Supporting Information

Spectroscopic/Bond Property Relationship in Group 11 Dihydrides via Relativistic Four-Component Methods

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Methodology and Computational Details

Methodological details of the 4c-CCSD(T) geometry optimizations

Geometries have been optimized at the 4c-CCSD(T) level by performing the numerical first derivatives of the energy with respect to the nuclear coordinates, by considering several conditions: i) the geometries are expected to be linear from previous calculations\(^1\text{"4}\); ii) the two M-H bonds are considered to be equal, on the basis of the complexes linear centrosymmetric symmetry (D\(\infty h\)). According to these conditions, we could optimize the MH\(_2\) complexes by only accounting for one degree of freedom (the M-H bond) in an iterative approach. At each step, three single-point calculations were performed and a second order Newton’s interpolation procedure was used for obtaining the minimum energy and the corresponding bond length. The steps have been repeated until convergence between the two bond lengths obtained after two consecutive steps was reached (10\(^{-4}\) Å). Using this approach, it was possible to optimize the geometries with a computationally demanding state-of-the-art method in a reasonable amount of time.

Methodological details of the 4c-CCSD(T) vibrational frequencies calculations

The Hessian matrix has been calculated considering that, since in this class of linear triatomic centrosymmetric molecules the stretching and bending modes are not coupled, we could neglect any motion along the x and y axis and considering motion only along the z-axis. In this way, the Hessian is simplified and becomes a 3x3 matrix.

The elements of the Hessian have been calculated via numerical derivatives. The most convenient approach in our case is the central difference approximation. In this way first derivatives can be expressed as follows:

\[
f'(x_0) = \frac{f(x_0+h)-f(x_0-h)}{2h} + \epsilon h^2
\]  

(1)

where \(h\) is the displacement from the equilibrium \(x_0\) value; \(f(x_0+h)\) and \(f(x_0-h)\) represent the function evaluated at both forward and backward displacements and \(\epsilon h^2\) represents the error due to the approximation. This is a more convenient way of evaluating derivatives with respect to backward of forward difference approximation, since the error scales as \(h^2\).

In our case, the diagonal elements of the Hessian can be simply expressed as:
Instead, in the case of non-diagonal elements, we need to perform subsequent first derivatives for calculating the gradients ($G^+_i$ and $G^-_i$) at first and then the element of the Hessian matrix:

$$k_{ij} = \frac{\delta^2 V}{\delta x_i \delta x_j} = \frac{\delta G_j}{\delta x} = \frac{G_j^+ - G_j^-}{2h} + \varepsilon h^2$$

A critical choice for a good approximation is in the value of $h$. A too small value of $h$ may cause problems in the sense that the difference between the function evaluated at backwards and forward displacement may be smaller than the precision of the calculations, therefore causing the final values to oscillate and therefore not being accurate. Instead, a too big value of $h$ may cause problems concerning a too big error in the estimation of the derivative and therefore a bad approximation of the latter.

With the aim of understanding which the optimal value of $h$ for introducing the smallest possible error was, we calculated the elements of the Hessian for CuH$_2^-$ with different values of $h$ ranging from 0.005 to 0.05. Then, rearranging Eqs. (2) and (3), we could find two expressions that, via linear or polynomial regression, could allow us to estimate the error we introduce in the approximation and therefore the real force constant.

For diagonal elements, rearranging Eq. (2) we obtain:

$$k_{ii}^{appr} = k_{ii}^{real} + \varepsilon_{ii} h^2$$

This means that in both cases we should be able, by plotting the $k_{ii}^{appr}$ values (which are the ones we determine through our calculations) versus $h^2$, by the means of a linear regression, we should be able to interpolate them to a straight line, whose intercept corresponds to the real force constant.

In the case of non-diagonal elements, manipulating the expressions for the gradients and the final derivative, we obtain the following expression:

$$k_{12}^{apparent} = k_{12}^{real} + \left(\frac{\varepsilon_{12}^- - \varepsilon_{12}^+}{2}\right) h + \varepsilon_{k12} h^2$$

This means that for $k_{12}$ (and $k_{13}$, for which one obtains the same equations), one can estimate the error due to the approximation by plotting the $k_{12}^{apparent}$ values versus $h$ and interpolate the data with a second-order polynomial.
Below are shown the plots for the four constants and the $k_{ij}^{\text{real}}$ values, comparing the results with the ones where the smallest value of $h$ is used (i.e. 0.005 Å).

