Supporting Information

IR Spectra of Hydrogen Bonded Complexes of Trifluoroacetic Acid with Acetone and Diethyl Ether in the Gas Phase. Interaction between CH and OH Stretching Vibrations

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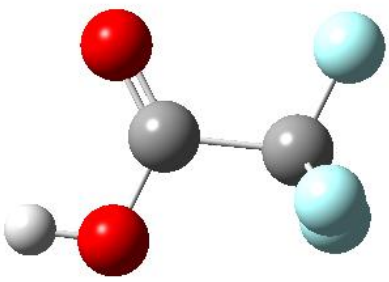
All calculations were performed at B3LYP 6 311++G(2df,2pd) level of theory.

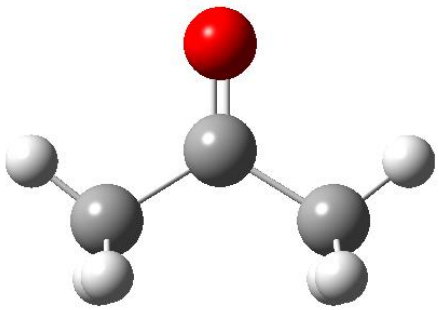
Table S1. The optimized structure and Cartesian coordinated of atoms of the molecules and complexes studied.

Trifluoroacetic acid, TFA



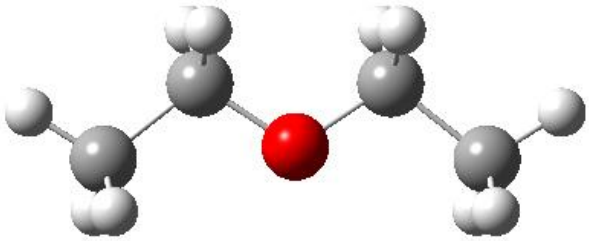
O	-1.493422	1.220237	-0.000006
O	-1.525672	-1.038815	-0.000007
H	-2.486241	-0.911850	0.000014
C	0.600189	-0.000925	0.000001
F	0.998501	-0.677509	-1.086394
F	0.998453	-0.677429	1.086456
F	1.191061	1.187451	-0.000034
C	-0.942380	0.162236	-0.000028

Acetone, DMK



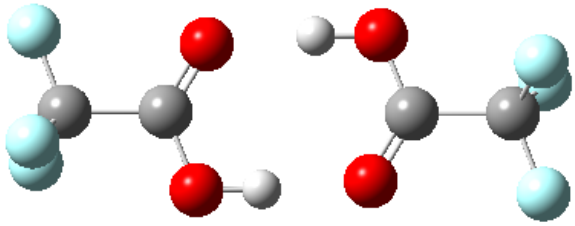
C	0.000000	0.184297	-0.000066
O	0.000000	1.393808	-0.000082
C	-1.288139	-0.611122	0.000045
H	-1.330236	-1.261110	-0.876629
H	-1.330249	-1.260800	0.876952
H	-2.142124	0.060518	-0.000069
C	1.288139	-0.611122	0.000045
H	1.330254	-1.260790	0.876959
H	1.330230	-1.261121	-0.876622
H	2.142124	0.060517	-0.000083

Diethyl ether, DEE



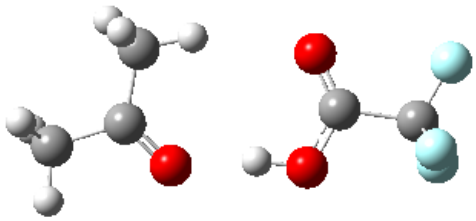
O	0.000000	-0.257800	-0.000064
C	-1.184671	0.517612	0.000039
H	-1.202877	1.169483	0.884301
H	-1.202899	1.169688	-0.884072
C	1.184671	0.517612	0.000060
H	1.202921	1.169678	-0.884058
H	1.202856	1.169493	0.884316
C	-2.380449	-0.412451	-0.000056
H	-2.370843	-1.050886	0.883203
H	-3.307242	0.162645	0.000009
H	-2.370850	-1.050694	-0.883455
C	2.380449	-0.412451	0.000006
H	2.370808	-1.050890	0.883262
H	2.370886	-1.050691	-0.883396
H	3.307242	0.162645	0.000111

Dimer of trifluoroacetic acid, TFA…TFA



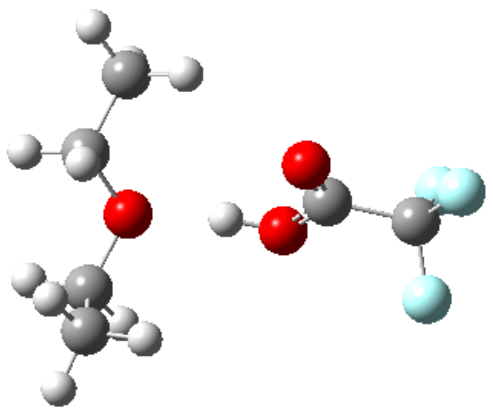
O	1.257219	-1.061928	-0.000407
O	1.411038	1.188862	-0.000507
H	0.411605	1.181850	-0.000945
C	3.436646	-0.028802	0.000188
F	3.897240	0.603154	1.086741
F	3.897811	0.603110	-1.086153
F	3.902494	-1.271762	0.000340
C	1.884745	-0.024577	-0.000213
O	-1.257218	1.061932	-0.000263
O	-1.411033	-1.188858	-0.000675
H	-0.411606	-1.181801	-0.001007
C	-3.436646	0.028800	0.000198
F	-3.897816	-0.602937	-1.086242
F	-3.897235	-0.603336	1.086648
F	-3.902501	1.271758	0.000556
C	-1.884743	0.024580	-0.00021200

Complex of acetic acid and acetone, TFA…DMK



O	0.503449	1.283822	-0.178860
O	0.341610	-0.955360	0.082308
H	-0.647229	-0.830847	0.053052
C	2.511738	-0.042230	0.000954
F	2.898502	-0.858962	-0.991590
F	2.871618	-0.603980	1.166077
F	3.166825	1.108763	-0.126755
C	0.976495	0.187679	-0.044792
C	-3.224662	-0.093898	0.015079
O	-2.325620	-0.918406	0.007331
C	-4.659092	-0.536380	-0.099648
H	-5.269266	-0.069517	0.675179
H	-5.061140	-0.202471	-1.059401
H	-4.731067	-1.618308	-0.035964
C	-2.960214	1.380666	0.142041
H	-3.548800	1.939417	-0.587234
H	-3.293230	1.711450	1.129783
H	-1.902884	1.602409	0.026960

