Table S1 Principal axis coordinates obtained from the ab initio calculations for diethyldifluorosilane (MP2(Full)/6-311+G(2d,2p)) and diethylsilane (MP2(Full)/6-311+G(2df,2pd). All coordinates are in Angstroms.

Diethyldifluorosilane, trans-trans conformer

Si1	0.000000	0.049755	0.000000
C2	1.574592	1.018603	0.000000
H3	1.574039	1.673265	-0.870452
H4	1.574039	1.673265	0.870452
C5	-1.574592	1.018603	0.000000
H6	-1.574039	1.673265	-0.870452
H7	-1.574039	1.673265	0.870452
C8	-2.826445	0.132491	0.000000
H9	-2.850973	-0.508524	0.875893
H10	-3.732686	0.729905	0.000000
H11	-2.850973	-0.508524	-0.875893
C12	2.826445	0.132491	0.000000
H13	2.850973	-0.508524	0.875893
H14	2.850973	-0.508524	-0.875893
H15	3.732686	0.729905	0.000000
F16	0.000000	-0.925996	1.276396
F17	0.000000	-0.925996	-1.276396

Diethyldifluorosilane, trans-gauche conformer

Si1	0.028215	0.263907	-0.046619
C2	1.793386	0.149058	-0.583757
H3	1.824278	0.120839	-1.671819
H4	2.292983	1.071559	-0.292542
C5	-1.049979	-1.174834	-0.479366
H6	-0.618875	-2.072526	-0.038408
H7	-1.012694	-1.320137	-1.558362
C8	-2.500937	-0.999648	-0.014024
H9	-2.952882	-0.122117	-0.466007
H10	-3.107230	-1.859926	-0.279569
H11	-2.552837	-0.876793	1.063475
C12	2.526157	-1.062649	0.004654
H13	2.511920	-1.040629	1.090433
H14	2.068189	-1.996294	-0.310494
H15	3.564474	-1.087783	-0.310473
F16	-0.006855	0.452330	1.548698
F17	-0.627199	1.596750	-0.655484

Diethyldifluorosilane, gauche-gauche conformer

Si1	0.000000	0.422822	0.000000
C2	1.292254	-0.575464	0.867245
H3	2.013097	0.110142	1.309211
H4	0.825416	-1.098196	1.700511
C5	-1.292254	-0.575464	-0.867245
H6	-0.825416	-1.098196	-1.700511
H7	-2.013097	0.110142	-1.309211
C8	-1.999341	-1.570185	0.060889
H9	-2.483546	-1.059972	0.888690
H10	-2.761259	-2.133769	-0.468205
H11	-1.299116	-2.286502	0.483043
C12	1.999341	-1.570185	-0.060889
H13	1.299116	-2.286502	-0.483043
H14	2.483546	-1.059972	-0.888690
H15	2.761259	-2.133769	0.468205
F16	0.717720	1.387068	-1.063729
F17	-0.717720	1.387068	1.063729

Diethyldifluorosilane, gauche-gauche' conformer

Si1	0.307011	0.354271	−0.047801
C2	1.156838	−1.248754	−0.409018
C3	−1.381638	0.591418	−0.771498
H4	−1.365105	0.255688	−1.807729
H5	−1.567488	1.663856	−0.810928
C6	−2.507452	−0.105350	0.002670
H7	−2.547090	0.245625	1.028885
H8	−3.473802	0.087918	−0.452547
H9	−2.370619	−1.181943	0.033400
C10	0.349857	−2.496084	−0.031472
H11	0.059671	−2.479120	1.015232
H12	−0.557488	−2.575139	−0.623214
H13	0.924804	−3.401613	−0.198105
H14	2.105529	−1.237499	0.125889
H15	1.411594	−1.269699	−1.467615
F16	0.186780	0.513127	1.546523
F17	1.257407	1.548266	−0.544830

Diethylsilane, trans-trans conformer

Si1	0.000000	0.396846	0.000000
H2	0.000000	1.273312	−1.193228
H3	0.000000	1.273312	1.193228
C4	1.558159	−0.644984	0.000000
H5	1.536124	−1.300803	0.871764
H6	1.536124	−1.300803	−0.871764
C7	−1.558159	−0.644984	0.000000
H8	−1.536124	−1.300803	0.871764
H9	−1.536124	−1.300803	−0.871764
C10	−2.837360	0.190364	0.000000
H11	−2.887445	0.833597	−0.876545
H12	−3.728476	−0.433979	0.000000
H13	−2.887445	0.833597	0.876545
C14	2.837360	0.190364	0.000000
H15	2.887445	0.833597	−0.876545
H16	2.887445	0.833597	0.876545
H17	3.728476	−0.433979	0.000000

