		
symmetry	assignment	ν	*Int*	ν	*Int*	$\Delta\nu$	ν	*Int*	$\Delta\nu$
A	ν_1	3220.2	25.0	3211.1	34.4	-9.1	3237.0	2.1	16.8
	ν_2	3143.0	2.2	3137.5	4.9	-5.5	3141	2.4	-2.0
	ν_3	3119.5	42.3	3111.1	34.4	-8.4	3125.8	32.5	6.3
	ν_4	1538.2	2.7	1532.1	0.3	-6.1	1533.6	2.1	-4.6
	ν_5	1465.3	21.6	1465.4	20.4	0.1	1464.0	22.4	-1.3
	ν_6	1438.3	134.8	1436.7	100.2	-1.6	1438.2	132.7	-0.1
	ν_7	1416.4	55.6	1420.0	41.9	3.6	1415.0	47.8	-1.4
	ν_8	1348.9	329.8	1342.7	384.6	-6.2	1346.3	297.2	-2.6
	ν_9	1321.5	32.4	1319.1	16.7	-2.4	1320.3	26.3	-1.2
	ν_{10}	1311.1	22.4	1311.6	55.6	0.5	1310.6	23.9	-0.5
	ν_{11}	1283.2	458.2	1282.8	371.2	-0.4	1282.6	465.5	-0.6
	ν_{12}	1257.5	215.5	1254.7	194.0	-2.8	1255.7	244.1	-1.8
	ν_{13}	1215.2	50.1	1216.0	24.2	0.8	1213.3	38.1	-1.9
	ν_{14}	1211.1	101.0	1209.8	107.4	-1.3	1205.9	119.3	-5.2
	ν_{15}	1166.0	171.9	1170.6	140.1	4.6	1164.2	0.7	-1.8
	ν_{16}	1145.3	173.4	1142.4	145.6	-2.9	1144.2	157.3	-1.1
	ν_{17}	1091.5	128.8	1093.1	107.5	1.6	1084.6	129.0	-6.9

ν_{18}	1060.8	27.0	1056.4	20.2	-4.4	1059.2	28.8	-1.6
ν_{19}	928.3	50.3	926.2	42.3	-2.1	927.2	47.7	-1.1
ν_{20}	902.1	20.2	902.0	25.5	-0.1	901.1	18.5	-1.0
ν_{21}	749.3	7.4	748.8	8.3	-0.5	749.0	7.4	-0.3
ν_{22}	697.0	49.4	696.0	42.0	-1.0	696.2	40.7	-0.8
ν_{23}	611.0	6.7	612.2	5.7	1.2	610.8	5.9	-0.2
ν_{24}	582.9	5.8	578.0	5.7	-4.9	583.0	7.7	0.1
ν_{25}	556.1	2.0	555.6	2.6	-0.5	556.0	2.1	-0.1
ν_{26}	542.5	3.6	542.3	2.4	-0.2	542.2	3.5	-0.3
ν_{27}	526.3	11.5	528.2	13.5	1.9	526.3	10.8	0.0
ν_{28}	452.8	2.2	450.7	1.4	-2.1	453.5	2.5	0.7
ν_{29}	366.9	4.7	368.4	4.5	1.5	367.5	3.5	-0.6
ν_{30}	336.2	1.3	335.2	1.2	-1.0	336.1	1.1	-0.1
ν_{31}	297.9	1.9	302.6	2.7	4.8	299.2	1.9	1.3
ν_{32}	295.6	1.7	297.2	0.2	1.5	295.7	1.0	0.1
ν_{33}	225.1	2.0	222.8	1.8	-2.3	225.3	1.6	0.2
ν_{34}	191.2	0.3	193.3	0.3	2.1	194.6	0.3	3.4
ν_{35}	166.2	4.4	161.4	3.0	-4.8	168.6	4.2	2.4
ν_{36}	111.4	4.5	106.0	6.6	-5.4	117.0	3.3	5.6
ν_{37}	70.7	0.5	76.7	0.7	6.0	80.7	0.3	10.0
ν_{38}	54.8	1.1	57.2	0.2	2.4	62.5	0.8	7.7

