Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Probing halogen bonding interactions between heptafluoro-2-iodopropane and three azabenzenes with Raman spectroscopy and density functional theory

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Table S1: Cartesian coordinates (in Å) of the HFP···Pyridine complex optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	3.802068	-1.16662	0.094547
C	5.18654	-1.21566	0.187816
C	5.895577	-0.02197	0.179192
C	5.193936	1.171822	0.077706
C	3.809163	1.122976	-0.01104
N	3.123837	-0.02178	-0.00299
H	6.974755	-0.02203	0.250233
H	3.212322	-2.07507	0.097913
H	5.690831	-2.16833	0.265122
H	5.70413	2.124421	0.06713
H	3.22507	2.03152	-0.09146
C	-2.48726	1.30687	0.125385
C	-1.89155	-0.02731	-0.3887
C	-2.49676	-1.28009	0.2921
F	-1.97507	-2.39163	-0.24351
F	-2.25443	-1.29039	1.608692
F	-3.82617	-1.33958	0.115604
F	-2.2185	-0.11171	-1.71708
F	-1.95764	2.336691	-0.54805
F	-2.24437	1.484184	1.429942
F	-3.81625	1.352976	-0.05804
I	0.303777	-0.0219	-0.17851

Table S2: Cartesian coordinates (in Å) of the HFP···Pyrimidine complex optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	0.033867	-2.96342	0.07551
C	1.229725	-4.85655	0.394219
C	1.655651	-4.39225	1.630694
C	1.195435	-3.14472	2.020007
N	0.38277	-2.42502	1.244477
H	1.545469	-5.82272	0.018164
H	-0.62604	-2.37728	-0.55256
H	2.313487	-4.97322	2.260122
H	1.477876	-2.70577	2.969367
C	-1.34923	2.196281	4.321934
C	-1.17218	2.176039	2.781752

C	-2.43167	2.638217	2.004444
F	-2.18196	2.645769	0.689171
F	-3.47436	1.831502	2.234409
F	-2.78626	3.884604	2.351475
F	-0.18374	3.077512	2.492407
F	-0.20499	1.84002	4.920009
F	-2.31369	1.357112	4.717311
F	-1.66267	3.425079	4.759175
I	-0.55016	0.176838	2.110423
N	0.417888	-4.14739	-0.39048

Table S3: Cartesian coordinates (in Å) of the HFP···Pyridazine complex optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	-1.38585	1.990148	4.399675
C	-1.03835	2.029251	2.889999
C	-2.10792	2.74343	2.025197
F	-1.71043	2.789089	0.747759
F	-3.28703	2.112976	2.081442
F	-2.296	4.009984	2.429602
F	0.109375	2.769843	2.776755
F	-0.39059	1.412628	5.086018
F	-2.51199	1.30442	4.628957
F	-1.54566	3.22684	4.896794
I	-0.67003	-0.00331	2.133112
N	-0.02011	-2.63327	1.205538
C	0.948852	-3.3543	1.761086
C	1.277832	-4.63485	1.327379
C	0.548753	-5.14639	0.276166
C	-0.45117	-4.33715	-0.25792
N	-0.72522	-3.11787	0.194953
H	2.072277	-5.19175	1.803498
H	1.470259	-2.87685	2.580258
H	0.735004	-6.13223	-0.12602
H	-1.0665	-4.6677	-1.08435

Table S4: Cartesian coordinates (in Å) of HFP optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	-0.92415	1.296886	0.00245
C	0.594177	1.300067	0.03931
C	1.155121	-0.11084	0.002398
F	0.746785	-0.80286	1.097581
F	-1.41498	0.660703	1.097627
F	-1.36437	0.65434	-1.10984
F	-1.39345	2.569538	-0.02043
F	0.721977	-0.75819	-1.10988
F	2.511041	-0.07391	-0.02055
F	1.01416	1.920441	-1.13987
I	1.319992	2.372061	1.763694

Table S5: Cartesian coordinates (in Å) of Pyridine optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	-0.69026	-0.8943	0.00000
C	0.71662	-0.8943	0.00000
C	1.38331	0.3323	0.00000
C	0.62923	1.50709	-0.00024
C	-0.77397	1.40428	-0.00038
N	-1.4335	0.22933	-0.00020
H	2.48185	0.37208	-0.00095
H	-1.25581	-1.84313	0.00012
H	1.27135	-1.84121	0.00026
H	1.11327	2.49201	-0.00034
H	-1.40732	2.30935	-0.00046

Table S6: Cartesian coordinates (in Å) of Pyrimidine optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
C	-0.50386	-0.71241	0.00000
N	0.85725	-0.71241	0.00000
C	1.44513	0.50232	0.00000
C	0.7019	1.69859	0.00000
C	-0.70106	1.57567	-0.00002
N	-1.32035	0.37665	0.00003
H	2.54973	0.51154	-0.00002
H	-1.0002	-1.70491	-0.00003
H	1.19178	2.67806	0.00000
H	-1.35629	2.465	-0.00002

Table S7: Cartesian coordinates (in Å) of Pyridazine optimized at the M06-2X/aVTZ level of theory.

