Supporting Information for

Second-order many-body perturbation study of solid hydrogen fluoride under pressure

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1. Optimized Geometries

Below are shown the optimized geometries of the hydrogen fluoride crystal as a function of pressure (P) in GPa. The bond distances and the lattice constants (a,b,c) are given in Å. The angles are in degrees, the volume is in Å^3 and the molar volume is in cm^3/mol.

HF/aug-cc-pVDZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.913	1.77	2.68	177	126	3.56	4.77	5.48	93.09	14.02
1	0.913	1.75	2.66	178	122	3.20	4.65	5.21	77.39	11.65
2	0.913	1.73	2.64	176	121	3.07	4.59	5.07	71.42	10.75
3	0.914	1.71	2.62	176	120	3.02	4.54	4.93	67.79	10.21
4	0.914	1.69	2.60	176	119	2.97	4.49	4.86	64.86	9.77
5	0.914	1.68	2.59	176	119	2.92	4.46	4.82	62.78	9.45
6	0.914	1.67	2.58	176	118	2.88	4.43	4.78	61.02	9.19
8	0.914	1.65	2.56	177	117	2.82	4.38	4.72	58.22	8.77
10	0.914	1.63	2.54	177	117	2.78	4.33	4.66	56.09	8.44
12	0.915	1.61	2.53	177	116	2.74	4.29	4.61	54.20	8.16
14	0.915	1.60	2.51	177	116	2.71	4.25	4.57	52.67	7.93
16	0.914	1.59	2.50	178	115	2.68	4.23	4.53	51.31	7.73
18	0.915	1.58	2.49	178	115	2.65	4.20	4.50	50.13	7.55
20	0.915	1.56	2.48	178	115	2.63	4.18	4.47	49.08	7.39

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cp-HF/aug-cc-pVDZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.914	1.79	2.70	179	126	3.78	4.81	5.59	101.73	15.32
1	0.914	1.76	2.67	177	122	3.31	4.68	5.25	81.16	12.22
2	0.915	1.74	2.66	176	121	3.14	4.61	5.09	73.79	11.11
3	0.915	1.73	2.64	176	120	3.07	4.57	4.97	69.62	10.48
4	0.915	1.71	2.62	176	119	3.02	4.52	4.89	66.72	10.04
5	0.916	1.69	2.61	176	118	2.96	4.48	4.85	64.32	9.68
6	0.916	1.68	2.60	176	118	2.92	4.45	4.80	62.35	9.39
8	0.916	1.66	2.57	176	117	2.85	4.39	4.74	59.31	8.93
10	0.917	1.64	2.55	177	117	2.80	4.34	4.68	56.89	8.56
12	0.917	1.62	2.53	177	116	2.76	4.30	4.63	54.95	8.27
14	0.917	1.60	2.52	177	116	2.73	4.27	4.58	53.30	8.02
16	0.917	1.59	2.51	178	116	2.69	4.24	4.55	51.90	7.81
18	0.917	1.58	2.49	178	115	2.66	4.21	4.53	50.69	7.63
20	0.917	1.56	2.48	178	115	2.63	4.19	4.50	49.59	7.47

HF/aug-cc-pVTZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.913	1.76	2.67	177	130	3.76	4.84	5.63	102.36	15.41
1	0.914	1.73	2.65	177	123	3.32	4.65	5.34	82.42	12.41
2	0.915	1.71	2.62	177	123	3.17	4.61	5.11	74.69	11.25
3	0.915	1.70	2.61	177	121	3.08	4.54	5.00	69.94	10.53
4	0.916	1.68	2.59	177	120	3.01	4.50	4.95	67.01	10.09
5	0.916	1.66	2.58	177	120	2.97	4.46	4.86	64.42	9.70
6	0.916	1.65	2.56	177	119	2.91	4.42	4.83	62.16	9.36
8	0.917	1.62	2.54	177	118	2.84	4.37	4.76	59.09	8.90
10	0.918	1.60	2.52	178	118	2.78	4.32	4.70	56.50	8.51
12	0.918	1.59	2.50	178	117	2.73	4.28	4.66	54.58	8.22
14	0.918	1.57	2.49	178	117	2.70	4.24	4.63	52.93	7.97
16	0.919	1.56	2.47	179	116	2.67	4.21	4.59	51.53	7.76
18	0.919	1.54	2.46	179	116	2.64	4.18	4.56	50.29	7.57
20	0.919	1.53	2.45	179	116	2.62	4.15	4.53	49.22	7.41

