Supplementary Material (ESI) for *PCCP*

Supporting Information

for:

Halogen Bonding to a Divalent Sulfur Atom: an Experimental Study of the Interactions of CF_3X (X = Cl, Br, I) with Dimethyl Sulfide †

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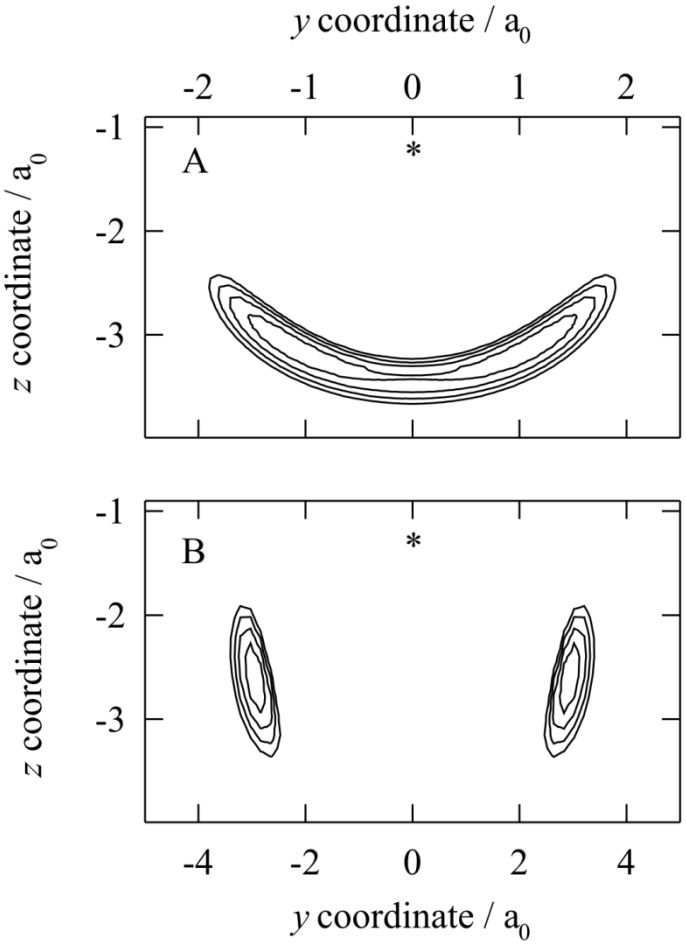

Figure S1. The electrostatic potential for dimethyl sulfide (A) and dimethyl ether (B) in the (*y*,*z*)-plane, with *z* along the twofold axis and *y* perpendicular to the plane of the heavy atom skeleton. The position of the heteroatom is indicated by an asterisk.

