Structural and Dynamical Features of the 2,2,2-Trifluoroethanol···Ammonia Complex

Javix Thomas, Isabel Peña,* Colton Carlson, Yisi Yang, Wolfgang Jäger, Yunjie Xu*

* Corresponding Authors, Email: ipencal@qf.uva.es; yunjie.xu@ualberta.ca

Supplementary Information

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Table S1. B3LYP-D3BJ/6-311++G(2d,p) rotational constants (in MHz), nuclear quadrupole coupling constants (in MHz), dipole moment components (in Debye) and relative binding energies (in $kJmol^{-1}$) of the most stable conformers of the TFE···NH_3 complex.

Parameter	*i g* TFE···NH_3 I	*a t* TFE··· NH_3 II	*a g* TFE···NH_3 III
A	3602	4903	3283
B	1493	1001	1570
C	1332	986	1340
$\lvert\mu_a\rvert$	3.2	5.8	0.7
$\lvert\mu_b\rvert$	1.6	2.3	1.4
$\lvert\mu_c\rvert$	1.5	0.0	0.0
χ_{aa}	0.01	-3.92	0.95
$\chi_{bb} - \chi_{cc}$	-4.06	-0.08	4.89
$\Delta D_0{}^a$	0.0	9.0	22.1
$\Delta E_b{}^b$	33.8	31.8	11.7

[a]ZPE and BSSE corrected relative dissociation energy with respect to the global minimum **I**. [b]ZPE and BSSE corrected binding energy which is the difference between the dimer and its subunits. We choose to represent binding energy as a positive value.

Table S2. Principal axis coordinates of the *ig* TFE···NH_3 I conformer from B3LYP-D3BJ/def2-TZVPD calculations.

Atom	X	Y	Z	Atom #
C	-0.010925	1.014821	-0.689453	1
C	0.816973	-0.077623	-0.026312	2
O	-1.101622	1.410111	0.081632	3
F	1.298485	0.288273	1.171159	4
H	-0.293880	0.636530	-1.679343	5
H	0.650718	1.871481	-0.829617	6
H	-1.811885	0.728393	0.018955	7
F	0.094663	-1.210397	0.167438	8
F	1.869857	-0.411597	-0.805256	9
N	-3.049081	-0.636626	-0.025553	10
H	-3.640554	-0.738982	-0.842603	11
H	-3.655542	-0.559697	0.783780	12
H	-2.508357	-1.488922	0.076835	13

Table S3. Principal axis coordinates of the *ag* TFE···NH_3 III conformer from B3LYP-D3BJ/def2-TZVPD calculations.

Atom	X	Y	Z	Atom #
C	-0.247163	0.685042	0.811382	1
C	0.756422	-0.150506	0.037646	2
O	-0.920934	1.599035	-0.025635	3
F	0.181764	-0.890799	-0.925393	4
F	1.681967	0.634257	-0.567536	5
F	1.414051	-0.987327	0.862308	6
H	0.293038	1.178915	1.624562	7
H	-1.001398	0.014734	1.221210	8
H	-0.291845	2.243160	-0.370874	9
N	-3.062351	-0.701447	0.041441	10
H	-2.754779	-1.402565	-0.623743	11
H	-2.864011	0.205363	-0.369820	12
H	-4.068524	-0.787894	0.128260	13

Table S4. Principal axis coordinates of the *at* TFE···NH_3 II conformer from B3LYP-D3BJ/def2-TZVPD calculations.

Atom	X	Y	Z	Atom #
C	-0.413489	0.544688	0.000000	1
C	1.024274	0.064678	0.000000	2
O	-1.262961	-0.563992	0.000000	3
F	1.319110	-0.673962	1.083892	4
F	1.319110	-0.673962	-1.083892	5
F	1.859452	1.131276	0.000000	6
H	-0.532334	1.175898	-0.889541	7
H	-0.532334	1.175898	0.889541	8
H	-2.196161	-0.255136	0.000000	9
N	-4.004300	0.209360	0.000000	10
H	-4.247215	1.194023	0.000000	11
H	-4.434181	-0.210122	0.817637	12
H	-4.434181	-0.210122	-0.817637	13

Table S5. Measured transition frequencies of the *ig* TFE···$^{14}NH_3$ isotopologue (parent species).

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	**Frequency**/ MHz	**Δν**/ MHz[a]
2	1	2	2	1	0	1	2	7607.3379	-0.0017
2	1	2	2	1	0	1	1	7607.4359	0.0033
2	1	2	3	1	0	1	2	7607.8662	-0.0015
2	1	2	1	1	0	1	0	7608.0248	0.0032
2	1	2	1	1	0	1	1	7608.2545	0.0004
2	1	1	1	1	0	1	0	8089.9620	0.0002
2	1	1	1	1	0	1	1	8090.1952	0.0008
2	1	1	3	1	0	1	2	8090.3403	0.0010
2	1	1	2	1	0	1	2	8090.7677	-0.0001
2	1	1	2	1	0	1	1	8090.8612	0.0004
3	1	3	2	2	1	2	1	8125.1371	0.0035
3	1	3	3	2	1	2	2	8125.1708	0.0041
3	1	3	4	2	1	2	3	8125.2217	-0.0009
3	0	3	3	2	0	2	3	8337.5000	0.0000
3	0	3	3	2	0	2	2	8337.6392	0.0059
3	0	3	4	2	0	2	3	8337.6917	0.0016
3	2	2	3	2	2	1	2	8371.6705	-0.0003
3	2	2	4	2	2	1	3	8371.7704	-0.0001
3	2	2	2	2	2	1	1	8371.8295	0.0036
3	1	2	2	2	1	1	2	8606.9799	0.0002
3	1	2	3	2	1	1	2	8607.5175	-0.0117
3	1	2	4	2	1	1	3	8607.5505	-0.0001
3	1	2	2	2	1	1	1	8607.6455	-0.0006
3	1	2	3	2	1	1	3	8607.9576	-0.0001
4	0	4	3	3	1	3	2	9255.2071	-0.0010
4	0	4	5	3	1	3	4	9255.3447	-0.0003
4	0	4	4	3	1	3	3	9255.6666	0.0001

3	1	3	3	2	0	2	3	10159.8496	0.0018
3	1	3	3	2	0	2	2	10159.9800	-0.0012
3	1	3	4	2	0	2	3	10160.4314	-0.0004
3	1	3	2	2	0	2	1	10160.5617	-0.0005
3	1	3	2	2	0	2	2	10160.7713	0.0017
4	1	4	4	3	1	3	4	10823.5418	-0.0015
4	1	4	4	3	1	3	3	10824.1259	-0.0015
4	1	4	5	3	1	3	4	10824.1652	-0.0016
4	1	4	3	3	1	3	3	10824.9092	-0.0020
4	0	4	4	3	0	3	4	11077.8222	-0.0020
4	0	4	4	3	0	3	3	11078.0176	0.0033
4	0	4	5	3	0	3	4	11078.0857	-0.0010
4	0	4	3	3	0	3	3	11078.3448	0.0004
3	1	2	2	2	0	2	1	11125.0132	-0.0017
3	1	2	4	2	0	2	3	11125.2329	0.0015
3	1	2	3	2	0	2	2	11125.7725	0.0006
4	2	3	4	3	2	2	4	11155.4936	-0.0021
4	2	3	4	3	2	2	3	11155.4936	-0.0021
4	2	3	5	3	2	2	4	11155.5435	-0.0028
4	2	3	3	3	2	2	3	11155.5613	0.0019
4	2	3	3	3	2	2	2	11155.5613	0.0020
4	3	2	4	3	3	1	3	11178.4694	0.0052
4	3	2	5	3	3	1	4	11178.5426	0.0020
4	3	2	3	3	3	1	2	11178.5709	-0.0023
4	3	1	4	3	3	0	3	11180.1697	-0.0016
4	3	1	5	3	3	0	4	11180.2417	-0.0031
4	3	1	3	3	3	0	2	11180.2732	-0.0035
4	2	2	5	3	2	1	4	11239.6167	-0.0001
4	2	2	4	3	2	1	3	11239.6409	0.0046
4	1	3	3	3	1	2	3	11465.4078	0.0003