Figure M1. Plot of $h^2$ values versus the calculated $k_{ii}$ elements (top panel) and $h$ values versus calculated $k_{ij}$ elements (bottom panel) for CuH$_2^-$. The calculations have been carried out with the 4c-CCSD(T) approach and a dyall.tvz basis set.

| Force constant | $k^{\text{real}}$ (N/m) | $k$ with $h=0.005$ Å (N/m) |
|----------------|--------------------------|------------------------------|
| $k_{11}$      | 159.485 ± 0.002          | 159.495                      |
| $k_{12}$      | -141.919 ± 0.002         | -141.946                     |
| $k_{22}$      | 283.840 ± 0.001          | 283.859                      |
| $k_{13}$      | -17.563 ± 0.001          | -17.563                      |
Table M1. Comparison between “real” extrapolated \( k \) values (\( k_{\text{real}} \)) and \( k \) values calculated with \( h=0.005 \) Å for CuH\(_2^+\).

The polynomial interpolations are very accurate (as shown by the \( R^2 \) values equal or extremely close to 1). We show how the \( k_{ij}^{\text{real}} \) values obtained are extremely close to the ones we report using a finite \( h \) value of 0.005 Å, leading to practically identical stretching frequencies. At this point, it is reasonable to believe that the central differences approximation works very well for estimating the stretching frequencies of CuH\(_2^+\), with \( h=0.005 \) Å being an appropriate value of displacement to perform these calculations.

**Computational details of the DKS-CD analysis**

The CD analysis has also been applied to quantify the rearrangement of the electron density in the MH\(_2^+\) complexes at relativistic four-component Dirac-Kohn-Sham level\(^5\) using BERTHA code\(^6\)–\(^9\) with the following computational set-up. The large component of the basis set for all the atoms was generated by uncontracting triple-\( \zeta \) quality Dyall’s basis sets\(^10\)–\(^13\). The corresponding small component basis was generated using the restricted kinetic balance relation\(^14\). For the metal atoms (i.e. Cu, Ag, Au, Rg), a previously optimized auxiliary basis set for density fitting denoted as B20 was used\(^15\). For H atoms, accurate auxiliary basis sets were generated using a simple procedure starting from available DeMon\(^16\) Coulomb fitting basis set. It is worth recalling that the Hermite Gaussian Type Functions (HGTFs) used as fitting functions are grouped together in sets sharing the same exponents (analogous scheme is adopted in the nonrelativistic DFT code DeMon)\(^16\). The sets are formed so that to an auxiliary function of a given angular momentum all the functions of smaller angular momentum are associated. Consequently, due to the variational nature of the density fitting procedure implemented, a fitting basis set of increased accuracy can be generated by simply upshifting the angular momentum in the basis set definition\(^17\). For H we achieved a fitting basis set of higher accuracy (referred to as A2) simply by up-shifting of two units the angular momentum of all the DeMon Coulomb Fitting definitions. This assures an accuracy on the Coulomb energy of 0.03 mHartree. The PBE\(^18\) functional was used. An energy convergence criterion of \( 10^{-7} \) Hartree on the total energy was adopted.
Table S1. DFT SOC-ZORA optimized Au-H bond lengths in AuH$_2^-$ by using different exchange-correlation functionals. CCSD(T)-SO calculated Au-H bond length from ref. 2 is used as reference.

| Functional | Au-H Bond length (Å) | Functional | Au-H Bond length (Å) |
|------------|----------------------|------------|----------------------|
| BLYP       | 1.666                | S12H       | 1.661                |
| PBE        | 1.658                | M06-L      | 1.664                |
| BP86       | 1.657                | TPSS       | 1.659                |
| B3LYP      | 1.659                | M06        | 1.680                |
| PBE0       | 1.650                | TPSSh      | 1.656                |

Reference Au-H bond length: 1.647 Å

Table S2. DFT SR-ZORA optimized Au-H bond lengths in AuH$_2^-$ by using different exchange-correlation functionals. CCSD(T)-SO calculated Au-H bond length from ref. 2 is used as reference.

| Functional | Au-H Bond length (Å) | Functional | Au-H Bond length (Å) |
|------------|----------------------|------------|----------------------|
| BLYP       | 1.672                | S12H       | 1.667                |
| PBE        | 1.663                | M06-L      | 1.670                |
| BP86       | 1.662                | TPSS       | 1.665                |
| B3LYP      | 1.664                | M06        | 1.687                |
| PBE0       | 1.656                | TPSSh      | 1.662                |

Reference Au-H bond length: 1.647 Å
Table S3. 4-component relativistic (R^4C) and non relativistic (R^NR) calculated M-H equilibrium bond lengths for MH complexes. The Relativistic Bond Contraction (RBC) for each complex is reported. When available, the experimental value (R^EXP) from ref. 19 is reported for comparison.