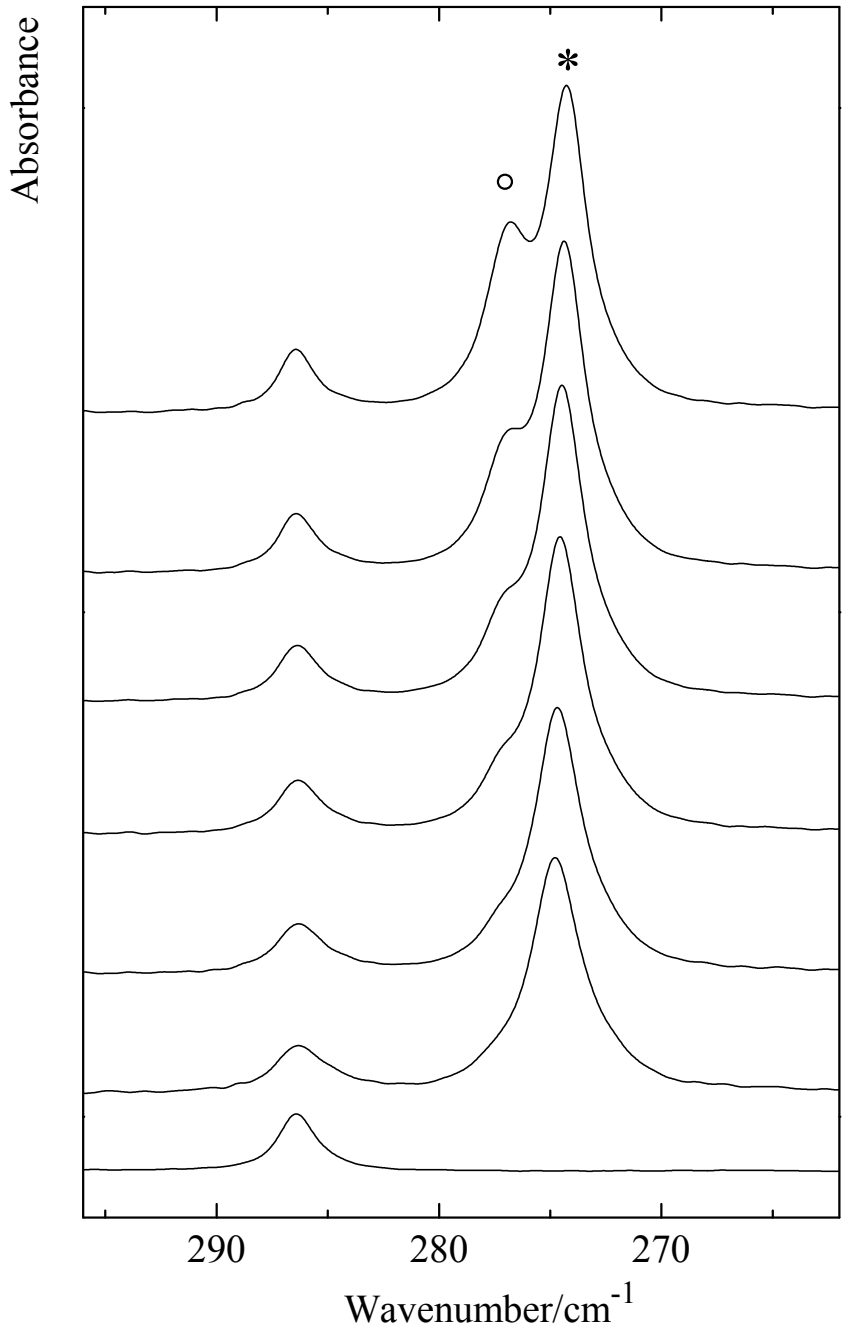

Figure S2. Temperature dependence of the $\nu_3^{CF_3X}$ region obtained for a solution in liquid krypton containing CF_3I and dimethyl sulfide. From top to bottom, the temperature in the solution increases from 118 K to 143 K. The lowest trace represents the spectrum of the CF_3I monomer recorded at 123 K. The new bands assigned to the 1:1 complex are marked with an asterisk (*); the bands assigned to the 2:1 complex are marked with a circle (°).

Table S1. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman scattering activities, in $Å^4$ amu^{-1}, for CF_3Cl·DMS.

Mode	$\nu_{monomer}$	IR Intensity	Raman scattering	$\nu_{complex}$	IR Intensity	Raman scattering	$\Delta\nu$
CF_3Cl							
ν_1 (a_1)	1096.4	496.6	1.5	1099.3	537.6	4.1	2.9
ν_2 (a_1)	764.7	24.8	9.3	761.4	20.0	16.7	-3.4
ν_3 (a_1)	479.9	0.1	4.8	477.1	2.2	15.2	-2.8
ν_4 (e)	1192.5	564.4	3.0	1184.6	539.9	2.8	-7.9
ν_5 (e)	545.9	2.8	1.6	545.8	2.7	1.6	-0.1
ν_6 (e)	347.1	0.004	1.7	349.5	0.02	1.6	2.4
DMS							
ν_1 (a_1)	3185.8	9.9	91.9	3186.7	7.9	91.6	0.8
ν_2 (a_1)	3061.7	31.7	338.3	3061.6	27.1	331.3	-0.2
ν_3 (a_1)	1473.6	0.3	7.6	1473.0	1.3	8.1	-0.5
ν_4 (a_1)	1352.5	0.8	0.9	1352.8	0.1	2.0	0.3
ν_5 (a_1)	1046.5	8.6	0.4	1046.8	7.5	0.3	0.3
ν_6 (a_1)	713.0	2.8	22.1	712.1	2.6	19.7	-0.9
ν_7 (a_1)	260.8	0.03	3.1	261.4	0.1	2.8	0.5
ν_8 (a_2)	3167.7	0.0	16.6	3167.9	0.2	14.5	0.2
ν_9 (a_2)	1450.1	0.0	10.3	1449.4	0.1	9.8	-0.8
ν_{10} (a_2)	945.7	0.0	0.1	947.9	0.0	0.3	2.3
ν_{11} (a_2)	172.3	0.0	0.1	173.5	0.02	0.1	1.2
ν_{12} (b_1)	3159.6	21.2	119.4	3160.5	21.6	110.1	1.0
ν_{13} (b_1)	1462.5	12.9	0.0	1461.9	12.3	0.2	-0.7
ν_{14} (b_1)	982.7	4.1	0.0	984.3	11.7	0.5	1.6
ν_{15} (b_1)	187.9	0.8	0.1	187.6	1.1	0.1	-0.3
ν_{16} (b_2)	3186.9	3.3	42.1	3187.7	2.4	36.8	0.8
ν_{17} (b_2)	3066.5	26.3	2.8	3066.0	22.5	3.4	-0.5
ν_{18} (b_2)	1464.2	13.6	0.0	1463.3	9.6	0.1	-1.0
ν_{19} (b_2)	1326.0	6.5	0.1	1326.3	4.4	0.1	0.4
ν_{20} (b_2)	912.9	0.2	0.2	913.2	0.2	0.1	0.9
ν_{21} (b_2)	764.8	0.2	8.5	763.6	0.3	7.6	-1.2

