Supporting information for

Matrix-isolation IR spectra of iodotrifluoroethylene (C_2F_3I)

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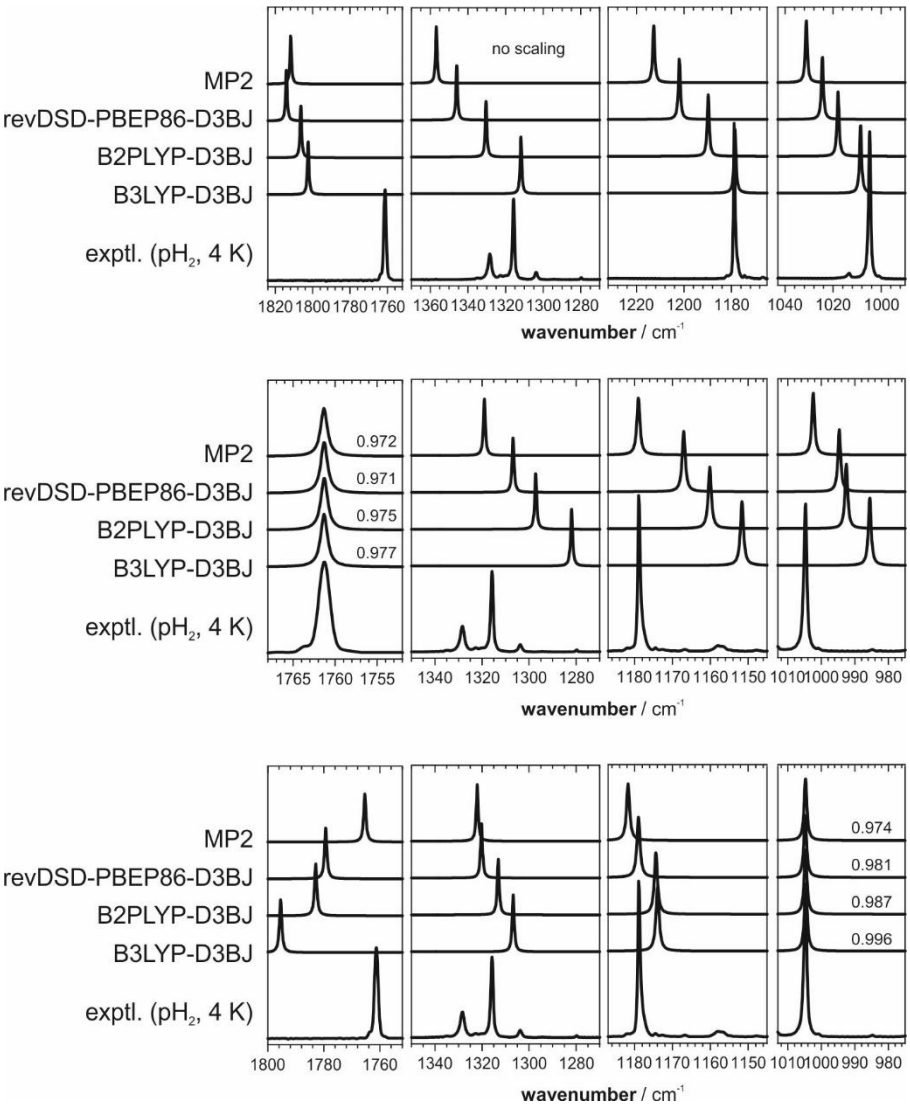

Fig. S1. Comparison of the IR spectra of ITFE computed within the harmonic approximation and experimental data recorded for a pH_2 matrix (1:1000, 4 K). Different bands were used as reference to set the frequency scaling factors, which are given alongside each spectrum.