Atom	X	Y	Z
N	-1.93365	-0.75381	0.00000
C	-0.56704	-0.75381	0.00000
C	0.17774	0.44049	0.00000
C	-0.54103	1.63871	0.00000
C	-1.94533	1.54378	-0.00001
N	-2.58863	0.33804	-0.00001
H	1.27493	0.42371	-0.00001
H	-0.08341	-1.74412	-0.00002
H	-0.03938	2.61464	0.00001
H	-2.59137	2.43666	-0.00002

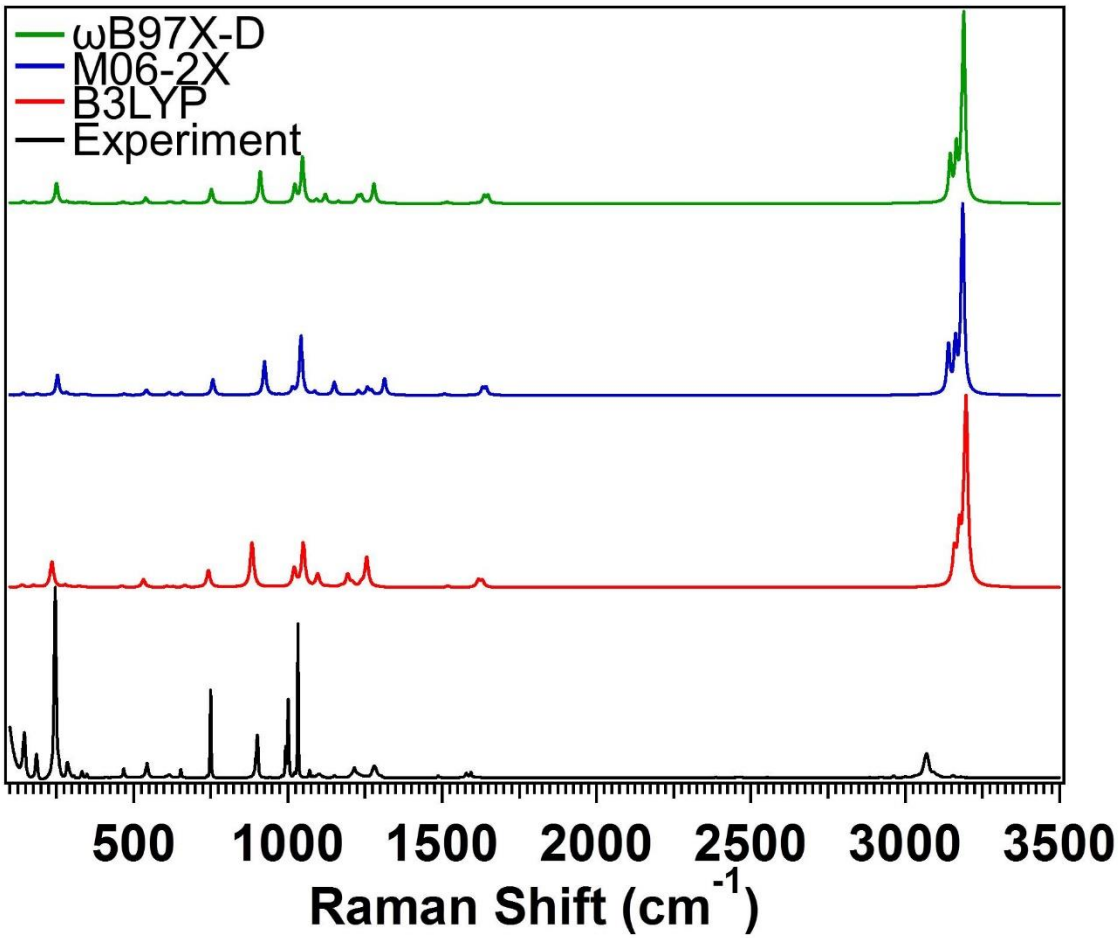

Figure S1. Theoretical Raman spectra of the HFP···Pyridine complex with the B3LYP, M06-2X, and ωB97X-D methods and aVTZ basis set compared to experimental results.

