

Supplementary Material: Appendices A, B, C and D  
for

## **The first-formed hydrogen and nitrogen defects in natural diamond**

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## **Appendix A**

Data from FTIR and PL spectra recorded from *Type Ib + IaA* diamonds and sample Z-16

**Tables A.1 – A.3**

**Table A.1.** Selected data from FTIR spectra recorded from *Type Ib + IaA* diamonds.

Sample no.	%IaA	N <sub>c</sub> (at.ppm)	N <sub>A</sub> (at.ppm)	N <sub>X</sub> (at.ppm)	N <sub>Y</sub> (at.ppm)	N <sub>tot</sub> (at.ppm)	3107 (cm <sup>-1</sup> )	3343 (cm <sup>-1</sup> )	3373 (cm <sup>-1</sup> )	3394 (cm <sup>-1</sup> )	1353 (cm <sup>-1</sup> )	1358 (cm <sup>-1</sup> )	1363 (cm <sup>-1</sup> )	1374 (cm <sup>-1</sup> )	1387 (cm <sup>-1</sup> )
501986	22.9	17.5	10.9	1.27	17.9	47.6	0.039	0.827	0.158	0.709	0.032	0.200	0.001	0.007	0.027
888257	23.9	27.5	16.5	2.20	22.9	69.1	0.049	0.552	0.078	0.436					
390746	22.8	14.8	9.7	1.01	17.2	42.7	0.047	0.292	0.056	0.239	0.044	0.159	0.007	0.019	0.013
665540	16.3	67.5	23.2	1.64	49.8	142.1	0.005	1.110	0.129	0.821	0.182	0.588	0	0.093	0.247
643299	26.5	5.0	7.3	0.66	14.6	27.6	0.005	0.672	0.338	0.885	0.024	0.115	0	0	0.017
761265	71.1	7.0	74.8	1.99	21.4	105.2	0.729	0.411	0.091	0.369	0.016	0.123	0.151	0.033	0.043
112167	18.0	105.0	38.0	4.40	63.9	211.2	0.018	0.779	0.059	0.483	0.186	0.373	0.024	0.125	0.186
187552	33.5	32.5	40.3	3.03	44.7	120.5	0.279	0.722	0.077	0.507	0.058	0.381	0.022	0.020	0.066
546866	26.0	26.3	19.8	2.59	27.3	75.9	0.066	0.717	0.149	0.662	0.064	0.328	0.123	0.104	0.197
501987	22.9	18.8	10.9	1.38	16.7	47.7	0.036	0.829	0.148	0.714					
866797	4.4	17.5	2.0	1.38	24.7	45.6	0.000	0.104	0.026	0.095	0.065	0.339	0.022	0.027	0.185
943822	12.0	8.8	2.6	0.83	9.2	21.3	0.000	0.109	0.021	0.116					
626035	84.8	20.0	213.0	1.47	16.8	251.3	0.647	0.031	0.000	0.010	0.143	0.084	0.041	0.053	0
210997	34.3	30.9	46.2	4.57	53.3	135.0	0.236	0.064	0.003	0.049	0.156	0.268	0.031	0.093	0.086
507406	48.8	17.4	66.7	3.34	49.4	136.9	0.394	0.233	0.033	0.213	0.162	0.315	0.053	0.087	0.102
023290	7.8	13.8	2.5	0.83	14.6	31.7	0.012	0.335	0.030	0.240					
359358	19.3	14.0	7.0	1.10	14.3	36.4	0.005	0.377	0.077	0.355					
955326	15.6	14.3	6.1	0.88	17.8	39.0	0.009	0.555	0.120	0.522	0.031	0.189	0.020	0.022	0.066
012525	27.4	10.5	9.6	1.21	13.7	35.1	0.023	0.772	0.198	0.804	0.030	0.175	0.001	0.001	0.027
852018	32.2	15.0	16.8	1.10	19.2	52.1	0.040	0.031	0.001	0.030	0.056	0.200	0.009	0.022	0.054
806596	42.4	20.6	25.5	1.02	13.0	60.2	0.112	0.059	0.000	0.020					
801720	39.7	3.8	11.3	0.93	12.4	28.5	0.145	0.203	0.047	0.220					
752510	80.9	20.1	227.3	4.06	29.6	281.1	0.875	0.024	0.000	0.012	0.280	0.069	0.121	0.205	0.049
714435	74.8	4.3	76.4	1.38	20.1	102.2	0.173	0.227	0.065	0.202	0.016	0.095	0.034	0.003	0.017
168429	26.9	20.5	14.4	1.27	17.4	53.6	0.146	0.375	0.031	0.248	0.038	0.199	0.026	0.013	0.025
794845	33.0	24.5	21.5	2.09	17.0	65.1	0.184	0.276	0.017	0.140					
437380	27.3	3.8	7.2	1.65	13.7	26.3	0.048	0.575	0.221	0.637	0.046	0.182	0.016	0.007	0.066
200959	28.6	7.3	9.6	1.60	15.0	33.4	0.063	0.586	0.161	0.637	0.028	0.171	0.057	0.038	0.092
482044	76.4	25.7	166.6	2.99	22.7	218.0	0.775	0.024	0.000	0.000	0.257	0.041	0.092	0.171	0.017
396560	72.2	21.7	119.3	2.60	21.6	165.2	0.971	0.039	0.000	0.006	0.317	0.091	0.128	0.211	0.036
012526	32.1	7.5	10.0	1.10	12.4	31.0	0.013	0.566	0.191	0.654					
180100	23.5	14.3	21.5	4.57	51.4	91.8	0.204	0.450	0.113	0.332					
669995	31.0	44.5	45.0	4.86	50.5	144.8	0.469	0.995	0.153	0.396	0.116	0.378	0.305	0.051	0.138
488963	20.8	19.6	10.9	1.31	20.7	52.5	0.054	0.340	0.039	0.244	0.031	0.167	0.017	0.001	0.030
648327	10.1	36.9	6.1	1.16	16.5	60.6	0.000	0.128	0.002	0.085					
725180	12.9	38.8	8.7	1.19	18.8	67.5	0.000	0.114	0.003	0.061					
761330	9.2	33.8	6.5	1.77	28.5	70.6	0.000	0.102	0.007	0.072	0.069	0.295	0.019	0.045	0.159
864441	25.9	11.3	8.0	0.50	11.2	30.9	0.054	0.336	0.081	0.343					
852019	25.9	34.5	28.6	3.04	44.1	110.2	0.165	0.130	0.007	0.092	0.139	0.337	0.027	0.068	0.092
887459	12.6	78.8	16.7	2.60	35.1	133.3	0.023	0.053	0.000	0.022	0.209	0.391	0	0.139	0.223
888257	23.8	26.0	16.4	2.20	24.3	69.0	0.050	0.546	0.077	0.431					
958943	8.4	82.5	12.4	2.85	50.3	148.0	0.000	0.151	0.004	0.106	0.086	0.352	0	0.035	0.137
106256	25.7	15.2	13.5	1.04	22.9	52.6	0.046	0.586	0.133	0.551	0.045	0.222	0.013	0.019	0.024
482178	17.0	26.6	9.0	1.10	16.3	53.0	0.159	0.769	0.119	0.633					
547515	30.1	24.3	19.4	1.12	19.4	64.2	0.299	0.672	0.034	0.356					
638331	21.2	33.2	49.9	15.95	135.8	234.8	0.338	0.306	0.080	0.230					
258372	28.2	5.5	10.5	0.92	20.3	37.3	0.041	0.907	0.444	1.147	0.047	0.196	0.024	0	0.047

