Table S1 Possible conformations with symmetry, energies (in kJ mol^{-1}) and three lowest-lying frequencies (cm^{-1}) for ITMS.

Conformer	Arrangement[a]	Energy difference[b]	Frequencies[c]
1 (C_{3v})	3S, 0E	0.0	162.5, 2 × 166.9
2 (C_s)	2S, 1E	+7.1	162.9*i*, 170.0, 173.6
3 (C_s)	1S, 2E	+14.7	179.0*i*, 169.6*i*, 175.2
4 (C_{3v})	0S, 3E	+23.6	197.7*i*, 2 × 182.9*i*

[a] S = Staggered (H-C-Si-I = 180º), E = Eclipsed (H-C-Si-I = 0º).

[b] Difference from the lowest energy conformer, calculated at the HF/3-21G* level.

[c] All frequencies relate to motions of the methyl groups relative to the Si-I bond.

Table S2 Natural coordinates defined for iodotrimethylsilane.

Number	**Description**	**Definition**
1-3	Si-C stretch	R_{1-3}
4-12	C-H stretch	R_{4-12}
13	Si-I stretch	R_{13}
14-16	symmetric methyl deformation	$6^{-1/2}(\alpha_{1,4,7}+\alpha_{2,5,8}+\alpha_{3,6,9}-\beta_{1,4,7}-\beta_{2,5,8}-\beta_{3,6,9})$
17-19	asymmetric methyl deformation	$6^{-1/2}(2\alpha_{1,4,7}-\alpha_{2,5,8}-\alpha_{3,6,9})$
20-22	asymmetric methyl deformation	$2^{-1/2}(\alpha_{2,5,8}-\alpha_{3,6,9})$
23-25	methyl rock	$6^{-1/2}(2\beta_{1,4,7}-\beta_{2,5,8}-\beta_{3,6,9})$
26-28	methyl rock	$2^{-1/2}(\beta_{2,5,8}-\beta_{3,6,9})$
29	symmetric SiC_3 deformation	$6^{-1/2}(\theta_1+\theta_2+\theta_3-\phi_1-\phi_2-\phi_{3,})$
30	asymmetric SiC_3 deformation	$6^{-1/2}(2\theta_1-\theta_2-\theta_{3,})$
31	asymmetric SiC_3 deformation	$2^{-1/2}(\theta_2-\theta_3)$
32	SiC_3 rock	$6^{-1/2}(2\phi_1-\phi_2-\phi_3)$
33	SiC_3 rock	$2^{-1/2}(\phi_2-\phi_3)$
34-36	C-Si torsion	$9^{-1/2}(\tau_{1,10,19}+\tau_{2,11,20}+\tau_{3,12,21}+\tau_{4,13,22}+\tau_{5,14,23}+\tau_{6,15,24}+\tau_{7,16,25}+\tau_{8,17,26}+\tau_{9,18,27})$

α: H-C-H angle, β: H-C-Si angle, θ: C-Si-C angle, ϕ: C-Si-I angle

Table S3 Geometric structures of $SiMe_3X$ (X = H, F, Cl, Br or I) at the HF level using the 3-21G* and 6-31G* basis sets, and at the MP2 level using the 6-31G* basis set. For ITMS, the SDB-cc-pVTZ basis set and ECP was used for iodine with the higher-level calculations.[a,b]

H-SiMe$_3$			
Parameter[c]	**HF/3-21G***	**HF/6-31G***	**MP2/6-31G***
C-Hα	108.8	108.7	109.5
C-Hβ	108.8	108.7	109.4
Si-C	188.7	189.1	188.6
Si-X	148.3	148.4	149.5
Si-C-Hα	111.2	111.3	110.9
Si-C-Hβ	111.2	111.4	111.4
C-Si-C	110.3	110.4	110.2
X-Si-C	108.6	108.6	108.8
Energy / Hartree	-406.2998	-408.3667	-408.8433
F-SiMe$_3$			
Parameter	**HF/3-21G***	**HF/6-31G***	**MP2/6-31G***
C-Hα	108.9	108.8	109.5
C-Hβ	108.8	108.7	109.4
Si-C	186.8	187.7	187.2
Si-X	160.5	161.0	163.6
Si-C-Hα	110.9	111.2	110.8
Si-C-Hβ	111.6	111.4	111.3
C-Si-C	110.9	111.4	111.2
X-Si-C	108.0	107.4	107.7
Energy / Hartree	-504.7284	-507.3023	-507.9508
Cl-SiMe$_3$			
Parameter	**HF/3-21G***	**HF/6-31G***	**MP2/6-31G***
C-Hα	108.9	108.8	109.5
C-Hβ	108.7	108.6	109.3
Si-C	187.3	187.9	187.4
Si-X	108.2	209.5	208.6
Si-C-Hα	110.6	110.5	110.5