Complex of acetic acid and diethyl ether, TFA…DEE



O	0.761161	0.827490	1.192569
O	0.370760	-0.282309	-0.737214
H	-0.598703	-0.092553	-0.580670
C	2.613394	-0.121688	-0.030875
F	3.018549	0.396592	-1.201157
F	2.802117	-1.451036	-0.078238
F	3.383097	0.374059	0.933873
C	1.118332	0.208690	0.228708
O	-2.258332	-0.006467	-0.513488
C	-2.926014	-1.273024	-0.555645
H	-3.933802	-1.120435	-0.954925
H	-2.367751	-1.863166	-1.281819
C	-2.976332	1.047118	0.141978
H	-3.999979	1.055439	-0.247153
H	-3.022890	0.852471	1.216479
C	-2.975506	-1.988922	0.784843
H	-3.571311	-1.446663	1.518318
H	-3.427790	-2.973185	0.654246
H	-1.972793	-2.127640	1.189024
C	-2.283732	2.365206	-0.129548
H	-1.276411	2.367603	0.284433
H	-2.229083	2.562449	-1.200031
H	-2.842903	3.175155	0.340089

Table S2. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of monomer of trifluoroacetic acid (TFA).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3579.7	18	3750	100	3566	81	ν(OH)
1829.8	17	1859	311	1826	231	ν(C=O)
1418.6	16	1403	34	1370	21	ν(C-C)+ν(C-O)+δ(OH) + (10 +8 comb), Fermi
1358.6				1317	7	(10 +8 comb) + 16, Fermi
1241.6	15	1249	73	1218	98	δ(OH)+ ν(CF)
1203.3	14	1195	308	1168	227	δ(OH)+ν(CF)
1194.6				1157	59	6+9, comb
1184.4	13	1162	300	1134	210	ν(CF)
1121.4	12	1137	308	1107	300	ν(C-O), δ(OH)
	11	793	3	783	3	ν(C-C)
	10	790	44	774	35	out of plane C(=O) + γ(OH)
	9	667	72	660	62	scissoring (O=C-O)
	8	592	95	602	57	γ(OH)
	7	584	7	577	8	scissoring(FCF)
	6	504	3	446	47	γ(OH)+γ(CF)
	5	422	0	416	0	scissoring(C-C-O)
	4	386	2	381	2	ν(C-C)
	3	243	0	237	0	twisting (CF_2)
	2	238	1	233	1	scissor(O=C-C)
	1	36	2	6	1	torsions around C-C

Table S3. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of monomer of aceton-H6 (DMK).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3455.3				3488	3	18+18 over
3017.2	24	3144	6	3003	9	ν(C-H)
2969.9	23	3143	12	3001	12	
2941.8	22	3089	17	2949	18	
2929.6	21	3081	0	2945	0	
	20	3036	7	2930	6	
	19	3029	1	2930	0	
2575.2				2551	0.48	11+13 comb
2449.9						
2244.9				2232	0.61	8+12 comb
2144.7				2117	0.83	6+12 comb
1995.4				2074	1.41	8+11 comb
1739.8 1728.5	18	1786		1771	90	Fermi resonance between ν(C=O), 8+8, 7+7, 5+11
				1755	52	
			199	1731	13	
				1722	41	
	17	1489	19	1443	12	twisting (CH_2) sym
1454.8	16	1472	31	1426	18	scissoring (CH_2) sym
	15	1467	0			deformation (CH_3) asym
	14	1461	1			deformation (CH_3) asym
1361.1	13	1389	20	1354	17	ν(C-C)sym + umbrella (CH_3) sym
1365.5	12	1388	55	1355	51	ν(C-C)asym + umbrella (CH_3) asym
1217.7	11	1234	73	1199	84	ν(C-C)asym
1091.7	10	1121	3	1092	3	out of plane C(=O)
	9	1085	0	1064	0	wagging (CH_2) sym
894.4	8	887	10	879	12	wagging (CH_2) asym
	7	886	0	871	0	twisting (CH_2) asym
	6	783	2	764	2	ν(C-C) sym
	5	537	14	532	13	δ(C=O)
	4	492	1	488	0	out of plane C(=O)
	3	381	2	383	2	scissoring (C-C-C)
	2	135	0	119	0	torsion (CH_3) sym
	1	46	0	143	0	torsion (CH_3) asym

Table S4. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of monomer of aceton-D6 (DMKD6).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3580.8						
3450.8				3473	4	18+18 over
2263.4	24	2331	4	2253	6	ν(CD)
2261.8	23	2329	4	2252	4	
2224.9	22	2285	9	2202	6	
	21	2278	0	2203	0	
2211.6	20	2182	1	2109	0	
	19	2177	0	2136	0	
1743.7				1764	28	7+16 comb
1732.0	18	1777	215	1747	162	ν(C=O)
1242.9	17	1240	132	1206	124	ν(C-C)asym+ umbrella (CD_3) asym
	16	1105	3	1083	3	ν(C-C) sym + umbrella (CD_3) sym
1053.7	15	1072	9	1048	7	twisting (CD_2) sym
	14	1061	0	1038	0	twisting (CD_2) asym
	13	1055	20	1034	18	scissoring (CD_2)sym
	12	1052	0	1032	0	scissoring (CD_2)asym
1004.7	11	1022	2	1004.8	2	umbrella(CD_3)asym
963.9	10	986	2	964	2	out of plane C(=O)
960.6				973	0.8	2+9 comb?
	9	897	0	883	0.5	scissoring (CD) sym
	8	714	1	706	1	ν(C-C)asym
	7	694	1	679	1	ν(C-C)sym
	6	674	0	659	0	twisting (CD_3) asym
	5	484	14	480	13	δ(C=O)
	4	408	1	405	0.5	out of plane C(=O)
	3	320	1	319	1	Scissor (C-C-C)
	2	100	1	86	0	torsion (CD_3) sym
	1	33	0	64	0	torsion (CD_3) asym