539470	66.6	23.8	98.8	2.33	23.4	148.4	1.519	0.577	0.052	0.288	0.217	0.277	0.201	0.188	0.148
612193	20.9	31.3	19.6	3.00	39.7	93.6	0.139	0.662	0.110	0.507	0.078	0.325	0.060	0.024	0.091
002730	29.2	8.9	13.1	1.06	21.8	44.8	0.105	1.082	0.518	1.356	0.056	0.233	0.107	0	0.140
028441	25.7	50.0	41.3	7.43	61.9	160.6	0.122	0.305	0.052	0.246	0.133	0.350	0.019	0.057	0.038
028455	18.2	18.8	8.4	1.38	17.6	46.1	0.022	0.776	0.134	0.653	0.050	0.209	0.013	0.007	0.041
634192	15.6	97.5	29.4	4.46	57.5	188.8	0.000	0.575	0.051	0.381	0.163	0.422	0	0.019	0.187
818236	33.7	16.9	22.2	2.20	24.5	65.9	0.293	0.741	0.128	0.621	0.072	0.291	0.099	0.046	0.103
597228	22.8	11.8	8.6	1.38	15.7	37.4	0.049	0.523	0.119	0.507	0.043	0.177	0.043	0	0.058
112169	22.1	30.5	19.6	1.38	37.1	88.6	0.000	0.797	0.198	0.796	0.049	0.271	0.065	0.060	0.136
940848	29.7	8.3	7.2	0.55	8.1	24.1	0.007	0.420	0.085	0.393					
369334	8.5	69.0	11.9	3.51	54.5	138.9	0.000	0.105	0.003	0.070	0.090	0.337	0.037	0.061	0.191
437378	10.9	73.0	13.6	2.37	35.3	124.3	0.000	0.013	0.000	0.008	0.082	0.260	0.012	0.055	0.063
870322	9.6	52.0	8.2	1.71	23.4	85.3	0.000	0.053	0.002	0.031					
636987	9.8	35.0	6.0	1.56	18.5	61.0	0.000	0.024	0.000	0.011					
941794	12.0	41.0	7.8	1.10	14.8	64.7	0.000	0.045	0.000	0.018					
941802	11.4	58.3	11.5	2.09	29.5	101.4	0.000	0.014	0.000	0.006	0.111	0.208	0.009	0.068	0.073
941805	13.4	79.5	17.2	2.81	28.2	127.6	0.046	0.035	0.000	0.013	0.245	0.308	0.041	0.175	0.200
961783	11.5	31.3	6.3	0.94	16.3	54.8	0.004	0.096	0.000	0.057					
653150	8.5	45.2	7.5	2.64	32.4	87.7	0.004	0.032	0.000	0.017					
742012	9.1	18.8	2.9	0.39	9.9	31.9	0.003	0.002	0.000	0.002					
720976	79.9	11.6	188.0	4.40	31.3	235.3	0.674	0.010	0.000	0.004					
067177	65.9	2.3	46.2	1.80	19.8	70.1	1.432	0.062	0.000	0.000					
224790	39.3	19.0	30.3	1.67	26.2	77.1	0.221	0.054	0.000	0.034					
224791	79.0	2.5	66.8	1.55	13.7	84.5	1.783	0.066	0.000	0.043					
283281	68.8	7.0	42.4	1.12	11.2	61.7	0.611	0.014	0.000	0.009					
537675	64.7	26.4	101.4	2.51	26.4	156.6	0.509	0.012	0.000	0.000	0.186	0.102	0.035	0.120	0.043
544792	71.8	9.6	60.5	1.52	12.6	84.1	0.890	0.032	0.000	0.017					
194938	55.4	4.1	33.2	2.86	19.8	60.0	1.403	0.175	0.006	0.074					
099984	65.2	2.6	41.8	2.53	17.2	64.1	1.328	0.076	0.000	0.031	0.013	0.111	0.182	0.013	0.084
660864	67.3	19.1	119.3	3.37	35.5	177.2	0.613	0.054	0.000	0.027	0.230	0.178	0.066	0.144	0.024
665973	66.1	9.4	98.9	3.11	38.2	149.6	0.386	0.046	0.000	0.044	0.109	0.121	0.081	0.077	0.067
396199	64.5	2.2	35.0	1.55	15.6	54.4	0.815	0.124	0.007	0.083					
444171	60.5	27.3	131.5	5.54	52.9	217.2	0.417	0.017	0.000	0.000	0.198	0.060	0.062	0.125	0.026
444176	57.3	23.3	58.6	1.78	18.7	102.4	0.279	0.048	0.000	0.019	0.157	0.122	0.047	0.107	0.036
444201	71.9	18.5	155.5	3.67	38.6	216.3	0.872	0.054	0.000	0.019	0.315	0.214	0.111	0.198	0.034
214026	48.2	11.3	35.8	2.97	24.2	74.2	0.365	0.111	0.015	0.065					
754667	32.4	23.3	21.2	2.09	18.8	65.3	0.382	0.371	0.011	0.169					
547284	61.0	14.5	35.0	1.16	6.8	57.3	0.676	0.079	0.000	0.017					
581359	41.7	29.0	48.3	3.03	35.5	115.8	0.379	0.098	0.000	0.058	0.216	0.234	0.079	0.145	0.098
035257	51.5	18.3	48.9	1.82	26.0	95.0	0.324	0.048	0.000	0.029					
909735	42.9	3.7	13.9	1.27	13.5	32.4	0.258	0.241	0.042	0.212	0.023	0.101	0.057	0.001	0.041
275200	38.9	6.3	12.6	0.99	12.6	32.5	0.213	0.095	0.013	0.065					
287182	39.9	0.0	23.0	4.29	30.4	57.6	0.558	0.059	0.000	0.035	0.074	0.268	0.102	0.001	0.022
290482	76.5	6.4	94.2	1.72	20.9	123.2	0.389	0.019	0.000	0.009	0.141	0.158	0.031	0.079	0.001
290488	40.4	21.6	50.2	3.49	48.9	124.1	0.284	0.055	0.012	0.055	0.200	0.301	0.065	0.116	0.116
448936	81.5	17.5	280.5	4.10	42.1	344.2	1.610	0.031	0.000	0.008	0.298	0.037	0.117	0.209	0.031
648730	83.6	16.8	100.4	1.05	1.8	120.1	2.377	0.013	0.000	0.000	0.007	0.069	0.289	0.018	0.031
995708	60.0	5.5	57.8	4.57	28.5	96.3	1.230	0.059	0.000	0.021					
001392	48.4	0.0	17.6	1.60	17.2	36.4	0.349	0.059	0.002	0.019	0.012	0.163	0.017	0	0.019
331293	53.9	20.7	71.7	3.54	37.1	133.1	0.474	0.059	0.000	0.031	0.136	0.204	0.044	0.113	0.227