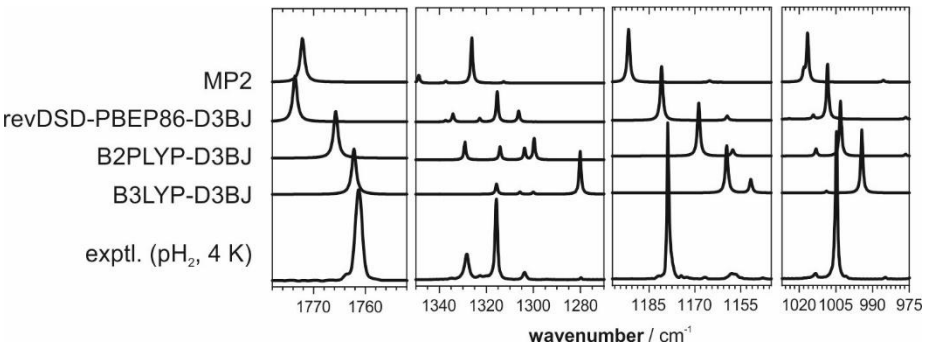

Fig. S2. Comparison of the fingerprint region of the experimental spectrum of ITFE recorded in pH_2 matrix (1:1000, 4 K) and the computed spectra obtained with the VPT2 approach to account for anharmonic effects. No frequency scaling factor was applied.

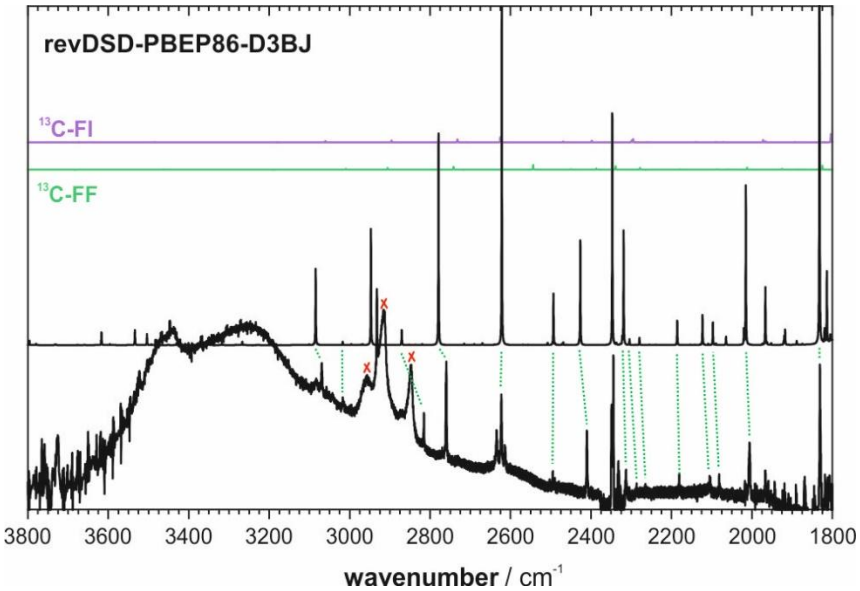

Fig. S3. Comparison of the experimental spectrum of ITFE recorded in pH_2 matrix (1:1000, 4 K) and the computed spectra obtained with the VPT2 approach to account for anharmonic effects. The red X mark known background artefacts that particularly strong next to the very weak bands of ITFE in this range.

