Calculation and analysis of the harmonic vibrational frequencies in molecules at extreme pressure: methodology and diborane as a test case.

Supporting Information

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Contents

TABLE S1. Amount of the electronic charge lying outside of the cavity hosting diborane , Q_{out}(in $-e$), as a function of the cavity scaling factor f and of the pressure, p(in GPa). Results refer to the PCM/DFT/M062X/ 6-311++G(d,p) level, and for the step barrier potentials $V_0(6)$ (harder) and $V_0(3)$ (softer).

	$V_0(3)$		$V_0(6)$	
f	$p(GPa)$	$Q_{out}(-e)$	$p(GPa)$	$Q_{out}(-e)$
1.200	0.98	0.147	0.98	0.147
1.150	1.30	0.184	1.87	0.182
1.100	2.50	0.230	4.05	0.228
1.075	2.91	0.281	5.30	0.266
1.050	4.30	0.304	8.20	0.287
1.025	6.50	0.328	12.68	0.306
1.000	8.90	0.357	17.23	0.329
0.975	11.20	0.401	25.57	0.357
0.950	16.10	0.438	38.08	0.373

TABLE S2. Energy gradients $G^{\alpha}_{el-rep}(E_h a_0^{-1})$ of diborane with respect to the rBH_t and rBH_b bond leghts, and as a function of the pressure p (in GPa). Values refer to the PCM/M062X/6-311++G(d,p) level of calculation with the step barrier potential $V_0(6)$ and at the equilibrium geometry in gas phase.

$p(GPa)$	$G^{rBH_t}_{e-r}$	$G^{rBH_b}_{e-r}$
0.98	0.00089	0.00010
1.87	0.00161	0.00030
4.05	0.00287	0.00072
5.30	0.00391	0.00107
12.68	0.00692	0.00219
17.23	0.00936	0.00324
25.58	0.01263	0.00441
38.08	0.01696	0.00618

TABLE S3. Harmonic vibrational frequencies (in cm^{-1}) of diborane as a function of the pressure, p(in GPa). Results refer to the PCM/DFT/M06/ 6-311++G(d,p) level with the barrier potential $V_0(3)$. Data at 0.0 GPa refer to the gas phase.

Mode	Symmetry	$p(GPa)$								
		1.0	1.3	2.5	2.91	4.3	6.5	8.9	11.2	16.1
1	A_g	2681	2688.8	2700.1	2708.4	2717.9	2729.8	2746.0	2765.9	2791.2
2	A_g	2180	2182.4	2187.2	2191.8	2197.3	2204.2	2218.8	2227.6	2249.5
3	A_g	1207	1210.1	1214.6	1218.3	1222.9	1227.9	1234.9	1243.0	1254.5
4	A_g	821	824.4	829.9	834.0	839.2	845.2	856.6	863.9	879.0
5	A_u	866	869.1	875.2	877.5	883.5	891.3	901.1	910.8	926.3
6	B_{2g}	1882	1885.1	1890.3	1894.5	1899.9	1905.9	1920.3	1928.8	1949.2
7	B_{2g}	901	903.7	908.0	910.2	914.7	919.8	927.9	933.7	945.2
8	B_{2u}	2770	2777.9	2790.2	2799.0	2809.3	2822.3	2839.4	2861.2	2888.2
9	B_{2u}	955	957.3	960.0	961.8	964.5	968.3	971.3	978.0	984.8
10	B_{2u}	337	339.8	344.4	348.5	354.2	361.6	367.2	379.5	392.5
11	B_{1g}	2758	2765.9	2778.6	2787.6	2798.2	2811.4	2828.7	2850.9	2878.3
12	B_{1g}	930	931.9	934.7	937.1	940.5	944.3	949.4	955.1	963.7
13	B_{1u}	2015	2020.9	2029.4	2036.0	2044.2	2054.1	2072.6	2084.5	2111.0
14	B_{1u}	1001	1003.4	1007.2	1008.6	1012.7	1017.8	1024.1	1030.7	1041.2
15	B_{3g}	1054	1056.1	1058.9	1060.3	1063.0	1067.2	1070.9	1077.8	1085.3
16	B_{3u}	2666	2673.6	2685.3	2693.8	2703.6	2716.0	2732.5	2753.1	2779.0
17	B_{3u}	1704	1704.1	1706.2	1708.7	1712.0	1716.0	1727.4	1733.7	1751.3
18	B_{3u}	1193	1194.9	1198.6	1202.0	1206.0	1210.5	1217.0	1224.4	1235.2

TABLE S4. Quadratic force constants $\tilde{k}_i(p)$ (in $mDyne\mathring{A}^{-1}$) of diborane as a function of the pressure, p(in GPa). Results refer to the PCM/DFT/M06/ 6-311++G(d,p) level for the barrier potential $V_0(6)$, at the equilibrium geometry dependent from the pressure. Data at 0.0 GPa refer to the gas phase.

