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Comparison of the interactions in the rare gas hydride and Group 2 metal hydride anions

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We study both the rare gas hydride anions, RG–H− (RG = He–Rn) and Group 2 (Group IIa) metal hydride anions, MIIaH− (MIIa = Be–Ra), calculating potential energy curves at the CCSD(T) level with augmented quadruple and quintuple basis sets, and extrapolating the results to the basis set limit. We report spectroscopic parameters obtained from these curves; additionally, we study the Be–He complex. While the RG–H− and Be–He species are weakly bound, we show that, as with the previously studied BeH− and MgH− species, the other MIIaH− species are strongly bound, despite the interactions nominally also being between two closed shell species; M(ns2) and H−(1s2). We gain insight into the interactions using contour plots of the electron density changes and population analyses. For both series, the calculated dissociation energy is significantly less than the ion/induced-dipole attraction term, confirming that electron repulsion is important in these species; this effect is more dramatic for the MIIaH− species than for RG–H−. Our analyses lead us to conclude that the stronger interaction in the case of the MIIaH− species arises from sp and spd hybridization, which allows electron density on the MIIa atom to move away from the incoming H−. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4865749]

I. INTRODUCTION

The BeH− system, on first inspection, might be expected to be unremarkable, but in fact it has recently been highlighted.1 Beryllium, being a closed-shell system in its ground electronic state, has a lower electronegativity on the Pauling scale than that of hydrogen (1.57 vs. 2.00, respectively).2 Since also hydrogen has an electron affinity of 0.75 eV2 and the beryllium anion has a negative electron affinity, and so is unstable,2 the negative charge on BeH− would be expected to reside on the hydrogen atom. This would then lead to an interaction between two closed-shell 1S systems, which could be expected to yield a weakly bound species; however, a recent publication by Verdicchio1 drew attention to the peculiarities of this system. In that work, a valence full-configuration-interaction (FCI) study was conducted, with the surprising conclusion that this molecular ion is in fact strongly bound by 2.1 eV. This was interpreted as being due to the beryllium atom undergoing sp hybridization, and the subsequent formation of a σ bonding orbital between an empty Be sp hybrid orbital and the H 1s orbital.

In fact, BeH− has been studied theoretically several times previously. In 1975, Kenney and Simons2 undertook an equations-of-motion (EOM) study using Slater-type orbitals, which was focused on obtaining the vertical detachment energy. During that study the equilibrium bond length and limited spectroscopic constants were also calculated. In addition, a description of the bonding of this species in terms of a σ bond between an sp orbital on Be and the 1s orbital on H was proposed. Slightly later, Rosmus and Meyer4 reported the results of pseudo-natural orbital, coupled electron pair approximation calculations on a range of first- and second-row hydride anions including BeH− and MgH−. Although electron affinities were the main aim, the equilibrium bond length and various spectroscopic parameters were produced; similar results were published in 1986 by Frenking and Koch.5 Polášek and Zahradník6 performed MP2/6-31++G** geometry optimizations on a range of beryllium hydrides, including BeH−, and also reported the harmonic vibrational frequency for the latter. As noted, Verdicchio et al.1 recently studied this species, employing up to cc-pV6Z basis sets (note the absence of diffuse functions – see below), and full configuration interaction (full-CI) results; the effect of diffuse functions and core (Be 1s) correlation was examined separately with quadruple-ζ basis sets. The main conclusion from this work was that as the BeH− species formed, the negative charge from the H− moved towards the Be atom, eventually forming a “BeH species at short R, with the negative charge located on the opposite side of Be. Arguments for this were supported by the changes in occupations of the relevant orbitals and the forms of contour plots of the natural orbitals. Very recently, Koput7 has reported results on BeH− using the multireference averaged-coupled-pair function (MR-ACPF) approach. In that work, up to a aug-cc-pV7Z basis set was employed (truncated at f functions), and it was demonstrated that the use of diffuse functions was important in obtaining reliable curves, and so spectroscopic parameters. The values from the above studies are collected together in Table I.