817225	54.0	18.8	52.1	2.02	23.6	96.5	0.358	0.007	0.000	0.002					
244878	69.8	20.1	115.3	3.01	26.7	165.1	0.538	0.030	0.000	0.009	0.194	0.073	0.091	0.157	0.058
829325	75.6	23.2	162.7	2.51	26.9	215.3	0.590	0.017	0.000	0.006	0.253	0.115	0.078	0.176	0.046
744446	69.8	26.6	123.5	2.62	24.2	176.9	0.884	0.068	0.000	0.030	0.331	0.140	0.167	0.279	0.160
566076	72.3	14.3	139.9	3.40	35.9	193.5	0.601	0.007	0.000	0.005					
566118	72.4	17.8	232.9	8.17	62.8	321.6	0.959	0.004	0.000	0.002					
566139	84.4	28.5	162.2	1.40	0.0	192.1	0.815	0.018	0.000	0.001					
741542	66.8	5.7	34.4	1.52	9.9	51.5	1.478	0.064	0.008	0.028					
119492	83.9	41.2	223.2	1.76	0.0	266.1	0.699	0.009	0.000	0.002					
482178	28.5	14.3	13.2	1.54	17.4	46.4	0.158	0.780	0.123	0.659					
974426	72.8	14.3	58.3	1.54	6.0	80.2	1.080	0.065	0.000	0.000					
668125	67.8	30.6	120.7	3.52	23.2	178.0	0.947	0.023	0.000	0.000					
940817	86.2	0.0	73.1	1.65	10.1	84.8	1.276	0.027	0.000	0.008					
941063	84.2	3.9	197.8	3.16	30.0	234.8	0.711	0.005	0.000	0.001					
941328	73.2	22.7	125.8	2.43	20.9	171.9	0.665	0.018	0.000	0.003					
916919	73.8	21.7	180.5	3.52	38.8	244.5	0.625	0.054	0.000	0.023					
946826	62.4	22.8	102.6	2.77	36.2	164.4	0.492	0.091	0.006	0.068					
954052	47.6	52.2	83.1	3.80	35.7	174.7	1.120	0.364	0.000	0.096					
954067	50.5	34.1	91.1	4.10	51.2	180.6	0.546	0.128	0.008	0.092					
992045	54.4	9.8	41.0	3.19	21.4	75.4	0.480	0.055	0.002	0.033					
007388	42.9	71.5	75.0	2.68	25.6	174.9	0.185	0.033	0.000	0.000	0.343	0.118	0.038	0.234	0.065
007393	34.5	35.5	39.6	3.85	35.9	114.7	0.432	0.085	0.005	0.046	0.287	0.318	0.111	0.198	0.119
029732	76.7	0.0	233.3	4.38	66.4	304.1	0.832	0.221	0.111	0.247	0.031	0.111	0.013	0	0.019
862154	70.9	25.0	173.3	4.69	41.5	244.5	0.717	0.032	0.000	0.008	0.235	0.069	0.077	0.137	0.016
932303	58.4	38.4	105.6	4.29	32.4	180.7	0.965	0.046	0.000	0.021	0.421	0.200	0.126	0.266	0.042
935246	58.0	4.4	33.1	2.31	17.2	57.1	0.682	0.077	0.000	0.038					
568883	78.1	24.6	177.3	2.64	22.5	227.0	0.623	0.040	0.000	0.011	0.248	0.045	0.087	0.169	0.022
568904	73.6	17.8	118.2	2.69	22.0	160.7	0.472	0.005	0.000	0.002	0.099	0.049	0.024	0.062	0.005
632367	74.7	16.9	225.2	5.13	54.4	301.6	0.642	0.019	0.000	0.003	0.249	0.042	0.105	0.184	0.034
761265	70.9	5.4	74.3	2.59	22.5	104.8	0.740	0.417	0.088	0.370	0.015	0.128	0.148	0.031	0.039
818236	33.9	19.3	22.4	2.20	22.1	66.0	0.291	0.740	0.129	0.638					
083719	48.3	11.3	27.8	2.04	16.5	57.5	0.535	0.028	0.000	0.015					
000198	10.9	11.5	2.0	0.12	4.9	18.6	0.000	0.000	0.000	0.000					
009063	10.6	36.5	6.3	1.05	15.9	59.8	0.000	0.054	0.003	0.017					
011290	14.0	70.8	16.2	2.37	26.7	116.1	0.022	0.039	0.000	0.013	0.241	0.358	0.004	0.170	0.179
027762	5.2	7.5	0.5	0.22	0.9	9.1	0.000	0.000	0.000	0.000					
027763	15.1	94.8	23.0	3.19	31.1	152.1	0.025	0.021	0.005	0.003	0.242	0.307	0.008	0.158	0.167
036542	8.5	13.8	2.8	1.05	14.6	32.2	0.010	0.075	0.000	0.075					
037162	18.7	57.1	17.9	1.76	18.7	95.4	0.015	0.009	0.006	0.003					
042869	14.4	24.5	5.3	0.33	6.6	36.7	0.000	0.003	0.007	0.004					
050156	17.8	22.5	6.9	0.55	9.0	38.9	0.009	0.035	0.004	0.013					
059052	11.9	20.8	3.7	0.28	6.0	30.8	0.000	0.009	0.000	0.001					
061832	9.7	31.3	5.6	1.71	19.6	58.2	0.000	0.065	0.001	0.052					
061921	18.8	78.4	25.0	2.26	27.1	132.8	0.012	0.033	0.003	0.003	0.243	0.191	0.019	0.176	0.107
075105	10.0	33.8	5.7	1.16	16.1	56.7	0.000	0.038	0.006	0.024					
106883	6.6	15.3	1.9	0.55	11.5	29.3	0.000	0.000	0.004	0.003					
134661	3.8	35.0	1.6	0.55	3.8	40.9	0.000	0.006	0.002	0.002					
209050	9.5	26.3	4.5	1.38	15.7	47.9	0.000	0.032	0.000	0.018					
293760	22.0	57.2	21.4	1.36	17.4	97.3	0.000	0.032	0.006	0.010					
296297	15.3	16.1	4.2	0.39	7.0	27.7	0.000	0.028	0.000	0.012					