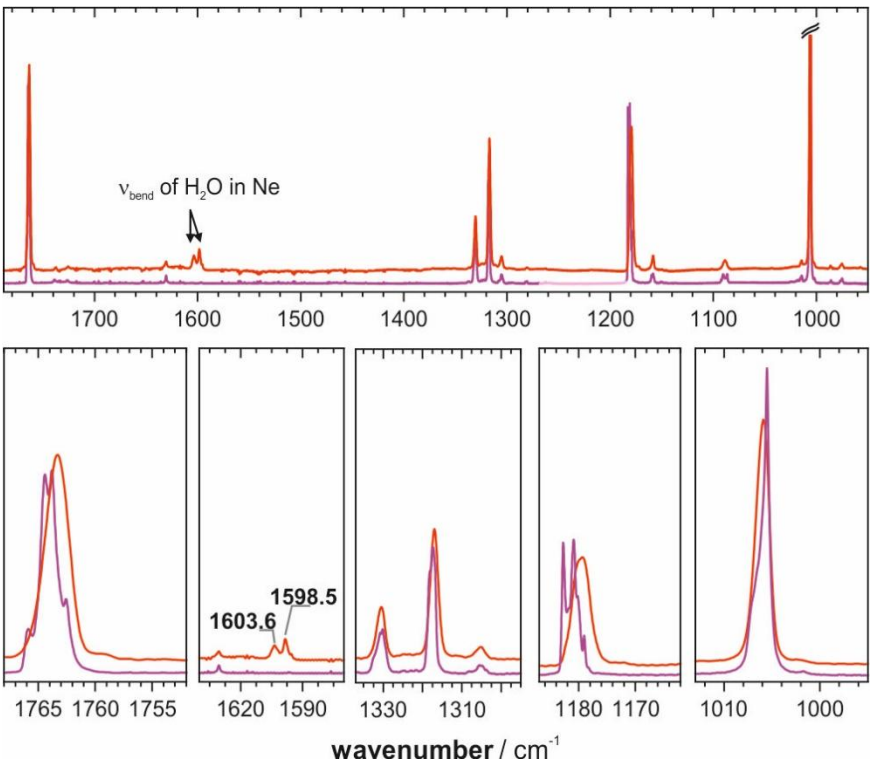

Fig. S4. Detailed views on the MI-IR spectra of ITFE in Ne matrix, which detail that the strong site splitting breaks down in the presence of trace amounts of H_2O in the matrix.

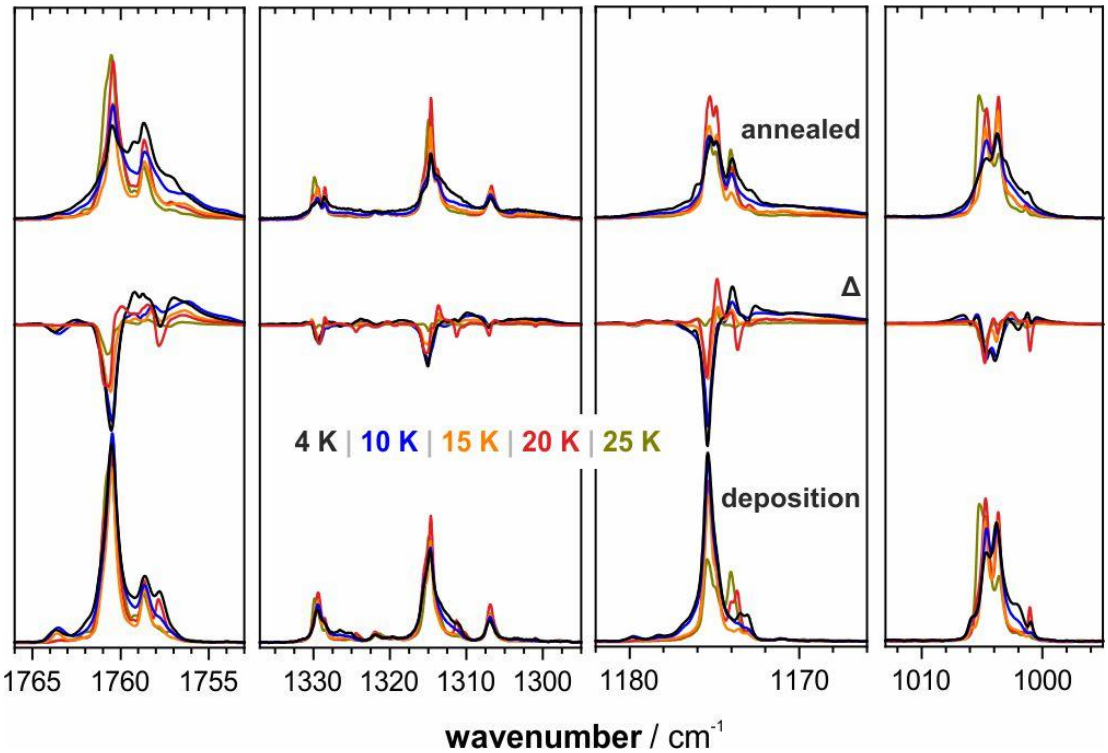

Fig. S5. Difference spectra for ITFE/Ar (1:3600) depositions at different temperatures (bottom), the corresponding spectra after annealing (top) and the difference spectrum Δ = [annealed] – [deposited].