| Group 11 hydride | R^EXP (Å) | R^4C (Å) | R^NR (Å) | RBC (pm) |
|------------------|-----------|----------|----------|----------|
| Cu               | 1.463     | 1.458    | 1.484    | 2.6      |
| Ag               | 1.618     | 1.615    | 1.691    | 7.6      |
| Au               | 1.524     | 1.521    | 1.740    | 21.9     |
| Rg               | /         | 1.521    | 1.925    | 40.4     |
Figure S1. Correlation between the square of the atomic number ($Z^2$) and the relativistic bond contraction (RBC) in MH complexes. $R^2=0.998$. 
Table S4. DFT SR-ZORA ($\Delta E_{\text{INT}}^{\text{SR}}$) and SOC-ZORA ($\Delta E_{\text{INT}}^{\text{SOC}}$) calculated interaction energies for AuH$_2^-$ by using different exchange-correlation functionals.

| Functional | $\Delta E_{\text{INT}}^{\text{SR}}$ (kcal/mol) | $\Delta E_{\text{INT}}^{\text{SOC}}$ (kcal/mol) | Functional | $\Delta E_{\text{INT}}^{\text{SR}}$ (kcal/mol) | $\Delta E_{\text{INT}}^{\text{SOC}}$ (kcal/mol) |
|------------|--------------------------------------|--------------------------------------|------------|--------------------------------------|--------------------------------------|
| BLYP       | 90                                   | 83                                   | S12H       | 87                                   | 85                                   |
| PBE        | 89                                   | 87                                   | M06-L      | 85                                   | 83                                   |
| BP86       | 88                                   | 86                                   | TPSS       | 89                                   | 87                                   |
| B3LYP      | 86                                   | 84                                   | M06        | 87                                   | 85                                   |
| PBE0       | 90                                   | 88                                   | TPSSh      | 89                                   | 87                                   |
**Figure S2.** Non relativistic and 4c-CCSD(T) calculated PESs for the HCu---H bond. The energy has been shifted according to the two fragments being at infinite distance.
**Figure S3.** Non relativistic and 4c-CCSD(T) calculated PESs for the HAg---H$^-$ bond. The energy has been shifted according to the two fragments being at infinite distance.
Figure S4. Non relativistic and 4c-CCSD(T) calculated PESs for the HAu----H bond. The energy has been shifted according to the two fragments being at infinite distance.
Figure S5. Non relativistic and 4c-CCSD(T) calculated PESs for the HRg—H bond. The energy has been shifted according to the two fragments being at infinite distance.
**Figure S6.** Top: DKS-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the CuH$_2^-$ complex. The isovalue for the upper three surfaces (i.e. $\Delta \rho$, $\Delta \rho_1$, $\Delta \rho_2$) is $\pm 0.001 \ e \ \text{a}_0^{-3}$, whereas for the three lower surfaces (i.e. $\Delta \rho_3$, $\Delta \rho_4$, $\Delta \rho_5$) the isovalue is $\pm 0.0001 \ e \ \text{a}_0^{-3}$ . Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas.

Bottom: corresponding DKS-CD curves for the CuH$_2^-$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
Figure S7. *Top:* DKS-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the AgH$_2^-$ complex. The isovalue for the upper three surfaces (i.e. $\Delta \rho$, $\Delta \rho_1$, $\Delta \rho_2$) is $\pm 0.001\ e\ a_0^{-3}$, whereas for the three lower surfaces (i.e. $\Delta \rho_3$, $\Delta \rho_4$, $\Delta \rho_5$) the isovalue is $\pm 0.0001\ e\ a_0^{-3}$. Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas.

*Bottom:* corresponding DKS-CD curves for the AgH$_2^-$ complex. Red dots indicate the position of the nuclei along the $z$ axis. The vertical line marks the isodensity boundary.
Figure S8. Top: DKS-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the AuH$_2^-$ complex. The isovalues for the upper three surfaces (i.e. $\Delta \rho$, $\Delta \rho_1$, $\Delta \rho_2$) is $\pm 0.001$ e $\text{a}_0^{-3}$, whereas for the three lower surfaces (i.e. $\Delta \rho_3$, $\Delta \rho_4$, $\Delta \rho_5$) the isovalues is $\pm 0.0001$ e $\text{a}_0^{-3}$. Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas.

Bottom: corresponding DKS-CD curves for the AuH$_2^-$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
**Figure S9.** Top: SR-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the CuH$_2^-$ complex (the isovalue is ±0.005 e $a_0^{-3}$). Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas. 