Table S5. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of monomer of diethyl ether-H10 (DEE).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
2989.3	39	3108	57	2970	63	ν(CH) in CH_3
	38	3108	0	2970	0	
	37	3103	38	2983	41	
	36	3103	16	2980	1	
	35	3039	7	2901	3	
2945	34	3038	32	2943	15	
	33	2979	0	2841	0	ν(CH) in CH_2
2869.3	32	2976	114	2838	115	
	31	2962	114	2774	29	
	30	2951	12	2834	9	
1977.0				1950	3	10+14 comb
1737						
1728						
	29	1533	2	1494	3	Scissor HCH sym CH_2
	28	1517	2	1477	1	Scissor HCH asym CH_2
	27	1502	3	1461	2	Scissor HCH sym CH_3
	26	1499	3	1458	4	Scissor HCH asym CH_3
1449.3	25	1485	12	1445	6	twisting CH_3 sym
	24	1485	0	1443	0	twisting CH_3 asym
	23	1446	5	1408	5	wagging CH_2 sym
1386.7	22	1413	22	1382	17	Umbrella CH_3 asym
1365.4	21	1407	1	1376	1	Umbrella CH_3 sym
1353.7	20	1383	34	1352	31	wagging CH_2 asym
1302.2	19	1301	4	1274	3	twisting CH_2sym
1219.9	18	1297	0	1269	0	twisting CH_2 asym
	17	1197	10	1173	8	rocking CH_2 sym
1190.7	16	1176	21	1149	21	scissor C-O-C + scissor C-C-O sym + rocking CH_3
	15	1169	0	1144	0	rocking CH_2 asym
1141.0	14	1149	211	1120	122	ν(C-O) asym
1080	13	1095	16	1068	32	ν(C-C) asym + wagging(CH_3) asym
	12	1050	13	1022	7	ν(C-C) sym + ν(C-O) sym
	11	943	5	926	5	rocking CH_3 + rocking CH_2
	10	855	8	841	8	δ(CH_3) sym
	9	829	1	824	1	γ(CH_2) sym
	8	818	0	814	0	γ(CH_2) asym
	7	438	0	434	0	scissor C-O-C + scissor C-C-O sym
	6	435	3	434	3	scissor C-C-O asym
	5	250	1	236	1	twist CH_3 sym
	4	246	0	232	0	twist CH_3 asym
	3	193	1	180	1	scissor C-O-C
	2	107	5	103	5	out of plane CH_3 sym +out of plane O
	1	101	0	98	0	out of plane CH_3 asym

Table S6. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of monomer of diethyl ether-D10 (DEED10).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
2242.9	39	2303	29	2229	27	ν(CD) CD_3
	38	2303	0	2229	0	
	37	2298	17	2217	6	
2234.0	36	2298	8	2221	10	
	35	2213	0	2137	0	ν(CD) CD_2
2164	34	2209	71	2098	22	
	33	2183	1	2089	1	ν(CD) CD_3
	32	2183	14	2071	5	
2084.6	31	2151	74	2059	41	ν(CD) CD_2
	30	2142	7	2042	8	
	29	1254	2	1216	3	ν(C-C) sym + scissor (C-O-C)
1190.5	28	1203	147	1170	36	ν(C-C) asym
	27	1158	4	1133	3	Scissor (CD_2) sym
1138	26	1152	90	1121	37	Scissor (CD_2) asym
1080.9	25	1100	10	1079	14	Umbrella(CD_3) asym
	24	1096	1	1077	1	Umbrella(CD_3) sym
	23	1079	1	1057	2	Scissor (CD_3) sym
1052.1	22	1079	15	1050	6	Scissor (CD_3) asym
	21	1070	6	1050	6	Twisting (CD_3) sym
	20	1070	0	1050	0	Twisting (CD_3) asym
1012.6	19	1039	24	1011	11	ν(C-O) sym
	18	1026	16	1013	9	ν(C-O) asym
	17	1001	2	985	2	rocking CD_2 + rocking CD_3 sym
	16	990	0	974	0	rocking CD_2 + rocking CD_3 asym
	15	952	9	934	6	twisting (CD_2) sym
	14	913	1	898	1	wagging (CD_3) asym
	13	902	0	886	0	twisting (CD_2) asym
	12	884	8	869	8	wagging (CD_3) sym
	11	770	2	753	1	Scissor (CCD) asym
	10	698	1	691	1	Scissor (CCD) sym
	9	605	0	603	0	rocking (CD_2) + rocking CD_3 sym
	8	596	0	594	0	rocking (CD_2) + rocking CD_3 asym
	7	391	0	388	0	Scissor (C-O-C)
	6	374	2	373	2	Scissor (C-C-O) asym
	5	189	2	178	2	rocking (CD_2) + rocking CD_3 sym
	4	182	0	172	0	rocking (CD_2) + rocking CD_3 asym
	3	168	1	163	0	Scissor (C-O-C)
	2	95	3	85	3	twisting (CD_2)+twisting(CD_3) sym
	1	80	0	74	0	rocking (CD_2) + rocking CD_3 asym

Table S7. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of dimer of trifluoroacetic acid (TFA…TFA).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3022[1]	42	3205	3162	2897	1732	ν(OH) asym
	41	3097	0	2741	0	ν(OH) sym
1788.4	40	1808	717	1772	483	ν(C=O) asym
	39	1749	0	1690	0	ν(C=O) sym
	38	1498	0	1451	0	δ(OH) sym + ν(C-C) sym
1466.1	37	1484	38	1444	28	δ(OH) asym + ν(C-C) asym
	36	1342	0	1318	1	δ(OH) sym
1298.1	35	1336	109	1301	92	δ(OH) asym
1239.0	34	1224	698	1201	691	ν(CF) asym
1208.2	33	1223	0	1199	26	ν(CF) sym
	32	1191	0	1171	0	Umbrella (CF_3) sym
1198.0				1188	30	19+20 comb
1185.8	31	1181	562	1160	470	Umbrella (CF_3) asym
1175.6	30	1171	618	1160	519	ν(CF) asym
	29	1168	0	1159	1	ν(CF) sym
	28	976	144	951	113	γ(OH) asym
	27	942	0	916	1	γ(OH) sym
	26	826	25	814	13	ν(CF) + Scissor (OCO) asym
	25	814	0	805	0	ν(CF) + Scissor (OCO) sym
	24	790	0	802	0	Out of plane C(-O, =O) sym
	23	785	10	785	12	Out of plane C(-O, =O) asym
	22	715	93	712	56	Scissor (OCO) asym
	21	701	0	698	0	Scissor (OCO) sym
	20	601	14	599	6	Scissor (CCO) asym
	19	591	0	589	0	Scissor (CCO) sym
	18	519	0	514	0	γ(CF) sym
	17	517	6	512	5	γ(CF) asym
	16	455	36	453	44	ν(O…H) + ν(CF_2) asym
	15	435	0	430	0	ν(O…H) + ν(CF_2) sym
	14	420	0	417	0	ν(C-C) sym
	13	394	2	391	3	ν(C-C) asym
	12	295	42	294	38	
	11	268	0	276	0	twisting CF_2 sym
	10	266	0	263	0	ν(O…HO) asym
	9	255	2	265	2	twisting CF_2 asym
	8	126	0	131	0	δ(O…HO) sym
	7	114	0	110	0	ν(O…HO) sym
	6	90	6	82	6	δ(O…HO) asym
	5	83	1	99	2	twisting (OCO) asym
	4	82	0	136	0	γ(O…HO) asym
	3	30	0	82	0	γ(O…HO) sym
	2	29	0	81	0	rotation CF_3 sym
	1	15	0	220	84	rotation CF_3 asym

[1]The experimental value of the center of gravity M_1. See article text for definition.