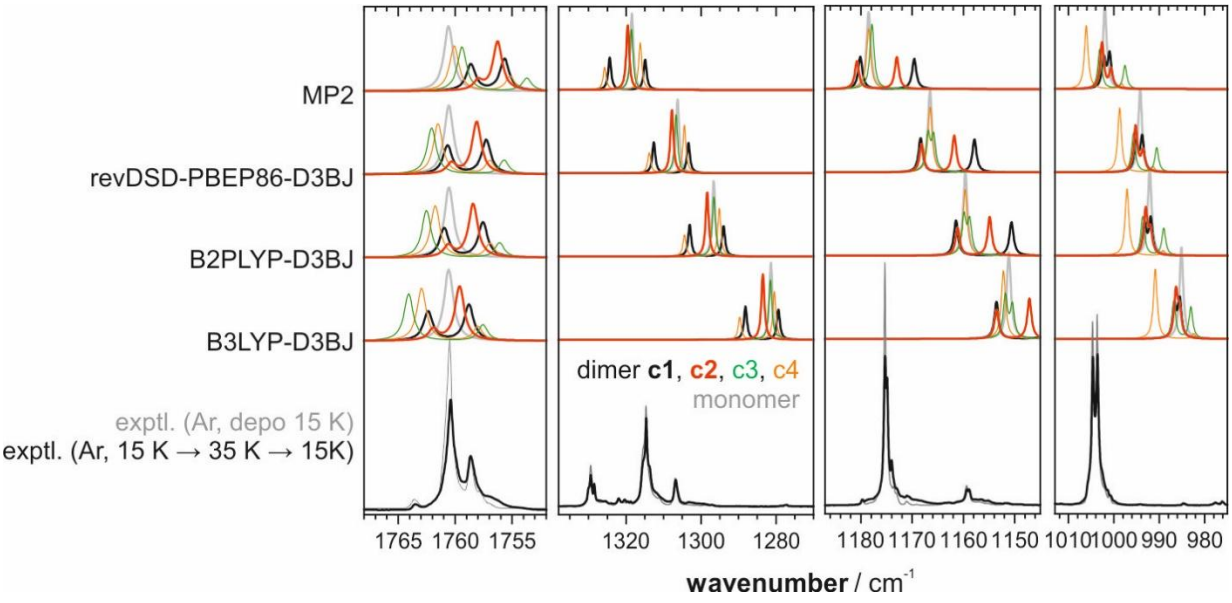

Fig. S6. Comparison of the experimental spectra of ITFE recorded in Ar matrix (1:3600, 15 K, annealed at 35 K) and the computed spectra of the four lowest-energy dimers obtained at the harmonic level. Frequency scaling factor chosen based on the C=C stretching band.