	ν_{39}	31.0	0.0	38.4	0.1	7.4	30.5	0.0	-0.5
Benzene									
A_{1g}	ν_1	3246.8	0.0	3249.0	0.2	2.2	3247.9	0.2	1.1
	ν_2	1017.0	0.0	1015.9	0.2	-1.1	1015.7	0.3	-1.3
A_{2g}	ν_3	1358.9	0.0	1358.6	0.0	-0.3	1358.8	0.0	-0.1
	ν_4	686.0	90.9	692.5	108.5	6.5	690.2	111.7	4.2
B_{1u}	ν_5	3209.4	0.0	3212.0	0.8	2.6	3210.9	0.1	1.5
	ν_6	1007.0	0.0	1006.7	0.0	-0.4	1006.6	0.0	-0.4
B_{2g}	ν_7	961.9	0.0	962.5	0.0	0.5	962.2	0.0	0.3
	ν_8	633.9	0.0	625.0	0.0	-8.9	627.0	0.0	-6.9
B_{2u}	ν_9	1472.4	0.0	1473.6	0.0	1.3	1473.0	0.0	0.6
	ν_{10}	1163.4	0.0	1164.3	0.0	1.0	1161.3	144.1	-2.1
E_{1g}	ν_{11}	858.9	0.0	864.5	0.6	5.6	863.1	0.2	4.2
		858.9	0.0	863.6	0.7	4.7	862.5	0.2	3.6
E_{1u}	ν_{12}	3236.9	29.7	3240.9	16.1	4.0	3238.6	20.8	1.7
		3236.9	29.7	3237.7	18.5	0.8	3237.6	29.7	0.7
	ν_{13}	1505.0	7.6	1503.9	9.3	-1.1	1504.1	9.3	-0.9
		1505.0	7.6	1503.7	8.2	-1.3	1504.0	8.8	-1.0
	ν_{14}	1061.3	4.4	1061.1	4.7	-0.2	1061.1	3.5	-0.2
		1061.3	4.4	1060.6	2.9	-0.7	1060.7	3.6	-0.6
E_{2g}	ν_{15}	3220.4	0.0	3224.6	0.6	4.2	3223.0	0.3	2.6

			3220.4	0.0	3222.3	0.0	1.9	3221.4	0.4	1.0
		ν_{16}	1649.7	0.0	1646.9	0.0	-2.8	1647.3	0.0	-2.4
			1649.7	0.0	1646.5	0.0	-3.2	1647.0	0.0	-2.7
		ν_{17}	1190.7	0.0	1191.7	0.5	1.0	1191.4	0.1	0.7
			1190.7	0.0	1190.5	0.3	-0.2	1190.5	0.1	-0.2
		ν_{18}	605.6	0.0	605.3	0.0	-0.3	605.2	0.0	-0.4
			605.6	0.0	604.8	0.0	-0.8	604.8	0.0	-0.8
E_{2u}		ν_{19}	953.7	0.0	957.4	0.0	3.7	956.1	0.1	2.4
			953.7	0.0	956.2	0.0	2.5	955.8	0.0	2.1
		ν_{20}	400.9	0.0	399.8	0.0	-1.1	400.3	0.0	-0.6
			400.9	0.0	399.0	0.0	-1.9	399.6	0.0	-1.3
	vdW									
		ν_1			52.7	0.2		52.7	0.2	
		ν_2			50.9	0.9		50.0	0.2	
		ν_3			45.0	0.1		43.0	0.1	
		ν_4			34.3	0.1		19.1	0.1	
		ν_5			21.8	0.3		11.8	0.2	
		ν_6			7.9	0.0		7.8	0.0	

Table S3 MP2/aug-cc-pvdz infrared harmonic vibrational frequencies ν, in cm^{-1}, intensities *Int*, in km mol^{-1} and complexation shifts $\Delta\nu$, in cm^{-1}, for sevoflurane, benzene and the complexes of sevoflurane with benzene