Table S8. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of complex of trifluoroacetic acid and acetone-H6 (TFA…DMK).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3032[1]	48	3190	1931	2944	646	ν(OH)
	47	3149	9	3020	4	ν(CH)
	46	3149	5	3004	16	
	45	3092	7	2980	8	
	44	3084	4	2973	0	
	43	3038	6	2915	4	
	42	3030	4	2899	1	
1802.4	41	1823	370	1788	291	ν(C=O) TFA
1715.2	40	1747	270	1699	220	ν(C=O) DMK
1585.6				1587	2	8+39 comb
1539				1528	5	2+36
	39	1494	18	1463	1	Scissor (HCH)
	38	1475	13	1423	0	Scissor (HCH)
	37	1465	7	1407	9	Scissor (HCH)
1430	36	1464	26	1449	7	Scissor (HCH)
	35	1460	1	1401	3	δ(OH) + Scissor (HCH)
1372	34	1401	43	1365	74	Umbrella (CH_3)
	33	1395	42	1369	17	Umbrella (CH_3)
1287	32	1316	61	1282	55	δ(OH)+ν(C-C) TFA
	31	1257	64	1227	59	ν(C-C) asym DMK
1228.1	30	1208	377	1182	341	ν(C-F) + ν(C-O)
1187.4	29	1176	272	1152	184	ν(C-F) + ν(C-O)
1166.0	28	1154	302	1141	268	ν(C-F)
	27	1125	4	1098	5	out of plane C(=O) DMK
	26	1095	2	1070	1	wagging (CH_2) sym
1034.9						
1031.2						
1029.5						
	25	961	71	949	10	γ(OH)
	24	911	6	889	3	wagging (CH_2) asym
	23	888	4	857	4	twisting (CH_2)
	22	808	24	803	14	Scissor (OCO)+ν(CF)
	21	800	1	783	1	ν(C-C) sym DMK
	20	785	9	784	10	out of plane C(=O) TFA
	19	701	68	698	47	Scissor (OCO) + umbrella (CF_3)
	18	590	2	588	2	Scissor (FCF)
	17	556	18	554	13	Scissor (CC=O) DMK
	16	517	3	505	3	Scissor (FCF)
	15	497	0	517	2	out of plane C(=O) DMK
	14	434	13	432	24	
	13	399	11	417	4	
	12	393	1	378	2	

[1]The experimental value of the center of gravity M_1. See article text for definition.

Table S8. Continue

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
	11	267	19	264	17	
	10	259	2	267	1	
	9	137	7	157	20	
	8	134	0	140	7	
	7	104	1	122	18	
	6	95	0	-44	2	
	5	83	2	32	1	
	4	68	4	63	31	
	3	36	1	195	213	
	2	29	1	88	6	
	1	15	1	366	3538	

Table S9. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of complex of trifluoroacetic acid and acetone-D6 (TFA…DMKD6).

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
3042[1]	48	3189	1935	2943	684	ν(OH)
	47	2337	2	2273	1	ν(CD)
	46	2334	2	2242	3	
	45	2286	3	2211	4	
	44	2279	1	2217	1	
	43	2184	1	2124	0	
	42	2179	5	2148	2	
1802.2	41	1823	367	1787	228	ν(C=O) TFA
1768.4				1728	73	23+26 comb
1706.2	40	1737	298	1688	146	ν(C=O) DMKD6
1472.6						
	39	1462	10	1416	0	δ(OH) + scissor (OCO)
1436.5				1438	11	15+18 comb
1333						
1262.2	38	1316	65	1283	61	δ(OH) + ν(C-C) TFA
1226.7	37	1264	113	1239	89	ν(C-C) asym DMKD6
1188.4	36	1208	376	1182	231	ν(C-F)
1166.2	35	1176	271	1152	177	ν(C-O)+Umbrella(CF_3)
	34	1155	302	1141	272	ν(C-F)
	33	1117	4	1098	0	Umbrella (CD_3) sym
	32	1074	9	1058	5	Umbrella (CD_3) asym
	31	1061	1	1026	2	Scissoring (CD_2)
1034.8	30	1055	1	1020	3	δ(CD) asym
1030.5	29	1050	20	1042	15	Scissoring (CD_2)
	28	1029	1	1005	3	Scissoring (CD_2)

[1]The experimental value of the center of gravity M_1. See article text for definition.

Table S9. Continue

	27	991	9	973	2	Out of plane C(=O) DMKD6
	26	958	69	940	38	γ(OH)
	25	906	4	889	3	Scissoring (C-C-C)
	24	808	24	802	20	ν(C-C)+Scissoring (OCO)+ν(CF)
	23	785	9	787	13	Out of plane C(=O) TFA
	22	731	0	716	0	wagging (CD_2) asym
	21	715	0	700	1	ν(C-C) sym DMKD6
	20	701	68	698	31	Scissoring (OCO) + Umbrella(CF_3)
	19	672	0	658	1	twisting (CD_2)
	18	590	2	588	1	Scissoring (CCO) TFA
	17	517	3	512	3	γ(CF)
	16	506	21	506	18	Scissoring (CCO) DMKD6
	15	433	10	429	10	Scissoring (CCO) TFA
	14	412	0	428	1	Out of plane C(=O) DMKD6
	13	397	6	393	5	ν(C-C) TFA
	12	333	8	338	10	
	11	266	17	262	15	
	10	259	2	269	1	
	9	131	6	139	5	
	8	105	1	245	411	
	7	98	0	77	7	
	6	82	1	69	26	
	5	67	2	111	1	
	4	63	2	-21	2	
	3	35	1	90	0	
	2	28	1	34	2	
	1	13	1	389	3598	

Table S10. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of complex of trifluoroacetic acid and diethyl ether-H10 (TFA…DEE). In anharmonic calculations only vibrations 63 – 24 were taken into account using SelectAnharmonicModes option.

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
2867[1]	63	3126	1552	2777	143	ν(OH)
	62	3120	65	3020	198	
	61	3115	12	2988	3	
	60	3106	42	2940	22	
2981.2	59	3102	44	2942	95	
2949.2	58	3082	5	2952	29	ν(CH)
2912.8	57	3045	34	2876	15	
2889.4	56	3042	9	2997	6	
	55	3038	6	3012	17	
	54	3011	116	2859	50	
	53	3000	84	2852	54	
1795.9	52	1825	294	1791	207	ν(C=O)

[1]The experimental value of the center of gravity M_1. See article text for definition.

