Supplemental material

Phase stability and lattice dynamics of Ammonium Azide under hydrostatic compression

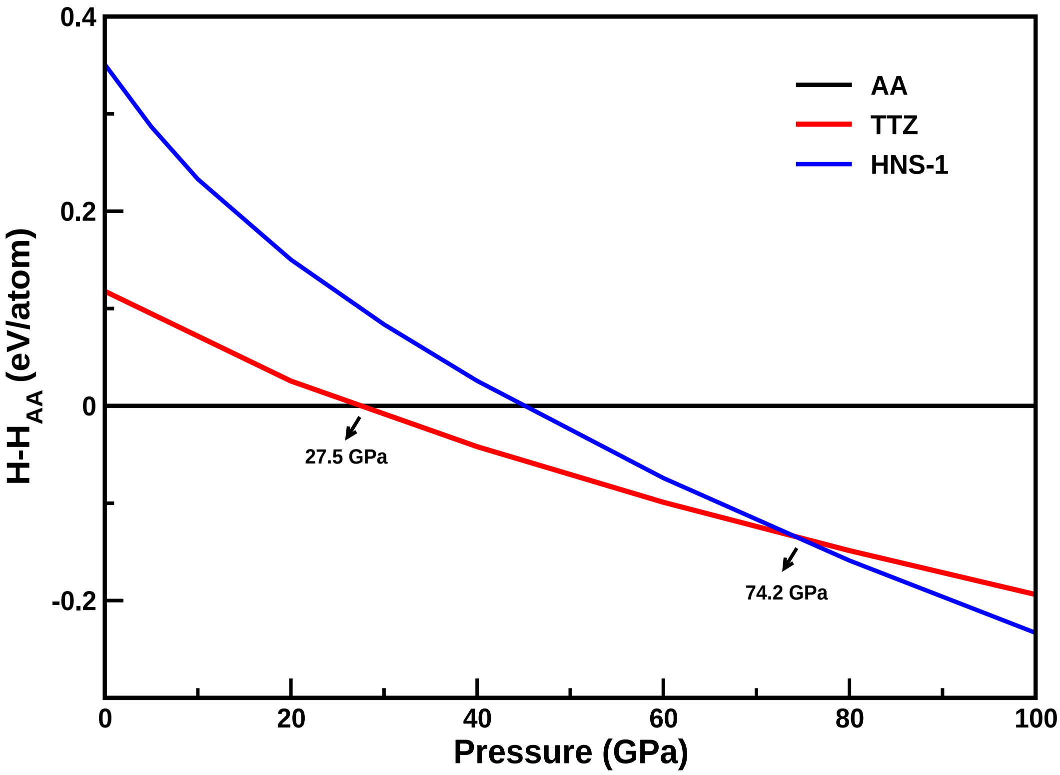

FIG. 1: (Colour online) Calculated relative enthalphies of TTZ, HNS-1, and HNS-2 polymorphic phases of N_4H_4 with respect to AA with USPP approach using CASTEP package.