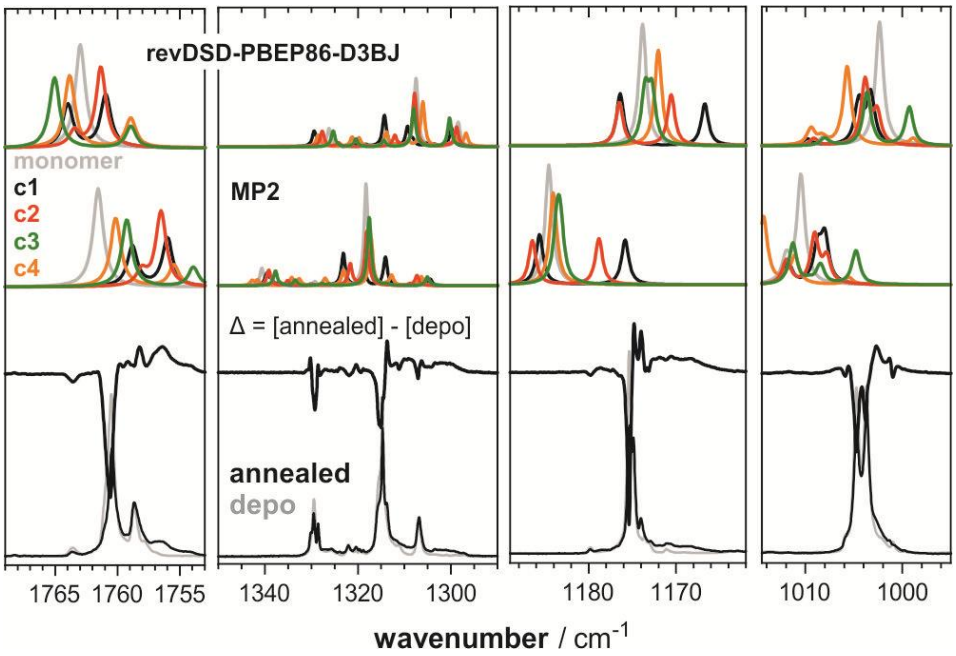

Fig. S7. Comparison of the experimental spectra of ITFE/Ar (1:3600) deposited at 15 K and annealed at 35 K, and the computed anharmonic spectra obtained from revDSD-PBEP86-D3BJ and MP2 electronic structure calculations at the VPT2 level.

Table S1. Relative zero-point corrected energies (in kcal/mol) of all considered dimers of ITFE obtained at the revDSD-PBEP86-D3BJ and MP2 levels of theory with the def2TZVP basis. Relative single-point energies from DLPNO-CCSD(T) are given in parenthesis

	B3LYP-D3BJ	**revDSD-PBEP86-D3BJ**	**MP2**
π-π c1	0.00 (0.00)	0.00 (0.00)	0.03 (0.00)
π-π c2	0.07 (0.08)	0.05 (0.04)	0.00 (0.11)
π-π c3	0.2 (0.3)	0.3 (0.3)	0.3 (0.3)
π-π c4	0.5 (0.5)	0.3 (0.4)	0.7 (0.4)
π-π c5	0.9 (1.1)		1.3 (1.1)
I-I	1.4 (2.8)		2.3 (2.2)
I-F	1.6 (1.9)		2.4 (2.5)
I-π	1.7 (2.1)		2.2 (2.1)
I-π 2	1.7 (2.0)		2.2 (2.0)
π-π c6	-		0.9 (0.7)

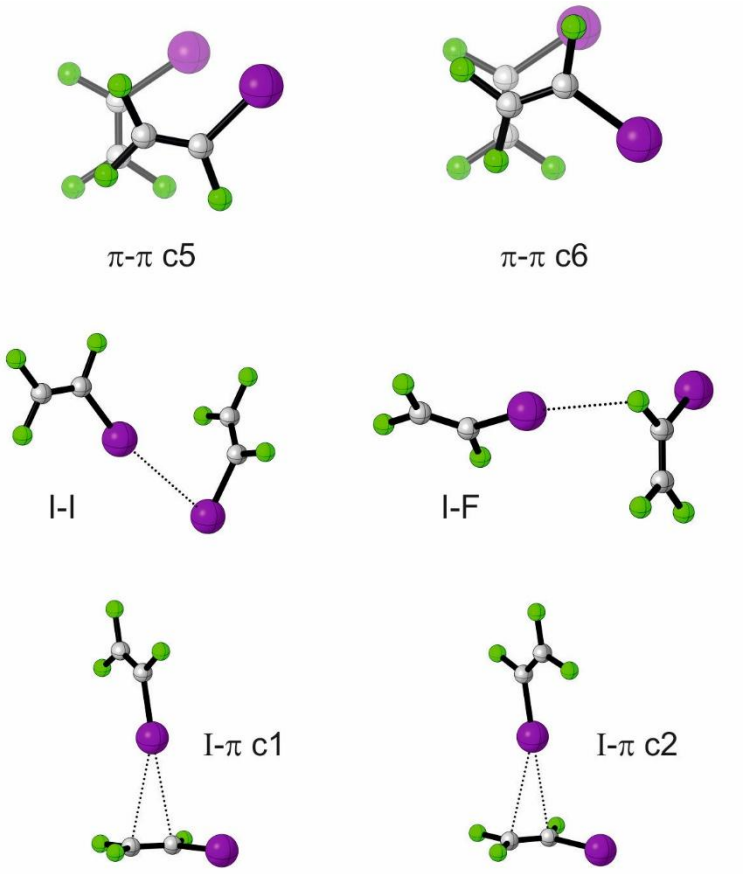

Fig. S8 Structures of the six dimer structures not discussed in the main text.