Si-C-Hβ	111.3	111.4	111.2
C-Si-C	111.5	111.5	111.4
X-Si-C	107.3	107.3	107.5
Energy / Hartree	-863.1956	-867.3338	-867.9373
Br-SiMe$_3$			
Parameter	**HF/3-21G***	**HF/6-31G***	**MP2/6-31G***
C-Hα	108.9	108.8	109.5
C-Hβ	108.7	108.6	109.3
Si-C	187.3	187.8	187.3
Si-X	222.1	224.5	224.8
Si-C-Hα	110.3	110.3	110.2
Si-C-Hβ	111.4	111.4	111.2
C-Si-C	110.9	111.3	111.4
X-Si-C	108.1	107.6	107.5
Energy / Hartree	-2966.0659	-2977.7481	-2978.3360
I-SiMe$_3$			
Parameter	**HF/3-21G***	**HF/GEN[d]**	**MP2/GEN[d]**
C-Hα	108.9	108.8	109.6
C-Hβ	108.6	108.5	109.4
Si-C	1.876	188.2	187.7
Si-X	2.501	250.3	248.7
Si-C-Hα	110.1	110.1	110.1
Si-C-Hβ	111.4	111.5	111.1
C-Si-C	111.2	111.4	111.5
X-Si-C	107.7	107.5	107.3
Energy / Hartree	-7293.6875	-419.0258	-419.6477

[a] Distances in pm, angles in °

[b] See Figure 1 (main text) for a general structural overview of the molecules.

[c] α = unique methyl hydrogen atom; β = symmetry-equivalent hydrogen atoms.

[d] 6-31G* on H, C and Si, SDB-cc-pVTZ on I

Table S4 Interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the GED structure of ITMS with those calculated at the HF/6-31G*//SDB-cc-pVTZ level (u_{calc}).[a.b]

Number	Atom pair	r_a / pm	u_{h1} / pm	Restraint	k_{h1} / pm	u_{calc} / pm
1	C(3)-H(5)	108.9(3)	8.4(3)	7.5(7)	0.4	7.5
2	Si(1)-C(3)	187.3(1)	4.5(1)	-	0.1	5.1
3	Si(1)-I(2)	248.5(2)	4.5(3)	-	0.0	5.8
4	C(3)...C(7)	310.2(2)	10.0(6)	-	-0.2	10.0
5	I(2)...C(3)	350.9(2)	9.8(3)	-	-0.3	10.6
6	I(2)...H(5)	361.6(10)	25.6(17)	24.2(24)	0.4	24.2
7	I(2)...H(4)	448.0(7)	12.1(18)	-	-3.3	12.1
8	H(5)...H(6)	175.6(5)	12.0(fixed)	-	-0.1	12.0
9	Si(1)...H(4)	246.8(12)	11.8(fixed)	-	-0.3	11.8
10	Si(1)...H(5)	247.7(7)	11.6(fixed)	-	-0.3	11.6
11	H(5)...H(14)	306.1(13)	32.4(fixed)	-	-3.7	32.4
12	H(4)...H(9)	317.3(28)	32.2(fixed)	-	-3.1	32.2
13	C(3)...H(10)	329.4(6)	22.2(fixed)	-	0.4	22.2
14	C(3)...H(9)	334.2(13)	22.1(fixed)	-	0.3	22.1
15	H(4)...H(10)	359.7(10)	35.0(fixed)	-	-0.9	35.0
16	C(3)...H(8)	402.0(5)	11.6(fixed)	-	-2.8	11.6
17	H(5)...H(10)	425.5(11)	22.3(fixed)	-	-2.9	22.3
18	H(4)...H(8)	431.3(13)	22.0(fixed)	-	-3.1	22.0
19	H(5)...H(8)	484.5(12)	14.5(fixed)	-	-4.7	14.5

[a] Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

[b] Amplitudes not refined were fixed at the values obtained using a force field obtained at the HF level with the 6-31G* basis set on H, C and Si, and the SDB-cc-pVTZ basis set on I.

Table S5 Least-squares correlation matrix (× 100) for the GED refinement of ITMS.[a]

	k_2
u_2	58
u_3	63

[a] Only elements with absolute values ≥50% are shown; k_2 is a scale factor.