Intermolecular vibrations: 91.3 cm^{-1}, 6.7 km mol^{-1}, 0.6 $Å^4$ amu^{-1}; 59.9 cm^{-1}, 0.02 km mol^{-1}, 0.7 $Å^4$ amu^{-1}; 58.8 cm^{-1}, 0.3 km mol^{-1}, 0.6 $Å^4$ amu^{-1}; 29.1 cm^{-1}, 1.1 km mol^{-1}, 0.2 $Å^4$ amu^{-1}; 28.0 cm^{-1}, 0.3 km mol^{-1}, 0.8 $Å^4$ amu^{-1}; 2.2 cm^{-1}, 0.4 km mol^{-1}, 0.1 $Å^4$ amu^{-1}.

Table S2. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman scattering activities, in $Å^4$ amu^{-1}, for CF_3Br·DMS.

Mode	$\nu_{monomer}$	IR Intensity	Raman activity	$\nu_{complex}$	IR Intensity	Raman activity	$\Delta\nu$
CF_3Br							
ν_1 (a_1)	1078.3	496.2	3.1	1083.1	563.2	9.5	4.8
ν_2 (a_1)	739.5	30.4	9.0	734.2	22.0	20.7	-5.3
ν_3 (a_1)	360.9	0.03	5.9	353.4	3.5	25.9	-7.5
ν_4 (e)	1180.2	509.7	3.3	1168.3	496.0	3.2	-11.8
ν_5 (e)	531.4	1.8	1.5	530.1	1.8	1.5	-1.3
ν_6 (e)	305.5	0.02	1.5	306.9	0.02	1.5	1.4
DMS							
ν_1 (a_1)	3185.8	9.9	91.9	3188.0	7.0	90.1	2.1
ν_2 (a_1)	3061.7	31.7	338.3	3062.3	25.2	317.2	0.5
ν_3 (a_1)	1473.6	0.3	7.6	1472.2	1.9	8.8	-1.4
ν_4 (a_1)	1352.5	0.8	0.9	1352.7	0.1	4.0	0.3
ν_5 (a_1)	1046.5	8.6	0.4	1047.2	7.3	0.4	0.7
ν_6 (a_1)	713.0	2.8	22.1	711.1	3.1	19.2	-1.9
ν_7 (a_1)	260.8	0.03	3.1	261.1	0.1	2.7	0.2
ν_8 (a_2)	3167.7	0.0	16.6	3169.9	0.3	14.7	2.2
ν_9 (a_2)	1450.1	0.0	10.3	1448.9	0.1	9.3	-1.2
ν_{10} (a_2)	945.7	0.0	0.1	948.7	0.001	0.3	3.1
ν_{11} (a_2)	172.3	0.0	0.1	172.8	0.01	0.1	0.5
ν_{12} (b_1)	3159.6	21.2	119.4	3162.7	18.3	110.6	3.1
ν_{13} (b_1)	1462.5	12.9	0.0	1461.7	13.2	0.3	-0.9
ν_{14} (b_1)	982.7	4.1	0.0	984.7	13.5	0.6	2.1
ν_{15} (b_1)	187.9	0.8	0.1	187.7	1.5	0.3	-0.2
ν_{16} (b_2)	3186.9	3.3	42.1	3189.0	1.9	34.7	2.1
ν_{17} (b_2)	3066.5	26.3	2.8	3066.8	19.9	4.9	0.3
ν_{18} (b_2)	1464.2	13.6	0.0	1462.4	9.1	0.2	-1.9
ν_{19} (b_2)	1326.0	6.5	0.1	1326.5	3.8	0.1	0.5
ν_{20} (b_2)	912.9	0.2	0.2	914.5	0.2	0.2	1.6
ν_{21} (b_2)	764.8	0.2	8.5	762.9	0.4	7.4	-1.9

