Supplementary Material (ESI) for PCCP

The complexes of halothane with benzene: the temperature dependent direction of the complexation shift of the aliphatic C-H stretching

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SUPPLEMENTARY INFORMATION

Figure S1 (A). Scatter plots of the integrated intensity of the 681 cm^{-1} complex band versus the product $(I_{halothane})^m \times (I_{benzene})^n$ of the intensities of monomer halothane (3007.1 cm^{-1} band) and benzene (674.8 cm^{-1} band).

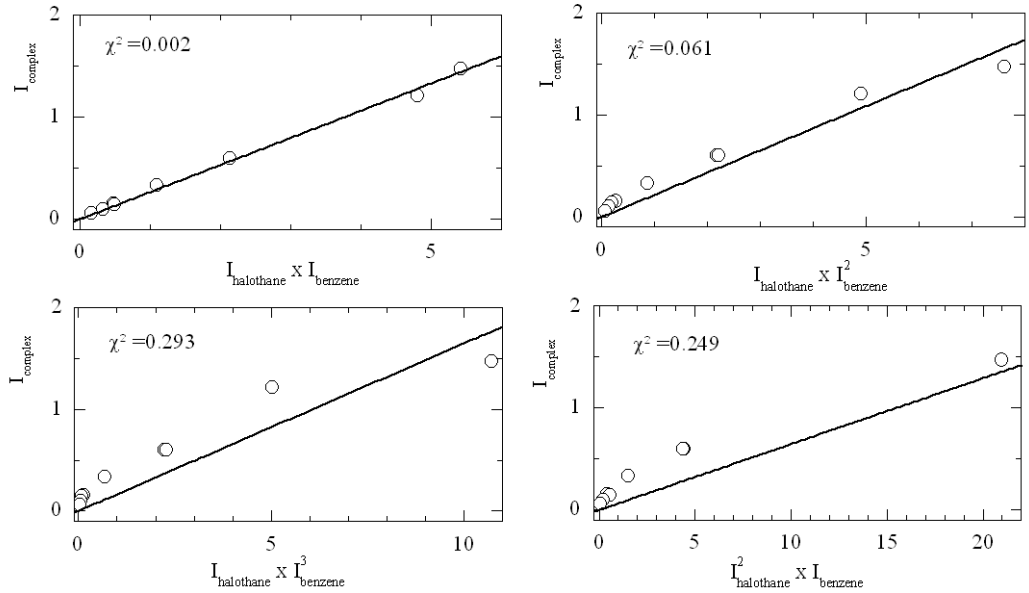

Figure S1 (B). Scatter plots of the integrated intensity of the 686 cm^{-1} complex band versus the product $(I_{halothane})^m \times (I_{benzene})^n$ of the intensities of monomer halothane (3007.1 cm^{-1} band) and benzene (674.8 cm^{-1} band).