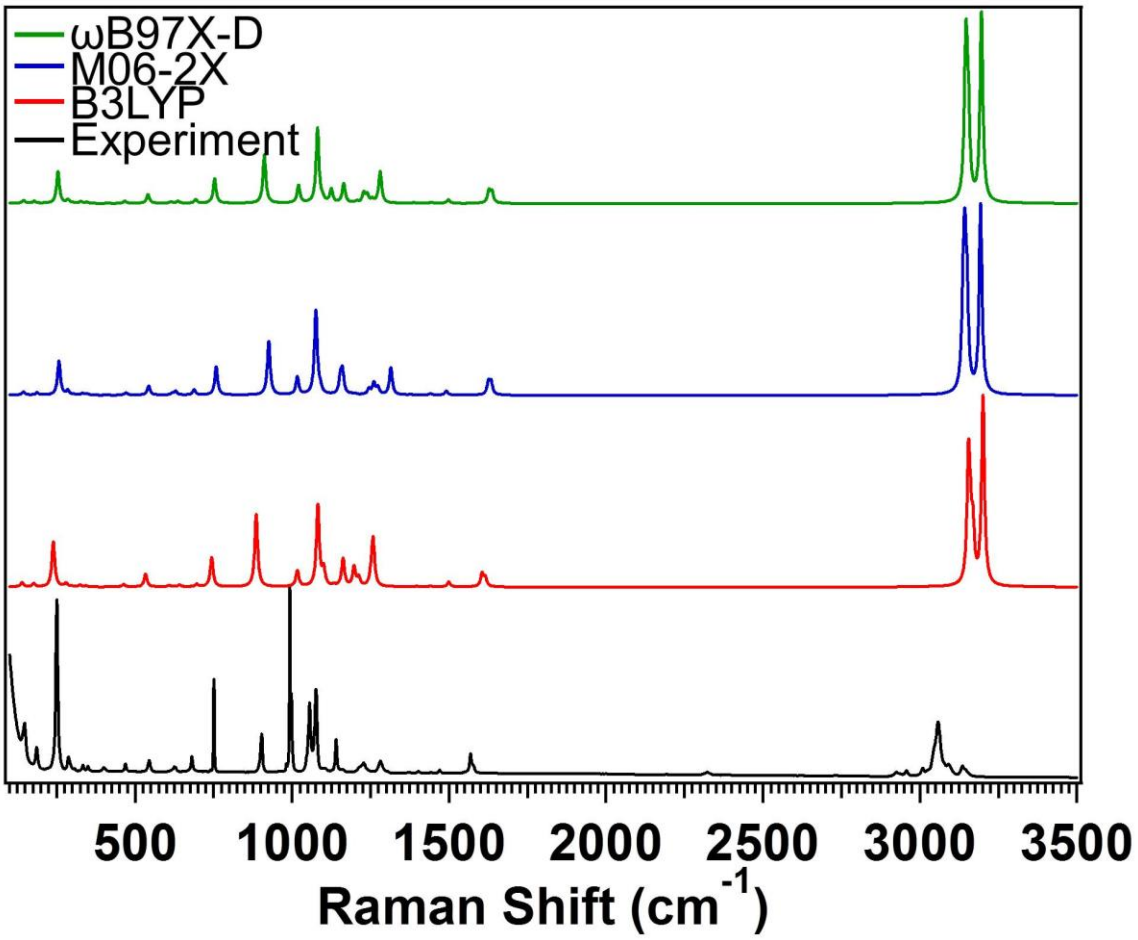

Figure S2. Theoretical Raman spectra of the HFP···Pyrimidine complex with the B3LYP, M06-2X, and ωB97X-D methods and aVTZ basis set compared to experimental results.

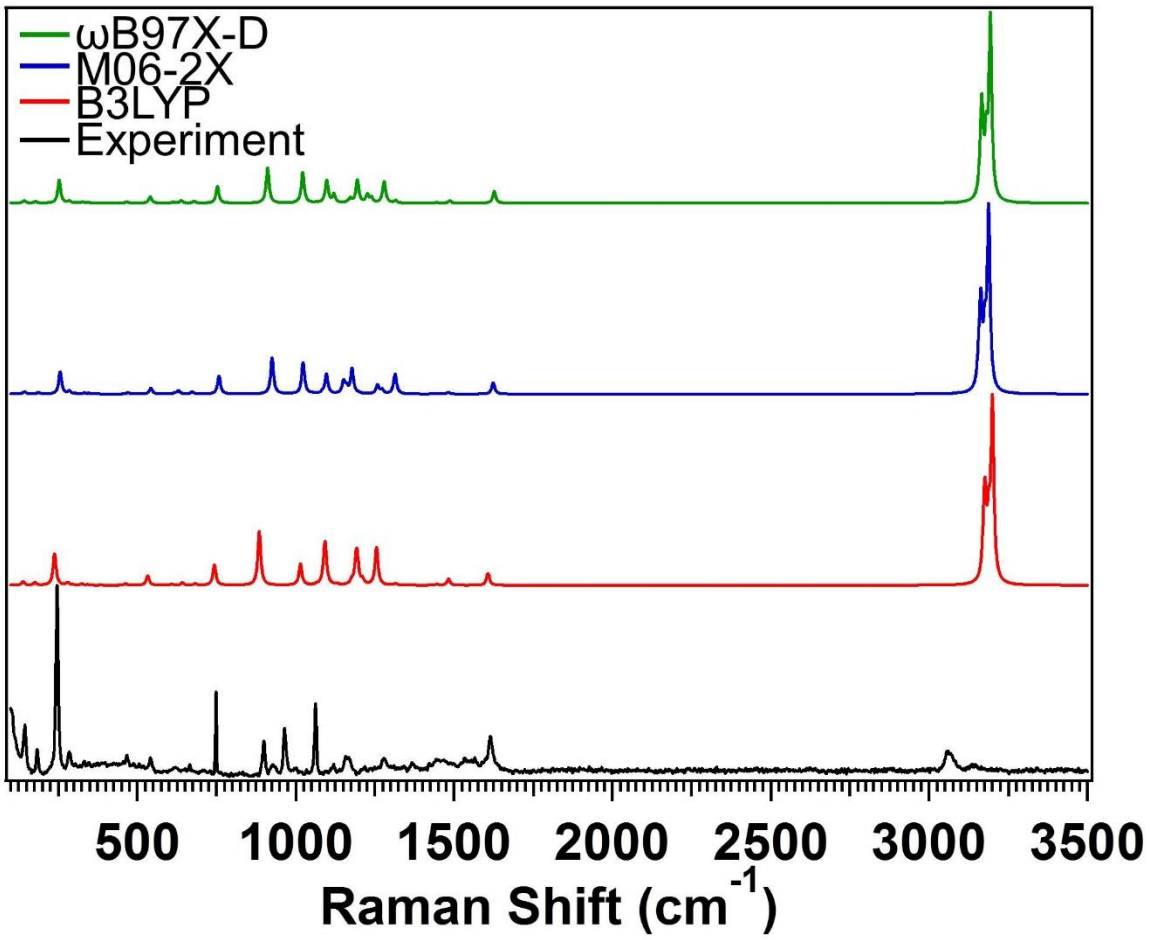

Figure S3. Theoretical Raman spectra of the HFP···Pyridazine complex with the B3LYP, M06-2X, and ωB97X-D methods and aVTZ basis set compared to experimental results.

