Supporting Information for

Dibridged, Monobridged, Vinylidene-Like, and Linear Structures for the Alkaline Earth Dihydrides, Be$_2$H$_2$, Mg$_2$H$_2$, Ca$_2$H$_2$, Sr$_2$H$_2$, and Ba$_2$H$_2$. Proposals for Observations

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Computational Methods

The search for the global minimum of Be$_2$H$_2$, Mg$_2$H$_2$, and Ca$_2$H$_2$ at singlet states was performed using the Coalescence Kick program (10,000 trial structures for each stoichiometry) at the PBE0/3-21G level of theory. The lowest in energy isomers then were reoptimized at PBE0/6-311++G** and CCSD(T)/cc-pVQZ levels. The Gaussian-16 software was used for the geometry optimization and frequency calculations. In order to assess the multireference character of wavefunctions of investigated systems, the CASSCF/cc-pvqz (for Be, Mg, and Ca containing structures) and CASSCF/def2qzvp (for Sr and Ba containing structures) calculations were performed via the ORCA software. The active space was chosen in such a way, to account for all valence electrons and six lowest unoccupied molecular orbitals (6e, 9o). The PBE0/cc-qcvp wavefunctions were chosen as initial guesses for those calculations. The geometries obtained at the CCSD(T)/cc-pvqz level were used, the ZPE correction was taken into account using values calculated at the CCSD(T)/cc-pvqz level. Dynamical correlation is added through the second-order N-electron valence state perturbation theory (NEVPT2) method. The chemical bonding pattern was analyzed using the AdNDP 2.0 code at PBE0/6-311++G** level of theory.

Table S1. Relative energies [kcal/mol] of E$_2$H$_2$ singlet species calculated at CASSCF(6e,9o)/NEVPT2 level of theory.

Spin state	Linear HE-EH	Dibridged	Monobridged	Vinylidene-like	Linear E···H-E-H
Be$_2$H$_2$	0.0	+34.0	+39.7	+23.8	+26.1
Mg$_2$H$_2$	0.0	+8.8	+25.7	+2.4	+6.24
Ca$_2$H$_2$	0.0	-8.8	-1.0	+13.2	+7.5
Sr$_2$H$_2$	0.0	-17.6	-7.3	+10.4	+0.9
Ba$_2$H$_2$	0.0	-25.6	-13.9	+0.8	-4.3

Table S2. Relative energies [kcal/mol] of singlet and triplet dibridged E_2H_2 species calculated at CASSCF(6e,9o)/NEVPT2 level of theory.

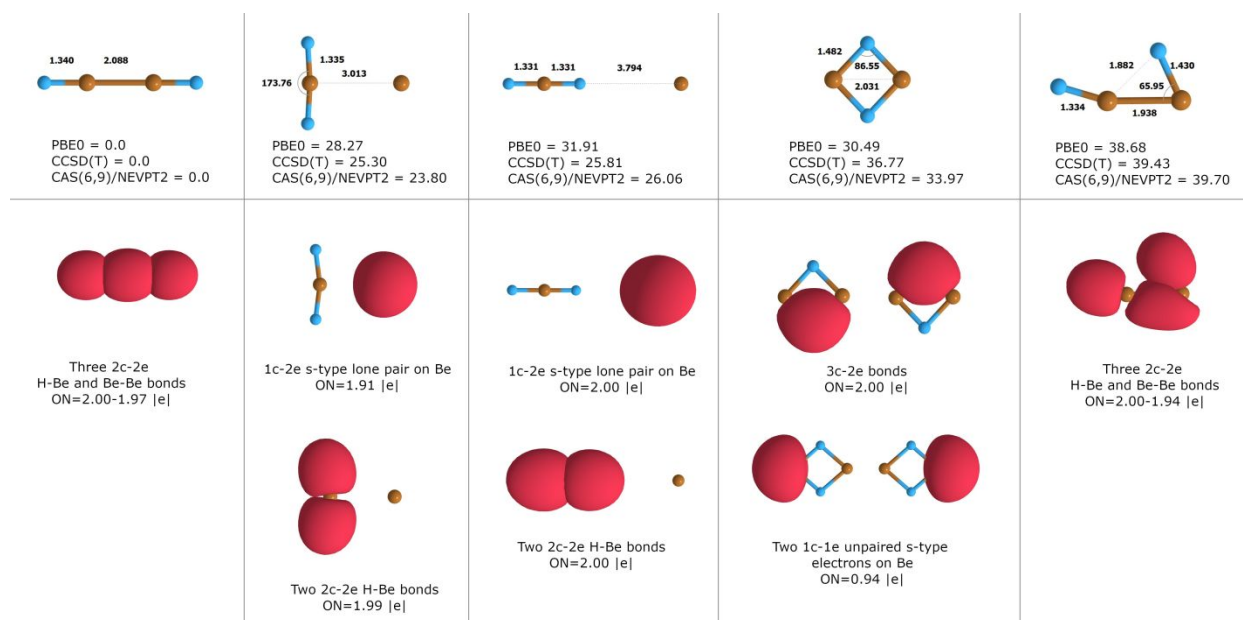|	Spin state	Energy
Be_2H_2	Singlet	0.0
	Triplet	+6.9
Mg_2H_2	Singlet	0.0
	Triplet	+9.0
Ca_2H_2	Singlet	0.0
	Triplet	+1.5
Sr_2H_2	Singlet	0.0
	Triplet	+1.2
Ba_2H_2	Singlet	0.0
	Triplet	+2.9