Diethylsilane, trans-gauche conformer

Si1	0.033261	−0.749286	0.141223
H2	0.493536	−1.997146	−0.506814
H3	0.066508	−0.958004	1.606653
C4	−1.722699	−0.355537	−0.386081
H5	−1.750591	−0.279133	−1.474176
H6	−2.359491	−1.202753	−0.127973
C7	1.216671	0.637860	−0.296274
H8	0.881896	1.552175	0.195527
H9	1.146207	0.827800	−1.368776
C10	2.662445	0.332815	0.092540
H11	3.025290	−0.561838	−0.409874
H12	3.332556	1.149800	−0.167130
H13	2.753900	0.161829	1.163612
C14	−2.265511	0.924468	0.247646
H15	−2.243040	0.867091	1.334706
H16	−1.676355	1.791902	−0.043542
H17	−3.294780	1.116392	−0.048382

Diethylsilane, gauche-gauche conformer

Si1	0.000000	1.041090	0.000000
H2	0.493105	1.906170	-1.094193
H3	-0.493105	1.906170	1.094193
C4	1.407363	-0.031502	0.623047
H5	2.223340	0.616700	0.945154
H6	1.076111	-0.561829	1.516943
C7	-1.407363	-0.031502	-0.623047
H8	-1.076111	-0.561829	-1.516943
H9	-2.223340	0.616700	-0.945154
C10	-1.902619	-1.023817	0.427698
H11	-2.241227	-0.511700	1.327057
H12	-2.733905	-1.621763	0.059756
H13	-1.113536	-1.712247	0.725664
C14	1.902619	-1.023817	-0.427698
H15	1.113536	-1.712247	-0.725664
H16	2.241227	-0.511700	-1.327057
H17	2.733905	-1.621763	-0.059756

Diethylsilane, gauche-gauche' conformer

Si1	-0.026945	1.012190	0.224074
H2	-0.069762	2.426608	-0.205724
H3	0.118408	0.978508	1.697335
C4	1.466500	0.161058	-0.537021
H5	1.230085	-0.095113	-1.571633
H6	2.276826	0.889498	-0.590252
C7	-1.646029	0.192552	-0.254669
H8	-1.812677	0.364983	-1.319377
H9	-2.448992	0.721959	0.261098
C10	-1.721533	-1.302153	0.050765
H11	-1.518377	-1.505875	1.100908
H12	-2.704851	-1.708804	-0.177117
H13	-0.996121	-1.861902	-0.535727
C14	1.941196	-1.076950	0.223846
H15	2.219854	-0.822268	1.244373
H16	1.166625	-1.837834	0.283341
H17	2.809105	-1.530671	-0.250683

Table S2 Observed and calculated transition frequencies for diethylsilane and diethyldifluorosilane

Transition frequencies for diethylsilane:

trans-trans species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
6	0	6	5	1	5	6460.4630	6460.4630	0.0000
1	1	0	1	0	1	11865.9619	11865.9621	-0.0002
2	1	1	2	0	2	11950.1382	11950.1403	-0.0021
3	1	2	3	0	3	12077.2413	12077.2406	0.0007
4	1	3	4	0	4	12248.2633	12248.2602	0.0032
5	1	4	5	0	5	12464.5224	12464.5233	-0.0009
6	1	5	6	0	6	12727.6774	12727.6758	0.0016
7	1	6	7	0	7	13039.6740	13039.6758	-0.0018
1	1	1	0	0	0	14729.6778	14729.6792	-0.0014