Bottom: corresponding SR-CD curves for the CuH$_2^-$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
Figure S10. Top: SR-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the AgH$_2$ complex (the isovalue is $\pm 0.005$ e $a_0^{-3}$). Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas. Bottom: corresponding SR-CD curves for the AgH$_2$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
Figure S11. Top: SR-CD calculated isodensity surfaces of the total ($\Delta \rho$) and of its first five NOCV components for the AuH$_2$ complex (the isovalue is $\pm 0.005$ e $a_0^{-3}$). Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas. Bottom: corresponding SR-CD curves for the AuH$_2$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
Figure S12. Top: SR-CD calculated isodensity surfaces of the total ($\Delta\rho$) and of its first five NOCV components for the RgH$_2$ complex (the isovalue is $\pm 0.005 \text{ e a}_0^{-3}$). Blue regions indicate electron charge accumulation areas, whereas red regions indicate depletion areas. 
Bottom: corresponding SR-CD curves for the RgH$_2$ complex. Red dots indicate the position of the nuclei along the z axis. The vertical line marks the isodensity boundary.
Table S5. SR-CD calculated charge Transfer (CT) values corresponding to NOCVs for MH$_2^-$ complexes calculated by scalar relativistic Charge Displacement analysis (SR-CD).

| Complex | $\Delta\rho$ | $\Delta\rho_1$ | $\Delta\rho_2$ | $\Delta\rho_3$ | $\Delta\rho_4$ | $\Delta\rho_5$ |
|---------|--------------|----------------|----------------|----------------|----------------|----------------|
| CuH$_2^-$ | 0.219 | 0.244 | -0.024 | 0.006 | -0.004 | -0.004 |
| AgH$_2^-$ | 0.230 | 0.269 | -0.021 | -0.008 | -0.004 | -0.004 |
| AuH$_2^-$ | 0.329 | 0.385 | -0.036 | -0.001 | -0.010 | -0.010 |
| RgH$_2^-$ | 0.401 | 0.475 | -0.034 | -0.003 | -0.019 | -0.019 |
Figure S13. DKS-CD curves of the $\Delta \rho_1$ component (red line) and of parent NOCV-pairs densities $|\Phi_{-1}|^2$ (orange line) and $|\Phi_{+1}|^2$ (green line) for the CuH$_2^-$ complex. The isodensity pictures (isovalue: $\pm 0.005$ e $a_0^{-3}$) corresponding to the two parent densities have been also reported, where red and blue regions correspond to electron charge depletion and accumulation areas, respectively.

Figure S14. DKS-CD curves of the $\Delta \rho_1$ component (red line) and of parent NOCV-pairs densities $|\Phi_{-1}|^2$ (orange line) and $|\Phi_{+1}|^2$ (green line) for the AgH$_2^-$ complex. The isodensity pictures (isovalue: $\pm 0.005$ e $a_0^{-3}$) corresponding to the two parent densities have been also reported, where red and blue regions correspond to electron charge depletion and accumulation areas, respectively.
Figure S15. DKS-CD curves of the $\Delta \rho_1$ component (red line) and of parent NOCV-pairs densities $|\Phi_{-1}|^2$ (orange line) and $|\Phi_{+1}|^2$ (green line) for the AuH$_2^+$ complex. The isodensity pictures (isovalue: $\pm 0.005 \text{ e } \text{a}_0^{-3}$) corresponding to the two parent densities have been also reported, where red and blue regions correspond to electron charge depletion and accumulation areas, respectively.

Figure S16. DKS-CD curves of the $\Delta \rho_1$ component (red line) and of parent NOCV-pairs densities $|\Phi_{-1}|^2$ (orange line) and $|\Phi_{+1}|^2$ (green line) for the RgH$_2^+$ complex. The isodensity pictures (isovalue: $\pm 0.005 \text{ e } \text{a}_0^{-3}$) corresponding to the two parent densities have been also reported, where red and blue regions correspond to electron charge depletion and accumulation areas, respectively.
Table S6. Population of (n+1)s and nd orbitals of the metal atoms of the Group 11 anion dihydrides (n=4 for Cu, n=4 for Ag, n=5 for Au and n=6 for Rg) calculated by the means of non-relativistic (NR) and 4-component (4c) projection analysis.

| Atomic Orbital | Cu (NR) | Cu (4c) | Ag (NR) | Ag (4c) | Au (NR) | Au (4c) | Rg (NR) | Rg (4c) |
|---------------|---------|---------|---------|---------|---------|---------|---------|---------|
| nd_{5/2,1/2}  | 1.87    | 1.88    | 1.78    |         |         |         |         |         |
| nd_{5/2,-3/2} | 1.99    | 1.99    | 1.98    | 1.96    |         |         |         |         |
| nd_{5/2,5/2}  | 2.00    | 2.00    | 2.00    | 1.99    | 1.96    | 1.99    |         |         |
| nd_{3/2,1/2}  | 1.92    | 1.93    | 1.90    | 1.86    |         |         |         |         |
| nd_{3/2,-3/2} | 2.00    | 2.00    | 2.00    | 1.99    |         |         |         |         |
| (n+1)s_{1/2}  | 1.11    | 1.15    | 1.11    | 1.15    | 1.40    | 1.15    | 1.68    |         |
Figure S17. Correlation between the populations of (n+1)s orbitals of the metal atom for Group 11 dihydrides (calculated at the 4-component level by the means of projection analysis) and the calculated extent of the sd hybridization ($\Delta_{HYBR}$).
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