Analysis of selected isotopologues frequency shifts

While the energies are overall lower going from the main to the ^{13}C isotopologues, this is not the case for the fundamental of mode 2 and the combination 6+5. Looking at 2^1 (second panel, Fig. 2 of the main text), is harmonic energy is virtually the same between ITFE and ^{13}CFI (about 1746 cm^{-1}). The VPT2 correction leads to a small shift (1316 and 1318 cm^{-1}, see Tab. S2). Applying the variational correction further increases the energy difference, with the final position predicted at 1315 cm^{-1} for the main isotopologue and 1322.723 for ^{13}CFI, allowing us to univocally assign the small feature observed experimentally. This example also shows the importance of a full VPT2 treatment including the variational correction, the relative energy of 2^1 in resonance with it (Tab. S3) explaining the lowering in energy for the main isotopologue and conversely the increase for ^{13}CFI. In the case of revDSD-PBEP86, this results in a near perfect overlap with the combination band 9+3 of the main isotopologue, also at 1322 cm^{-1}. The shift is more readily visible with MP2 since this overlap does not occur there. A similar trend is observed for the combination 6+5 (third panel, Fig. 2 of main text), but with a more dramatic change. At the harmonic level, the energy for the main isotopologue is predicted higher (1174 cm^{-1}) than for ^{13}CFI (1169). The difference is preserved at the VPT2 level (1162 vs 1157). However, because of the large difference in the energy of the fundamental 3^1 (1180 and 1153, see Tables S4 and S5), the result of the variational correction is an inversion of the relative energies and an important intensity transfer (the intensity of the combination in ^{13}CFI is four times more intense than in the main isotopologue).

Tab S2. Polyads involving the fundamental of mode 2 at the revDSD-PBEP86-D3BJ/def2-TZVP level for the main isotopologue (top) and ^{13}CFI (bottom). The diagonal values are the DVPT2 energies, with resonance terms removed from the VPT2 equations. The off-diagonal terms are the coupling terms reintroduced variationally.

	$\|2^1\rangle$	$\|9^1 3^1\rangle$	$\|7^1 4^1\rangle$	$\|5^2\rangle$
$\|2^1\rangle$	1316.33	2.98	-6.07	-4.20
$\|9^1 3^1\rangle$	2.98	1321.76	0.00	0.00
$\|7^1 4^1\rangle$	-6.07	0.00	1332.30	0.00
$\|5^2\rangle$	-4.20	0.00	0.00	1308.90

	$\|2^1\rangle$	$\|9^1 3^1\rangle$	$\|7^1 4^1\rangle$	$\|5^2\rangle$
$\|2^1\rangle$	1318.36	3.03	-6.21	-4.01
$\|9^1 3^1\rangle$	3.03	1296.37	0.00	0.00
$\|7^1 4^1\rangle$	-6.21	0.00	1310.65	0.00
$\|5^2\rangle$	-4.01	0.00	0.00	1303.12

Tab S3: Polyads involving the fundamental of mode 2 at the MP2/def2-TZVP level for the main isotopologue (top) and ^{13}CFI (bottom). The diagonal values are the DVPT2 energies, with resonance terms removed from the VPT2 equations. The off-diagonal terms are the coupling terms reintroduced variationally.

	$\|2^1\rangle$	$\|9^1 3^1\rangle$	$\|7^1 4^1\rangle$	$\|5^2\rangle$
$\|2^1\rangle$	1328.46	2.83	-6.26	-3.91
$\|9^1 3^1\rangle$	2.83	1335.10	0.00	0.00
$\|7^1 4^1\rangle$	-6.26	0.00	1345.27	4.09
$\|5^2\rangle$	-3.91	0.00	4.09	1315.55

	$\|2^1\rangle$	$\|9^1 3^1\rangle$	$\|7^1 4^1\rangle$	$\|5^2\rangle$
$\|2^1\rangle$	1328.20	2.89	-6.37	-3.73
$\|9^1 3^1\rangle$	2.89	1309.06	0.00	0.00
$\|7^1 4^1\rangle$	-6.37	0.00	1321.54	0.00
$\|5^2\rangle$	-3.73	0.00	0.00	1308.86

Tab S4. Polyads involving the combination $6^1 5^1$ at the revDSD-PBEP86-D3BJ/def2-TZVP level for the main isotopologue (top) and ^{13}CFI (bottom). The diagonal values are the DVPT2 energies, with resonance terms removed from the VPT2 equations. The off-diagonal terms are the coupling terms reintroduced variationally.