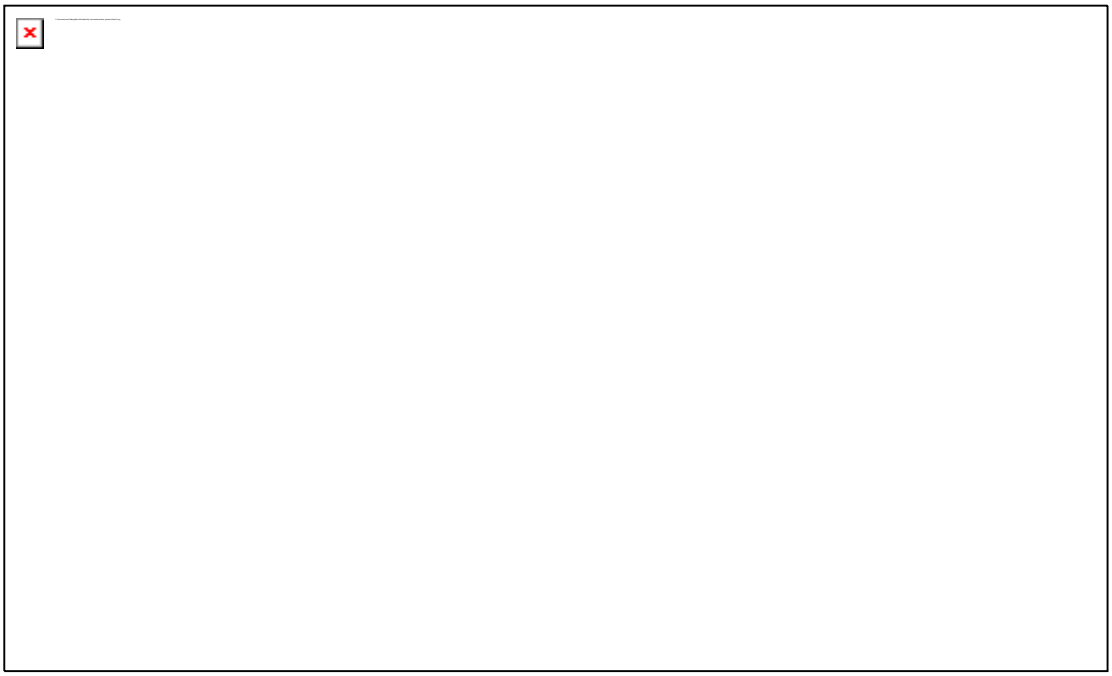

Figure S2. Infrared spectra of the $\nu_{11}+\nu_{19}$ and the $\nu_7+\nu_{11}$ absorptions in LKr. Trace a shows the mixture, trace b the monomer halothane, trace c the monomer benzene and trace d the spectrum of the complex obtained after subtracting traces b and c from trace a.

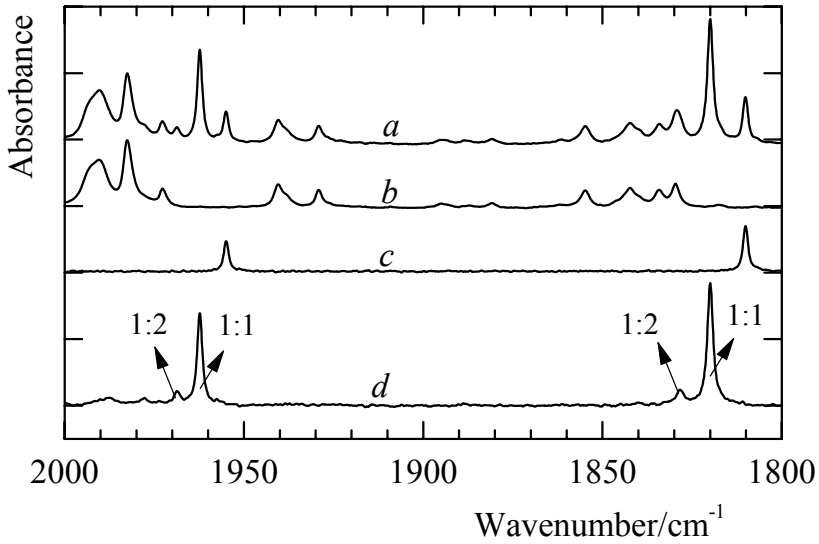

Figure S3. Van't Hoff plots for the 1:1 and 2:1 complexes of halothane and benzene observed in liquid krypton

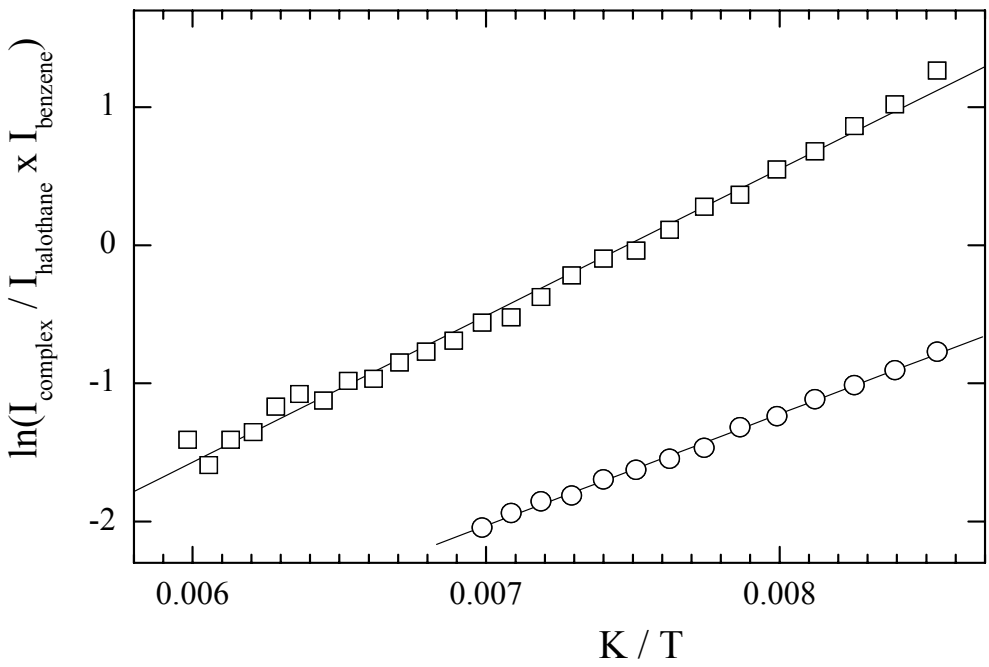
ln(I complex / I halothane x I benzene)
1
0
-1
-2
0.006
0.007
0.008
K / T

Table ST1. MP2/aug-cc-pVDZ harmonic vibrational frequencies (cm^{-1}), infrared intensities (km mol^{-1}) and complexation shifts for halothane, benzene($-d_6$) and the complexes of halothane with benzene($-d_6$).