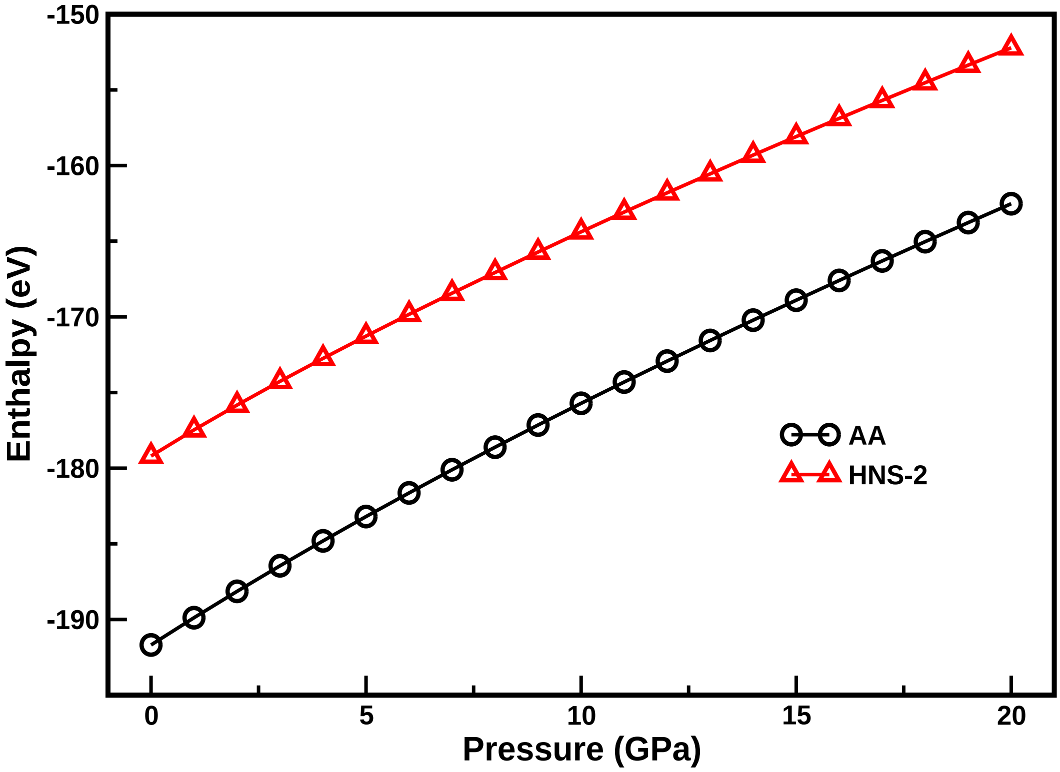

FIG. 2: (Colour online) Calculated enthalphies of AA and HNS-2 polymorphic phases of N_4H_4 up to 20 GPa with TS-SCS scheme with VASP package.

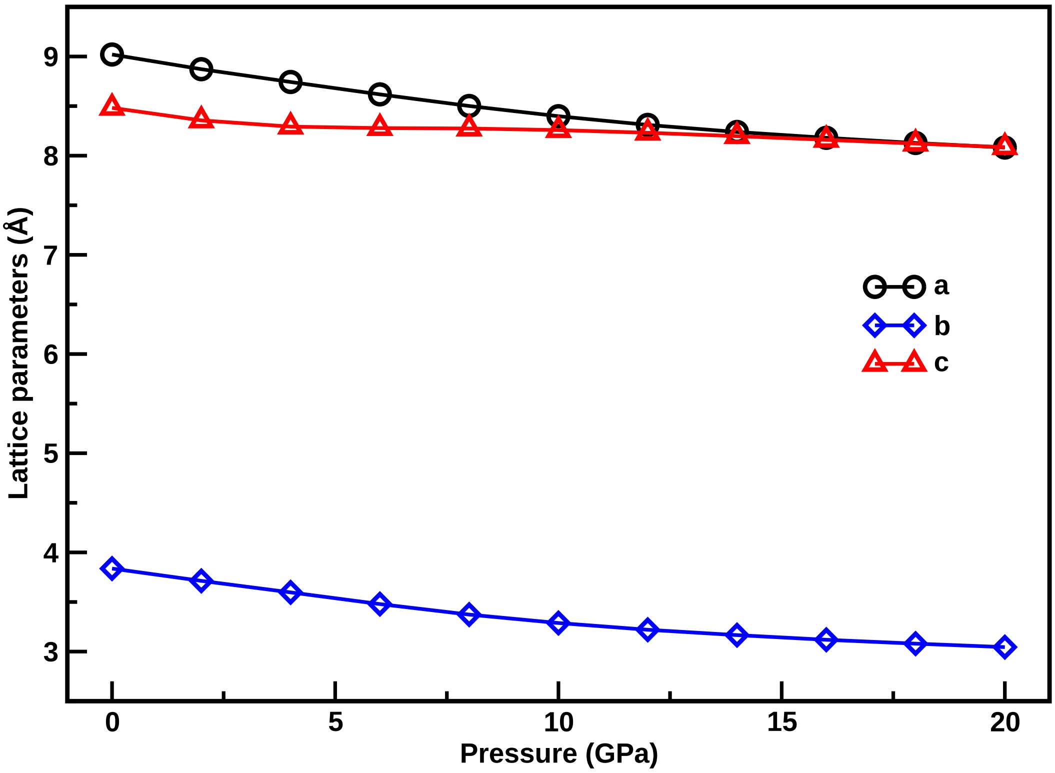

FIG. 3: (Colour online) Calculated lattice constants of AA as a function of pressure up to 20 GPa with TS-SCS scheme with VASP package.