300321	1.7	15.7	0.4	0.00	9.3	25.4	0.000	0.013	0.000	0.001						
322563	8.4	43.5	6.1	1.38	21.0	72.0	0.000	0.033	0.007	0.016						
324223	5.3	20.5	2.4	2.59	20.3	45.8	0.000	0.030	0.004	0.023						
327579	0.0	9.5	0.0	0.00	6.2	15.7	0.000	0.016	0.005	0.007						
369044	18.7	85.3	26.2	2.26	26.2	139.9	0.000	0.024	0.008	0.003	0.254	0.218	0.013	0.160	0.094	
377658	6.7	17.8	1.8	0.35	7.5	27.4	0.000	0.003	0.009	0.002						
390416	9.6	34.5	5.7	1.21	18.1	59.5	0.000	0.003	0.008	0.003						
397877	7.0	40.4	5.9	3.36	35.1	84.8	0.000	0.026	0.007	0.017						
402295	4.2	16.5	0.9	0.22	3.8	21.5	0.000	0.000	0.000	0.000						
436060	0.8	17.9	0.2	0.08	8.1	26.2	0.000	0.004	0.008	0.007						
462372	9.3	63.4	10.0	2.92	30.9	107.2	0.005	0.024	0.006	0.010	0.129	0.386	0.030	0.099	0.237	
471606	0.0	5.8	0.0	0.00	4.0	9.8	0.000	0.000	0.000	0.000						
484804	13.5	73.8	16.5	2.05	30.0	122.4	0.000	0.088	0.007	0.034	0.171	0.247	0.013	0.117	0.121	
501656	1.0	16.8	0.2	0.28	4.6	21.8	0.000	0.000	0.000	0.000						
580998	19.9	38.5	14.4	1.05	18.7	72.6	0.050	0.015	0.007	0.002						
659786	21.4	99.6	33.5	2.64	20.5	156.2	0.050	0.019	0.007	0.001	0.382	0.215	0.021	0.268	0.118	
700411	15.3	63.8	15.6	1.82	21.2	102.4	0.000	0.014	0.006	0.003	0.092	0.130	0	0.065	0.061	
718316	6.1	13.0	1.0	0.15	2.6	16.7	0.000	0.000	0.000	0.000						
718753	7.3	43.3	6.3	3.36	33.5	86.4	0.000	0.027	0.007	0.023						
748824	12.3	55.8	11.5	1.87	24.7	93.8	0.000	0.010	0.002	0.010						
749141	13.3	53.8	12.0	1.98	22.5	90.2	0.001	0.032	0.007	0.015						
770419	10.0	60.3	9.8	2.59	25.1	97.7	0.000	0.010	0.000	0.008						
770421	9.1	48.0	7.7	2.64	26.2	84.5	0.000	0.037	0.005	0.020						
782182	9.4	43.0	7.5	2.09	26.9	79.5	0.000	0.056	0.033	0.005						
852149	18.3	105.8	30.6	2.92	28.0	167.3	0.029	0.039	0.000	0.008	0.318	0.318	0.030	0.235	0.175	
875409	73.3	5.1	192.9	5.45	59.7	263.1	1.152	0.060	0.005	0.039	0.024	0.187	0.174	0.019	0.020	
902805	1.4	11.0	0.2	0.00	1.5	12.6	0.000	0.000	0.008	0.006						
911836	13.3	60.0	13.4	1.77	25.1	100.2	0.005	0.027	0.008	0.005	0.121	0.223	0.006	0.091	0.095	
939411	6.4	15.6	1.6	0.25	7.5	25.0	0.000	0.026	0.006	0.015						
980672	11.5	54.5	11.3	2.09	30.2	98.1	0.000	0.012	0.004	0.004						
994753	11.2	35.9	6.7	1.01	16.3	59.9	0.000	0.044	0.005	0.020						
763528	26.0	23.3	16.7	2.08	22.1	64.2	0.045	0.826	0.157	0.723	0.007	0.033	0.005	0.005	0.012	
<b>Average</b>	<b>35.0</b>	<b>27.9</b>	<b>46.6</b>	<b>2.2</b>	<b>24.4</b>	<b>101.1</b>	<b>0.313</b>	<b>0.189</b>	<b>0.035</b>	<b>0.151</b>	<b>0.140</b>	<b>0.209</b>	<b>0.059</b>	<b>0.089</b>	<b>0.083</b>	

The C-, A-, X-, and Y-center content was calculated using the excel spreadsheet *Caxbd\_Inherit\_2024\_lb* from ref. [1]. The absorption coefficients (cm<sup>-1</sup>) for all discrete peaks were calculated using the automated baseline and normalization routine from the *DiaMap* Excel spreadsheet.

The normalized intensity of the 1353, 1358, 1363, 1374, and 1387 cm<sup>-1</sup> peaks could not be determined for all samples as such peaks could not be reliably differentiated from noise due to atmospheric H<sub>2</sub>O in some samples.

#### References:

[1] Day, M. C. *et al.* Infrared spectroscopy of natural *Type Ib + IaA* diamond: insights into the formation of Y-centers and the early aggregation of nitrogen. *Am. Min.* (Accepted, in-press), <https://doi.org/10.2138/am-2024-9722>.

**Table A.2.** Selected data from FTIR spectra recorded from sample Z-16.

Zone	%IaA	N <sub>c</sub> (at.ppm)	N <sub>A</sub> (at.ppm)	N <sub>X</sub> (at.ppm)	N <sub>Y</sub> (at.ppm)	N <sub>tot</sub> (at.ppm)	3107 (cm <sup>-1</sup> )	3343 (cm <sup>-1</sup> )	3372 (cm <sup>-1</sup> )	3394 (cm <sup>-1</sup> )	1353 (cm <sup>-1</sup> )	1358 (cm <sup>-1</sup> )	1363 (cm <sup>-1</sup> )	1374 (cm <sup>-1</sup> )	1387 (cm <sup>-1</sup> )
colorless	25.2	2.0	3.1	0.1	7.1	12.3	0	0	0	0	0.0309	0.0333	0	0	0
colorless	34.9	0.9	4.7	0.1	7.8	13.5	0	0	0	0	0.0273	0.0275	0	0	0
colorless	19.8	2.7	1.9	0.1	4.9	9.6	0	0	0	0	0.0119	0.0385	0	0	0
colorless	20.2	2.5	2.0	0.1	5.3	9.9	0	0	0	0	0.0167	0.0376	0	0	0
colorless	25.0	2.2	3.0	0.1	6.8	12.1	0	0	0	0	0.0132	0.0344	0	0	0
colorless	25.9	2.3	4.4	0.1	10.1	16.9	0	0	0	0	0.0179	0.0440	0	0	0
<b>avg.</b>	<b>25.2</b>	<b>2.1</b>	<b>3.2</b>	<b>0.1</b>	<b>7.0</b>	<b>12.4</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0.0197</b>	<b>0.0359</b>	<b>0</b>	<b>0</b>	<b>0</b>
yellow	21.0	9.6	6.8	0.6	15.3	32.2	0.0010	0.0029	0.0005	0.0014	0.0216	0.0609	0	0.0148	0.0164
yellow	29.5	8.8	9.6	0.7	13.5	32.6	0.0019	0.0021	0.0004	0.0013	0.0140	0.0494	0	0.0147	0.0151
yellow	18.0	9.0	6.2	0.6	18.9	34.7	0.0006	0.0017	0.0005	0.0012	0.0221	0.0821	0	0.0124	0.0188
yellow	23.3	10.2	9.8	0.7	21.4	42.1	0.0015	0.0019	0	0.0011	0.0354	0.0903	0	0.0181	0.0277
<b>avg.</b>	<b>22.9</b>	<b>9.4</b>	<b>8.1</b>	<b>0.7</b>	<b>17.3</b>	<b>35.4</b>	<b>0.0013</b>	<b>0.0022</b>	<b>0.0004</b>	<b>0.0013</b>	<b>0.0233</b>	<b>0.0707</b>	<b>0</b>	<b>0.0150</b>	<b>0.0195</b>

The C-, A-, X-, and Y-center content was calculated using the excel spreadsheet *Caxbd\_Inherit\_2024\_Ib* from ref [1]. The absorption coefficients (cm<sup>-1</sup>) for H-related peaks were calculated using the automated baseline and normalization routine from the *DiaMap* Excel spreadsheet.

**References:**

[1] Day, M. C. *et al.* Infrared spectroscopy of natural *Type Ib + IaA* diamond: insights into the formation of Y-centers and the early aggregation of nitrogen. *Am. Min.* (Accepted, in-press), <https://doi.org/10.2138/am-2024-9722> .