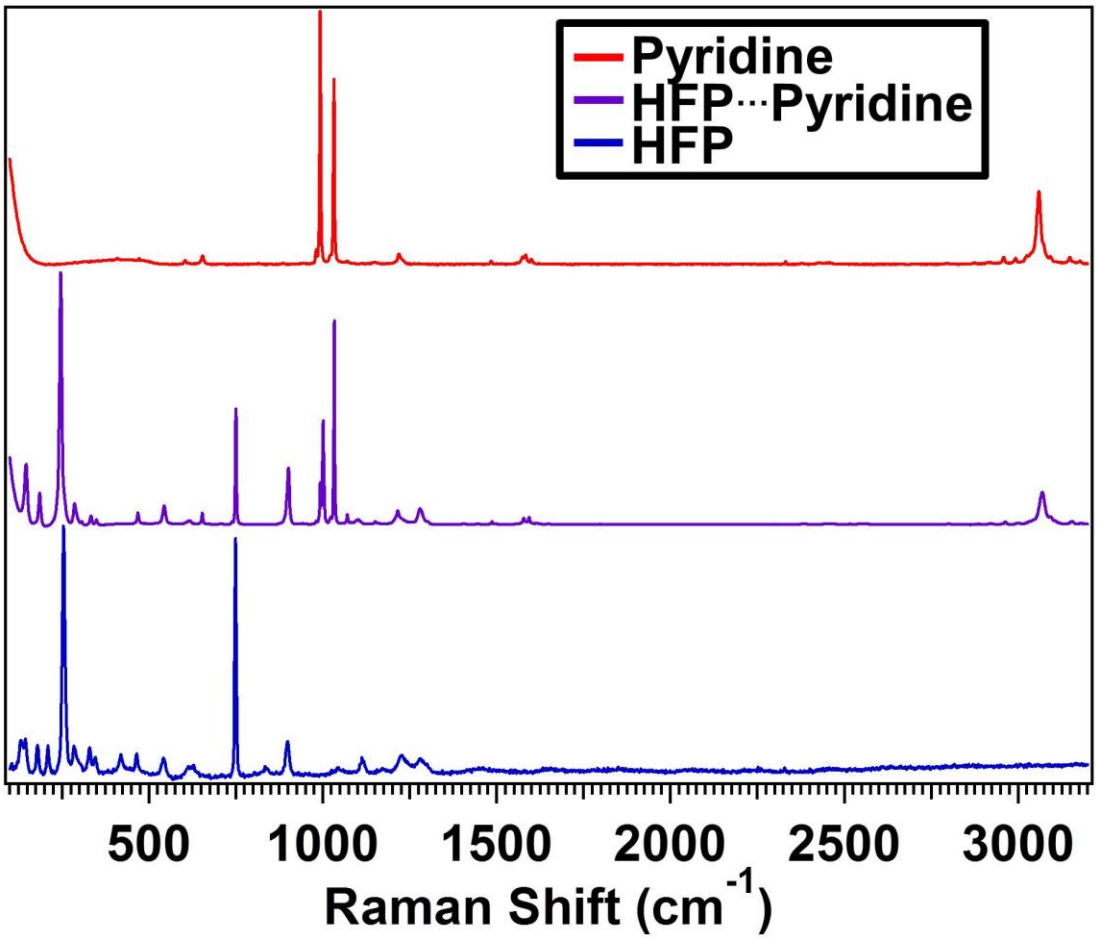

Figure S4. Raman spectrum of the HFP···Pyridine complex (purple) compared to the individual molecules' spectra (pyridine, red; HFP blue).