Figure S1. The relative energies [kcal/mol], optimized structures (bond lengths are given in [Å], angles are given in [degrees]), and chemical bonding patterns (the abbreviation ON denote the occupancy number) for the five lowest isomers of Be_2H_2.
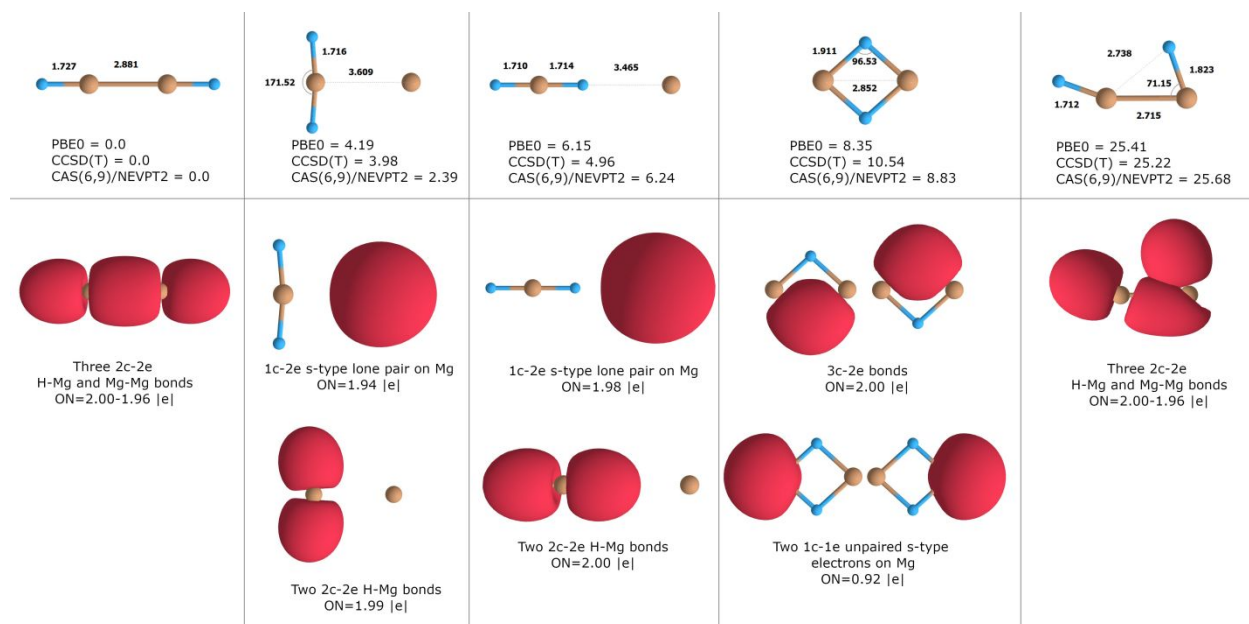
Figure S2. The relative energies [kcal/mol], optimized structures (bond lengths are given in [Å], angles are given in [degrees]), and chemical bonding patterns (the abbreviation ON denote the occupancy number) for the five lowest isomers of Mg_2H_2.
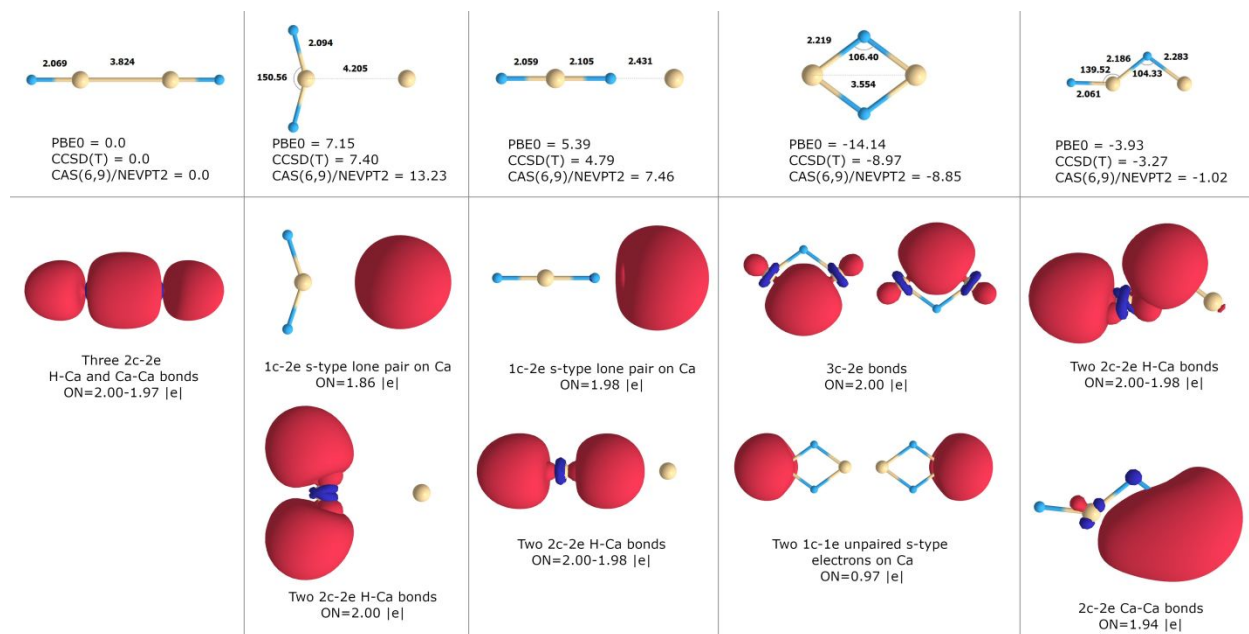

Figure S3. The relative energies [kcal/mol], optimized structures (bond lengths are given in [Å], angles are given in [degrees]), and chemical bonding patterns (the abbreviation ON denote the occupancy number) for the five lowest isomers of Ca_2H_2.

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