4	1	3	5	3	1	2	4	11465.9142	-0.0000
4	1	3	3	3	1	2	2	11465.9569	-0.0002
4	1	3	4	3	1	2	4	11466.2991	-0.0025
5	0	5	4	4	1	4	3	12219.4462	0.0014
5	0	5	6	4	1	4	5	12219.5337	-0.0007
5	0	5	5	4	1	4	4	12219.8114	0.0009
2	2	1	1	1	1	0	1	12303.9434	0.0031
2	2	1	2	1	1	0	1	12304.0965	0.0011
2	2	1	3	1	1	0	2	12304.4874	-0.0011
2	2	1	1	1	1	0	0	12305.1774	0.0048
2	2	0	1	1	1	0	1	12312.4700	0.0021
2	2	0	2	1	1	0	1	12312.6757	0.0004
2	2	0	3	1	1	0	2	12313.0334	-0.0014
2	2	0	2	1	1	0	2	12313.1700	0.0018
2	2	0	1	1	1	0	0	12313.7050	0.0049
2	2	1	1	1	1	1	0	12464.5870	0.0037
2	2	1	3	1	1	1	2	12465.2402	0.0017
2	2	1	2	1	1	1	1	12465.7365	-0.0017
2	2	0	1	1	1	1	0	12473.1140	0.0031
2	2	0	3	1	1	1	2	12473.7843	-0.0005
2	2	0	2	1	1	1	1	12474.3177	-0.0004
4	1	4	4	3	0	3	3	12646.4722	-0.0030
4	1	4	5	3	0	3	4	12646.9059	-0.0027
4	1	4	3	3	0	3	2	12647.0034	0.0009
5	1	5	5	4	1	4	4	13515.7973	-0.0032
5	1	5	6	4	1	4	5	13515.8366	0.0019
5	0	5	5	4	0	4	4	13788.2764	0.0050
5	0	5	6	4	0	4	5	13788.3578	0.0016
5	2	4	5	4	2	3	4	13933.4911	0.0050
5	2	4	6	4	2	3	5	13933.5214	-0.0002

5	3	3	5	4	3	2	4	13979.0644	0.0052
5	3	3	6	4	3	2	5	13979.0918	-0.0025
5	3	3	4	4	3	2	3	13979.1095	0.0045
5	3	2	5	4	3	1	4	13985.0033	-0.0038
5	3	2	6	4	3	1	5	13985.0346	-0.0011
5	3	2	4	4	3	1	3	13985.0493	0.0042
5	2	3	6	4	2	2	5	14097.5903	0.0016
5	2	3	5	4	2	2	4	14097.6344	-0.0018
4	1	3	3	3	0	3	2	14253.2892	-0.0004
4	1	3	5	3	0	3	4	14253.4547	-0.0009
4	1	3	4	3	0	3	3	14254.0323	-0.0008
5	1	4	5	4	1	3	4	14314.1053	0.0004
5	1	4	6	4	1	3	5	14314.1306	0.0008
5	1	4	4	4	1	3	3	14314.1517	-0.0039
3	2	2	3	2	1	1	2	14933.7474	-0.0014
3	2	2	4	2	1	1	3	14934.1759	-0.0014
3	2	2	2	2	1	1	1	14934.4189	0.0036
3	2	1	3	2	1	1	2	14976.4188	-0.0009
3	2	1	4	2	1	1	3	14976.7608	-0.0006
3	2	1	2	2	1	1	1	14976.9708	0.0017
5	1	5	5	4	0	4	4	15084.2607	-0.0008
5	1	5	6	4	0	4	5	15084.6553	-0.0013
5	1	5	4	4	0	4	3	15084.7255	0.0025
6	0	6	5	5	1	5	4	15170.5677	0.0020
6	0	6	7	5	1	5	6	15170.6255	-0.0002
6	0	6	6	5	1	5	5	15170.8451	0.0001
3	2	2	2	2	1	2	1	15416.3525	-0.0030
3	2	2	4	2	1	2	3	15416.6462	-0.0027
3	2	2	3	2	1	2	2	15417.1740	-0.0030
3	2	1	2	2	1	2	1	15458.9085	-0.0008

3	2	1	4	2	1	2	3	15459.2326	-0.0005
3	2	1	3	2	1	2	2	15459.8491	0.0012
6	1	6	6	5	1	5	5	16199.3179	-0.0046
6	1	6	5	5	1	5	4	16199.3370	-0.0002
6	1	6	7	5	1	5	6	16199.3587	0.0040
6	0	6	6	5	0	5	5	16466.8334	-0.0016
6	0	6	7	5	0	5	6	16466.9253	-0.0007
6	2	5	6	5	2	4	5	16704.2563	-0.0040
6	2	5	7	5	2	4	6	16704.2926	0.0018
6	3	4	6	5	3	3	5	16782.1677	-0.0011
6	3	4	7	5	3	3	6	16782.1898	0.0042
6	3	3	7	5	3	2	6	16797.9160	0.0027
6	2	4	7	5	2	3	6	16979.7433	-0.0011
6	2	4	6	5	2	3	5	16979.8025	-0.0008
6	1	5	6	5	1	4	5	17148.5478	-0.0029
6	1	5	7	5	1	4	6	17148.5808	-0.0020
6	1	5	5	5	1	4	4	17148.6048	0.0036
4	2	3	4	3	1	2	3	17481.7133	-0.0019
4	2	3	5	3	1	2	4	17482.1720	-0.0010
4	2	3	3	3	1	2	2	17482.3242	-0.0043
5	1	4	4	4	0	4	3	17489.3601	0.0028
5	1	4	6	4	0	4	5	17489.4985	-0.0002
5	1	4	5	4	0	4	4	17490.1216	-0.0021
4	2	2	4	3	1	2	3	17608.5242	-0.0025
4	2	2	5	3	1	2	4	17608.8240	-0.0036
4	2	2	3	3	1	2	2	17608.9419	-0.0009

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S6. Measured transition frequencies of the *ig* TFE···$^{15}NH_3$ isotopologue.

J'	K_a'	K_c'	J''	K_a''	K_c''	**Frequency**/ MHz	**Δν**/ MHz[a]
2	1	2	1	0	1	7501.5787	0.0015
3	1	3	2	1	2	7921.9759	-0.0002
2	1	1	1	0	1	7963.9002	0.0023
3	0	3	2	0	2	8126.9462	-0.0003
3	2	2	2	2	1	8157.8718	0.0009
3	2	1	2	2	0	8188.7718	0.0006
3	1	2	2	1	1	8384.0179	0.0004
4	0	4	3	1	3	8934.8356	-0.0003
3	1	3	2	0	2	9992.7005	0.0007
4	1	4	3	1	3	10554.0319	0.0012
4	0	4	3	0	3	10800.5883	-0.0009
4	2	3	3	2	2	10870.9856	-0.0011
4	3	2	3	3	1	10891.8806	0.0009
4	3	1	3	3	0	10893.3440	-0.0002
3	1	2	2	0	2	10917.0621	0.0002
4	2	2	3	2	1	10947.3877	-0.0002
4	1	3	3	1	2	11168.8922	-0.0010
4	3	2	4	2	2	11380.9534	-0.0009
4	3	1	4	2	2	11382.6633	0.0001
3	3	1	3	2	1	11436.4624	-0.0001
3	3	0	3	2	1	11436.7090	0.0020
3	3	1	3	2	2	11475.1198	-0.0013
3	3	0	3	2	2	11475.3659	0.0003
4	3	2	4	2	3	11496.0144	0.0003
4	3	1	4	2	3	11497.7229	-0.0001
5	3	3	5	2	4	11537.4890	0.0004
5	3	2	5	2	4	11544.3050	0.0010
6	3	4	6	2	5	11608.5012	-0.0013