Sevoflurane		monomer		isopropyl-bonded complex			fluoromethyl-bonded complex		
		ν	*Int*	ν	*Int*	$\Delta\nu$	ν	*Int*	$\Delta\nu$
A	ν_1	3225.5	10.2	3216.3	15.7	-9.1	3231.9	4.1	6.4
	ν_2	3120.8	15.7	3111.5	15.2	-9.3	3113.5	7.9	-7.3
	ν_3	3116.2	16.1	3107.9	26.7	-8.3	3121.6	14.7	5.4
	ν_4	1524.4	0.7	1518.6	0.8	-5.8	1515.9	0.7	-8.5
	ν_5	1431.1	8.8	1430.2	7.9	-1.0	1428.7	10.8	-2.4
	ν_6	1413.9	86.0	1410.2	55.9	-3.6	1412.7	87.5	-1.2
	ν_7	1392.1	56.1	1393.7	45.3	1.6	1389.6	46.3	-2.5
	ν_8	1311.8	191.1	1305.2	173.5	-6.6	1308.1	162.6	-3.7
	ν_9	1293.1	20.2	1295.9	100.3	2.8	1292.9	16.4	-0.2
	ν_{10}	1281.3	42.6	1274.8	54.4	-6.5	1278.5	40.5	-2.8
	ν_{11}	1219.3	522.4	1216.1	401.6	-3.2	1218.1	510.8	-1.2
	ν_{12}	1207.6	245.8	1202.3	231.8	-5.3	1204.7	284.4	-2.9
	ν_{13}	1188.4	64.2	1186.1	53.2	-2.3	1182.5	72.6	-5.9
	ν_{14}	1152.0	12.2	1149.9	16.3	-2.1	1149.7	9.6	-2.3
	ν_{15}	1138.7	144.4	1142.1	132.4	3.4	1133.8	118.8	-4.9
	ν_{16}	1098.1	159.0	1092.7	120.2	-5.4	1095.9	144.8	-2.2
	ν_{17}	1042.8	42.7	1039.3	45.8	-3.5	1039.0	30.1	-3.8

ν_{18}	1012.7	161.5	1006.7	124.2	-5.9	1005.2	124.4	-7.5
ν_{19}	906.1	56.7	902.9	45.7	-3.2	904.7	53.5	-1.4
ν_{20}	880.7	19.6	880.1	31.1	-0.6	878.2	17.1	-2.5
ν_{21}	726.1	5.7	725.0	7.8	-1.1	725.6	5.7	-0.5
ν_{22}	674.8	43.9	673.6	34.9	-1.2	674.2	46.9	-0.6
ν_{23}	592.2	9.2	593.8	7.9	1.6	592.4	7.3	0.2
ν_{24}	559.1	4.5	551.2	4.7	-7.9	558.4	6.6	-0.7
ν_{25}	535.0	1.7	533.6	2.3	-1.3	534.8	2.0	-0.2
ν_{26}	519.5	3.0	519.4	1.9	-0.2	519.2	2.9	-0.3
ν_{27}	504.9	9.9	507.4	12.2	2.4	504.9	8.9	0.0
ν_{28}	439.1	1.8	437.3	0.8	-1.8	440.1	2.0	1.0
ν_{29}	361.4	5.2	363.7	4.8	2.3	362.8	3.7	1.4
ν_{30}	326.8	1.4	325.7	1.3	-1.0	326.6	1.1	-0.2
ν_{31}	292.2	2.5	297.9	2.3	5.6	294.9	2.0	4.7
ν_{32}	288.7	0.8	290.4	0.2	1.8	288.6	0.5	-0.1
ν_{33}	220.3	1.9	220.1	1.8	-0.2	220.9	1.5	0.6
ν_{34}	190.6	0.2	194.8	0.3	4.2	196.4	0.3	5.8
ν_{35}	163.1	3.9	160.0	2.9	-3.1	166.3	3.6	3.2
ν_{36}	103.1	5.0	108.4	8.6	5.3	112.0	3.5	8.9
ν_{37}	69.4	0.9	81.2	0.8	11.7	87.3	0.5	17.9
ν_{38}	51.3	1.6	54.9	0.5	3.6	58.8	1.2	7.5