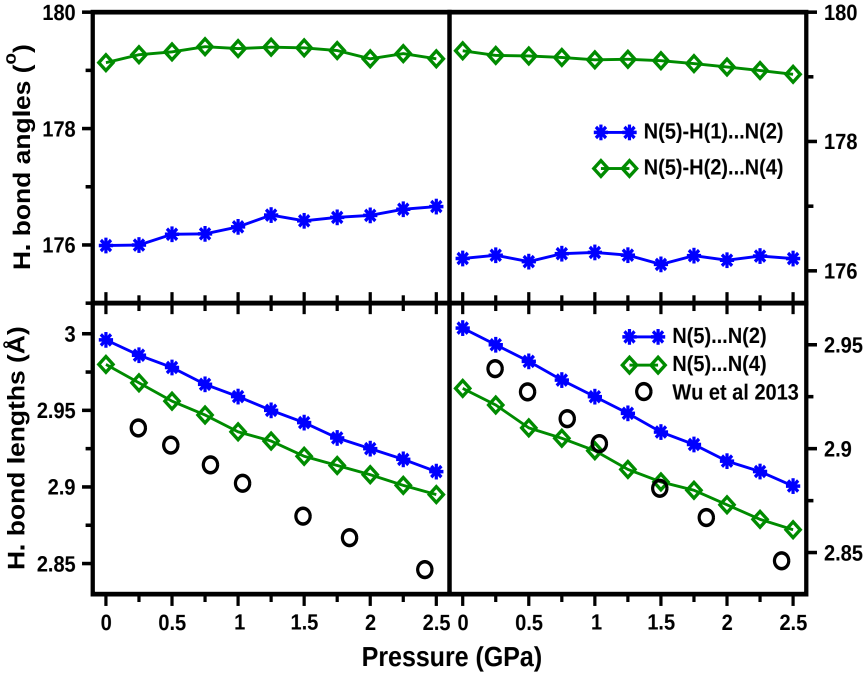

FIG. 4: (Colour online) Calculated Hydrogen bond lengths and angles of AA as a function of pressure. The left and right panels correspond to PBE and vdW-TS, respectively. The experimental data is taken from Ref.[1]

TABLE I: The calculated zone-center optical modes of AA with (vdW-TS) dispersion corrected functional

Mode	Symmetry	vdW-TS	Assignment
M96	B_{3g}	3102.9	N-H Asym. Str.
M95	B_{3g}	3083.5	N-H Asym. Str.
M94	B_{1g}	3015.5	N-H Asym. Str.
M93	B_{3u}	3015.1	N-H Asym. Str.
M92	B_{1u}	3012.4	N-H Asym. Str.
M91	B_{1u}	2989.2	N-H Asym. Str.
M90	B_{1g}	2986.7	N-H Asym. Str.
M89	B_{3u}	2983.2	N-H Asym. Str.
M88	A_g	3069.4	N-H Symm. Str.
M87	A_u	3006.0	N-H Symm. Str.
M86	B_{2g}	3004.5	N-H Symm. Str.
M85	B_{2u}	3001.2	N-H Symm. Str.
M84	A_g	2997.8	N-H Symm. Str.
M83	B_{2u}	2988.6	N-H Symm. Str.
M82	B_{2g}	2983.7	N-H Symm. Str.
M81	A_u	2980.9	N-H Symm. Str.
M80	A_u	1953.1	N=N=N (Type-I) Asymm. str.
M79	B_{2u}	1930.3	N=N=N (Type-II) Asymm. str.
M78	B_{3u}	1894.7	N=N=N (Type-I) Asymm. str.
M77	B_{1u}	1888.3	N=N=N (Type-II) Asymm. str.
M76	A_g	1724.3	N-H Scissor.
M75	A_u	1704.8	N-H Scissor. + Bend.
M74	B_{2u}	1712.2	N-H Bend.
M73	A_g	1711.4	N-H Bend.
M72	B_{2g}	1701.8	N-H Bend.
M71	B_{2u}	1693.4	N-H Bend.