**Table A.3.** Data from PL spectra recorded from colorless and yellow H-bearing zones in sample Z-16.

Peak (nm)	Intensity		Possible Defects	$\lambda$ (nm)	Sample	Ref.
	colorless zone	yellow zone				
470.2	0.16	-	$(C_2)_i^{+/-} / (N-C)_i^+ / (V_2Ni)N_3^{0/+}$	457	ird/HT / ND	1
488.8	0.22	-	$V_2N_4^0 / (V_2Ni)N_3 / VSi^- / (C_2)_iN_2^+ / (V_3Ni_2)^+$	457	ird/HT / ND	1
489.6	-	0.18	$(C_2)_iN_2^+ / VNi_2^- / B/Al$ -related	457	ird/HT/ syn/ ND	1
489.8	0.29	-	$VNi_2^-$	457	HT / ND	1
490.2	-	0.16	$VNi_2^- / VN_3^- / B/Al$ -related	457	HT/ syn/ ND	1
<b>503.2</b>	0.53	0.26	$VN_2^0 / NV^0 / VN^{2+} / (C_2)_i^{+/-} / (C_2)_iN_2^-$	457	ird/HT / ND	1, 2
510.8	0.26	-	$VNi_2^0 / VN^0 / (C_2)_i^-$	457	Ird/HT / ND	1
511.7	6.64	0.95	-	457	ND	1
520.1	0.99	0.59	$V_3Ni_2^+ / NV^0 / VN_3^- / Ni$ -related	457	ird/HT/ syn/ ND	1
523.7	0.25	0.25	Si-related / $VNi_3^{0/+} / (C_2)_iN_2^-$	457	ird/HT/ syn/ ND	1
524.8	0.49	0.26	$VSi^0 / (C_2)_i^-$	457	ird/HT / ND- <i>lb</i>	1
525.3	0.31	0.49	$(C_2)_i^- / Cr-Fe-Ni-Cu$ -related / $VSi^0$	457	ird/ syn/ ND	1
<b>575.0</b>	2.32	3.59	$NV^0$	457	ND/ syn	1, 3
624.5	0.11	0.27	Ni-related	457	HT/ syn	1
635.1	-	0.45	<i>H-related?</i>	457	ND- <i>lb</i>	-
635.4	0.05	0.61	$N^+ / N^+ + B^0 / (C_2)_i^0 / VN_3^0 / V_3Si_2^0$	457	ird/ ND	1, 4
<b>637.1</b>	0.14	0.37	$NV^- / VNi_2^-$	457	HT/ ND	1, 5
648.2	0.06	0.33	$N^+ + B^0 / N^{2+} + B^0$	457	ird/ ND	1
671.5	-	0.40	<i>H-related?</i>	457	ND- <i>lb</i>	-
685.1	-	0.27	$V^0 / NV^- / V_3Si_2^+ / Ni$ -related	457/633	ird/ syn/ ND	1
689.4	0.27	1.09	<i>Y-center</i> / $N^{2+} + B^0 / Ni$ -related	457/633	ird/HT/ syn/ ND	1, 6
698.0	0.80	0.92	$N^+ + B^0$	457/633	syn/ND	1
<b>700.0</b>	-	0.17	$V^0 / Ni$ -related	457	ird/HT/ ND	1
701.9	0.13	-	$NV^- / VNi^+ / N^+ + B^0$	633	ird/HT ND- <i>lb</i>	1
703.7	-	0.17	<i>H-related?</i>	633	ND- <i>lb</i>	-
705.6	-	0.18	<i>H-related?</i>	633	ND- <i>lb</i>	-
709.4	0.10	-	-	457	ND- <i>lb</i>	-
740.2	0.29	-	-	633	ND- <i>lb</i>	-
742.1	9.91	4.71	$V^0 / VCr^0$	633	ird/HT/ syn/ ND	1
749.7	0.28	0.34	Ni-related	633	ND	3
761.6	0.14	0.24	$VNi^0$	633	syn/ ND	1
869.2	-	0.19	Ni-related	830	ND- <i>lb</i>	1, 7
874.9	0.20	-	<i>Y-center</i>	830	ND- <i>lb</i>	7
900.1	0.07	0.47	<i>Y-center</i>	830	ND- <i>lb</i>	7
902.6	2.13	-	$VN_2^-$	830	HT/ ND	1
904.3	0.73	1.32	$V_2Ni^+$	830	HT/syn	1
919.0	0.97	-	-	830	-	-
953.4	0.11	0.08	-	830	-	-
991.5	-	0.07	-	830	-	-

All PL spectra were recorded from a single polished plate (sample Z-16) of uniform thickness and thus were not Raman normalized. PL peak intensities are reported as raw counts/ $1 \times 10^4$ . Raman diamond bands at 486, 691 and 933 nm for 457, 633 and 830 nm excitation wavelengths, respectively, were not included.

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Defects with assigned lines within  $\pm 0.1$  nm of the corresponding peak position are shown in bold, other peaks are listed if assigned lines are within  $\pm 0.5$  nm of the corresponding peak position. Abbreviations: ird (irradiated); HT (heat treated); syn (synthetic); ND (natural diamond). Broad peaks (unknown vibronic structure) are not indicated here.