Table S10. Continue

	51	1527	3	1497	1	Scissoring of CH_2 and CH_3
	50	1511	6	1487	2	
1455	49	1507	3	1460	27	
	48	1495	3	1453	11	
	47	1491	7	1449	14	
1393	46	1491	4	1435	25	
	45	1465	7	1420	3	δ(OH)
	44	1431	14	1401	3	ν(C-C)+umbrella(CH_3)+wagging(CH_2)
1359	43	1419	22	1386	15	ν(C-C)+umbrella(CH_3)+wagging(CH_2)
	42	1411	1	1375	11	Umbrella(CH_3) sym
	41	1399	7	1367	4	Umbrella(CH_3) asym
1302	40	1333	19	1298	73	twisting (CH_2)
	39	1322	56	1290	22	δ(OH)
	38	1306	0	1282	7	twisting (CH_2)
1230.0	37	1213	123	1214	219	ν(C-O) DEE
	36	1208	296	1156	45	ν(CF)
	35	1182	13	1172	56	rocking (CH_2)
1184.3	34	1173	259	1139	145	ν(C-O) TFA
1169.9	33	1152	312	1126	255	ν(CF)
	32	1126	64	1097	72	ν(C-O) DEE
	31	1121	43	1088	5	ν(C-O) DEE
	30	1084	79	1043	21	ν(C-O) DEE
1103.9	29	1026	35	995	48	ν(C-C) DEE
	28	980	48	944	13	γ(OH)
	27	919	7	878	8	ν(C-C) DEE
	26	840	20	856	13	
	25	825	6	797	2	rocking(CH_2)
	24	807	26	798	14	scissoring(OCO)+ν(CC)+umbrella(CF_3)
	23	797	13			
	22	785	10			
	21	701	68			
	20	590	1			
	19	517	3			
	18	504	2			
	17	434	14			
	16	398	8			
	15	372	3			
	14	331	13			
	13	267	11			
	12	260	3			
	11	259	1			
	10	222	1			
	9	138	4			
	8	113	2			
	7	99	1			
	6	69	1			
	5	63	0			
	4	42	1			
	3	34	1			
	2	21	1			
	1	12	0			

Table S11. Experimental (ν_{exp}) wavenumber of band maxima, the number of harmonic vibration (n), calculated in harmonic (ν_{harm}) and anharmonic (ν_{anh}) approximation frequencies, calculated intensities (I_{harm} and I_{anh}), and tentative assignment of the band in the spectra of complex of trifluoroacetic acid and diethyl ether-D10 (TFA…DEED10). In anharmonic calculations only vibrations 63 – 24 were taken into account using SelectAnharmonicModes option.

ν_{exp}, cm^{-1}	n	ν_{harm}, cm^{-1}	I_{harm}, km/mole	ν_{anh}, cm^{-1}	I_{anh}, km/mole	Interpretation
2868[1]	63	3123	1731	2797	18	ν(OH)
2241.6 2218 2199 2166 2102.3	62	2313	6	2241	5	ν(CD)
	61	2308	17	2240	3	
	60	2301	9	2225	7	
	59	2297	10	2220	15	
	58	2286	5	2212	9	
	57	2260	17	2204	13	
	56	2196	35	2174	5	
	55	2187	9	2167	1	
	54	2184	9	2063	2	
	53	2180	21	2081	1	
1796.4	52	1825	294	1789	251	ν(C=O)
1446.8	51	1466	10	1423	5	δ(OH)
1316.3	50	1324	63	1291	20	δ(OH)+ν(C-C)+ν(C-O)
1229.2	49	1221	52	1189	365	ν(C-C)+umbrella(CD_3)+wagging(CD_2)
	48	1209	372	1187	87	ν(CF)
1183.6	47	1189	49	1159	104	ν(C-C)+umbrella(CD_3)+wagging(CD_2)
1168.4	46	1173	254	1145	183	ν(C-O)+umbrella(CF_3)
	45	1152	312	1129	216	ν(CF)
	44	1145	36	1125	241	ν(C-O)+scissoring(CD_2) DEED10
1126	43	1124	52	1104	19	ν(C-O)+scissoring(CD_2) DEED10
1114	42	1098	15	1067	25	deformation CD_2 and CD_3
	41	1091	11	1078	9	
1077	40	1086	11	1084	19	
1056	39	1081	22	1033	23	
1035	38	1077	5	1048	11	
1029	37	1071	2	1055	32	
	36	1067	34	1050	16	
	35	1017	33	988	6	
	34	996	1	977	3	
	33	992	25	1011	38	
	32	978	37	926	0	γ(OH)
	31	930	3	906	2	deformation CD_2 and CD_3
	30	913	4	875	12	
	29	909	5	892	10	
	28	864	18	846	8	
	27	807	24	796	20	ν(C-C)+scissoring(OCO)+ν(CF)
	26	785	10	777	7	out of plane C(=O) TFA
	25	760	2	754	0	ν(C-C) DEED10
	24	701	39	699	37	Scissor(OCO)+umbrella(CF_3)
	23	697	41			
	22	605	1			

[1]The experimental value of the center of gravity M_1. See article text for definition.

Table S11. Continue

	21	591	0			
	20	590	1			
	19	517	3			
	18	442	6			
	17	431	8			
	16	397	7			
	15	328	5			
	14	289	21			
	13	260	3			
	12	257	3			
	11	192	0			
	10	167	1			
	9	126	3			
	8	105	2			
	7	90	1			
	6	66	1			
	5	55	0			
	4	39	1			
	3	33	0			
	2	18	0			
	1	11	0			

Table S12. Calculated energies of complexation: taking account BSSE (ΔE_e), taking account BSSE and zero point vibrational energy (ΔE_0).

complex	ΔE_e, kcal/mole	ΔE_0, kcal/mole
TFA…TFA	−16.79	−15.66
TFA…DMK	−12.02	−13.00
TFA…DMKD6		−12.92
TFA…DEE	−10.97	−11.98
TFA…DEED10		−11.81

Table S13. The spectral feature of the ν(OH) band in the spectra of TFA…DMK and TFA…DMKD6.

TFA…DMK		TFA…DMKD6			
Present study		Present study		Previous study[1]	
wavenumber, cm^{-1}	description	wavenumber, cm^{-1}	description	wavenumber, cm^{-1}	description
3245	submaximum	3244	submaximum		
3167	submaximum	3186	global max		
3094	subminimum	3091	subminimum		
3070	global max	3058	submaximum	3060	global max
2726	submaximum	2729	submaximum	2720	submaximum
2579	submaximum	2580	submaximum	2580	submaximum
2454	submaximum	2456	submaximum	2450	submaximum

[1] Wierzejewska-Hnat, M.; Mielke, Z.; Ratajczak, H. Infrared Matrix Isolation and Gas Phase Studies of Complexes between Trifluoroacetic Acid and Diethylether and Acetone. *Spectrochim. Acta Part A Mol. Spectrosc.* **1987**, *43*, 675–678. (Ref. 25 in the article)

Table S14. The spectral feature of the ν(OH) band in the spectra of TFA…DEE and TFA…DEED10.