M70	A_u	1696.1	N-H Bend.
M69	B_{2g}	1686.7	N-H Bend.
M68	B_{3g}	1473.8	N-H Wagg. + Rock.
M67	B_{1u}	1462.1	N-H Wagg. + Rock.
M66	B_{3g}	1457.9	N-H Wagg. + Rock.
M65	B_{3u}	1456.8	N-H Wagg. + Rock.
M64	B_{1g}	1452.7	N-H Wagg. + Rock.
M63	B_{3u}	1437.7	N-H Wagg. + Rock.
M62	B_{1u}	1435.5	N-H Wagg. + Rock.
M61	B_{1g}	1431.8	N-H Wagg. + Rock.
M60	A_g	1452.4	N-H Scissor. + Wagg.
M59	B_{2u}	1424.4	N-H Scissor. + Wagg.
M58	B_{2g}	1421.7	N-H Scissor. + Wagg.
M57	A_u	1419.9	N-H Scissor. + Wagg.
M56	B_{3g}	1234.0	N=N=N (Type-II) Symm str.
M55	A_g	1233.8	N=N=N (Type-II) Symm str.
M54	B_{3g}	1228.7	N=N=N (Type-I) Symm str.
M53	A_g	1228.4	N=N=N (Type-I) Symm str.
M52	B_{2u}	649.5	N_3 (Type-I) Bend. + NH_4 Rot.
M51	B_{1u}	647.8	N_3 (Type-I) Bend. + NH_4 Rot.
M50	A_u	631.0	N_3 (Type-II) Bend. + NH_4 Rot.
M49	B_{3u}	630.9	N_3 (Type-II) Bend. + NH_4 Rot.
M48	B_{2u}	599.5	N_3 (Type-I) Bend.
M47	B_{1u}	599.4	N_3 (Type-I) Bend.
M46	B_{1u}	594.6	N_3 (Type-II) Bend.
M45	B_{2u}	593.7	N_3 (Type-II) Bend.
M44	B_{3g}	525.1	NH_4 Torsion.
M43	A_g	515.6	NH_4 Torsion.
M42	B_{2g}	513.1	NH_4 Torsion.
M41	B_{1u}	509.2	NH_4 Torsion.

M40	B_{2u}	508.3	NH_4 Torsion.
M39	B_{1g}	507.8	NH_4 Torsion.
M38	B_{3u}	507.1	NH_4 Torsion.
M37	A_u	505.8	NH_4 Torsion.
M36	B_{3g}	497.8	NH_4 Torsion.
M35	B_{1u}	486.9	NH_4 Torsion.
M34	B_{1g}	484.8	NH_4 Torsion.
M33	B_{3u}	476.5	NH_4 Torsion.
M32	B_{2g}	271.1	Lattice Rot.
M31	B_{3g}	260.7	NH_4 Trans.
M30	B_{3g}	238.7	NH_4 Trans.
M29	B_{1g}	258.3	N_3 (Type-I) Rot. + NH_4 Trans.
M28	B_{1g}	233.7	N_3 Rot. + NH_4 Trans.
M27	B_{2g}	227.9	N_3 Rot. + NH_4 Trans.
M26	A_g	193.1	NH_4 and N_3 (Type-II) Trans.
M25	B_{1u}	246.6	NH_4 and N_3 (Type-I) Trans.
M24	B_{2u}	224.9	NH_4 and N_3 (Type-I) Trans.
M23	A_u	182.9	NH_4 and N_3 (Type-II) Trans.
M22	B_{1u}	182.6	NH_4 and N_3 (Type-II) Trans.
M21	B_{3u}	203.3	NH_4 and N_3 (Type-II) Trans.
M20	B_{3u}	211.6	Lattice Trans.
M19	B_{2u}	180.0	Lattice Trans.
M18	A_u	167.2	Lattice Trans.
M17	B_{1u}	118.0	Lattice Trans.
M16	B_{3u}	113.5	Lattice Trans.
M15	A_u	99.3	Lattice Trans.
M14	B_{2g}	145.3	N_3 Rot. + NH_4 Trans.
M13	B_{3g}	136.8	N_3 (Type-II) Rot. + NH_4 Trans.
M12	A_g	129.8	N_3 (Type-II) Rot. + NH_4 Trans.
M11	B_{1g}	120.5	N_3 Rot. + NH_4 Trans.

M10	B_{1g}	111.0	N_3 Rot. + NH_4 Trans.
M9	B_{1g}	92.8	N_3 Rot. + NH_4 Trans.
M8	B_{2g}	83.8	N_3 (Type-I) Rot + NH_4 Trans.
M7	B_{2u}	109.8	N_3 Trans.
M6	B_{1u}	109.0	NH_4 and N_3 Trans.
M5	B_{2u}	87.9	NH_4 and N_3 Trans.
M4	B_{1u}	80.4	NH_4 and N_3 (Type-II) Trans.

[1] X. Wu, H. Cui, J. Zhang, R. Cong, H. Zhu, Q. Cui, *Appl. Phys. Lett.*, 2013, **102**, 121902.