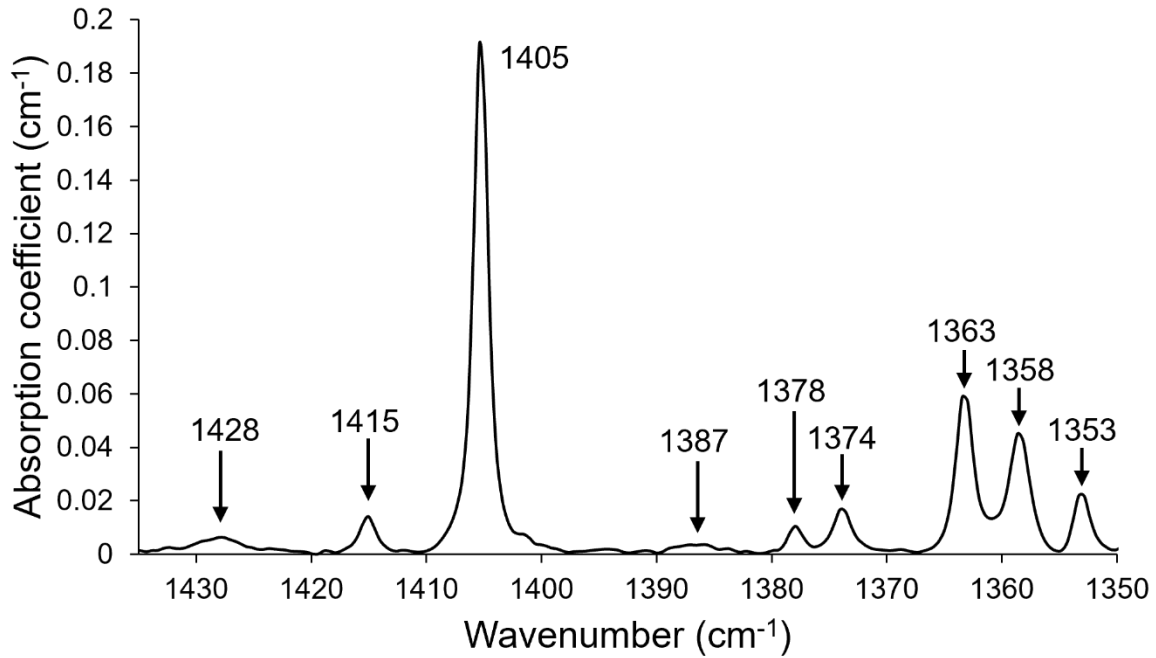
**References:**

- [1] Dischler, B. Handbook of Spectral Lines in Diamond. (2012).
- [2] Fritsch, E. & Delaunay, A. What Truly Characterises a Chameleon Diamond? An Example of an Atypical 25.85 ct Stone. *The Journal of Gemmology* **36**, 142–151 (2018).
- [3] Kazuchits, V. N. *et al.* Rapid HPHT annealing of synthetic IB-TYPE diamonds. *Carbon* **174**, 180–189 (2021).
- [4] Kupriyanov, I. N. *et al.* Effect of HPHT Treatment on Spectroscopic Features of Natural Type Ib-IaA Diamonds Containing Y Centers. *Crystals* **10**, 378 (2020).
- [5] Smit, K. V. *et al.* Deformation-related spectroscopic features in natural Type Ib-IaA diamonds from Zimmi (West African craton). *Mineral Petrol* **112**, 243–257 (2018).
- [6] Vasilev, E. *et al.* Point defects in coated diamonds. *Diam Relat Mater* **148**, 111519 (2024).
- [7] Vasilev, E. *et al.* The enigma of cuboid diamonds: the causes of inverse distribution of optical centers within the growth zones. *Journal of Geosciences* **65**, 59–70 (2020).
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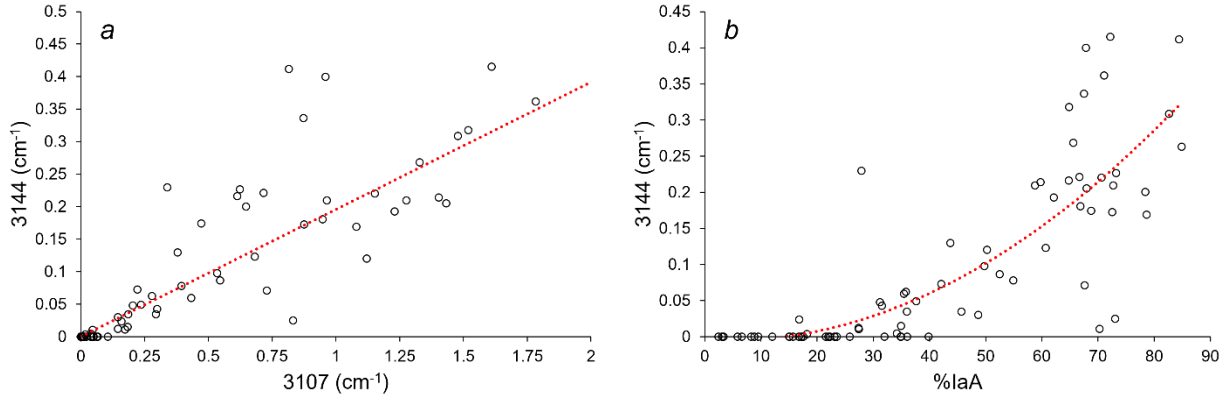
## **Appendix B**

Data from FTIR spectra recorded from *Type Ib + IaA* diamonds

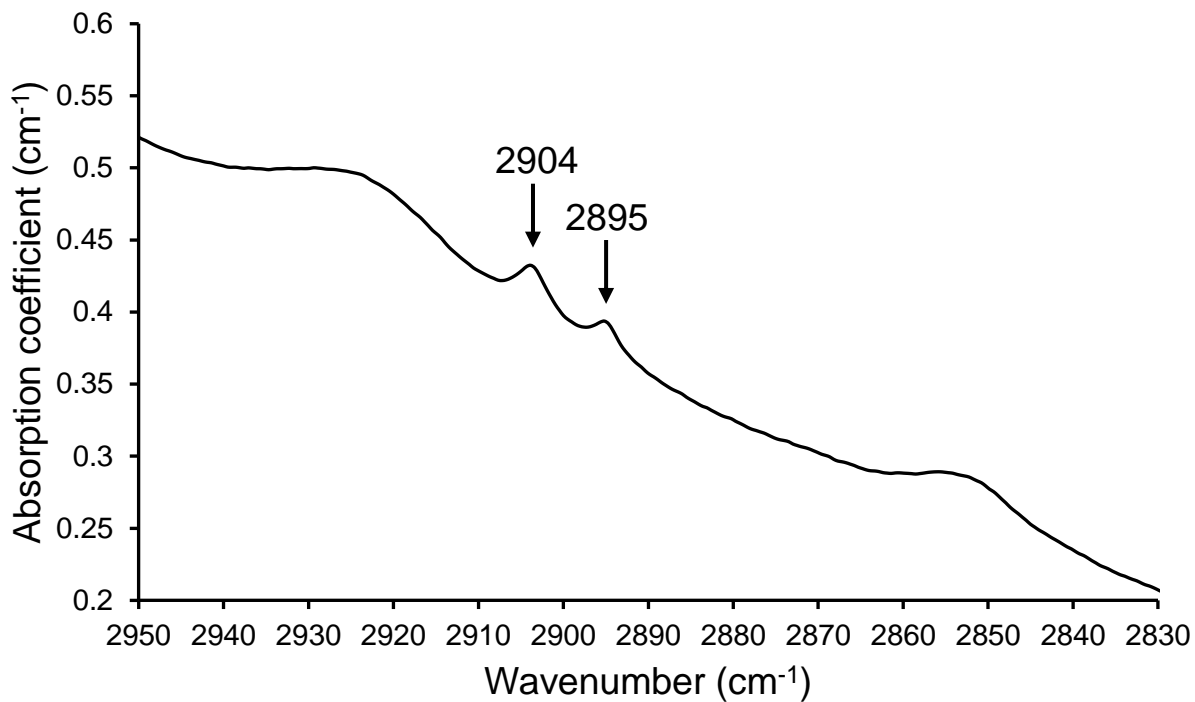
**Figures B.1 – B.3**



**Fig. B.1.** Peaks observed in the one-phonon region (1450-1350 cm<sup>-1</sup>) of the FTIR spectra recorded from one *Type Ib + IaA* spectrum. Peaks from 1353 to 1387 cm<sup>-1</sup> are attributed to (self-)interstitial complexes, 1405 cm<sup>-1</sup> is the C-H bending mode of the VN<sub>3</sub>H<sup>0</sup> defect, and the 1415 and 1428 cm<sup>-1</sup> peaks may be C-H bending modes of the NH<sup>0</sup> and N<sub>2</sub>H<sup>0</sup> defects.



**Fig. B.2.** (a) The normalized 3144 cm<sup>-1</sup> peak intensity plotted as a function of the normalized 3107 cm<sup>-1</sup> peak intensity. (b) The normalized 3144 cm<sup>-1</sup> peak intensity plotted as a function of %laA.



**Fig. B.3.** Peaks observed at 2904 and 2895 cm<sup>-1</sup> in the FTIR spectra recorded from one *Type /b + /aA* spectrum. These peaks likely represent overtone bands that involve the  $\nu_B$  ( $2 \times \nu_B$ ) of NH<sup>0</sup> and/or N<sub>2</sub>H<sup>0</sup> (see Table 3). Broad peaks at ~2920 and ~2850 cm<sup>-1</sup> are due to a hydrocarbon contaminant such as glue or grease.

## Appendix C

C-H stretching frequencies from *ab initio* simulations of H-related defects from selected studies

### Table C.1

**Table C.1.** C-H stretching frequencies from 3200 to 3500 cm<sup>-1</sup> for H-related defects in diamond from *ab initio* simulations of IR spectra from selected studies.