cp-HF/aug-cc-pVTZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.913	1.76	2.68	177	128	3.83	4.82	5.69	104.89	15.79
1	0.915	1.73	2.64	177	125	3.33	4.68	5.37	83.71	12.60
2	0.915	1.71	2.63	177	123	3.15	4.62	5.21	75.87	11.42
3	0.915	1.69	2.60	177	122	3.06	4.56	5.09	71.14	10.71
4	0.916	1.67	2.59	177	121	3.00	4.51	4.99	67.61	10.18
5	0.916	1.66	2.57	177	121	2.96	4.47	4.91	64.95	9.78
6	0.916	1.65	2.56	178	120	2.91	4.43	4.89	63.00	9.48
8	0.917	1.62	2.54	178	119	2.84	4.37	4.81	59.68	8.99
10	0.918	1.60	2.52	178	118	2.78	4.33	4.75	57.17	8.61
12	0.918	1.58	2.50	179	118	2.74	4.29	4.69	55.14	8.30
14	0.918	1.57	2.49	179	117	2.70	4.25	4.65	53.45	8.05
16	0.919	1.56	2.47	179	117	2.68	4.22	4.60	51.95	7.82
18	0.919	1.54	2.46	179	117	2.65	4.19	4.57	50.72	7.64
20	0.919	1.53	2.45	180	116	2.63	4.16	4.54	49.62	7.47

MP2/aug-cc-pVDZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.948	1.62	2.57	179	118	3.20	4.40	4.99	70.20	10.57
1	0.949	1.61	2.55	179	117	3.09	4.35	4.89	65.64	9.88
2	0.949	1.60	2.54	179	116	3.01	4.31	4.82	62.67	9.44
3	0.950	1.58	2.53	180	116	2.98	4.28	4.75	60.50	9.11
4	0.950	1.57	2.52	180	116	2.91	4.26	4.73	58.77	8.85
5	0.951	1.56	2.51	180	115	2.88	4.23	4.71	57.29	8.63
6	0.951	1.55	2.50	180	115	2.85	4.21	4.67	56.01	8.43
8	0.951	1.54	2.49	180	114	2.80	4.18	4.62	53.92	8.12
10	0.952	1.52	2.47	180	114	2.76	4.14	4.57	52.27	7.87
12	0.952	1.51	2.46	179	113	2.73	4.12	4.52	50.76	7.64
14	0.952	1.50	2.45	179	113	2.70	4.09	4.49	49.49	7.45
16	0.953	1.49	2.44	179	113	2.67	4.06	4.46	48.39	7.28
18	0.953	1.48	2.43	179	113	2.64	4.04	4.43	47.40	7.14
20	0.953	1.47	2.42	179	112	2.62	4.02	4.41	46.48	7.00

cp-MP2/aug-cc-pVDZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.948	1.66	2.61	179	119	3.37	4.48	5.19	78.45	11.81
1	0.949	1.64	2.59	179	118	3.21	4.43	4.99	70.94	10.68
2	0.949	1.62	2.57	179	116	3.10	4.37	4.94	66.89	10.07
3	0.950	1.61	2.56	180	116	3.02	4.34	4.89	64.00	9.64
4	0.951	1.59	2.54	180	115	2.97	4.30	4.83	61.75	9.30
5	0.951	1.58	2.53	180	116	2.92	4.29	4.79	59.98	9.03
6	0.951	1.57	2.52	180	115	2.89	4.26	4.74	58.41	8.79
8	0.952	1.56	2.51	180	115	2.83	4.23	4.68	55.94	8.42
10	0.952	1.54	2.49	179	114	2.78	4.19	4.63	53.95	8.12
12	0.953	1.52	2.48	179	114	2.74	4.16	4.60	52.34	7.88
14	0.953	1.51	2.46	178	114	2.70	4.13	4.56	50.95	7.67
16	0.954	1.50	2.45	178	114	2.68	4.10	4.53	49.72	7.49
18	0.955	1.49	2.44	178	113	2.65	4.08	4.50	48.64	7.32
20	0.955	1.48	2.43	178	113	2.63	4.06	4.47	47.67	7.18