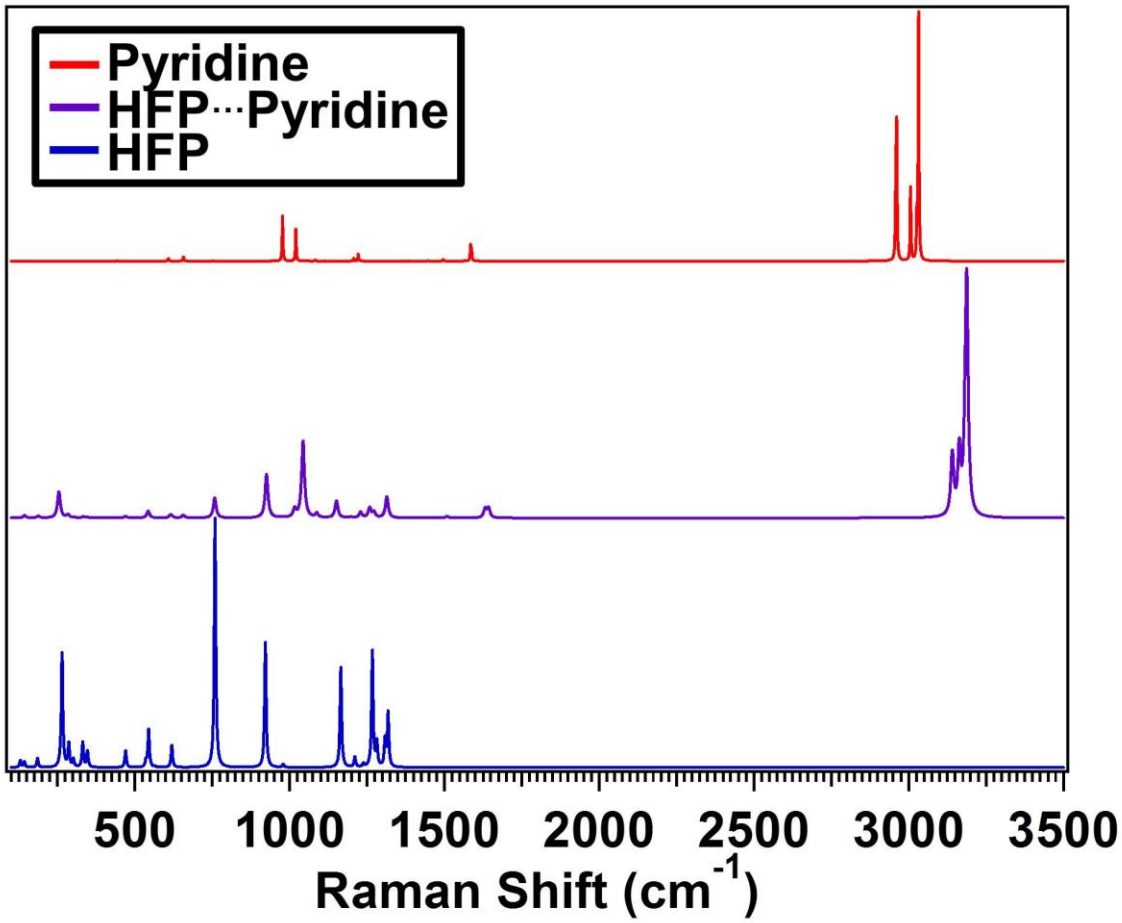

Figure S5. Theoretical Raman spectrum of the HFP···Pyridine complex (purple) compared to the individual molecules' spectra (pyridine, red; HFP blue) all at the M06-2X/aVTZ level of theory.

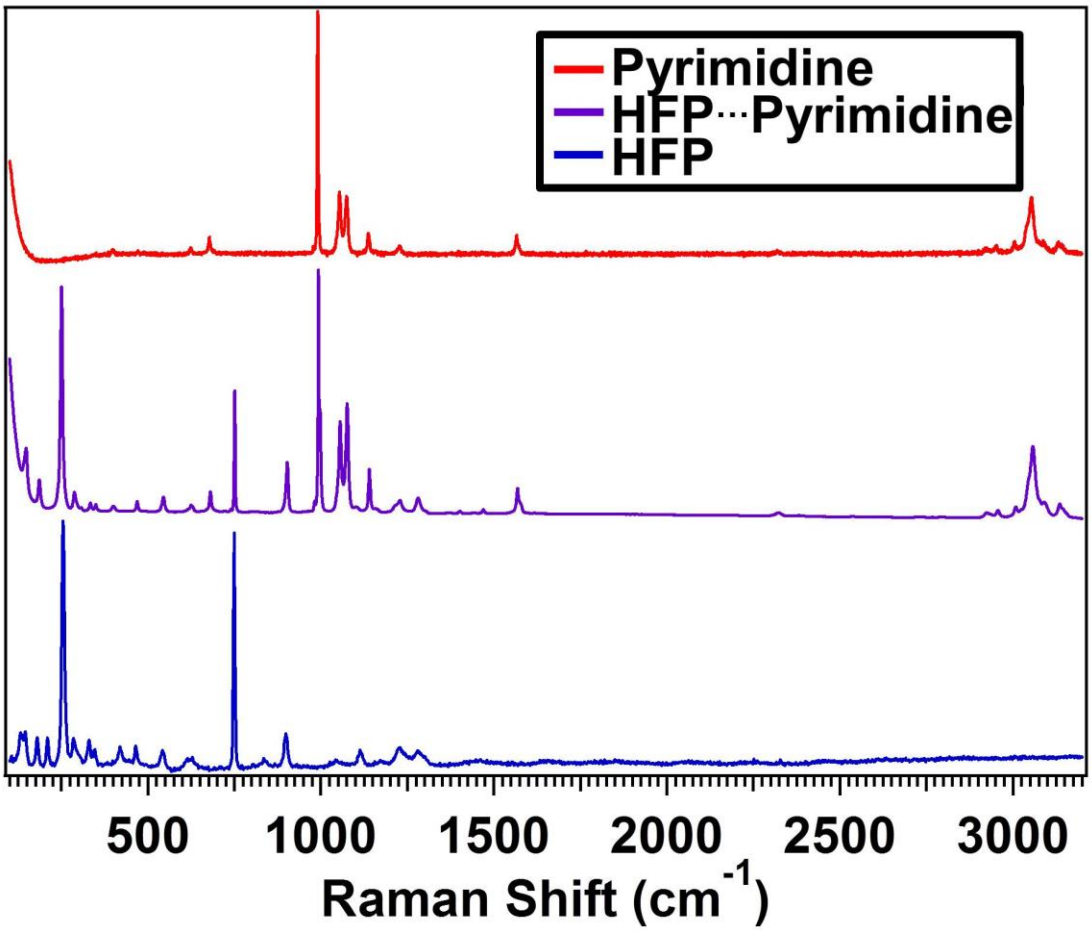

Figure S6. Raman spectrum of the HFP···Pyrimidine complex (purple) compared to the individual molecules' spectra (pyrimidine, red; HFP blue).