			MP2/aug-cc-pVDZ				
			monomer		**complex**		
			$\tilde{\nu}$	intensity	$\tilde{\nu}$	intensity	$\Delta\tilde{\nu}$
halothane	A	ν_1	3174.7	4.7	3184.9	59.8	10.2
		ν_2	1334.2	112.7	1330.7	92.7	-3.5
		ν_3	1277.5	129.2	1268.2	140.2	-9.3
		ν_4	1212.6	2.8	1203.9	5.9	-8.7
		ν_5	1171.7	209.4	1166.9	172.5	-4.8
		ν_6	1124.5	180.6	1116.9	176.9	-7.6
		ν_7	868.2	35.2	866.4	25.8	-1.7
		ν_8	825.2	79.0	822.7	61.1	-2.4
		ν_9	724.3	15.5	723.6	20.2	-0.7
		ν_{10}	653.5	25.0	653.8	22.3	0.4
		ν_{11}	537.9	3.8	537.5	3.2	-0.4
		ν_{12}	503.8	4.0	504.1	7.0	0.4
		ν_{13}	362.0	0.5	361.7	0.4	-0.4
		ν_{14}	311.2	0.5	309.9	0.4	-1.3
		ν_{15}	229.7	0.3	231.3	0.9	1.5
		ν_{16}	199.3	0.5	200.3	0.6	1.0
		ν_{17}	158.5	0.8	159.0	0.5	0.5
		ν_{18}	71.2	0.0	78.1	0.0	6.8
benzene	A_{1g}	ν_1	3239.4	0.0	3235.8	0.1	-3.7
		ν_2	1007.6	0.0	1001.8	0.5	-5.8
	A_{2g}	ν_3	1322.5	0.0	1323.1	0.0	0.5
	A_{2u}	ν_4	678.0	115.8	684.7	127.7	6.7
	B_{1u}	ν_5	3202.8	0.0	3201.5	0.1	-1.3
		ν_6	969.7	0.0	972.7	0.1	3.1
	B_{2g}	ν_7	904.2	0.0	906.6	0.0	2.4
		ν_8	577.5	0.0	566.8	0.0	-10.7
	B_{2u}	ν_9	1474.7	0.0	1474.0	0.0	-0.7
		ν_{10}	1155.3	0.0	1158.0	0.0	2.7
	E_{1g}	ν_{11}	845.3	0.0	850.5	1.3	5.2
			845.3	0.0	850.5	1.3	5.2
	E_{1u}	ν_{12}	3229.8	56.7	3226.6	13.8	-3.2
			3229.8	56.7	3225.9	14.2	-3.9
		ν_{13}	1469.6	10.8	1468.3	7.3	-1.2
			1469.6	10.8	1466.3	7.9	-3.2

		ν_{14}	1052.3	5.4	1050.3	4.2	-2.0
			1052.3	5.4	1047.3	4.1	-5.0
	E_{2g}	ν_{15}	3213.7	0.0	3211.5	0.0	-2.2
			3213.7	0.0	3211.5	0.0	-2.2
		ν_{16}	1625.2	0.0	1616.4	0.0	-8.8
			1625.2	0.0	1615.9	0.0	-9.3
		ν_{17}	1183.2	0.0	1183.9	0.2	0.7
			1183.2	0.0	1183.0	1.3	-0.2
		ν_{18}	595.0	0.0	593.3	0.1	-1.7
			595.0	0.0	593.3	0.1	-1.7
	E_{2u}	ν_{19}	926.9	0.0	931.6	0.0	4.6
			926.9	0.0	931.6	0.0	4.6
		ν_{20}	394.5	0.0	392.1	0.0	-2.5
			394.5	0.0	392.1	0.0	-2.5
vdW		ν_1			72.2	0.1	
		ν_2			67.9	0.1	
		ν_3			65.7	0.0	
		ν_4			28.4	0.0	
		ν_5			25.6	0.0	
		ν_6			4.6	0.0	