	$\|3^1\rangle$	$\|6^1 5^1\rangle$
$\|3^1\rangle$	1179.51	5.99
$\|6^1 5^1\rangle$	5.99	1161.56

	$\|3^1\rangle$	$\|6^1 5^1\rangle$
$\|3^1\rangle$	1153.04	-5.74
$\|6^1 5^1\rangle$	-5.74	1157.26

Tab S5. Polyads involving the combination $6^1 5^1$ at the MP2/def2-TZVP level for the main isotopologue (top) and ^{13}CFI (bottom). The diagonal values are the DVPT2 energies, with resonance terms removed from the VPT2 equations. The off-diagonal terms are the coupling terms reintroduced variationally.

	$\|3^1\rangle$	$\|6^1 5^1\rangle$
$\|3^1\rangle$	1190.96	6.04
$\|6^1 5^1\rangle$	6.04	1166.66

	$\|3^1\rangle$	$\|6^1 5^1\rangle$
$\|3^1\rangle$	1164.40	-5.78
$\|6^1 5^1\rangle$	-5.78	1161.61

Cartesian coordinates of ITFE and its lowest energy dimers computed at MP2 level

ITFE

C	0.00000000	0.88943900	0.00000000
C	1.28513700	1.23811300	0.00000000
F	2.28093900	0.38361500	0.00000000
F	1.70076100	2.48448000	0.00000000
F	-0.93309900	1.84731300	0.00000000
I	-0.66317400	-1.04158400	0.00000000

$(ITFE)_2$ π-π c1

C	1.44301600	1.13480000	-0.24106800
C	1.26853900	1.61245700	0.99050400
F	1.47184700	0.91554700	2.08320000
F	0.87419200	2.83766100	1.24583900
F	1.21469100	1.93324100	-1.28866800
I	2.05512300	-0.76962900	-0.64753200
C	-1.48100100	-0.18599600	0.97415200
C	-1.05774500	-1.38236900	1.37971300
F	-1.04029900	-2.45308600	0.62247100
F	-0.61136800	-1.62275800	2.59090200
F	-1.46484800	0.83488200	1.84125100
I	-2.15011900	0.22089900	-0.90859500

$(ITFE)_2$ π-π c2

C	1.48292700	0.56031400	0.83923400
C	1.07512400	1.82837200	0.80505300
F	1.04785200	2.56310100	-0.28153400
F	0.65809200	2.48657900	1.86103000
F	1.47743000	-0.09522200	2.00464000
I	2.11495700	-0.48542700	-0.79478200
C	-1.48292300	-0.56030800	0.83924600
C	-1.07511700	-1.82836500	0.80507200
F	-1.04784900	-2.56310200	-0.28151100
F	-0.65807800	-2.48656400	1.86105100
F	-1.47742100	0.09523600	2.00464800
I	-2.11496200	0.48542100	-0.79477500

$(ITFE)_2$ π-π c3

C	-1.48274800	0.19086700	-1.07954100
C	-1.29494500	1.50975600	-1.08867900
F	-1.46531700	2.28330500	-0.04058700
F	-0.91708400	2.18577700	-2.14859100
F	-1.28990800	-0.50027600	-2.20734300
I	-2.06143500	-0.86647200	0.56708800
C	1.48274700	0.19086700	1.07954100
C	1.29494500	1.50975600	1.08867900
F	1.46531500	2.28330500	0.04058800
F	0.91708400	2.18577700	2.14859200
F	1.28991000	-0.50027600	2.20734300
I	2.06143500	-0.86647100	-0.56708900

$(ITFE)_2$ π-π c4

C	1.21972200	0.97683900	0.43003200
C	0.90753800	1.87749900	-0.50101200
F	1.45018800	1.92573300	-1.69297400
F	0.01620000	2.82550600	-0.32026000
F	0.59271500	1.02439000	1.61217700
I	2.63586400	-0.47220100	0.19345300
C	-2.00704600	0.32575100	-0.41270900
C	-2.51018800	1.04795600	0.58706100
F	-2.70715800	0.58833300	1.79893500
F	-2.86252400	2.30690300	0.46891500
F	-1.84068400	0.89978800	-1.61142800
I	-1.45659600	-1.63165100	-0.24851900