6	3	3	6	2	5	11628.8447	-0.0006
7	3	5	7	2	6	11718.6079	0.0003
5	0	5	4	1	4	11827.3447	-0.0001
2	2	1	1	1	0	12243.8830	-0.0004
2	2	0	1	1	0	12251.6422	0.0005
2	2	1	1	1	1	12397.9929	-0.0012
2	2	0	1	1	1	12405.7526	0.0001
4	1	4	3	0	3	12419.7831	-0.0009
5	1	5	4	1	4	13179.4133	0.0005
5	0	5	4	0	4	13446.5396	0.0000
5	2	4	4	2	3	13578.8273	-0.0004
5	3	3	4	3	2	13620.3026	0.0004
5	3	2	4	3	1	13625.4090	0.0003
5	2	3	4	2	2	13728.2707	0.0002
5	1	4	4	1	3	13944.6271	-0.0007
4	1	3	3	0	3	13959.0065	-0.0021
6	0	6	5	1	5	14710.7913	0.0008
5	1	5	4	0	4	14798.6065	-0.0011
3	2	2	2	1	1	14809.0326	-0.0009
3	2	1	2	1	1	14847.6926	0.0005
3	2	2	2	1	2	15271.3554	0.0012
3	2	1	2	1	2	15310.0128	-0.0000
6	1	6	5	1	5	15797.2784	-0.0001
6	0	6	5	0	5	16062.8581	-0.0004
6	2	5	5	2	4	16280.1158	0.0000
6	3	4	5	3	3	16351.1299	0.0002
6	3	3	5	3	2	16364.6575	0.0004
6	2	4	5	2	3	16531.9570	0.0008
6	1	5	5	1	4	16708.0077	-0.0002

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S7. Measured transition frequencies of the *ig* TFE···$^{14}ND_3$ isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	2	3	2	1	1	2	7856.9376	0.0004
3	1	3	3	2	0	2	2	9525.0085	-0.0014
3	1	3	4	2	0	2	3	9525.4503	-0.0003
3	1	3	2	2	0	2	1	9525.5684	0.0004
4	1	4	4	3	1	3	4	9906.7475	0.0029
4	1	4	4	3	1	3	3	9907.3585	-0.0062
4	1	4	5	3	1	3	4	9907.4145	0.0062
4	1	4	3	3	1	3	3	9908.1940	-0.0050
4	0	4	4	3	0	3	3	10136.8726	0.0047
4	0	4	5	3	0	3	4	10136.9310	-0.0013
4	0	4	3	3	0	3	2	10136.9310	0.0034
3	1	2	2	2	0	2	1	10367.2719	0.0031
3	1	2	4	2	0	2	3	10367.4978	0.0008
4	1	3	3	3	1	2	3	10467.3935	0.0021
4	1	3	4	3	1	2	3	10467.8213	-0.0026
4	1	3	5	3	1	2	4	10467.8483	0.0012
4	1	3	3	3	1	2	2	10467.8836	-0.0036
4	1	3	4	3	1	2	4	10468.1893	-0.0019
4	1	4	4	3	0	3	3	11807.5898	-0.0062
4	1	4	5	3	0	3	4	11808.0324	0.0033
2	2	1	3	1	1	1	2	12051.1061	-0.0033
2	2	1	2	1	1	1	1	12051.6393	0.0050
2	2	0	3	1	1	1	2	12057.5534	0.0072
2	2	0	2	1	1	1	1	12058.1049	0.0049
5	1	5	5	4	1	4	4	12373.1823	0.0007
5	1	5	6	4	1	4	5	12373.2133	-0.0035
5	0	5	5	4	0	4	4	12625.5009	0.0052
5	0	5	6	4	0	4	5	12625.5716	0.0001

5	2	4	5	4	2	3	4	12736.0711	0.0054
5	2	4	6	4	2	3	5	12736.1137	0.0031
5	2	3	4	4	2	2	3	12860.9478	0.0003
5	2	3	6	4	2	2	5	12860.9478	-0.0021
5	2	3	5	4	2	2	4	12860.9763	-0.0020
5	1	4	5	4	1	3	4	13071.1811	0.0020
5	1	4	6	4	1	3	5	13071.2010	-0.0024
5	1	4	4	4	1	3	3	13071.2243	-0.0024
3	2	2	4	2	1	2	3	14741.5836	-0.0155
3	2	2	3	2	1	2	2	14742.1523	0.0016
6	1	6	6	5	1	5	5	14832.5803	-0.0042
6	1	6	7	5	1	5	6	14832.6198	0.0036
6	0	6	6	5	0	5	5	15088.3831	-0.0011
6	0	6	7	5	0	5	6	15088.4664	-0.0009
6	2	5	6	5	2	4	5	15271.2191	-0.0010
6	2	5	5	5	2	4	4	15271.2581	0.0013
6	3	3	6	5	3	2	5	15340.8054	0.0007
6	3	3	5	5	3	2	4	15340.8316	-0.0015
6	3	3	7	5	3	2	6	15340.8316	0.0033
6	2	4	5	5	2	3	4	15482.8513	0.0030
6	2	4	7	5	2	3	6	15482.8513	-0.0016
6	2	4	6	5	2	3	5	15482.8963	-0.0030
6	1	5	6	5	1	4	5	15664.4300	0.0028
6	1	5	7	5	1	4	6	15664.4534	-0.0028
6	1	5	5	5	1	4	4	15664.4728	0.0006

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S8. Measured transition frequencies of the *ig* TFEOD···$^{14}ND_3$ isotopologue.

J'	K_a'	K_c'	*F'*	*J"*	K_a"	K_c"	*F"*	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	2	3	2	1	1	2	7803.2132	-0.0051
3	1	2	4	2	1	1	3	7803.2437	-0.0048
3	1	3	3	2	0	2	2	9459.3313	-0.0005
3	1	3	2	2	0	2	1	9459.9109	0.0066
3	1	3	2	2	0	2	1	9459.9109	0.0066
5	0	5	5	4	1	3	4	9466.7010	-0.0064
5	0	5	6	4	1	3	5	9467.4289	-0.0014
4	1	4	4	3	1	3	4	9833.3668	0.0020
4	1	4	4	3	1	3	3	9833.9856	0.0042
4	1	4	3	3	1	3	2	9833.9856	0.0081
4	1	4	5	3	1	3	4	9834.0189	-0.0049
4	0	4	4	3	0	3	3	10063.8025	0.0018
4	0	4	5	3	0	3	4	10063.8680	0.0020
4	0	4	3	3	0	3	2	10063.8680	0.0053
4	2	3	4	3	2	2	3	10122.9728	0.0003
4	2	3	4	3	2	2	4	10122.9728	0.0003
4	2	3	5	3	2	2	4	10123.0336	-0.0046
4	2	3	3	3	2	2	3	10123.0520	-0.0031
4	2	3	3	3	2	2	2	10123.0520	-0.0030
4	3	2	4	3	3	1	3	10140.4338	-0.0050
4	3	2	5	3	3	1	4	10140.5526	0.0006
4	3	1	4	3	3	0	3	10141.5647	-0.0038
4	3	1	5	3	3	0	4	10141.6770	-0.0026
4	2	2	5	3	2	1	4	10187.2807	-0.0030
3	1	2	4	2	0	2	3	10304.3637	0.0047
3	1	2	3	2	0	2	2	10304.9025	-0.0070
4	1	3	3	3	1	2	3	10395.6635	0.0019

4	1	3	4	3	1	2	3	10396.1157	-0.0004
4	1	3	5	3	1	2	4	10396.1407	0.0027
4	1	3	3	3	1	2	2	10396.1903	0.0111
4	1	3	4	3	1	2	4	10396.4992	-0.0003
4	3	2	5	4	2	2	5	11341.7543	0.0005
4	3	1	4	4	2	2	4	11343.0708	-0.0034
3	3	1	3	3	2	2	3	11421.1132	0.0006
3	3	0	3	3	2	2	3	11421.3024	0.0010
4	3	2	5	4	2	3	5	11438.4387	-0.0001
4	3	2	4	4	2	3	4	11438.5846	0.0058
4	3	1	5	4	2	3	5	11439.7500	-0.0045
4	3	1	4	4	2	3	4	11439.8992	0.0018
2	2	1	2	1	1	0	1	11843.7494	-0.0029
2	2	1	3	1	1	0	2	11844.1280	-0.0012
2	2	0	3	1	1	0	2	11850.6310	-0.0022
2	2	1	3	1	1	1	2	11984.8278	0.0028
2	2	1	2	1	1	1	1	11985.3437	-0.0051
5	1	5	5	4	1	4	4	12281.3558	0.0029
5	1	5	4	4	1	4	3	12281.3558	-0.0037
5	1	5	6	4	1	4	5	12281.3852	-0.0024
5	0	5	5	4	0	4	4	12533.7349	0.0003
5	0	5	6	4	0	4	5	12533.8114	-0.0004
5	2	4	5	4	2	3	4	12645.4176	0.0034
5	2	4	6	4	2	3	5	12645.4589	0.0024
5	2	3	6	4	2	2	5	12771.5503	0.0018
5	1	4	5	4	1	3	4	12981.4061	0.0019
5	1	4	6	4	1	3	5	12981.4279	-0.0001
5	1	4	4	4	1	3	3	12981.4490	-0.0032
6	1	6	6	5	1	5	5	14722.2597	-0.0009
6	1	6	7	5	1	5	6	14722.2911	-0.0011