MP2/aug-cc-pVTZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.949	1.61	2.56	180	118	3.34	4.39	5.08	74.48	11.21
1	0.951	1.59	2.54	180	117	3.16	4.33	4.97	67.93	10.23
2	0.952	1.57	2.53	180	116	3.06	4.29	4.86	63.89	9.62
3	0.952	1.56	2.51	180	116	2.97	4.27	4.81	61.08	9.20
4	0.953	1.55	2.50	180	116	2.94	4.23	4.76	59.11	8.90
5	0.954	1.54	2.49	180	115	2.88	4.20	4.74	57.40	8.64
6	0.954	1.53	2.48	180	115	2.85	4.19	4.70	56.04	8.44
8	0.956	1.51	2.46	179	115	2.78	4.15	4.65	53.69	8.08
10	0.957	1.49	2.44	179	114	2.73	4.11	4.61	51.76	7.79
12	0.958	1.47	2.43	178	114	2.70	4.08	4.57	50.27	7.57
14	0.959	1.46	2.42	178	114	2.66	4.05	4.54	48.96	7.37
16	0.960	1.45	2.41	178	114	2.63	4.03	4.51	47.77	7.19
18	0.961	1.43	2.39	177	113	2.61	4.00	4.48	46.75	7.04
20	0.961	1.42	2.38	177	113	2.59	3.98	4.45	45.89	6.91

cp-MP2/aug-cc-pVTZ

P	H–F Bond	H…F Bond	F…F Bond	FHF Angle	FFF Angle	*a*	*b*	*c*	Volume	Molar Volume
0	0.947	1.62	2.56	180	121	3.36	4.46	5.21	78.09	11.76
1	0.949	1.60	2.55	179	119	3.17	4.38	5.09	70.82	10.66
2	0.950	1.58	2.53	179	118	3.06	4.34	5.00	66.37	9.99
3	0.951	1.56	2.51	179	118	2.98	4.30	4.94	63.33	9.53
4	0.952	1.55	2.50	179	117	2.93	4.27	4.89	61.08	9.20
5	0.952	1.54	2.49	179	117	2.88	4.24	4.84	59.14	8.90
6	0.953	1.53	2.48	179	117	2.85	4.22	4.79	57.65	8.68
8	0.954	1.51	2.46	178	116	2.78	4.18	4.73	55.01	8.28
10	0.955	1.49	2.45	178	116	2.74	4.14	4.68	53.16	8.00
12	0.956	1.48	2.43	177	115	2.70	4.11	4.64	51.50	7.75
14	0.957	1.46	2.42	177	115	2.67	4.08	4.59	50.08	7.54
16	0.958	1.45	2.41	177	114	2.65	4.05	4.56	48.88	7.36
18	0.958	1.44	2.40	177	114	2.63	4.02	4.52	47.80	7.20
20	0.958	1.43	2.39	176	114	2.60	4.01	4.50	46.88	7.06

2. Vibrational Frequencies

The harmonic vibrational frequencies in the stretching, librational, and pseudo-translational regions for both the hydrogen fluoride (FH) and deuterium fluoride (FD) crystals are shown below as a function of pressure (*P*) in GPa. All frequencies are obtained at the cp-MP2/aug-cc-pVDZ level and given in cm^{-1}.

FH

P				
0	3458	3555	3570	3584
1	3439	3531	3556	3574
2	3423	3513	3547	3564
3	3408	3495	3537	3555
4	3394	3479	3529	3547
5	3381	3462	3519	3540
6	3377	3457	3518	3539
8	3357	3433	3504	3527
10	3344	3415	3497	3521
12	3325	3393	3486	3511
14	3315	3379	3480	3507
16	3298	3358	3468	3497
18	3286	3343	3460	3491
20	3277	3330	3455	3487

P								
0	480	510	513	584	601	669	928	1003
1	451	501	497	594	607	685	947	1027
2	438	500	486	592	602	705	976	1056
3	428	494	484	600	605	714	991	1074
4	421	493	481	604	609	724	1006	1090
5	415	487	483	619	609	729	1017	1104
6	407	483	474	619	608	735	1027	1113
8	405	482	473	629	611	750	1050	1136
10	399	476	466	634	611	759	1068	1154
12	391	467	464	641	609	765	1088	1176
14	383	461	457	646	607	771	1102	1191
16	385	461	456	653	610	780	1119	1208
18	381	456	452	659	610	785	1132	1223
20	376	450	446	662	607	789	1143	1235