$(ITFE)_2$ π-π c5

C	2.36836200	0.10355200	0.26550500
C	2.40672900	1.13648900	-0.57501000
F	1.79000100	1.16584700	-1.73260100
F	3.05992400	2.24834000	-0.33073300
F	3.02467300	0.18694600	1.42763200
I	1.36438000	-1.63470600	-0.10443800
C	-1.42544100	1.18982800	-0.21313200
C	-0.62040000	1.62793100	0.75366600
F	-0.53230500	1.09155300	1.94707000
F	0.17870500	2.66436400	0.61508600
F	-1.41961400	1.81718600	-1.39334900
I	-2.70943600	-0.38255600	-0.01224300

$(ITFE)_2$ π-π c6

C	2.14001500	0.57295800	-0.12413500
C	1.65766500	1.36612500	-1.08019100
F	0.87084300	0.95827800	-2.04755100
F	1.91527100	2.65129800	-1.15659000
F	2.93057800	1.09914300	0.81711700
I	1.75530900	-1.42714900	0.00724100
C	-1.38561100	0.21793200	1.08504400
C	-0.76506800	1.39405400	1.16064900
F	-0.84918200	2.33142200	0.24340600
F	0.00608000	1.74968400	2.16254300
F	-1.23694200	-0.65980000	2.08195500
I	-2.55930600	-0.35542900	-0.48188500

$(ITFE)_2$ I-I

C	2.29955400	0.83100900	0.54468300
C	2.05370700	1.84711100	-0.28046200
F	1.99532100	1.73587200	-1.58573100
F	1.83388700	3.07513700	0.12582700
F	2.32774900	1.04812700	1.86240900
I	2.60713700	-1.08982000	-0.07860200
C	-3.05292200	0.47282700	0.00378700
C	-4.16768900	-0.25319100	0.06210400

F	-4.19194200	-1.56517300	0.08790900
F	-5.37436200	0.26562800	0.10043100
F	-3.14711000	1.80710400	-0.01793700
I	-1.16917100	-0.31936500	-0.05605600

$(ITFE)_2$ I-F

C	2.14861300	0.71513800	-0.37894700
C	2.17913400	1.74472700	0.46523900
F	2.68132100	1.69055100	1.67442800
F	1.69999600	2.93246200	0.17658500
F	1.59761000	0.89419000	-1.59027500
I	2.85981700	-1.14851000	0.03966900
C	-3.02749900	-0.24325500	0.64308500
C	-4.26522400	-0.31668100	0.15740500
F	-4.57639900	-0.11420600	-1.10126900
F	-5.31904100	-0.60188400	0.88890100
F	-2.82768900	-0.46959400	1.94658800
I	-1.37891800	0.19788300	-0.47882600

$(ITFE)_2$ I-π

C	-2.06725400	0.87257200	-0.43414300
C	-1.72470100	1.73116200	0.52807600
F	-1.88532600	1.50293500	1.80862400
F	-1.18455500	2.90394600	0.29402100
F	-1.85803700	1.21539200	-1.70961500
I	-2.92366900	-0.94872200	-0.09396100
C	3.13306300	-0.66621000	0.19183600
C	4.16985500	0.06947000	-0.20463800
F	4.06484000	1.26213700	-0.74157500
F	5.42076700	-0.31946900	-0.10145000
F	3.35846300	-1.87106600	0.72743100
I	1.18194900	-0.07555900	0.03766500

$(ITFE)_2$ I-π 2

C	2.18816700	0.75941300	-0.36032100
C	1.93389900	1.62491000	0.62287500
F	1.96075100	1.31883900	1.89702800
F	1.62579000	2.88380000	0.41828900
F	2.13363600	1.18604500	-1.62633800
I	2.68591000	-1.19798500	-0.06414600
C	-3.23763100	0.20474000	-0.16122900
C	-3.89715800	-0.88653800	0.22274500
F	-3.31974200	-1.97952700	0.66381400
F	-5.20682800	-0.99142200	0.20277600
F	-3.93009500	1.26359600	-0.59477900
I	-1.20091500	0.38011400	-0.13569400