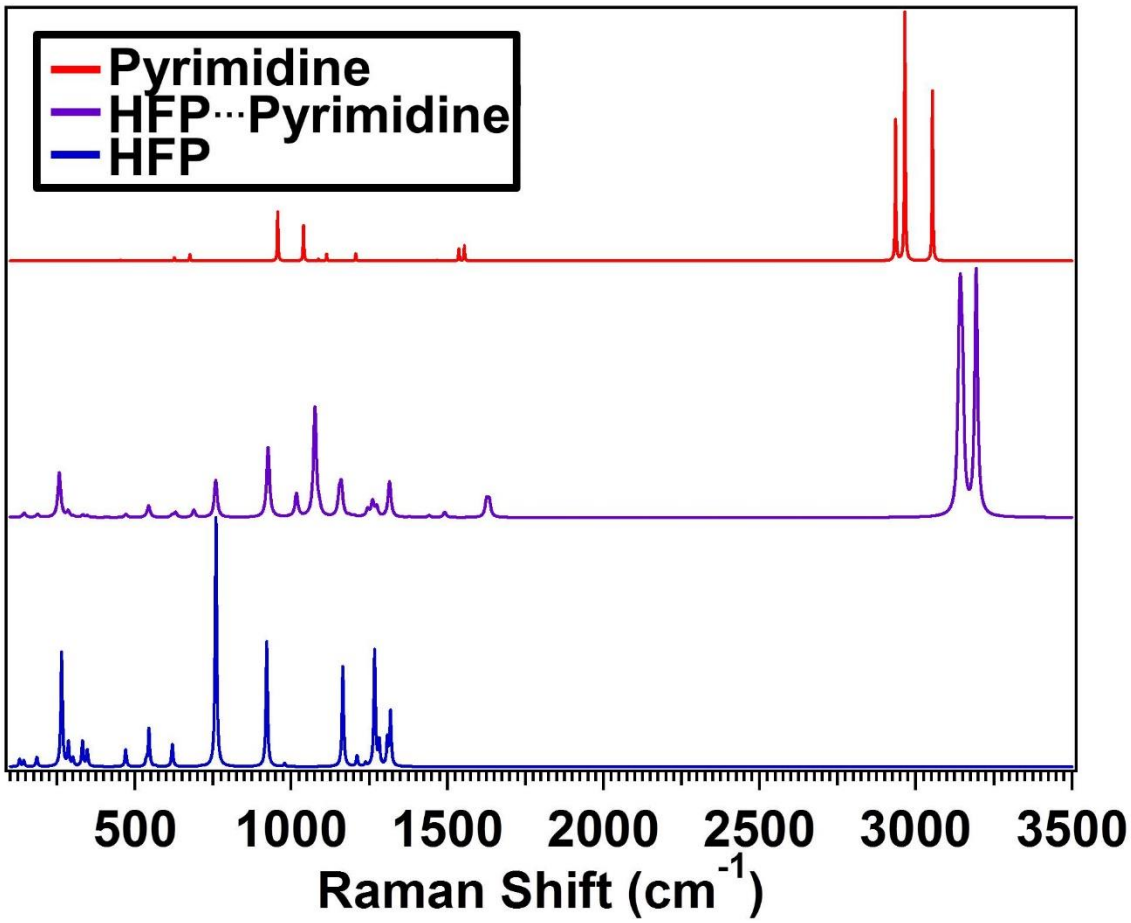

Figure S7. Theoretical Raman spectrum of the HFP···Pyrimidine complex (purple) compared to the individual molecules' spectra (pyrimidine, red; HFP blue) all at the M06-2X/aVTZ level of theory.