trans-gauche species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
3	0	3	2	1	2	4547.5193	4547.5211	-0.0018
3	1	3	3	0	3	5492.0130	5492.0171	-0.0041
2	1	2	2	0	2	5779.5607	5779.5562	0.0045
1	1	1	1	0	1	5977.6374	5977.6330	0.0044
1	1	0	1	0	1	6180.8354	6180.8316	0.0038
2	1	1	2	0	2	6389.1428	6389.1435	-0.0007
2	1	2	1	1	1	6695.1403	6695.1408	-0.0005
3	1	2	3	0	3	6711.0873	6711.0863	0.0010
2	0	2	1	0	1	6893.2200	6893.2176	0.0024
2	1	1	1	1	0	7101.5294	7101.5295	-0.0001
4	1	3	4	0	4	7157.7881	7157.7909	-0.0028
5	1	4	5	0	5	7743.5147	7743.5123	0.0025
4	0	4	3	1	3	8253.7501	8253.7482	0.0019
1	1	1	0	0	0	9426.7926	9426.7961	-0.0035
1	1	0	0	0	0	9629.9919	9629.9947	-0.0028
3	1	3	2	1	2	10039.5368	10039.5382	-0.0014
3	0	3	2	0	2	10327.0787	10327.0773	0.0014
3	2	2	2	2	1	10347.5749	10347.5747	0.0002
3	2	1	2	2	0	10367.9254	10367.9230	0.0024
3	1	2	2	1	1	10649.0189	10649.0201	-0.0012
2	1	2	1	0	1	12672.7748	12672.7738	0.0010
2	1	1	1	0	1	13282.3646	13282.3611	0.0035
4	1	4	3	1	3	13380.2440	13380.2393	0.0047
4	0	4	3	0	3	13745.7679	13745.7653	0.0026
4	1	3	3	1	2	14192.4665	14192.4700	-0.0035
3	1	3	2	0	2	15819.0911	15819.0944	-0.0033
6	0	6	5	1	5	15821.6134	15821.6140	-0.0006
5	1	5	4	1	4	16716.1945	16716.1952	-0.0007
3	1	2	2	0	2	17038.1597	17038.1635	-0.0038

gauche-gauche species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
4	1	3	4	0	4	5515.6429	5515.6437	-0.0008
3	1	2	2	2	1	5779.0780	5779.0786	-0.0006
2	0	2	1	1	1	6022.2331	6022.2320	0.0011
1	1	1	0	0	0	6969.8895	6969.8915	-0.0020
5	2	3	5	1	4	7050.5807	7050.5785	0.0022
5	1	4	5	0	5	7153.4255	7153.4235	0.0020
4	2	2	4	1	3	7160.3021	7160.3001	0.0020
3	2	1	3	1	2	7497.2031	7497.2016	0.0015
2	2	0	2	1	1	7917.2767	7917.2779	-0.0012
2	2	1	2	1	2	9150.0648	9150.0678	-0.0030
3	2	2	3	1	3	9819.1713	9819.1716	-0.0003
3	0	3	2	1	2	10607.5231	10607.5234	-0.0003
4	2	3	4	1	4	10722.3447	10722.3449	-0.0002
9	2	7	9	1	8	10844.4005	10844.4008	-0.0003
4	1	3	3	2	2	10871.7541	10871.7541	0.0001
2	1	2	1	0	1	10889.6964	10889.6964	0.0000
8	3	5	8	2	6	11108.5410	11108.5417	-0.0007
5	2	4	5	1	5	11860.5970	11860.5975	-0.0005
3	3	0	3	2	1	13977.7728	13977.7726	0.0002
3	3	1	3	2	2	14210.3602	14210.3600	0.0002
3	1	3	2	0	2	14615.5008	14615.5002	0.0006
4	0	4	3	1	3	15175.2820	15175.2820	0.0000
2	2	1	1	1	0	16989.6602	16989.6594	0.0008

Transition frequencies for diethyldifluorosilane:

trans-trans species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
1	1	1	0	0	0	4910.7870	4910.7834	0.0036
3	0	3	2	1	2	5393.7415	5393.7421	-0.0006
2	1	2	1	0	1	7467.0173	7467.0171	0.0002
4	0	4	3	1	3	7989.1986	7989.1978	0.0008
3	1	3	2	0	2	10015.2738	10015.2774	-0.0036
5	0	5	4	1	4	10591.9418	10591.9391	0.0027
4	1	4	3	0	3	12555.6633	12555.6649	-0.0016
6	0	6	5	1	5	13201.6344	13201.6365	-0.0021
5	1	5	4	0	4	15088.3445	15088.3423	0.0022