Intermolecular vibrations: 101.5 cm^{-1}, 10.5 km mol^{-1}, 2.0 $Å^4$ amu^{-1}; 65.1 cm^{-1}, 0.02 km mol^{-1}, 0.8 $Å^4$ amu^{-1}; 61.8 cm^{-1}, 0.3 km mol^{-1}, 1.0 $Å^4$ amu^{-1}; 31.5 cm^{-1}, 1.1 km mol^{-1}, 0.2 $Å^4$ amu^{-1}; 30.2 cm^{-1}, 0.2 km mol^{-1}, 0.9 $Å^4$ amu^{-1}; 1.9 cm^{-1}, 0.4 km mol^{-1}, 0.1 $Å^4$ amu^{-1}.

Table S3. MP2/aug-cc-pVDZ-PP vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman scattering activities, in $Å^4$ amu^{-1}, for CF_3I·DMS.

Mode	$\nu_{monomer}$	IR Intensity	Raman activity	$\nu_{complex}$	IR Intensity	Raman activity	$\Delta\nu$
CF_3I							
ν_1 (a_1)	1059.6	547.3	9.6	1069.1	611.5	21.0	9.5
ν_2 (a_1)	722.3	34.7	10.9	715.9	20.3	30.2	-6.4
ν_3 (a_1)	294.9	0.3	8.2	284.3	8.1	40.1	-10.6
ν_4 (e)	1162.6	455.5	3.5	1145.4	448.0	3.3	-17.2
ν_5 (e)	518.8	1.1	1.4	516.5	1.0	1.6	-2.3
ν_6 (e)	269.1	0.1	1.5	269.2	0.02	2.0	0.2
DMS							
ν_1 (a_1)	3185.8	9.9	91.9	3189.8	5.9	89.6	3.9
ν_2 (a_1)	3061.7	31.7	338.3	3063.6	23.3	305.3	1.8
ν_3 (a_1)	1473.6	0.3	7.6	1471.0	3.0	9.6	-2.6
ν_4 (a_1)	1352.5	0.8	0.9	1352.4	0.8	9.5	0.0
ν_5 (a_1)	1046.5	8.6	0.4	1047.7	9.8	0.6	1.2
ν_6 (a_1)	713.0	2.8	22.1	709.6	3.9	17.7	-3.3
ν_7 (a_1)	260.8	0.03	3.1	260.4	0.1	2.6	-0.4
ν_8 (a_2)	3167.7	0.0	16.6	3172.8	0.4	15.1	5.1
ν_9 (a_2)	1450.1	0.0	10.3	1448.3	0.3	8.5	-1.9
ν_{10} (a_2)	945.7	0.0	0.1	949.4	0.002	0.3	3.7
ν_{11} (a_2)	172.3	0.0	0.1	172.7	0.01	0.1	0.4
ν_{12} (b_1)	3159.6	21.2	119.4	3166.0	13.8	121.9	6.5
ν_{13} (b_1)	1462.5	12.9	0.0	1461.0	8.6	0.4	-1.6
ν_{14} (b_1)	982.7	4.1	0.0	985.1	17.2	0.6	2.4
ν_{15} (b_1)	187.9	0.8	0.1	188.5	2.5	0.6	0.5
ν_{16} (b_2)	3186.9	3.3	42.1	3190.8	1.2	31.8	3.9
ν_{17} (b_2)	3066.5	26.3	2.8	3168.1	16.5	8.4	1.6
ν_{18} (b_2)	1464.2	13.6	0.0	1461.3	14.1	0.5	-3.0
ν_{19} (b_2)	1326.0	6.5	0.1	1326.4	3.0	0.1	0.5
ν_{20} (b_2)	912.9	0.2	0.2	915.4	0.3	0.2	2.5
ν_{21} (b_2)	764.8	0.2	8.5	761.9	0.5	7.2	-2.9

Intermolecular vibrations: 115.5 cm^{-1}, 17.2 km mol^{-1}, 4.9 $Å^4$ amu^{-1}; 73.7 cm^{-1}, 0.02 km mol^{-1}, 1.0 $Å^4$ amu^{-1}; 67.4 cm^{-1}, 1.2 km mol^{-1}, 1.5 $Å^4$ amu^{-1}; 34.0 cm^{-1}, 1.1 km mol^{-1}, 0.3 $Å^4$ amu^{-1}; 33.0 cm^{-1}, 0.2 km mol^{-1}, 0.8 $Å^4$ amu^{-1}; 2.0 cm^{-1}, 0.4 km mol^{-1}, 0.1 $Å^4$ amu^{-1}.