Mode	Symmetry	$p(GPa)$					
		0.0	1.0	1.9	4.1	5.3	12.7
1	A_g	4.4166	4.4641	4.4993	4.56	4.6085	4.7507
2	A_g	2.8285	2.8417	2.8527	2.8763	2.9	2.987
3	A_g	0.9437	0.9507	0.9558	0.9654	0.9738	1.0001
4	A_g	1.6974	1.7237	1.7487	1.7957	1.8369	1.9699
5	A_u	0.4374	0.4451	0.4497	0.4592	0.4637	0.4915
6	B_{2g}	2.1372	2.1589	2.1681	2.1872	2.2049	2.272
7	B_{2g}	0.6971	0.7091	0.7148	0.7255	0.7319	0.7633
8	B_{2u}	5.0568	5.1063	5.1489	5.2232	5.2814	5.4523
9	B_{2u}	0.5867	0.5938	0.5973	0.6031	0.6078	0.6242
10	B_{2u}	0.0648	0.0674	0.069	0.0722	0.0754	0.0861
11	B_{1g}	5.005	5.0581	5.1008	5.1754	5.2341	5.4051
12	B_{1g}	0.7137	0.7174	0.7214	0.7292	0.7365	0.7612
13	B_{1u}	2.6688	2.6799	2.6982	2.7319	2.7612	2.8647
14	B_{1u}	0.656	0.6586	0.6627	0.6716	0.6762	0.7026
15	B_{3g}	4.3307	4.3752	4.4122	4.4759	4.5268	4.6746
16	B_{3u}	4.3307	4.3752	4.4122	4.4759	4.5268	4.6746
17	B_{3u}	1.8483	1.8203	1.8219	1.8307	1.8417	1.8897
18	B_{3u}	0.9409	0.9464	0.9515	0.9619	0.9717	1.0013

TABLE S5. Quadratic force constants $k_i(p)$ (in $mDyne\mathring{A}^{-1}$) of diborane as a function of the pressure, p(in GPa). Results refer to the PCM/DFT/M06/ 6-311++G(d,p) level for the barrier potential $V_0(6)$ and at the equilibrium geometry in gas phase.

Mode	Symmetry	$p(GPa)$				
		1.0	1.9	4.1	5.3	12.7
1	A_g	4.4333	4.4449	4.4633	4.4772	4.518
2	A_g	2.841	2.8451	2.8546	2.8623	2.8904
3	A_g	0.9525	0.9592	0.9724	0.9832	1.0169
4	A_g	1.7083	1.7217	1.75	1.773	1.849
5	A_u	0.4484	0.4555	0.4697	0.4788	0.5176
6	B_{2g}	2.1517	2.1505	2.1502	2.1488	2.1462
7	B_{2g}	0.7141	0.7232	0.7404	0.752	0.7967
8	B_{2u}	5.0698	5.085	5.1095	5.1279	5.1815
9	B_{2u}	0.5954	0.6013	0.6119	0.6207	0.651
10	B_{2u}	0.0716	0.0769	0.0873	0.0959	0.1246
11	B_{1g}	5.0223	5.0379	5.063	5.082	5.1364
12	B_{1g}	0.7213	0.7284	0.7426	0.7542	0.792
13	B_{1u}	2.6731	2.6823	2.6997	2.7127	2.7563
14	B_{1u}	0.6632	0.6707	0.686	0.6963	0.7379
15	B_{3g}	0.6598	0.6648	0.6738	0.6808	0.7081
16	B_{3u}	4.3445	4.3583	4.3802	4.3968	4.4457
17	B_{3u}	1.8196	1.8151	1.8112	1.8079	1.8015
18	B_{3u}	0.9496	0.957	0.9724	0.9851	1.0251

TABLE S6. Selected cubic force constant g_{iij} (in $AttoJamu^{-3/2}Ang^{-3}$) between the normal modes Q_i and the subset of the totally symmetric (TS) one (Q_1,Q_2) of diborane in gas phase. Results refer to the DFT/M062X/6-311++G(d,p) level.

Q_i	Q_j	g_{iij} ($AttoJamu^{-3/2}Ang^{-3}$)
1	1	-8.09
2	2	-4.95
3	1	1.03
5	1	1.26
6	2	-3.89
7	1	1.51
8	1	-9.30
9	2	0.803
10	1	1.03
11	1	-9.38
12	1	1.04
13	2	-3.01
14	1	1.30
15	2	0.83
16	1	-8.18
17	2	-4.01
18	1	1.06