trans-gauche species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
1	1	0	0	0	0	4254.7150	4254.7196	-0.0046
2	1	2	1	1	1	5428.7863	5428.7836	0.0027
2	0	2	1	0	1	5591.6820	5591.6824	-0.0004
2	1	1	1	1	0	5790.5750	5790.5737	0.0013
4	3	2	4	2	2	6595.6942	6595.6955	-0.0013
3	0	3	2	1	1	6694.9055	6694.9055	0.0000
2	1	2	1	0	1	6697.7662	6697.7637	0.0025
3	0	3	2	1	2	7237.5907	7237.5929	-0.0022
2	1	1	1	0	1	7240.4435	7240.4511	-0.0076
4	1	3	3	2	1	7905.2511	7905.2527	-0.0016
4	1	3	3	2	2	7994.0673	7994.0678	-0.0005
3	1	3	2	1	2	8132.4269	8132.4244	0.0025
3	0	3	2	0	2	8343.6767	8343.6742	0.0025
3	2	2	2	2	1	8414.5087	8414.5080	0.0007
3	2	1	2	2	0	8485.3337	8485.3290	0.0047
3	1	2	2	1	1	8673.9712	8673.9731	-0.0019
4	0	4	3	1	2	9070.0869	9070.0866	0.0003
3	1	3	2	0	2	9238.5033	9238.5057	-0.0024
2	2	1	1	1	0	9597.4766	9597.4785	-0.0019
2	2	0	1	1	0	9615.4731	9615.4726	0.0006
2	2	1	1	1	1	9778.3763	9778.3757	0.0006
2	2	0	1	1	1	9796.3713	9796.3698	0.0015
4	0	4	3	1	3	10154.3198	10154.3227	-0.0029
3	1	2	2	0	2	10322.7405	10322.7417	-0.0012
4	1	4	3	1	3	10824.6687	10824.6706	-0.0019
4	0	4	3	0	3	11049.1563	11049.1541	0.0022
5	0	5	4	1	3	11236.4273	11236.4260	0.0013
4	1	3	3	1	2	11541.5084	11541.5075	0.0009
4	1	4	3	0	3	11719.4997	11719.5021	-0.0024
3	2	2	2	1	1	12221.4115	12221.4127	-0.0012
3	2	1	2	1	1	12310.2310	12310.2278	0.0032
3	2	2	2	1	2	12764.1018	12764.1001	0.0017
3	2	1	2	1	2	12852.9196	12852.9152	0.0044
5	0	5	4	1	4	13037.4983	13037.4990	-0.0007
5	1	5	4	1	4	13504.0194	13504.0178	0.0016
4	1	3	3	0	3	13520.5754	13520.5750	0.0004
5	0	5	4	0	4	13707.8493	13707.8469	0.0024
5	1	5	4	0	4	14174.3639	14174.3657	-0.0018
5	1	4	4	1	3	14385.2611	14385.2622	-0.0011
6	1	5	5	2	4	14385.4338	14385.4333	0.0005
4	2	3	3	1	2	14752.7140	14752.7178	-0.0038

gauche-gauche species

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} (MHz)	ν_{calc} (MHz)	ν_{obs}-ν_{calc} (MHz)
2	0	2	1	1	1	5872.1544	5872.1538	0.0006
2	1	2	1	0	1	6240.5008	6240.5006	0.0002
2	2	1	1	1	0	7732.6504	7732.6509	-0.0005
2	2	0	1	1	1	8485.0715	8485.0701	0.0014
3	0	3	2	1	2	8778.9303	8778.9305	-0.0002
3	1	3	2	0	2	8890.3628	8890.3615	0.0013
3	1	2	2	2	1	9242.8189	9242.8194	-0.0005
3	2	2	2	1	1	10479.8858	10479.8864	-0.0006
4	0	4	3	1	3	11569.8393	11569.8430	-0.0037
4	1	4	3	0	3	11593.5865	11593.5849	0.0016
3	3	1	2	2	0	12069.2501	12069.2508	-0.0007
4	2	2	3	3	1	12205.1177	12205.1177	0.0000
3	3	0	2	2	1	12484.8502	12484.8492	0.0010
4	1	3	3	2	2	12492.6485	12492.6474	0.0012
3	2	1	2	1	2	12948.8416	12948.8426	-0.0010
4	2	3	3	1	2	13029.5531	13029.5533	-0.0002
5	0	5	4	1	4	14326.0511	14326.0588	-0.0077
5	1	5	4	0	4	14330.3022	14330.2939	0.0083

Table S3 Observed and calculated Stark coefficients (in units of MHz V^{-2} cm^2).