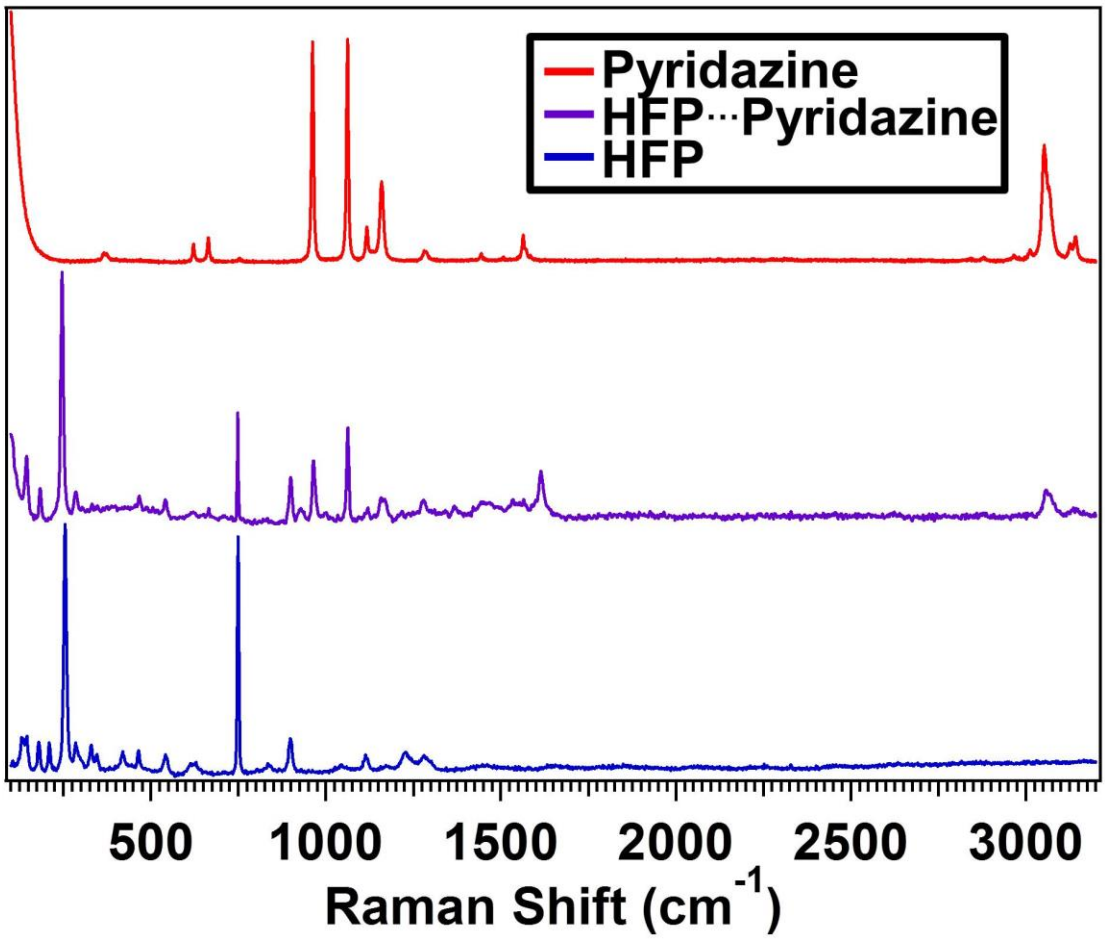

Figure S8. Raman spectrum of the HFP···Pyridazine complex (purple) compared to the individual molecules' spectra (pyridazine, red; HFP blue).

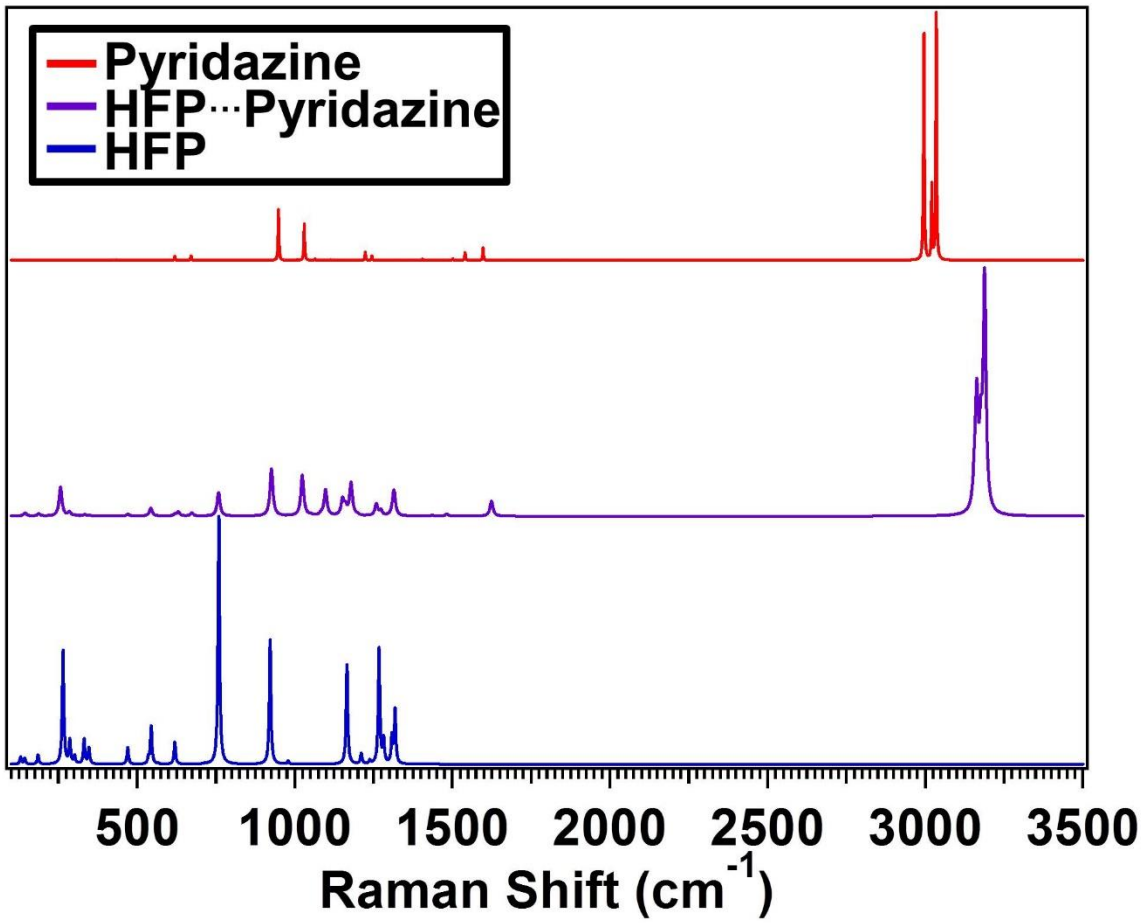

Figure S9. Theoretical Raman spectrum of the HFP···Pyridazine complex (purple) compared to the individual molecules' spectra (pyridazine, red; HFP blue) all at the M06-2X/aVTZ level of theory.