P									
0	44	70	71	85	129	194	231	297	322
1	56	87	103	102	169	205	259	308	346
2	69	94	119	122	190	214	278	315	365
3	72	98	132	134	210	222	295	326	383
4	77	104	144	145	227	230	311	335	399
5	76	107	153	151	242	236	324	347	415
6	82	113	163	161	256	241	336	351	425
8	91	120	178	179	278	250	356	361	446
10	97	127	192	193	298	260	375	373	467
12	99	128	201	205	312	271	400	385	490
14	105	132	211	216	327	279	411	400	507
16	111	137	222	227	341	288	426	411	524
18	115	141	230	237	354	295	439	420	539
20	120	145	239	247	366	302	451	429	553

FD

P				
0	2508	2577	2588	2598
1	2494	2560	2578	2590
2	2482	2547	2571	2582
3	2471	2534	2564	2576
4	2462	2522	2557	2570
5	2452	2510	2550	2564
6	2449	2506	2549	2563
8	2435	2489	2539	2554
10	2425	2476	2533	2549
12	2412	2460	2524	2542
14	2405	2450	2520	2539
16	2392	2435	2511	2531
18	2383	2423	2505	2526
20	2377	2415	2501	2523

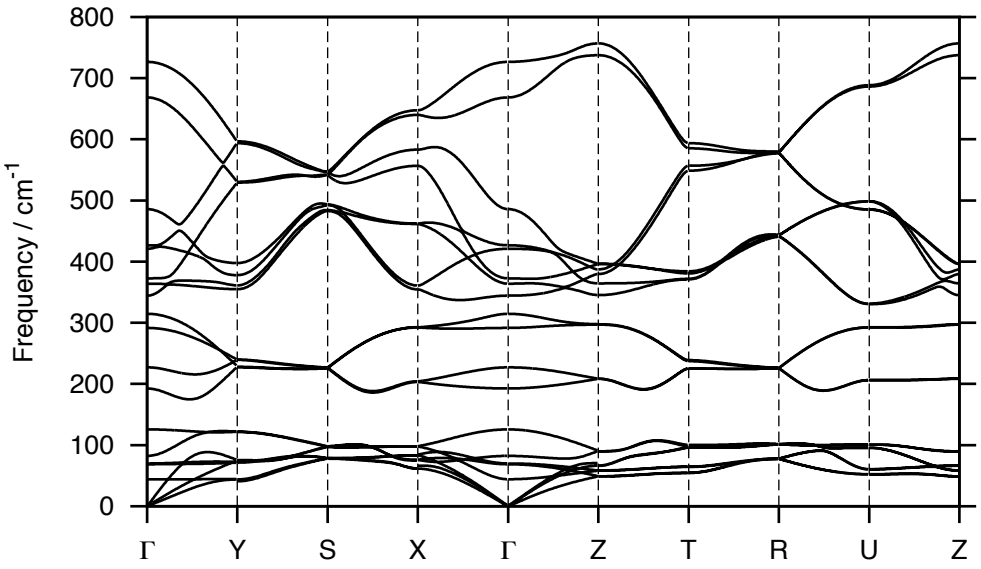
P								
0	344	364	373	421	427	486	669	727
1	325	353	367	428	431	497	682	745
2	318	345	366	431	426	512	703	765
3	314	343	362	437	428	519	713	778
4	290	341	361	441	430	526	725	789
5	291	343	357	450	433	529	732	799
6	287	337	354	450	431	534	739	805
8	287	335	353	458	433	545	756	821
10	282	330	348	462	434	552	769	834
12	280	328	342	467	432	556	783	849
14	275	324	338	471	431	560	794	860
16	276	323	338	476	433	567	806	872
18	273	320	334	480	432	571	816	882
20	269	316	330	483	431	574	824	891

P									
0	44	69	70	82	126	193	227	292	315
1	56	99	87	98	165	203	254	303	338
2	69	115	94	117	186	212	270	309	356
3	72	127	98	128	205	220	283	321	374
4	77	140	104	138	222	228	318	330	390
5	76	148	106	145	236	234	326	341	405
6	82	158	112	154	250	239	335	345	415
8	91	172	120	170	272	248	354	355	436
10	97	186	126	184	292	258	373	367	456
12	99	194	127	196	306	270	389	384	479
14	104	204	132	206	321	277	403	394	495
16	110	214	137	217	334	286	418	404	512
18	115	222	141	226	347	293	431	414	527
20	119	230	145	235	358	300	443	422	541

3. Phonon Dispersions

The phonon dispersion curves of deuterium fluoride (FD) crystal in the first Brillouin zone at 0 and 20 GPa are shown below. All frequencies are obtained at the cp-MP2/aug-cc-pVDZ level.

0 GPa



20 GPa