6	0	6	6	5	0	5	5	14977.7493	-0.0005
6	0	6	7	5	0	5	6	14977.8339	-0.0004
6	0	6	5	5	0	5	4	14977.8339	-0.0021
6	2	5	6	5	2	4	5	15162.3346	0.0078
6	2	5	5	5	2	4	4	15162.3646	0.0025
6	2	5	7	5	2	4	6	15162.3646	0.0044
6	2	4	7	5	2	3	6	15375.9918	-0.0004
6	2	4	5	5	2	3	4	15375.9918	0.0042
6	2	4	6	5	2	3	5	15376.0399	-0.0016
6	1	5	6	5	1	4	5	15556.4728	-0.0010
6	1	5	7	5	1	4	6	15556.4973	-0.0055
6	1	5	5	5	1	4	4	15556.5142	-0.0053

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S9. Measured transition frequencies of the *ig* TFE···$^{14}ND_2H$ isotopologue.

J'	K_a'	K_c'	*F'*	*J"*	K_a"	K_c"	*F"*	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	3	2	2	1	2	1	7673.7278	0.0054
3	1	3	3	2	1	2	2	7673.7515	0.0024
3	1	3	4	2	1	2	3	7673.8128	-0.0009
2	1	1	1	1	0	1	1	7743.3834	-0.0046
2	1	1	3	1	0	1	2	7743.5038	0.0047
2	1	1	2	1	0	1	1	7744.0417	-0.0025
3	0	3	3	2	0	2	3	7869.0218	0.0051
3	0	3	3	2	0	2	2	7869.1793	-0.0008
3	0	3	4	2	0	2	3	7869.2346	0.0002
3	2	2	2	2	2	1	2	7897.1321	-0.0110
3	2	2	3	2	2	1	2	7897.1321	-0.0109
3	2	2	4	2	2	1	3	7897.2806	0.0054
3	2	2	3	2	2	1	3	7897.2806	0.0055
3	2	2	2	2	2	1	1	7897.3405	-0.0080
3	1	2	3	2	1	1	2	8112.1426	0.0051
3	1	2	4	2	1	1	3	8112.1656	-0.0011
3	1	2	3	2	1	1	3	8112.5624	0.0030
3	1	3	3	2	0	2	2	9720.4736	-0.0015
3	1	3	4	2	0	2	3	9720.9285	-0.0017
3	1	3	2	2	0	2	1	9721.0644	0.0085
4	1	4	3	3	1	3	2	10223.7861	0.0028
4	1	4	4	3	1	3	3	10223.7861	-0.0009
4	1	4	5	3	1	3	4	10223.8290	-0.0007
4	0	4	4	3	0	3	3	10459.8441	-0.0040
4	0	4	5	3	0	3	4	10459.9153	-0.0016
4	0	4	3	3	0	3	2	10459.9153	0.0007
4	2	3	4	3	2	2	4	10523.9511	0.0022
4	2	3	4	3	2	2	3	10523.9511	0.0021

4	2	3	5	3	2	2	4	10524.0107	-0.0020
4	2	3	3	3	2	2	3	10524.0318	0.0026
4	2	3	3	3	2	2	2	10524.0318	0.0027
4	3	2	4	3	3	1	3	10542.6127	-0.0035
4	3	2	5	3	3	1	4	10542.7225	-0.0009
4	3	1	5	3	3	0	4	10544.0142	0.0020
4	2	2	4	3	2	1	3	10593.9045	-0.0028
4	2	2	5	3	2	1	4	10593.9045	-0.0009
3	1	2	2	2	0	2	1	10597.4831	0.0021
3	1	2	4	2	0	2	3	10597.7095	0.0003
3	1	2	2	2	0	2	2	10597.7369	0.0018
4	1	3	4	3	1	2	3	10807.2388	-0.0024
4	1	3	5	3	1	2	4	10807.2642	0.0008
4	1	3	3	3	1	2	2	10807.3017	-0.0038
2	2	1	3	1	1	0	2	11969.6858	0.0056
4	1	4	4	3	0	3	3	12075.0855	0.0034
4	1	4	5	3	0	3	4	12075.5151	-0.0104
2	2	1	3	1	1	1	2	12115.7463	-0.0007
2	2	0	3	1	1	1	2	12122.8263	-0.0052
5	1	5	5	4	1	4	4	12767.6626	0.0002
5	1	5	6	4	1	4	5	12767.6949	-0.0029
5	0	5	5	4	0	4	4	13024.9751	0.0036
5	0	5	6	4	0	4	5	13025.0522	-0.0002
5	0	5	4	4	0	4	3	13025.0522	-0.0013
5	2	4	5	4	2	3	4	13145.8821	0.0075
5	2	4	6	4	2	3	5	13145.9176	0.0013
5	1	4	5	4	1	3	4	13493.9972	0.0015
5	1	4	6	4	1	3	5	13494.0221	0.0016
6	1	6	6	5	1	5	5	15304.5722	-0.0003
6	1	6	7	5	1	5	6	15304.6037	-0.0014

6	0	6	6	5	0	5	5	15562.4666	-0.0008
6	0	6	5	5	0	5	4	15562.5548	-0.0027
6	0	6	7	5	0	5	6	15562.5548	-0.0007
6	2	5	6	5	2	4	5	15761.7783	0.0070
6	2	5	7	5	2	4	6	15761.8091	0.0042
6	2	5	5	5	2	4	4	15761.8091	0.0022
6	2	4	7	5	2	3	6	15993.1392	-0.0038
6	2	4	5	5	2	3	4	15993.1392	0.0009
6	2	4	6	5	2	3	5	15993.1878	-0.0078

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S10. Measured transition frequencies of the *ig* TFEOD···$^{14}ND_2H$ isotopologue.

J'	***K*$_a$'**	***K*$_c$'**	***F'***	***J"***	***K*$_a$"**	***K*$_c$"**	***F"***	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	3	2	2	1	2	1	7613.1507	-0.0021
3	1	3	4	2	1	2	3	7613.2479	0.0048
3	0	3	3	2	0	2	2	7808.8738	-0.0021
3	0	3	4	2	0	2	3	7808.9385	0.0089
3	2	2	4	2	2	1	3	7837.1472	0.0020
3	2	2	2	2	2	1	1	7837.2123	-0.0009
3	1	2	2	2	1	1	2	8051.9069	0.0083
3	1	2	4	2	1	1	3	8052.4561	-0.0029
3	1	2	3	2	1	1	3	8052.8605	0.0061
4	0	4	3	3	1	3	2	8535.6835	-0.0049
4	0	4	5	3	1	3	4	8535.8358	0.0062
4	0	4	4	3	1	3	3	8536.1608	0.0008
4	1	4	4	3	1	3	4	10142.3695	0.0002
4	1	4	3	3	1	3	2	10142.9701	-0.0008
4	1	4	5	3	1	3	4	10143.0192	0.0026
4	0	4	4	3	0	3	3	10379.2144	-0.0034