	ν_{39}	34.0	0.0	48.9	0.3	15.0	36.6	0.0	2.6
Benzene									
A_{1g}	ν_1	3233.5	0.0	3235.7	0.3	2.2	3234.5	0.4	1.0
	ν_2	1004.2	0.0	1003.2	0.8	-1.1	1002.5	52.4	-1.7
A_{2g}	ν_3	1324.0	0.0	1323.3	0.0	-0.7	1323.6	0.0	-0.4
	ν_4	678.0	115.9	686.9	134.8	8.9	684.7	125.8	6.7
B_{1u}	ν_5	3196.2	0.0	3199.3	0.3	3.0	3197.9	0.1	1.7
	ν_6	976.1	0.0	974.1	0.0	-2.0	973.9	0.1	-2.2
B_{2g}	ν_7	907.0	0.0	908.4	0.1	1.4	909.0	0.4	2.0
	ν_8	576.9	0.0	570.2	0.0	-6.7	571.9	0.0	-5.0
B_{2u}	ν_9	1469.9	0.0	1475.7	0.0	5.8	1474.2	0.0	4.3
	ν_{10}	1155.9	0.0	1157.8	0.6	1.9	1157.2	0.3	1.3
E_{1g}	ν_{11}	845.0	0.0	852.2	1.1	7.2	851.0	0.7	6.0
		845.0	0.0	850.7	1.9	5.7	849.8	0.5	0.8
E_{1u}	ν_{12}	3223.8	28.7	3227.9	12.8	4.1	3225.7	17.7	1.9
		3223.8	28.7	3224.5	15.2	0.7	3223.8	17.9	0.0
	ν_{13}	1469.6	5.3	1468.6	7.2	-1.1	1468.8	6.5	-0.8
		1469.6	5.3	1468.1	6.2	-1.5	1468.6	7.1	-1.0
	ν_{14}	1051.0	5.2	1050.5	4.3	-0.5	1050.5	6.0	-0.5
		1051.0	5.2	1049.6	3.1	-1.5	1050.0	3.7	-1.0
E_{2g}	ν_{15}	3207.5	0.0	3212.3	0.6	4.8	3210.5	0.8	3.0

			3207.5	0.0	3209.6	0.1	2.1	3207.9	0.4	0.4
		ν_{16}	1622.2	0.0	1618.6	0.0	-3.7	1619.8	0.0	-2.4
			1622.2	0.0	1618.0	0.0	-4.3	1619.2	0.0	-3.0
		ν_{17}	1183.1	0.0	1183.9	2.5	0.8	1184.1	14.2	1.0
			1183.1	0.0	1182.7	2.6	-0.4	1182.8	0.3	-0.3
		ν_{18}	596.9	0.0	595.4	0.0	-1.5	595.4	0.0	-1.5
			596.9	0.0	594.7	0.1	-2.2	594.9	0.0	-2.0
E_{2u}		ν_{19}	929.7	0.0	932.9	0.1	3.1	933.2	0.3	35
			929.7	0.0	932.7	0.1	2.9	932.3	0.1	2.6
		ν_{20}	394.7	0.0	394.3	0.0	-0.4	395.0	0.1	0.3
			394.7	0.0	392.8	0.0	-1.9	393.6	0.0	-1.1
	vdW									
		ν_1			70.7	0.2		67.4	0.4	
		ν_2			68.3	0.6		62.2	0.1	
		ν_3			62.5	0.2		51.4	0.2	
		ν_4			46.2	0.4		30.7	0.2	
		ν_5			30.8	0.2		17.5	0.2	
		ν_6			12.9	0.0		10.2	0.0	