Defect	Frequency (cm <sup>-1</sup> )	Mode (x)	H/Ah	Intensity (km/mol)	S	Functional	Cell	Basis set	Comment	Ref.
VNH <sub>2</sub> <sup>+</sup>	3200	C-H <sub>asy</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sup>+</sup>	3210	C-H <sub>s</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	2
VN <sub>2</sub> H	3213	C-H <sub>s</sub> (a)	H	122 (20%)	1/2	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
VN <sub>4</sub> H	3221 3095	C-H <sub>s</sub>	H			LDA***	68	Planewave	Model 1 position MP 6x6x2 mesh	4
VNH	3224	C-H <sub>s</sub> (a)	H	129 (21%)	0	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
VNH <sub>2</sub> <sup>0</sup>	3230	C-H <sub>asy</sub>	H		1/2	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH	3231	C-H <sub>s</sub>	H		1/2	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G <sup>(*)</sup> (H) Γ point sampling	5
VN <sub>3</sub> H	3249	C-H <sub>s</sub>	H	50 (100%)		B3LYP**	32	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	6
VN <sub>3</sub> H	3250	C-H <sub>s</sub> (a)	H	621 (100%)		B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
VN <sub>3</sub> H	3250	C-H <sub>s</sub>	H	50 (100%)		B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	6
VN <sub>3</sub> H	3250	C-H <sub>s</sub>	H	619 (100%)		B3LYP**	64	Gaussian ( <i>all electron</i> )	Freq. calc. includes only defect atoms MP 4x4x4 mesh	7
VN <sub>3</sub> H	3251	C-H <sub>s</sub>	H	50 (100%)		B3LYP**	128	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	6
VH <sub>2</sub>	3253 3477	C-H <sub>asy</sub> C-H <sub>sy</sub>	Ah	29	1	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	8
VN <sub>3</sub> H	3262	C-H <sub>s</sub>	H	608 (100%)		B3LYP**	216	Gaussian ( <i>all electron</i> )	Freq. calc. includes only defect atoms MP 2x2x2 mesh	7
VN <sub>3</sub> H	3271	C-H <sub>s</sub>	H			B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G Γ point sampling	9
VH <sub>2</sub>	3275 3526	C-H <sub>asy</sub> C-H <sub>sy</sub>	H	29	1	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	8
NH	3309	C-H <sub>s</sub>	H			LDA*	64	Gaussian ( <i>atom centered</i> )	MP 2x2x2 mesh	10
VH <sup>+</sup>	3310	C-H <sub>s</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>2</sub> <sup>0</sup>	3310	C-H <sub>sy</sub>	H		1	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
NH	3318	C-H <sub>s</sub>	H			LDF*	64	Gaussian	<sup>13</sup> C-H isotopes Atom and bond centered basis sets	11
VN <sub>2</sub> H <sub>2</sub>	3320	C-H <sub>asy</sub>	H			PBE*	1000	Gaussian ( <i>atom centered</i> )	Gaussian basis set	1
NH	3324	C-H <sub>s</sub>	H			LDF*	64	Gaussian	Atom and bond centered basis sets	11

VH <sub>2</sub> <sup>-</sup>	3330	C-H <sub>sy</sub>	H		1/2	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>2</sub> <sup>0</sup>	3337 3060	C-H <sub>s</sub> C-H <sub>s</sub>	H		1	GGA*	216	Gaussian	MP 2x2x2 mesh	12
VH <sub>2</sub> <sup>-</sup>	3339 3118	C-H <sub>s</sub> C-H <sub>s</sub>	H			GGA*	216	Gaussian	MP 2x2x2 mesh	12
VH <sub>2</sub> <sup>0</sup>	3350	C-H <sub>asy</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>2</sub> <sup>0</sup>	3356 3525	C-H <sub>s</sub> C-H <sub>s</sub>	H		0	GGA*	216	Gaussian	MP 2x2x2 mesh	12
VN <sub>2</sub> H <sub>2</sub> <sup>0</sup>	3370 3540	C-H <sub>asy</sub> C-H <sub>sy</sub>	H			PBE*	1000	Gaussian ( <i>atom centered</i> )	Basis set: 8-31G (C) 4-31G (N), 3-21G (H) Γ point sampling	13
VH <sub>2</sub> <sup>+</sup>	3370	C-H <sub>sy</sub>	H		1/2	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>2</sub>	3378 3552	C-H <sub>asy</sub> C-H <sub>sy</sub>	Ah	395	0	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	8
BH	3394 3455	C-H <sub>s</sub> C-H <sub>s</sub>	Ah H			B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G Γ point sampling	9
VNH <sub>2</sub>	3402 3580	C-H <sub>asy</sub> (b) C-H <sub>sy</sub> (b)	Ah	88 (14%)	1/2	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
VNH <sub>2</sub> <sup>+</sup>	3410	C-H <sub>sy</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VNH <sub>2</sub>	3417 3615	C-H <sub>asy</sub> (b) C-H <sub>sy</sub> (b)	H	88 (14%)	1/2	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
NH	3408	C-H <sub>s</sub>	Ah			B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G Γ point sampling	9
VNH <sub>2</sub> <sup>0</sup>	3420	C-H <sub>sy</sub>	H		1/2	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>3</sub> <sup>+</sup>	3420 3450	C-H <sub>asy</sub> (b) C-H <sub>asy</sub> (b)	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>2</sub>	3426 3606	C-H <sub>asy</sub> C-H <sub>sy</sub>	H	395	0	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) Γ point sampling	8
VH	3428	C-H <sub>sy</sub>	Ah		1/2	HF**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G <sup>(t)</sup> (H) Γ point sampling	5
VH <sub>3</sub> <sup>-</sup>	3430	C-H <sub>sy</sub>	H		0	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1
VH <sub>3</sub> <sup>0</sup>	3450 3460	C-H <sub>asy</sub> (b) C-H <sub>asy</sub> (b)	H		1/2	PBE*	1000	Gaussian ( <i>atom centered</i> )	Γ point sampling	1

VN <sub>2</sub> H <sub>2</sub>	3469 3664	C-H <sub>asy</sub> (b) C-H <sub>sy</sub> (b)	H	346 (56%)	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
VN <sub>2</sub> H <sub>2</sub>	3470 3641	C-H <sub>asy</sub> (b) C-H <sub>sy</sub> (b)	Ah	346 (56%)	B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G (C/N) 6-31G (H) MP8 sampling	3
NH	3471	C-H <sub>s</sub>	H		B3LYP**	64	Gaussian ( <i>all electron</i> )	Basis set: 6-21G $\Gamma$ point sampling	9
VN <sub>2</sub> H <sub>2</sub>	3490	C-H <sub>sy</sub>	H		PBE*	1000	Gaussian ( <i>atom centered</i> )	$\Gamma$ point sampling	1

All data was adapted from Day et al., 2024, see reference 14 below.

The defect charge state  $q$  (e.g. VN<sup>0</sup>), and the harmonic (H) or anharmonic (Ah) calculated frequencies are only included if explicitly specified in the corresponding reference. Where more than one H-atom is present, both symmetric (C-H<sub>sy</sub>) and anti-symmetric (C-H<sub>asy</sub>) stretching modes are expected and reported only if explicitly specified in the corresponding reference, otherwise stretching modes are indicated as C-H<sub>s</sub>.

Calculated peak intensities are reported in km/mol. In cases where the VN<sub>3</sub>H defect is simulated, relative intensities were normalized and reported (as %) in comparison to the VN<sub>3</sub>H C-H stretching mode, which is always the most intense H-related peak observed in experiment.

Isotopes <sup>12</sup>C, <sup>1</sup>H and <sup>14</sup>N are assumed unless otherwise specified.

Total spin quantum number =  $S$ ;  $S = 0$  (singlet),  $S = 1$  (triplet),  $S = 3/2$  (quartet),  $S = 1/2$  (doublet),  $S = 2$  (quadruplet).