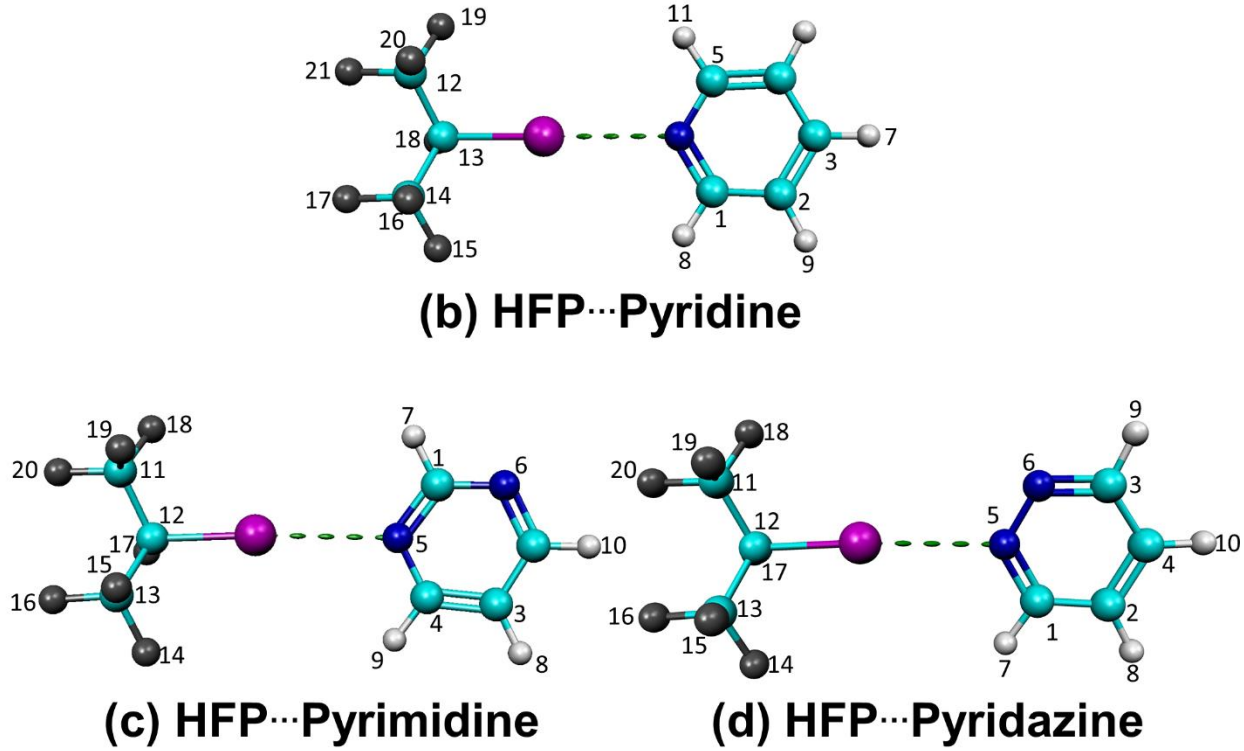

Figure S10. Numbering of molecular structures used in Table 3, 4, and 5.

Table S8. Changes in natural electron configuration for atoms in the HFP···Pyridine complex in millielectrons (me-).

Atom		Δq (me^-)
C	1	0
C	2	-10
C	3	-20
C	4	-10
C	5	0
N	6	40
H	7	-10
H	8	-10
H	9	0
H	10	0
H	11	-10
C	12	0
C	13	50
C	14	0
F	15	20
F	16	10
F	17	0
F	18	10
F	19	20
F	20	10
F	21	0
I	22	-30

Table S9. Changes in natural electron configuration for atoms in the HFP···Pyrimidine complex in millielectrons (me-).

Atom		Δq (me-)
C	1	-20
C	2	0
C	3	10
C	4	-30
N	5	40
N	6	-10
H	7	0
H	8	-10
H	9	-10
H	10	0
C	11	0
C	12	40
C	13	0
F	14	20
F	15	10
F	16	0
F	17	20
F	18	20
F	19	10
F	20	0
I	21	-40

Table S10. Changes in natural electron configuration for atoms in the HFP···Pyridazine complex in millielectrons (me-).

Atom		Δq (me^-)
C	1	-10
C	2	10
C	3	-10
C	4	0
N	5	50
N	6	-10
H	7	-10
H	8	-10
H	9	-10
H	10	-10
C	11	0
C	12	50
C	13	0
F	14	20
F	15	10
F	16	0
F	17	10
F	18	20
F	19	10
F	20	0
I	21	-50

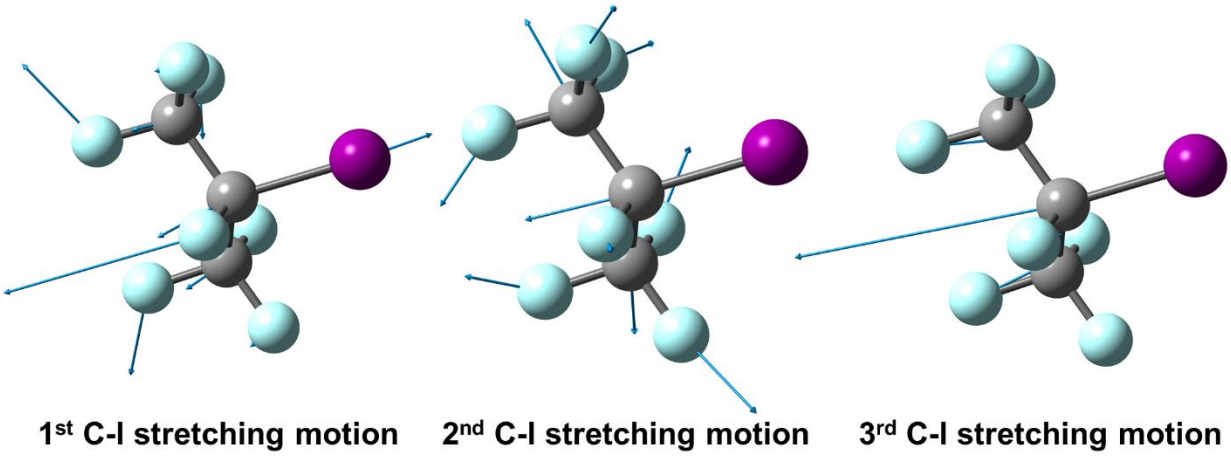

Figure S11. Displacement vectors of the stretching motions within the HFP molecule.