4	0	4	5	3	0	3	4	10379.2781	-0.0080
4	2	3	4	3	2	2	3	10443.7477	0.0027
4	2	3	5	3	2	2	4	10443.8027	-0.0019
4	2	3	3	3	2	2	2	10443.8240	0.0041
4	3	2	4	3	3	1	3	10462.4999	-0.0041
4	3	2	5	3	3	1	4	10462.5986	-0.0038
4	2	2	5	3	2	1	4	10514.2025	0.0018
3	1	2	2	2	0	2	1	10530.6675	-0.0013
3	1	2	4	2	0	2	3	10530.8913	-0.0011
3	1	2	3	2	0	2	2	10531.4392	-0.0022
4	1	3	5	3	1	2	4	10727.5908	-0.0016
4	1	3	3	3	1	2	2	10727.6308	-0.0037
5	3	2	5	5	2	3	5	11080.5210	-0.0025
5	3	2	6	5	2	3	6	11080.6158	-0.0006
3	3	0	4	3	2	2	4	11262.1640	0.0069
4	3	2	5	4	2	3	5	11280.7452	0.0082
4	3	1	5	4	2	3	5	11282.2549	-0.0051
4	3	1	4	4	2	3	4	11282.3956	0.0028
5	0	5	6	4	1	4	5	11316.7509	-0.0009
5	0	5	5	4	1	4	4	11317.0382	-0.0049
5	3	2	6	5	2	4	6	11324.4798	-0.0099
5	3	2	5	5	2	4	5	11324.6202	-0.0008
5	1	5	5	4	1	4	4	12666.5718	0.0028
5	1	5	6	4	1	4	5	12666.5998	-0.0037
5	0	5	5	4	0	4	4	12923.8549	-0.0035
5	0	5	6	4	0	4	5	12923.9311	-0.0077
5	2	4	5	4	2	3	4	13045.5609	0.0025
5	2	4	6	4	2	3	5	13045.6061	0.0081
5	2	3	6	4	2	2	5	13183.4990	0.0061
5	2	3	5	4	2	2	4	13183.5387	0.0071

5	1	4	5	4	1	3	4	13394.2997	-0.0009
5	1	4	6	4	1	3	5	13394.3208	-0.0040
5	1	4	4	4	1	3	3	13394.3426	-0.0071
5	1	5	5	4	0	4	4	14273.3777	-0.0065
5	1	5	6	4	0	4	5	14273.7897	-0.0008
3	2	2	4	2	1	1	3	14372.3858	0.0083
3	2	2	3	2	1	1	3	14372.3858	0.0083
3	2	2	2	2	1	1	1	14372.6108	-0.0012
3	2	2	2	2	1	2	1	14811.3647	-0.0008
3	2	2	4	2	1	2	3	14811.6653	-0.0026
3	2	1	4	2	1	2	3	14847.2481	-0.0022
3	2	1	3	2	1	2	2	14847.8708	-0.0043
6	1	6	6	5	1	5	5	15183.1635	0.0054
6	1	6	7	5	1	5	6	15183.1952	0.0051
6	0	6	6	5	0	5	5	15440.7383	-0.0030
6	0	6	7	5	0	5	6	15440.8263	-0.0025
6	2	4	7	5	2	3	6	15874.2296	0.0048
6	2	4	6	5	2	3	5	15874.2858	0.0075
6	1	5	6	5	1	4	5	16049.6928	-0.0024
6	1	5	7	5	1	4	6	16049.7196	-0.0059

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S11. Measured transition frequencies of the *ig* TFE···$^{14}NH_2D$ isotopologue.

J'	K_a'	K_c'	*F'*	*J"*	K_a"	K_c"	*F"*	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	3	2	2	1	2	2	7929.9160	0.0040
3	0	3	3	2	0	2	2	8136.2014	-0.0018
3	0	3	2	2	0	2	1	8136.2441	-0.0057
3	0	3	4	2	0	2	3	8136.2617	0.0023
3	2	2	3	2	2	1	2	8168.8133	0.0034
3	1	2	4	2	1	1	3	8398.3356	0.0018
3	1	2	3	2	1	1	3	8398.7378	0.0044
3	1	3	3	2	0	2	2	9942.4058	0.0017
3	1	3	4	2	0	2	3	9942.8494	-0.0030
4	1	4	4	3	1	3	3	10563.0638	0.0000
4	1	4	3	3	1	3	2	10563.0638	0.0042
4	1	4	5	3	1	3	4	10563.1027	-0.0014
4	0	4	4	3	0	3	3	10810.9862	-0.0036
4	0	4	5	3	0	3	4	10811.0609	-0.0005
4	0	4	3	3	0	3	2	10811.0609	-0.0007
3	1	2	4	2	0	2	3	10881.2995	-0.0008
3	1	2	3	2	0	2	2	10881.8418	0.0001
4	2	3	4	3	2	2	3	10885.2536	-0.0028
4	2	3	5	3	2	2	4	10885.3024	-0.0083
4	2	2	5	3	2	1	4	10965.8743	0.0033
4	1	3	4	3	1	2	3	11187.3479	-0.0020
4	1	3	5	3	1	2	4	11187.3749	0.0045
4	1	3	3	3	1	2	2	11187.4093	-0.0035
2	2	0	2	1	1	0	1	12095.8761	0.0031
2	2	0	3	1	1	0	2	12096.2239	-0.0037
2	2	1	1	1	1	1	0	12243.7463	0.0014
2	2	1	3	1	1	1	2	12244.3971	-0.0007
2	2	1	2	1	1	1	1	12244.9071	0.0056

2	2	0	3	1	1	1	2	12252.5833	0.0003
2	2	0	2	1	1	1	1	12253.1140	-0.0059
4	1	4	4	3	0	3	3	12369.2664	0.0018
4	1	4	5	3	0	3	4	12369.6973	0.0003
5	1	5	5	4	1	4	4	13189.9671	0.0003
5	1	5	4	4	1	4	3	13189.9775	0.0029
5	1	5	6	4	1	4	5	13189.9966	-0.0047
5	0	5	5	4	0	4	4	13456.7695	0.0033
5	0	5	6	4	0	4	5	13456.8501	0.0001
5	0	5	4	4	0	4	3	13456.8501	-0.0025
5	2	4	5	4	2	3	4	13596.0702	0.0044
5	2	4	6	4	2	3	5	13596.1023	-0.0008
5	3	3	5	4	3	2	4	13639.7668	0.0028
5	3	3	6	4	3	2	5	13639.7995	-0.0038
5	2	3	6	4	2	2	5	13753.4315	0.0028
5	2	3	5	4	2	2	4	13753.4713	-0.0020

[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S12. Measured transition frequencies of the *ig* TFEOD···$^{14}NH_2D$ isotopologue.

J'	***K*$_a$'**	***K*$_c$'**	***F'***	***J"***	***K*$_a$"**	***K*$_c$"**	***F"***	**Frequency**/ MHz	**Δν**/ MHz[a]
3	1	3	3	2	1	2	3	7862.0866	-0.0003
3	1	3	4	2	1	2	3	7862.6724	-0.0031
3	0	3	4	2	0	2	3	8069.5277	0.0009
3	1	2	2	2	1	1	2	8330.8582	0.0006
3	1	2	4	2	1	1	3	8331.4364	-0.0019
3	1	2	2	2	1	1	1	8331.5378	0.0028
3	1	2	3	2	1	1	3	8331.8533	-0.0001
4	0	4	5	3	1	3	4	8922.0001	-0.0001
4	1	4	4	3	1	3	4	10473.8136	-0.0007

4	1	4	4	3	1	3	3	10474.4057	0.0028
4	1	4	5	3	1	3	4	10474.4432	0.0010
4	1	4	3	3	1	3	3	10475.1924	0.0002
4	0	4	4	3	0	3	3	10721.9809	0.0045
4	0	4	5	3	0	3	4	10722.0483	-0.0005
4	2	2	5	3	2	1	4	10877.0535	-0.0008
4	1	3	3	3	1	2	3	11097.6537	-0.0013
4	1	3	5	3	1	2	4	11098.1688	-0.0030
4	1	3	3	3	1	2	2	11098.2145	-0.0008
2	2	0	2	1	1	0	1	12030.5799	0.0018
2	2	0	3	1	1	0	2	12030.9419	-0.0025
2	2	1	3	1	1	1	2	12178.9701	0.0006
2	2	1	2	1	1	1	1	12179.4731	-0.0005
2	2	0	3	1	1	1	2	12187.1660	-0.0004
2	2	0	2	1	1	1	1	12187.7053	0.0011
5	1	5	5	4	1	4	4	13079.1483	0.0028
5	1	5	6	4	1	4	5	13079.1773	-0.0024
5	0	5	5	4	0	4	4	13345.4619	0.0038
5	0	5	4	4	0	4	3	13345.5416	-0.0048
5	0	5	6	4	0	4	5	13345.5416	-0.0015
5	2	4	5	4	2	3	4	13484.9177	0.0009
5	2	4	4	4	2	3	3	13484.9519	-0.0044
5	2	4	6	4	2	3	5	13484.9519	0.0000
5	2	3	4	4	2	2	3	13642.4717	0.0028
5	2	3	6	4	2	2	5	13642.4717	-0.0013
5	2	3	5	4	2	2	4	13642.5246	0.0034
5	1	4	5	4	1	3	4	13855.1284	0.0001
5	1	4	6	4	1	3	5	13855.1530	0.0002