TFA…DEE		TFA…DEED10			
Present study		Present study		Previous study[1]	
wavenumber, cm^{-1}	description	wavenumber, cm^{-1}	description	wavenumber, cm^{-1}	description
3242	submaximum	3242			
3118	submaximum	3110			
		2950	global max	2950	global max
2728	submaximum	2727	submaximum	2702	submaximum
2593	submaximum	2592	submaximum	2588	submaximum
2471	submaximum	2472	submaximum	2470	submaximum

[1] See footnote of the previous Table

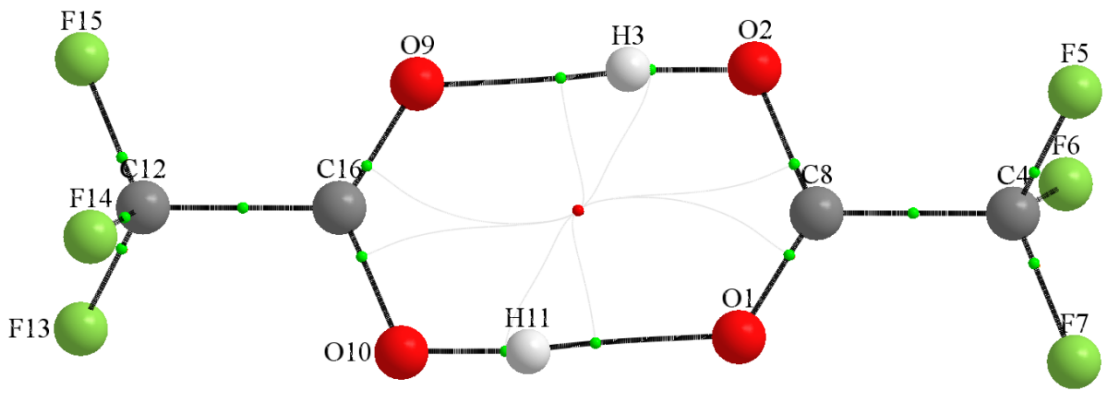


Figure S1. The bond critical points in the trifluoroacetic acid dimer (TFA…TFA)

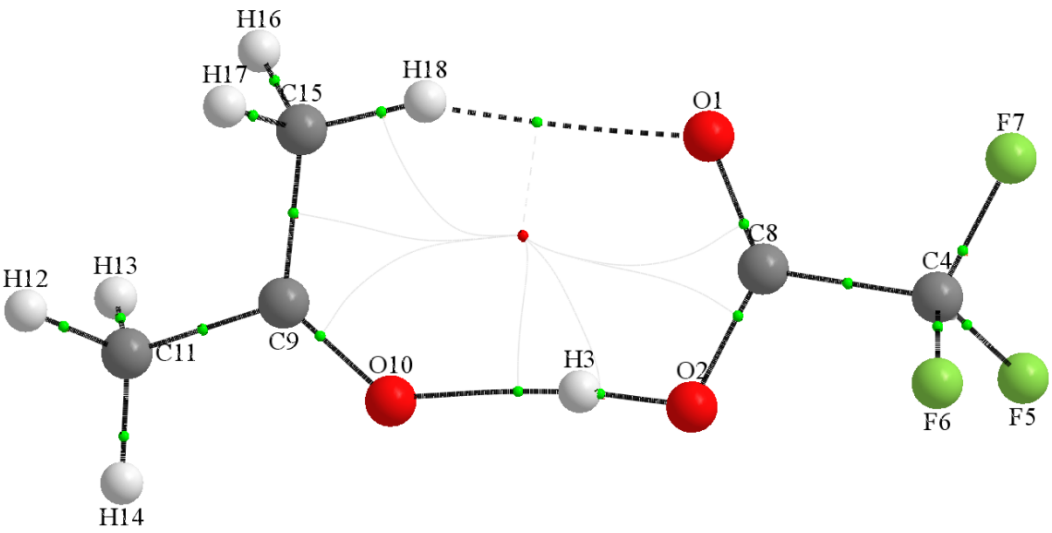


Figure S2. The bond critical points in the complex of trifluoroacetic acid and acetone (TFA…DMK)

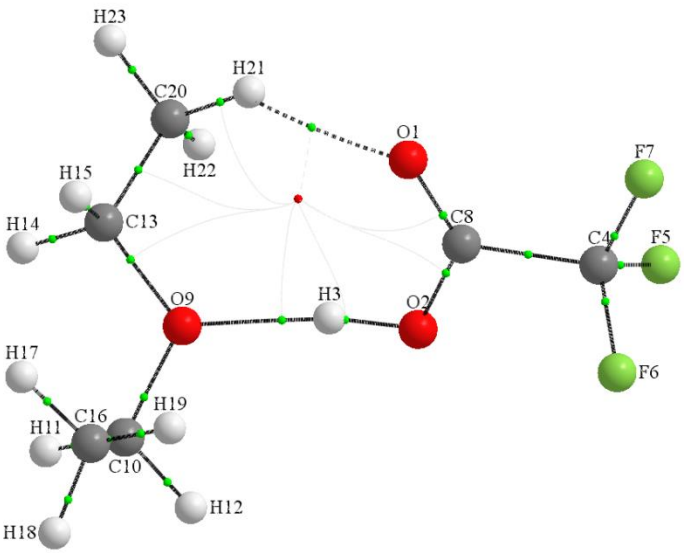


Figure S3. The bond critical points in the complex of trifluoroacetic acid and diethyl ether (TFA…DEE)

Table S15. The comparison of the AIM Properties of the Intermolecular Bond Critical Points of Complexes Studied: Electron Density (ρ), Laplacian of ρ ($\nabla^2\rho$), Potential Energy Density (V), Lagrangian Form of Kinetic Energy Density (G), the Estimated Bond Energies from V(ΔE(V)) and from G (ΔE(G))