Table S6 Experimental GED coordinates (Å) from the refinement of the C_{3v} structure of ITMS.

Atom	***x***	***y***	***z***
Si(1)	0.000	0.000	0.000
I(2)	2.486	0.000	0.000
C(3)	-0.536	1.794	0.000
H(4)	-1.626	1.868	0.000
H(5)	-0.164	2.317	0.883
H(6)	-0.164	2.317	-0.883
C(7)	-0.536	-0.897	-1.554
H(8)	-0.164	-1.923	-1.565
H(9)	-1.626	-0.934	-1.618
H(10)	-0.164	-0.394	-2.448
C(11)	-0.536	-0.897	1.554
H(12)	-1.626	-0.934	1.618
H(13)	-0.164	-1.923	1.565
H(14)	-0.164	-0.394	2.448

Table S7 Values of the scale factors associated with the normal coordinates defined for ITMS using the B3LYP method with three different basis sets.

		DFT / B3LYP	
	6-311G**	**LanL2DZdp**	**LanL2DZ**
SiC stretch	1.051	1.033	1.049
SiI stretch	0.981	0.923	1.139
CH stretch	0.915	0.914	0.896
CH_3 symmetric deformation	0.929	0.936	0.853
CH_3 asymmetric deformation	0.925	0.929	0.897
CH_3 rock	0.893	0.908	0.731
SiC_3 symmetric deformation	1.230	1.230	1.410
SiC_3 asymmetric deformation	1.108	1.083	1.131
SiC_3 rock	1.112	1.170	1.254
SiC torsion	1.000	1.000	1.000

Figure S1 Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for $ISiMe_3$.

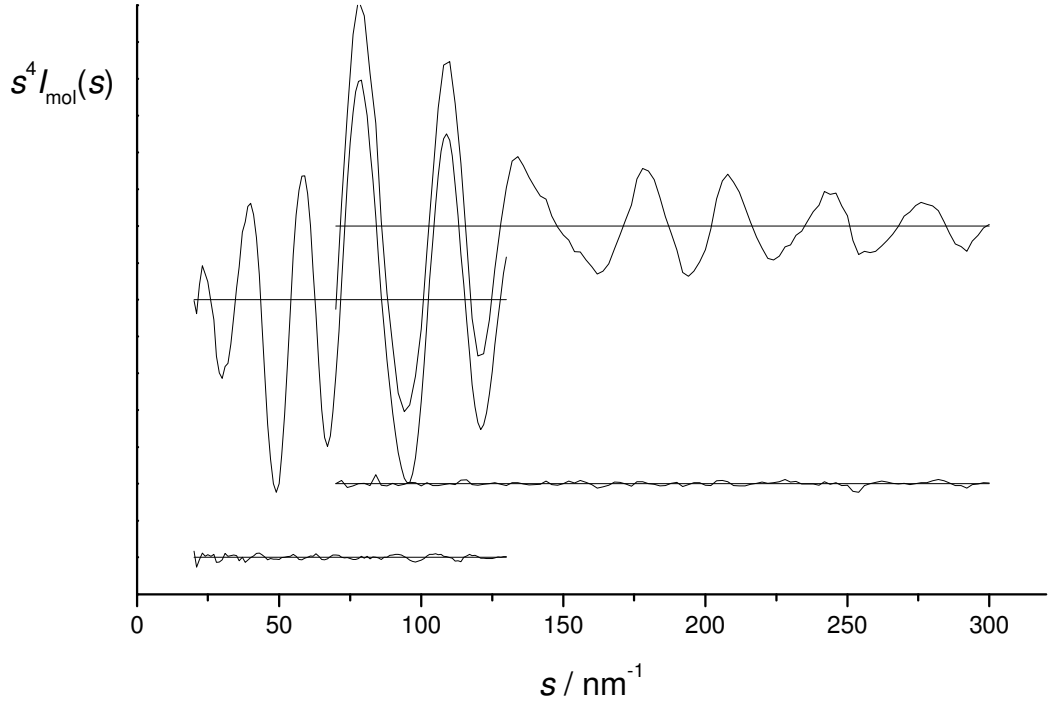

Figure S2 IR spectrum (liquid phase) (upper) compared with the calculated spectrum of the liquid using B3LYP/LanL2DZ and B3LYP/LanL2DZdp after scaling (lower), in the region from 3150 to 2850 cm^{-1}.