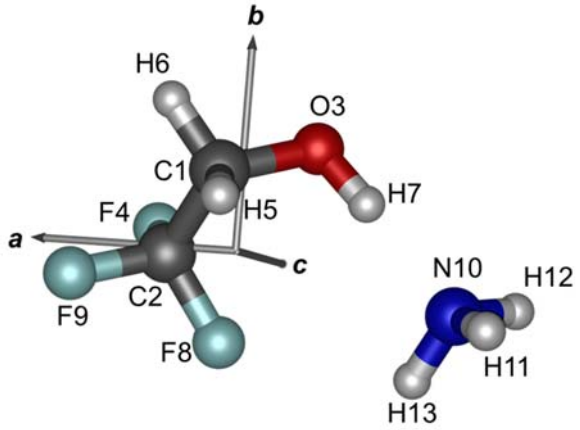
[a] $\Delta\nu = \nu_{EXP} - \nu_{CALC}$.

Table S13. Calculated rotational constants and *ZPE* for all possible deuterated *ig* TFE···NH3 I species, performed at the B3LYP-D3(BJ)/def2-TZVPD level of theory (see Figure 3 for atom numbering).

Isotopic Names	**Isotopologue**	**Rotational Constants** / MHz			***ZPE***
		A	***B***	***C***	kJ/mol
Non-deuterated TFE Species	**gTFE - ^{14}NH3**	3617	1474	1318	247.28
Non-deuterated TFE Species	**gTFE - ^{15}NH3**	3607	1436	1286	247.03
D11	**gTFE - ^{14}NHHD**	3586	1416	1273	238.98
D12	**gTFE - ^{14}NHDH**	3594	1416	1273	238.96
D13	**gTFE - ^{14}NDHH**	3562	1447	1290	238.91
D11, D12 (**H13**)	**gTFE - ^{14}NHDD**	3564	1364	1231	230.52
D11, D13 (**H12**)	**gTFE - ^{14}NDHD**	3535	1392	1246	230.47
D12, D13 (**H11**)	**gTFE - ^{14}NDDH**	3542	1392	1247	230.45
D11, D12, D13	**gTFE - ^{14}ND3**	3514	1341	1207	221.89
D7 (**TFEOD**)	**gTFE(OD) - ^{14}NH3**	3603	1460	1305	238.09
D7, **D11**	**gTFE(OD) - ^{14}NHHD**	3572	1404	1261	229.78
D7, **D12**	**gTFE(OD) - ^{14}NHDH**	3580	1404	1261	229.77
D7, **D13**	**gTFE(OD) - ^{14}NDHH**	3547	1434	1278	229.72
D7, D11, D12 **(H13)**	**gTFE(OD) - ^{14}NHDD**	3549	1353	1220	221.32
D7, D11, D13 (**H12**)	**gTFE(OD) - ^{14}NDHD**	3519	1380	1235	221.27
D7, D12, D13 (**H11**)	**gTFE(OD) - ^{14}NDDH**	3527	1381	1236	221.26
D7, D11, D12, D13	**gTFE(OD) - ^{14}ND3**	3499	1331	1197	212.68

Table S14. Comparison between experimental and B3LYP/def2-TVPVD rotational constants of the observed isotopologues with atom numbering on the right.

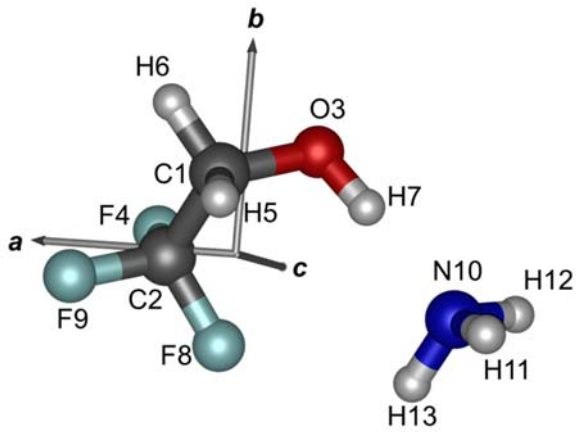
	TFE - $^{14}ND_2H$	TFE(OD) - $^{14}ND_2H$	TFE - $^{14}NH_2D$	TFE(OD) - $^{14}NH_2D$
		Experimental		
A/ MHz	3575.5880(18)	3557.98675(99)	3601.6636(22)	3583.5530(38)
B/ MHz	1389.37891(33)	1379.50536(34)	1439.75985(53)	1428.57792(47)
C/ MHz	1243.15825(31)	1232.99776(46)	1283.25385(44)	1272.20318(49)
		Theoretical		
Cal., Exp.-cal.	**H11**	**H11**	**D13**	**D13**
A, Δ*A* / MHz	3542, 33	3527, 31	3562, 40	3547, 36
B, Δ*B* / MHz	1392, -3	1381, -1	1447, -8	1434, -6
C, Δ*C* / MHz	1247, -4	1236, -3	1290, -7	1278, -5
Cal., Exp.-cal.	**H12**	**H12**	**D12**	**D12**
A, Δ*A* / MHz	3535, 41	3519, 39	3594, 7	3580, 3
B, Δ*B* / MHz	1392, -3	1380, -1	1416, 23	1404, 25
C, Δ*C* / MHz	1246, -3	1235, -2	1273, 10	1261, 11
Cal., Exp.-cal.	**H13**	**H13**	**D11**	**D11**
A, Δ*A* / MHz	3564, 12	3549, 9	3586, 15	3572, 11
B, Δ*B* / MHz	1364, 26	1353, 27	1416, 23	1404, 24
C, Δ*C* / MHz	1231, 12	1220, 13	1273, 11	1261, 11



[a] The exp.-cal. based on the DFT values provide a preference for the assignment of the H position in ND_2H to H11 or H12 and of the D position in NH_2D to D13. See main text for discussion.

Table S15. Comparison between experimental and MP2/6-311++G(2d,p) rotational constants of the observed isotopologues; atom numbering on the right.

	TFE - $^{14}ND_2H$	TFE(OD) - $^{14}ND_2H$	TFE - $^{14}NH_2D$	TFE(OD) - $^{14}NH_2D$
		Experimental		
A/ MHz	3575.5880(18)	3557.98675(99)	3601.6636(22)	3583.5530(38)
B/ MHz	1389.37891(33)	1379.50536(34)	1439.75985(53)	1428.57792(47)
C/ MHz	1243.15825(31)	1232.99776(46)	1283.25385(44)	1272.20318(49)
		Theorectical[a]		
Cal., Exp.-cal.	**H11**	**H11**	**D13**	**D13**
A, Δ*A* / MHz	3570, 5	3555, 3	3586, 15	3572, 12
B, Δ*B* / MHz	1402, -12	1390, -11	1459, -19	1446, -17
C, Δ*C* / MHz	1256, -13	1245, -12	1301, -18	1289, -17
Cal., Exp.-cal.	**H12**	**H12**	**D12**	**D12**
A, Δ*A* / MHz	3555, 20	3540, 18	3623, -22	3609, -26
B, Δ*B* / MHz	1404, -15	1393, -14	1427, 13	1414, 14
C, Δ*C* / MHz	1258, -15	1247, -14	1283, 0	1271, 1
Cal., Exp.-cal.	**H13**	**H13**	**D11**	**D11**
A, Δ*A* / MHz	3588, -13	3573, -15	3607, -6	3593, -9
B, Δ*B* / MHz	1375, 14	1364, 15	1430, 10	1418, 11
C, Δ*C* / MHz	1242, 1	1231, 2	1285, -2	1273, -1



[a] The exp.-cal. based on the MP2 values do not provide a clear preference for the assignment of the position of substituted H or D in the above isotopologues. See main text for discussion.