CP	ρ, a.u.	$\nabla^2\rho$, a.u.	G, a.u.	V, a.u.	ΔE (G)[a], kcal/mol	ΔE (V)[b], kcal/mol
TFA···TFA						
BCP (3,−1) O···HO	**B3LYP**					
	0.048443	0.09443	0.03482	−0.0460	9.0	8.9
	wB97XD					
	0.05056	0.10007	0.03877	−0.05252	10.2	10.2
	M062X					
	0.05057	0.10007	0.03877	−0.05253	10.2	10.2
TFA···DMK						
BCP (3,−1) OH···O	**B3LYP**					
	0.046627	0.097283	0.03417	−0.04402	8.9	8.6
	wB97XD					
	0.04864	0.09964	0.03594	−0.04698	9.4	9.1
	M062X					
	0.10000	0.35153	0.03980	−0.05460	10.4	10.6
BCP (3,−1) O···HC	**B3LYP**					
	0.009755	0.031818	0.00689	−0.00583	1.2	1.1
	wB97XD					
	0.01178	0.03897	0.00856	−0.00739	1.7	1.4
	M062X					
	0.01121	0.03874	0.00844	−0.00720	1.6	1.4
TFA···DEE						
BCP (3,−1) OH···O	**B3LYP**					
	0.050188	0.095592	0.03599	−0.04808	9.4	9.4
	wB97XD					
	0.05610	0.09578	0.03989	−0.05584	10.5	10.9
	M062X					
	0.06276	0.08791	0.04509	−0.06821	11.9	13.3
BCP (3,−1) O···HC	**B3LYP**[c]					
	0.005900	0.018796	0.00399	−0.00328	0.4	0.6
	wB97XD[d]					
	0.00624	0.02119	0.00454	−0.00379	0.5	0.7
	M062X[d]					
	0.00830	0.02799	0.00617	−0.00535	1.0	1.0

[a] ΔE (G) = (0.448·G − 0.0012)· 627.509 (Mata, I.; Alkorta, I.; Espinosa, E.; Molins, E. Relationships between Interaction Energy, Intermolecular Distance and Electron Density Properties in Hydrogen Bonded Complexes under External Electric Fields. *Chem. Phys. Lett.* **2011**, *507*, 185–189. Ref.56 in the Article)

[b] ΔE (V) = −0.31·V· 627.509 (same reference)

[c] HC of CH_3 group

[d] HC of CH_2 group

An additional discussion on Spectra Extraction

As it was mentioned in the article, the spectra of TFA dimers were obtained by subtraction of spectra of TFA recorded at certain pressure from the spectra obtained at different pressure with a coefficient that allow us to eliminate the obvious monomeric bands (including ν(OH) and ν(C=O) monomeric bands). The result of subtraction is the spectra of dimer of TFA. The spectra of monomeric form were obtained in same way. Using a number of pair of spectra of TFA recorded at different pressures the set of spectra of monomeric and dimeric forms of TFA were obtained. After they were averaged and the result is presented in Figure 2(B) in the article.

These spectra are correspond to some partial pressures of monomers (let us say P_M^0) and dimers (P_D^0). These pressures are unknown. If the shape of spectra weakly depends on the pressure (TFA itself and the pressure of hydrogen acceptors), then one may subtract the spectrum of monomer from experimental one with a coefficient α_M and conclude, that partial pressure of monomers during recording of spectra was $P_M = \alpha_M P_M^0$. Analogous coefficient α_D provides information about of partial pressure of dimer $P_D = \alpha_D P_D^0$.

In the condition of thermodynamic equilibrium P_M and P_D are connected as $\frac{(P_M)^2}{P_D P^\ominus} = K$, where $P^\ominus$ is the standard pressure, and K is the equilibrium constant that is constant at a certain temperature. So, it can be rewritten as

$$\frac{(\alpha_M P_M^0)^2}{\alpha_D P_D^0 P^\ominus} = K\,,$$

and

$$\frac{(\alpha_M)^2}{\alpha_D} = K\frac{P_D^0 P^\ominus}{(P_M^0)^2} = K'$$

We processed a number of experimental spectra of pure TFA to find α_M and α_D and calculate K'. The result is depicted in Figure S4. The weighted averaged of K'=3.0(1).

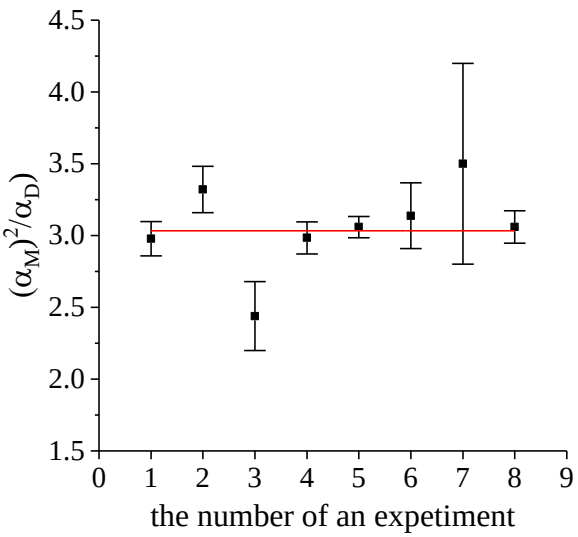


Figure S4. Finding K'

Thereby, the spectra of isolated complexes between TFA and hydrogen donors (acetone or diethyl ether) were obtained as follows: the previously recorded spectrum of donor monomer and the obtained spectrum of TFA monomer were subtracted from the experimental spectra of the mixture of TFA and the hydrogen donor using well-separated bands of the monomers. The coefficient α_M was found as the result of this procedure. The coefficient α_D was calculated as $\alpha_D = (\alpha_M)^2/K'$. After this, the obtained spectrum of TFA dimer multiplied by α_D was subtracted. The residual was an isolated spectrum of the complex. The spectra obtained by this way from experiments with different pressures of TFA and donor were averaged.

Toward finding the equilibrium constant

During the reviewing of the article Reviewer proposed to find a dimerization constant of monomer-dimer equilibrium in pure TFA. One can use the following procedure. If in the cell TFA in gaseous state is presented, than one can write

$$P_0 = P_M + P_D \tag{1}$$

where P_0 is total pressure in the cell (it can be measured with a gauge), P_M and P_D are the partial pressure of monomer and dimer respectively. Integrated intensity of a band $B_i = A_i C_i l$ ($i = M, D$), where A_i is the absolute integrated intensity of the band, C_i is concentration, and l is the optical path length. Because at certain temperature the pressure is proportional to the concentration (at low pressure), one can write $B_i = A_i^P P_i l$. After the expression pressure through B_i, Eq.(1) can be rewritten as