Table S4. MP2/aug-cc-pVDZ(-PP) complexation enthalpies, in vapour phase (vap) and corresponding liquid krypton (LKr)[a], and experimental complexation enthalpies for the complexes of CF_3Cl, CF_3Br and CF_3I with DMS. All data are in kJ mol^{-1}.

	CF_3Cl·DMS	CF_3Br·DMS	CF_3I·DMS
$\Delta H°$(vap,calc)	-10.4	-15.7	-22.2
$\Delta H°$(LKr,calc)[b]	-4.0(4)	-9.4(2)	-15.2(2)
Experimental			
$\Delta H°$(LKr)[b]		-9.5(5)	-17.4(1)

[a] The temperature at which the transformation was calculated is 149 K.
[b] Uncertainties are 2σ.

Table S5. Comparison of experimental frequencies, in cm^{-1}, for the vibrations of dimethyl sulfide in the gas phase[1] and dissolved in liquid krypton. Calculated frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman scattering activities, in $Å^4$ amu^{-1}, at the MP2/aug-cc-pVDZ level are shown as well.

Mode	$\nu_{exp, gas}$	$\nu_{exp, LKr}$	ν_{calc}	IR Intensity	Raman activity
ν_1 (a_1)	2997	2991.6	3185.8	9.9	91.9
ν_2 (a_1)	2925	2916.9	3061.7	31.7	338.3
ν_3 (a_1)	1447	1444.3	1473.6	0.3	7.6
ν_4 (a_1)	1337	1333.3	1352.5	0.8	0.9
ν_5 (a_1)	1030	1030.7	1046.5	8.6	0.4
ν_6 (a_1)	695	696.3	713.0	2.8	22.1
ν_7 (a_1)	280	276.8	260.8	0.03	3.1
ν_8 (a_2)	2970		3167.7	0.0	16.6
ν_9 (a_2)	1427	1423.9	1450.1	0.0	10.3
ν_{10} (a_2)	946		945.7	0.0	0.1
ν_{11} (a_2)	175		172.3	0.0	0.1
ν_{12} (b_1)	2970	2965.1	3159.6	21.2	119.4
ν_{13} (b_1)	1439	1432.2	1462.5	12.9	0.0
ν_{14} (b_1)	973	973.3	982.7	4.1	0.0
ν_{15} (b_1)	183	189.2	187.9	0.8	0.1
ν_{16} (b_2)	2998	2991.6	3186.9	3.3	42.1
ν_{17} (b_2)	2918	2920.3	3066.5	26.3	2.8
ν_{18} (b_2)	1442	1439.0	1464.2	13.6	0.0
ν_{19} (b_2)	1315	1310.1	1326.0	6.5	0.1
ν_{20} (b_2)	903	901.7	912.9	0.2	0.2
ν_{21} (b_2)	742	748.0	764.8	0.2	0.5

Table S6. Mole fractions used in the infrared and Raman study of mixtures of CF_3Br or CF_3I and DMS dissolved in liquid krypton.

		CF_3X	DMS
Figure 3			
Panel A (CF_3Br)	Trace *a*	4.3×10^{-5}	1.2×10^{-3}
Panel B (CF_3I)	Trace *a*	4.0×10^{-5}	7.1×10^{-4}
Figure 4			
Panels A and C (CF_3Br)	Trace *a*	1.5×10^{-3}	2.0×10^{-3}
Panels B and D (CF_3Br)	Trace *a*	4.7×10^{-3}	2.4×10^{-3}
Panels E and G (CF_3I)	Trace *a*	3.0×10^{-4}	1.2×10^{-3}
Panels F and H (CF_3I)	Trace *a*	2.4×10^{-3}	8.8×10^{-4}
	Trace *a*’	2.4×10^{-3}	3.1×10^{-3}
Figure 5			
Panel A (CF_3Br)	Trace *a*	6.8×10^{-3}	3.0×10^{-3}
Panel B (CF_3Br)	Trace *a*	4.7×10^{-3}	2.4×10^{-3}
Panel C (CF_3I)	Trace *a*	3.8×10^{-3}	1.8×10^{-3}
Panel D (CF_3I)	Trace *a*	2.4×10^{-3}	8.8×10^{-4}
	Trace *a*’	2.4×10^{-3}	3.1×10^{-3}
Figure 6			
Panel A (CF_3Br)	Trace *a*	6.8×10^{-3}	3.0×10^{-3}
Panel B (CF_3I)	Trace *a*	3.8×10^{-3}	1.8×10^{-3}
Panel C (CF_3I)	Trace *a*	2.4×10^{-3}	8.8×10^{-4}