Figure S1. a) A section of the experimental broadband spectrum (top) of TFE···NH_3 and the related simulated spectrum (bottom) produced with the experimental spectroscopic constants, a rotational temperature of 1 K, and the theoretical dipole moment components. The other strong lines are due mainly to the TFE monomer and dimers. b) The 3_{13}←2_{02} rotational transition of the parent species measured with higher resolution available with the cavity-based pulsed jet FTMW spectrometer. Each ^{14}N nuclear quadrupole component appears as a doublet due to the Doppler effect. Please note that the excitation frequency is set at ~10159.9 MHz near the F′←F″=3←2 nuclear hyperfine component. For this reason, the strongest component F′←F″=4←3 appears weaker.

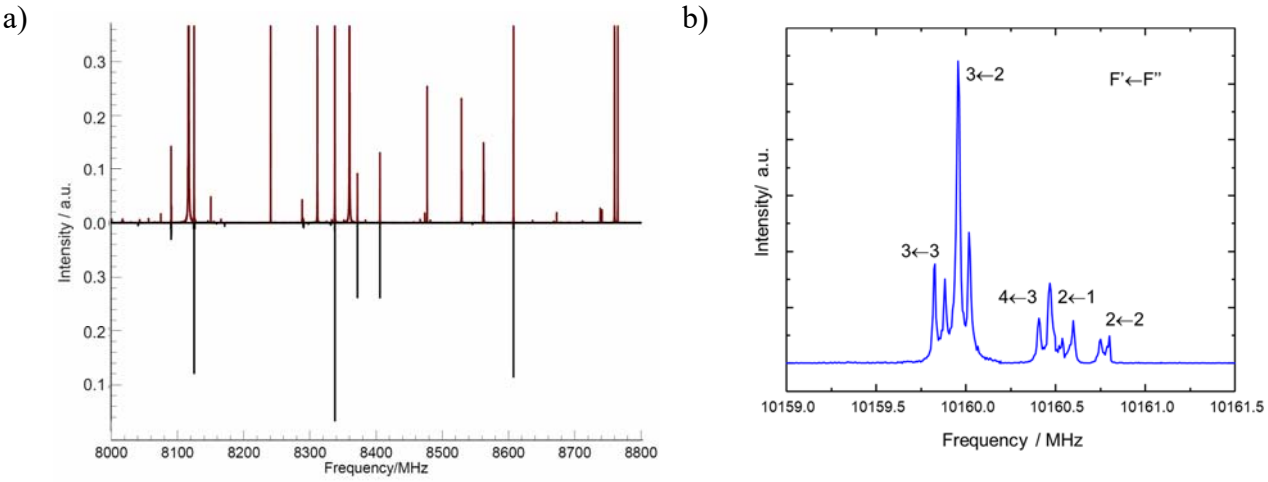


Figure S2. B3LYP/def2-TVPVD potential energy barrier for the rotation of the ammonia moiety. Zero-point energies (*ZPE*) are indicated (see text).

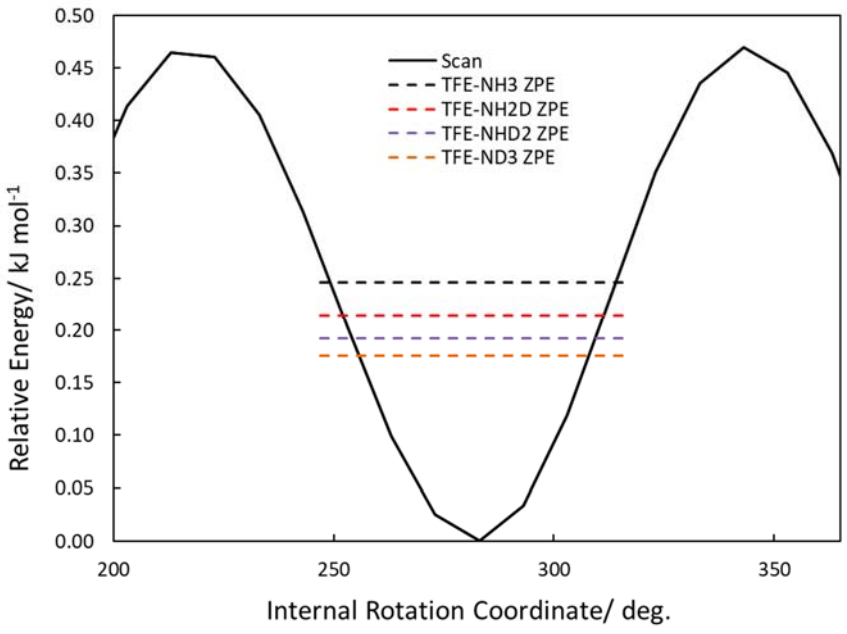


Table S16. ^{14}N nuclear quadrupole coupling constants of TFE···NH_3 calculated at every step (5°) of an NH_3 internal rotational scan at the B3LYP-D3BJ/def2-TZVPD level of theory.[a]

Point	χ_{aa}	χ_{bb}-χ_{cc}	Point	χ_{aa}	χ_{bb}-χ_{cc}	Point	χ_{aa}	χ_{bb}-χ_{cc}
1	-0.1483	-3.7983	26	-0.1952	-3.7510	51	-0.1455	-3.7999
2	-0.1613	-3.7819	27	-0.2179	-3.7237	52	-0.1490	-3.7894
3	-0.1809	-3.7560	28	-0.2370	-3.6974	53	-0.1550	-3.7728
4	-0.2028	-3.7248	29	-0.2519	-3.6734	54	-0.1625	-3.7527
5	-0.2239	-3.6929	30	-0.2615	-3.6529	55	-0.1735	-3.7279
6	-0.2433	-3.6617	31	-0.2655	-3.6368	56	-0.1849	-3.7025
7	-0.2578	-3.6356	32	-0.2624	-3.6269	57	-0.1968	-3.6778
8	-0.2656	-3.6161	33	-0.2543	-3.6217	58	-0.2062	-3.657
9	-0.2653	-3.6053	34	-0.2421	-3.6209	59	-0.2125	-3.6414
10	-0.2565	-3.6038	35	-0.2275	-3.6243	60	-0.2156	-3.6318
11	-0.2408	-3.6107	36	-0.2130	-3.6294	61	-0.2154	-3.6285
12	-0.2206	-3.6242	37	-0.2000	-3.6362	62	-0.2124	-3.6315
13	-0.1983	-3.6431	38	-0.1898	-3.6440	63	-0.2071	-3.6401
14	-0.1762	-3.6652	39	-0.1826	-3.6526	64	-0.1997	-3.6541
15	-0.1562	-3.6894	40	-0.1776	-3.6628	65	-0.1902	-3.6735
16	-0.1386	-3.7148	41	-0.1743	-3.6747	66	-0.1797	-3.6963
17	-0.1239	-3.7408	42	-0.1726	-3.6880	67	-0.169	-3.7210
18	-0.1141	-3.7643	43	-0.1705	-3.7041	68	-0.1573	-3.7473
19	-0.1074	-3.7862	44	-0.1680	-3.7216	69	-0.1482	-3.7703
20	-0.1065	-3.8020	45	-0.1656	-3.7394	70	-0.1414	-3.7894
21	-0.1101	-3.8123	46	-0.1618	-3.7576	71	-0.1384	-3.8015
22	-0.1190	-3.8148	47	-0.1570	-3.7750	72	-0.1405	-3.8049
23	-0.1326	-3.8094	48	-0.1521	-3.7891			
24	-0.1505	-3.7963	49	-0.1478	-3.7992			
25	-0.1719	-3.7762	50	-0.1453	-3.8031			

[a] This is a relaxed scan and the rest of the geometry is optimized at every step. Because of this, the rotational constants may not be exactly the same at every 120°.