Diethyldifluorosilane, trans-trans conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
2(1, 2) - 1(0, 1)	0	0.33175E-04	0.33093E-04	0.82437E-07	0.25
3(0, 3) - 2(1, 2)	0	0.29222E-05	0.28535E-05	0.68789E-07	2.35
3(0, 3) - 2(1, 2)	1	-0.10051E-04	-0.96049E-05	-0.44654E-06	4.44
3(1, 3) - 2(0, 2)	0	0.16921E-04	0.16509E-04	0.41176E-06	2.43
3(1, 3) - 2(0, 2)	1	0.56031E-04	0.56280E-04	-0.24895E-06	-0.44
RMS				0.29747E-06	2.51

Diethyldifluorosilane, trans-gauche conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
3(1, 3) - 2(0, 2)	0	0.17737E-05	0.16078E-05	0.16590E-06	9.35
3(1, 3) - 2(1, 2)	1	0.63608E-05	0.62817E-05	0.79081E-07	1.24
2(2, 1) - 1(1, 0)	0	0.11496E-04	0.11571E-04	-0.74749E-07	-0.65
2(2, 0) - 1(1, 1)	0	-0.25162E-04	-0.25053E-04	-0.10895E-06	0.43
2(2, 0) - 1(1, 0)	0	0.10810E-04	0.10844E-04	-0.33951E-07	-0.31
2(2, 1) - 1(1, 1)	0	-0.24255E-04	-0.24328E-04	0.73047E-07	-0.30
3(0, 3) - 2(1, 2)	1	-0.35317E-04	-0.35331E-04	0.13664E-07	-0.04
RMS				0.90954E-07	3.58

Diethyldifluorosilane, gauche-gauche conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
2(1, 2) - 1(0, 1)	0	0.52145E-04	0.47413E-04	0.47316E-05	9.07
2(1, 2) - 1(0, 1)	1	0.41630E-03	0.42136E-03	-0.50573E-05	-1.21
3(1, 3) - 2(0, 2)	1	0.41686E-04	0.37602E-04	0.40840E-05	9.80
3(1, 3) - 2(0, 2)	2	0.15706E-03	0.14635E-03	0.10711E-04	6.82
2(2, 1) - 1(1, 0)	0	0.43115E-04	0.38270E-04	0.48445E-05	11.24
RMS				0.63694E-05	8.40

Diethylsilane, trans-trans conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
1(1, 0) - 1(0, 1)	1	0.80110E-05	0.80647E-05	-0.53740E-07	-0.67
1(1, 1) - 0(0, 0)	0	0.89185E-05	0.88974E-05	0.21118E-07	0.24
2(1, 1) - 2(0, 2)	1	0.45636E-05	0.45076E-05	0.55987E-07	1.23
2(1, 1) - 2(0, 2)	2	0.94793E-05	0.94801E-05	-0.72396E-09	-0.01
RMS				0.40215E-07	0.71

Diethylsilane, trans-gauche conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
1(1, 0) - 0(0, 0)	0	0.28311E-05	0.25985E-05	0.23257E-06	8.21
1(1, 0) - 1(0, 1)	1	0.24588E-04	0.24657E-04	-0.68912E-07	-0.28
2(1, 2) - 1(0, 1)	1	0.66766E-05	0.66410E-05	0.35536E-07	0.53
2(1, 1) - 2(0, 2)	1	-0.44728E-05	-0.47623E-05	0.28947E-06	-6.47
2(1, 1) - 2(0, 2)	2	0.14447E-04	0.14694E-04	-0.24661E-06	-1.71
2(0, 2) - 1(0, 1)	0	0.12246E-04	0.11896E-04	0.34945E-06	2.85
2(1, 2) - 1(1, 1)	0	0.46891E-05	0.47586E-05	-0.69520E-07	-1.48
2(1, 2) - 1(1, 1)	1	0.20346E-04	0.20245E-04	0.10051E-06	0.49
RMS				0.20669E-06	3.92

Diethylsilane, gauche-gauche conformer

Transition	|M|	Observed	Calculated	Obs-Calc	Percent
1(1, 1) - 0(0, 0)	0	0.10026E-04	0.10030E-04	-0.44547E-08	-0.04
2(1, 2) - 1(0, 1)	0	0.29823E-05	0.29044E-05	0.77928E-07	2.61
2(1, 2) - 1(0, 1)	1	0.12928E-04	0.12946E-04	-0.18363E-07	-0.14
2(2, 0) - 2(1, 1)	1	-0.13503E-05	-0.13086E-05	-0.41675E-07	3.09
2(2, 0) - 2(1, 1)	2	-0.77504E-05	-0.77502E-05	-0.19918E-09	0.00
RMS				0.40414E-07	1.81