			MP2/aug-cc-pVDZ				
			monomer		**complex**		
			$\tilde{\nu}$	intensity	$\tilde{\nu}$	intensity	$\Delta\tilde{\nu}$
halothane	A	ν_1	3174.7	4.7	3184.9	59.7	10.2
		ν_2	1334.2	112.7	1332.5	57.9	-1.7
		ν_3	1277.5	129.2	1268.0	139.3	-9.5
		ν_4	1212.6	2.8	1203.5	6.1	-9.1
		ν_5	1171.7	209.4	1167.0	174.0	-4.7
		ν_6	1124.5	180.6	1116.9	178.2	-7.6
		ν_7	868.2	35.2	866.4	26.9	-1.8
		ν_8	825.2	79.0	823.4	63.3	-1.8
		ν_9	724.3	15.5	723.3	15.2	-1.0
		ν_{10}	653.5	25.0	653.9	25.3	0.4
		ν_{11}	537.9	3.8	537.5	3.1	-0.4
		ν_{12}	503.8	4.0	502.6	23.3	-1.2
		ν_{13}	362.0	0.5	361.7	0.4	-0.4
		ν_{14}	311.2	0.5	309.9	0.4	-1.3
		ν_{15}	229.7	0.3	231.2	0.9	1.5
		ν_{16}	199.3	0.5	200.3	0.6	1.0
		ν_{17}	158.5	0.8	159.0	0.5	0.5
		ν_{18}	71.2	0.0	76.9	0.0	5.7
benzene-d_6	A_{1g}	ν_1	2400.8	0.0	2402.6	0.1	1.8

		ν_2	957.4	0.0	954.5	0.3	-2.9
	A_{2g}	ν_3	1030.3	0.0	1029.2	0.0	-1.1
	A_{2u}	ν_4	498.1	62.5	505.1	54.1	7.0
	B_{1u}	ν_5	2352.4	0.0	2357.3	0.1	4.9
		ν_6	937.4	0.0	934.7	0.0	-2.7
	B_{2g}	ν_7	660.5	0.0	657.6	0.0	-2.9
		ν_8	560.1	0.0	552.6	0.0	-7.6
	B_{2u}	ν_9	1467.7	0.0	1470.8	0.0	3.1
		ν_{10}	819.9	0.0	820.9	0.0	1.0
	E_{1g}	ν_{11}	657.6	0.0	662.4	0.7	4.8
			657.6	0.0	662.8	0.0	5.2
	E_{1u}	ν_{12}	2388.2	31.0	2390.0	8.5	1.9
			2388.2	31.0	2390.5	8.3	2.3
		ν_{13}	1330.0	1.4	1325.4	3.5	-4.6
			1330.0	1.4	1324.2	37.0	-5.8
		ν_{14}	814.9	9.0	814.3	0.3	-0.6
			814.9	9.0	812.7	3.5	-2.2
	E_{2g}	ν_{15}	2366.9	0.0	2370.4	0.0	3.5
			2366.9	0.0	2370.8	0.0	3.9
		ν_{15}	1585.9	0.0	1578.9	0.0	-7.1
			1585.9	0.0	1578.1	0.0	-7.8
		ν_{17}	862.4	0.0	862.8	0.0	0.4
			862.4	0.0	861.8	0.1	-0.6
		ν_{18}	568.0	0.0	565.9	0.3	-2.2
			568.0	0.0	565.4	0.6	-2.6
	E_{2u}	ν_{19}	752.8	0.0	753.8	0.0	1.0
			752.8	0.0	753.4	0.0	0.7
		ν_{20}	344.6	0.0	343.0	0.0	-1.6
			344.6	0.0	342.7	0.0	-1.9
vdW		ν_1			67.0	0.1	
		ν_2			64.0	0.0	
		ν_3			63.4	0.1	
		ν_4			27.8	0.0	
		ν_5			25.1	0.0	
		ν_6			4.5	0.0	

Table ST2. The χ^2 values of the linear regression line between the integrated intensity of the complex band and the product of the integrated intensity of the monomers with appropriate powers $\left(I_{halothane}\right)^m \times \left(I_{benzene(-d_6)}\right)^n$, obtained by using the integrated band areas of the indicated complex band, the 3007.1 cm^{-1} band for monomer halothane, the 674.8 cm^{-1} of benzene and the 496.8 cm^{-1} band for monomer benzene(-d_6) at 119 K. The lowest χ^2 values are printed in italic.

	complex band	1:1	1:2	1:3	2:1	3:1
halothane·benzene	680.8 cm^{-1}	*0.0027*	0.0613	0.2931	0.2490	2.0580
	686.1 cm^{-1}	0.0108	0.0037	0.0074	*0.0006*	0.0235
halothane·benzene-d_6	501.9 cm^{-1}	*0.0031*	0.1185	0.5437	0.1362	0.9018
	506.3 cm^{-1}	0.0023	0.137	0.0487	*0.0006*	0.0088