Monkhorst-Pack sampling scheme denoted as MP $n$ , where a mesh of  $n \times n \times n$  points ( $k$ ) is used to sample the Brillouin Zone. Point symmetry of a given defect may reduce  $k$ . **AIMPRO\*** (*ab initio* modelling PROgram), **Crystal\*\*** and **Quantum ESPRESSO\*\*\*** density-functional modelling programs indicated in **Functional** column.

Note that many bands have calculated intensities significantly less than the intensity of the 3107cm<sup>-1</sup> band and are unlikely to be observed in experimental data.

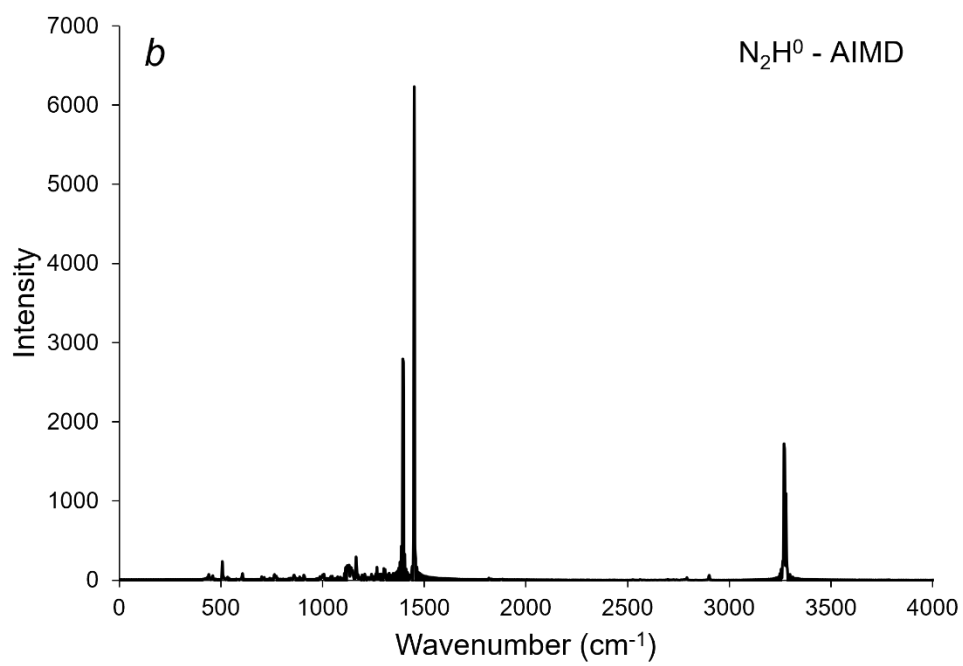
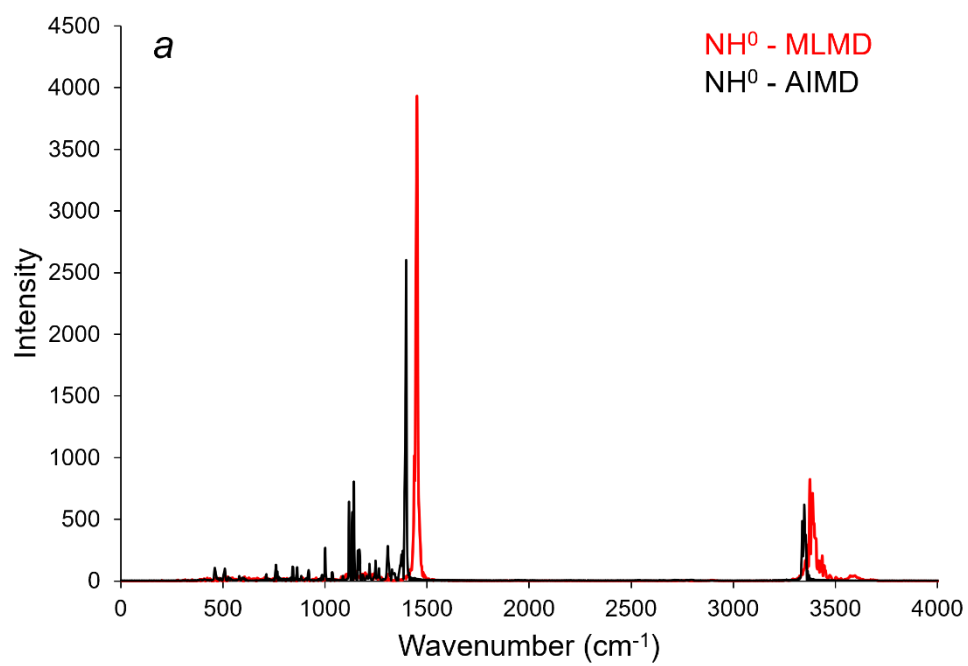
#### References:

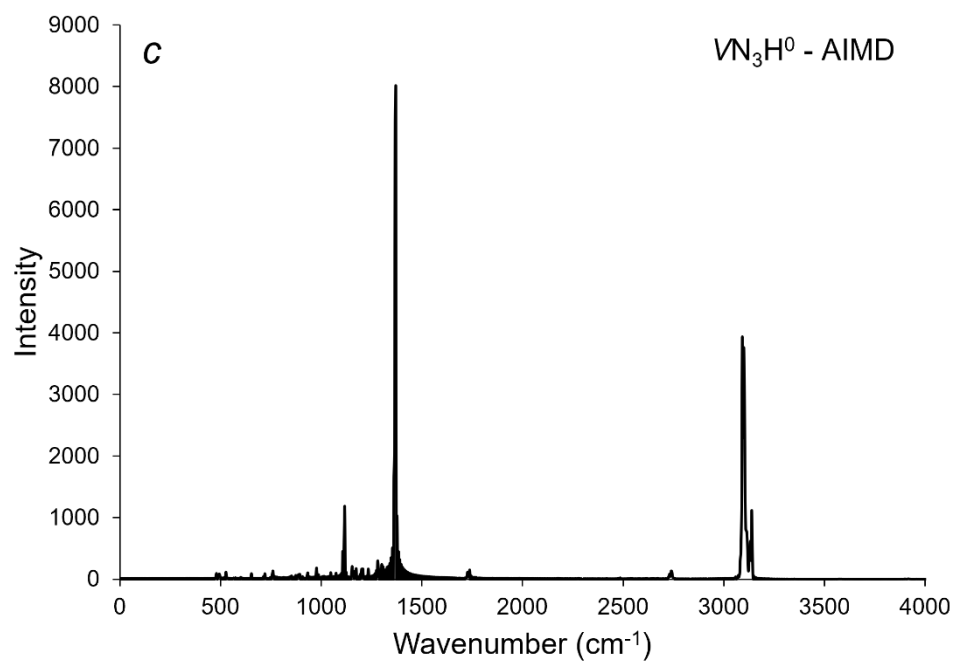
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## Appendix D

Vibrational spectra computed from MLMD simulations of  $\text{NH}^0$  and AIMD simulations of  $\text{NH}^0$ ,  $\text{N}_2\text{H}^0$  and  $\text{VN}_3\text{H}^0$

**Figure D.1**





**Fig. D.1.** The hydrogen vibrational spectrum computed from the self-correlation of the atomic velocities from (a) the MLMD (red line) and AIMD simulations of the NH<sup>0</sup> defect, (b) the AIMD simulation of the N<sub>2</sub>H<sup>0</sup> defect and (c) the AIMD simulation of the VN<sub>3</sub>H<sup>0</sup> defect.