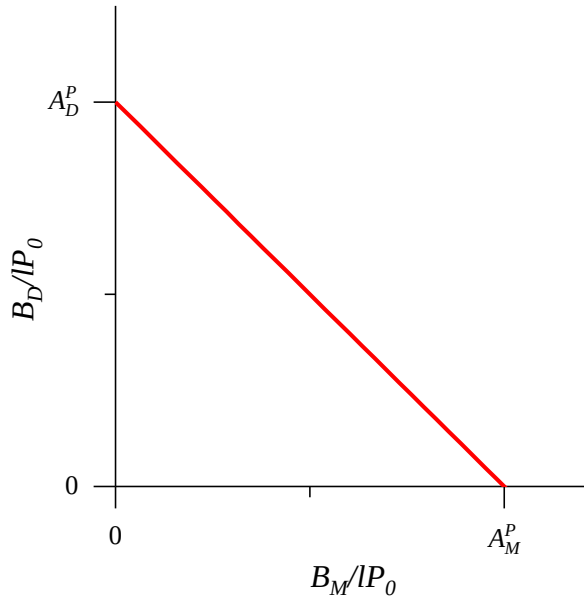


Figure S5. The theoretical plot of $\boldsymbol{B_D/P_0 l}$ vs $\boldsymbol{B_M/P_0 l}$.

$$P_0 = \frac{B_M}{A_M^P l} + \frac{B_D}{A_D^P l} \tag{2}$$

and

$$1 = \frac{B_M}{A_M^P l P_0} + \frac{B_D}{A_D^P l P_0} \tag{3}$$

If one plots the $B_D/P_0 l$ vs $B_M/P_0 l$, than points corresponding to the experiments at different total pressures should lie on one line (Figure S5). From parameters of this line, one can find the coefficients A_i^P, from B_i obtain P_i, and thereby equilibrium constant K. Moreover, from A_i^P one can derive absolute integral coefficients A_i, and,

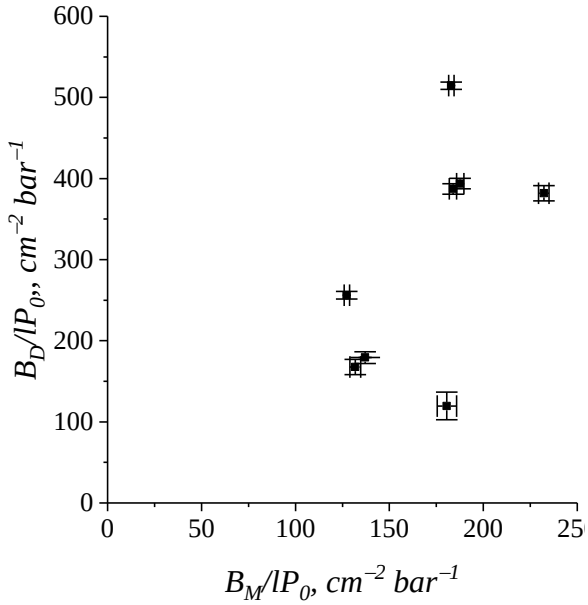


Figure S6. The plot of $\boldsymbol{B_D/P_0 l}$ vs $\boldsymbol{B_M/P_0 l}$ for TFA. $\boldsymbol{P_0}$ is pressure during admission.

for an example, compare it with values calculated by quantum-mechanical methods.

Unfortunately, in our experiments we controlled pressure only during the sample admission. The analysis of spectra showed that the pressure changed significantly in the first 5 – 10 minutes probably due to adsorption inside the cell. After that, the intensity of the spectra was more or less stable. We did not care about because it was not an aim to obtain some absolute values for bands. Thereby the attempt to find the equilibrium constant by mentioned method was failed (Figure S6).

Another possibility to estimate the partial pressures of monomer and dimers in the cell, and thus the equilibrium constants, is to use the calculated absolute intensities. The most quantum-mechanical programs present the intensity in km/mol units. Let us say that intensity of a band is equal to *A* km/mol. One can write:

$$A\ [\text{km/mol}] = A\cdot 10^5\ [\text{cm/mol}] = A\cdot 10^2\ [\text{l cm}^{-2}/\text{mol}] = \ldots \quad (4)$$

Because the molar volume is 22.4 T/273.15 [l atm/mol], where T is the temperature of the experiment, Eq.(4) can be follow

$$\ldots = A\cdot 10^2\ 273.15/22.4/T\ [\text{atm}^{-1}\ \text{cm}^{-2}] = A\cdot 10^2\ 12.19/(T\ 1.01325)\ [\text{bar}^{-1}\ \text{cm}^{-2}] = A\cdot 1203/T\ [\text{bar}^{-1}\ \text{cm}^{-2}]$$

We expressed the pressure in the bar units because the standard pressure is $P^{\ominus} = 1$ bar. Table S16 collects the values of the equilibrium constant obtained by intensity calculated in harmonic and anharmonic approximation as well as values calculated by literature data. The intensities of ν(C=O) in monomer and dimer spectra were used to calculate the equilibrium constants.

The value of equilibrium constant depends on the calculated intensities of the band, particular on harmonic or anharmonic calculations. The *K* estimated in present work is the same order as calculated from literature data. The value of thermodynamic parameters (Δ*H* and Δ*S*) was obtain from temperature range 45 – 195 °C by Lumbroso-Bader et al. and 350 – 415 °C by Frurip et al. Sauren et al. made their measurements in 293 – 313 K.

Table S16. The values of equilibrium constant obtained from present experimental and calculated data and calculated from literature data for temperature T = 293 K for standard pressure $P^{\ominus} = 1$ bar.

this study		literature data		
K_{harm} [1]	K_{anh} [2]	Lumbroso-Bader[3]	Frurip[4]	Sauren [5]
0.0010	0.0012	0.0090	0.0052	0.0029

[1] Equilibrium constant obtained with intensities calculated in harmonic approximation
[2] Equilibrium constant obtained with intensities calculated in anharmonic approximation
[3] Based on the constants reported in Lumbroso-Bader, N.; Coupry, C.; Baron, D.; Clague, D. .; Govil, G. Dimerization of Carboxylic Acids: A Vapor Phase NMR Study. *J. Magn. Reson.* **1975**, *17*, 386–392 (Ref. 34 in the Article)
[4] Based on the constants reported in Frurip, D. J.; Curtiss, L. A.; Blander, M. Vapor Phase Association in Acetic and Trifluoroacetic Acids. Thermal Conductivity Measurements and Molecular Orbital Calculations. *J. Am. Chem. Soc.* **1980**, *102*, 2610–2616. (Ref. 33 in the article)
5 Based on the constant reported in Sauren, H.; Winkler, A.; Hess, P. Kinetics and energetics of hydrogen bond dissociation in isolated acetic acid-d1 and –d4 and trifluoroacetic acid dimers. *Chem. Phys. Lett.* **1995**, *239*, 313-319 (Ref. 36 in the article)