Table S17. Rotational constants of TFE···NH_3 calculated at every step (5°) of an NH_3 internal rotational scan at the B3LYP-D3BJ/def2-TZVPD level of theory.[a]

Point	A	B	C	Point	A	B	C	Point	A	B	C
1	3.61682	1.47410	1.31836	26	3.62027	1.47184	1.31707	51	3.61790	1.47355	1.31813
2	3.61857	1.47301	1.31775	27	3.62124	1.47129	1.31676	52	3.61810	1.47357	1.31818
3	3.62007	1.47206	1.31720	28	3.62152	1.47123	1.31674	53	3.61795	1.47387	1.31838
4	3.62123	1.47144	1.31685	29	3.62109	1.47168	1.31703	54	3.61740	1.47447	1.31876
5	3.62168	1.47128	1.31677	30	3.62004	1.47259	1.31758	55	3.61658	1.47525	1.31923
6	3.62150	1.47156	1.31694	31	3.61837	1.47395	1.31840	56	3.61538	1.47630	1.31987
7	3.62052	1.47240	1.31744	32	3.61611	1.47575	1.31948	57	3.61396	1.47750	1.32057
8	3.61879	1.47379	1.31827	33	3.61362	1.47772	1.32065	58	3.61228	1.47886	1.32138
9	3.61641	1.47567	1.31940	34	3.61104	1.47974	1.32186	59	3.61049	1.48027	1.32220
10	3.61353	1.47789	1.32073	35	3.60865	1.48160	1.32296	60	3.60875	1.48160	1.32297
11	3.61048	1.48024	1.32214	36	3.60677	1.48303	1.32379	61	3.60724	1.48269	1.32360
12	3.60764	1.48238	1.32341	37	3.60550	1.48394	1.32430	62	3.60609	1.48345	1.32402
13	3.60531	1.48408	1.32441	38	3.60498	1.48424	1.32443	63	3.60542	1.48378	1.32417
14	3.60373	1.48516	1.32503	39	3.60515	1.48395	1.32422	64	3.60521	1.48371	1.32408
15	3.60299	1.48552	1.32521	40	3.60584	1.48324	1.32375	65	3.60541	1.48329	1.32380
16	3.60302	1.48527	1.32502	41	3.60693	1.48222	1.32310	66	3.60602	1.48257	1.32333
17	3.60366	1.48453	1.32455	42	3.60832	1.48096	1.32232	67	3.60703	1.48155	1.32270
18	3.60495	1.48330	1.32379	43	3.60977	1.47969	1.32154	68	3.60819	1.48048	1.32205
19	3.60655	1.48188	1.32293	44	3.61124	1.47842	1.32078	69	3.60970	1.47920	1.32129
20	3.60854	1.48022	1.32193	45	3.61273	1.47718	1.32005	70	3.61136	1.47789	1.32052
21	3.61067	1.47855	1.32094	46	3.61405	1.47612	1.31945	71	3.61314	1.47659	1.31977
22	3.61287	1.47689	1.31998	47	3.61517	1.47525	1.31896	72	3.61498	1.47531	1.31905
23	3.61503	1.47534	1.31908	48	3.61613	1.47456	1.31859				
24	3.61705	1.47394	1.31827	49	3.61691	1.47405	1.31834				
25	3.61885	1.47274	1.31758	50	3.61751	1.47370	1.31818				

[a] This is a relaxed scan and the rest of the geometry is optimized at every step. Because of this, the rotational constants may not be exactly the same at every 120°.

Table S18. Coordinates of the three H atoms of NH_3 in TFE···NH_3 calculated at every step (10°) of an NH_3 internal rotational scan at the B3LYP-D3BJ/def2-TZVPD level of theory.[a]

Points	Angle/°	H11			H12			H13		
		X / Å	Y / Å	Z / Å	X / Å	Y / Å	Z / Å	X / Å	Y / Å	Z / Å
1	3.1	-3.86	-0.26	-0.37	-3.05	-0.90	0.90	-2.61	-1.30	-0.63
2	13.1	-3.81	-0.32	-0.52	-3.18	-0.80	0.91	-2.54	-1.35	-0.49
3	23.1	-3.74	-0.38	-0.66	-3.31	-0.69	0.89	-2.48	-1.39	-0.33
4	33.1	-3.65	-0.47	-0.77	-3.44	-0.59	0.84	-2.45	-1.41	-0.17
5	43.1	-3.55	-0.56	-0.86	-3.56	-0.49	0.77	-2.45	-1.41	0.00
6	53.1	-3.43	-0.66	-0.93	-3.66	-0.40	0.67	-2.47	-1.40	0.17
7	63.1	-3.31	-0.77	-0.97	-3.78	-0.32	0.54	-2.51	-1.60	0.34
8	73.1	-3.17	-0.88	-0.97	-3.83	-0.26	0.39	-2.57	-1.31	0.49
9	83.1	-3.03	-0.99	-0.95	-3.88	-0.22	0.23	-2.65	-1.24	0.62
10	93.1	-2.89	-1.09	-0.89	-3.90	-0.21	0.05	-2.75	-1.15	0.74
11	103.1	-2.76	-1.19	-0.80	-3.90	-0.22	-0.13	-2.86	-1.06	0.83
12	113.1	-2.65	-1.27	-0.68	-3.88	-0.25	-0.30	-2.98	-0.95	0.88
13	123.1	-2.56	-1.33	-0.55	-3.83	-0.30	-0.46	-3.11	-0.84	0.91
14	133.1	-2.50	-1.38	-0.40	-3.77	-0.36	-0.60	-3.25	-0.73	0.90
15	143.1	-2.45	-1.40	-0.23	-3.69	-0.44	-0.73	-3.38	-0.63	0.87
16	153.1	-2.44	-1.41	-0.07	-3.59	-0.52	-0.83	-3.51	-0.53	0.81
17	163.1	-2.45	-1.41	0.09	-3.48	-0.61	-0.90	-3.62	-0.44	0.72
18	173.1	-2.49	-1.39	0.25	-3.37	-0.71	-0.95	-3.71	-0.36	0.61
19	183.1	-2.54	-1.35	0.40	-3.24	-0.81	-0.98	-3.79	-0.29	0.48
20	193.1	-2.60	-1.29	0.54	-3.11	-0.91	-0.97	-3.85	-0.25	0.33
21	203.1	-2.68	-1.22	0.66	-2.98	-1.02	-0.93	-3.89	-0.22	0.17
22	213.1	-2.77	-1.13	0.76	-2.86	-1.12	-0.87	-3.90	-0.21	0.01
23	223.1	-2.87	-1.04	0.84	-2.74	-1.21	-0.78	-3.90	-0.23	-0.15
24	233.1	-2.99	-0.94	0.89	-2.65	-1.28	-0.67	-3.88	-0.25	-0.31
25	243.1	-3.11	-0.84	0.91	-2.57	-1.33	-0.55	-3.84	-0.29	-0.45
26	253.1	-3.23	-0.74	0.91	-2.52	-1.38	-0.42	-3.79	-0.35	-0.58
27	263.1	-3.34	-0.65	0.88	-2.48	-1.40	-0.28	-3.72	-0.41	-0.69
28	273.1	-3.46	-0.56	0.83	-2.45	-1.41	-0.14	-3.63	-0.48	-0.79
29	283.1	-3.56	-0.48	0.76	-2.44	-1.41	0.01	-3.54	-0.57	-0.87
30	293.1	-3.66	-0.41	0.67	-2.46	-1.40	0.16	-3.43	-0.66	-0.93
31	303.1	-3.74	-0.34	0.56	-2.49	-1.37	0.31	-3.32	-0.75	-0.96
32	313.1	-3.81	-0.29	0.43	-2.54	-1.32	0.45	-3.19	-0.85	-0.97
33	323.1	-3.86	-0.25	0.28	-2.61	-1.27	0.58	-3.10	-0.95	-0.96
34	333.1	-3.89	-0.22	0.12	-2.70	-1.19	0.70	-2.94	-1.05	-0.91
35	343.1	-3.90	-0.21	-0.04	-2.80	-1.10	0.79	-2.82	-1.15	-0.84
36	353.1	-3.89	-0.23	-0.21	-2.92	-1.00	0.86	-2.71	-1.23	-0.75

[a] This is a relaxed scan and the rest of the geometry is optimized at every step. Because of this, the rotational constants may not be exactly the same at every 120°.