We note that Rackwitz et al.8 have recorded photodetachment spectra of BeH−, MgH−, and CaH−, but that there was not sufficient resolved structure present to make any detailed

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TABLE I. Spectroscopic constants for the MgH− complexes calculated at the CCSD(T)/EBS level. R e is the equilibrium bond length, D e the equilibrium dissociation energy, \( \omega_0 \) the harmonic vibrational frequency, \( \omega_0\alpha_0 \) the anharmonicity constant, B e the equilibrium rotational constant, \( \alpha_0 \) the vibration-rotation constant, \( \nu_{0,1} \) is the wavenumber separation between the \( \nu = 0 \) and \( \nu = 1 \) vibrational levels, and \( k \) is the harmonic force constant. The most prevalent naturally occurring isotope was considered for each atom.

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<th>( D_{0,1}/\text{cm}^{-1} )</th>
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<th>( B_e/\text{cm}^{-1} )</th>
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aMR-ACPF/aug-cc-pCVTZ(i) with corrections - see text.
bMR-ACPF/aug-cc-pVTZ.
cMR-ACPF/aug-cc-pVQZ.
dFrozen-core full CI results using a cc-pVQZ basis set.
eCore electron correlated MRCI/aug-cc-pVQZ.

fBond lengths and vibrational frequencies obtained employing MP2/6-31G(df); dissociation energies employing MP4(SDTQ)/6-311+++(3df,3pd)

\#PNO-CI.

bCEPA.

eEquations of motion results.

fMP2/6-31+G**.

deductions on bonding motifs or structure. However, employing the electron affinities measured in that work, Rosmus and Meyer estimate \( D_0 \) values using available corresponding values for the neutral species, available at that time.

The aim of the present study is to expand the above investigations to the whole family of Group 2 (Group IIA) hydride anions (M\(_{\text{IIa}}\)H\(^{-}\)), to establish whether all are strongly bound and to allow trends to be deduced. By bringing different computational techniques to bear, it is hoped that a deeper understanding of the bonding in the M\(_{\text{IIa}}\)H\(^{-}\) species can be obtained. In particular, we shall compare the results for the titular species with results for RG–H\(^{-}\) (RG = He–Rn) complexes, which are expected to be physically bound.

The RG–H\(^{-}\) anions have been studied by a number of groups. Bendazzoli et al.\(^{10}\) used HF, MP2, CISD, CCSD, and FCI calculations with extended basis sets to answer the question as to whether He–H\(^{-}\) is stable or not. They concluded that the species was stable, but with a long \( R_e \) value (~6.9 Å) and a \( D_e \) value of between 4 and 8.5 cm\(^{-1}\), depending on the method employed. Shalabi et al.\(^{11}\) also concentrated on He–H\(^{-}\), examining the effect of adding bond functions to the basis set and using QCISDT calculations; this was found to be considerable, with a tenfold increase in the depth of the potential well (from ~2 cm\(^{-1}\) to ~23 cm\(^{-1}\)), with \( R_e \) decreasing from ~8 Å to ~5 Å. In 2001, Vallet et al.\(^{12}\) studied the three lightest RG–H\(^{-}\) hydrides using extended basis sets and the CCSD[T] method. \( R_e \) values for He–H\(^{-}\), Ne–H\(^{-}\), and Ar–H\(^{-}\) of 6.6 Å, 4.6 Å, and 3.7 Å were obtained, with \( D_e \) values of 3.7, 26.9, and 272.8 cm\(^{-1}\), respectively. Harmonic vibrational frequencies were also calculated, and the values are collected in Table II. We shall discuss these values alongside our own results in the below.

We note that there have been two papers on the three lightest RG–H\(^{-}\) species, where the interaction was investigated using model potentials. The first of these by Robincheaux\(^{13}\) looked at a set of triatomic molecules that have “Tango states.” A model in which the extra electron of He–H\(^{-}\) is loosely bound, whereas all other electrons are bound, was examined and He–H\(^{-}\) was considered. The model was very sensitive to one of the parameters, so it is not possible to place much weight on the dissociation energies obtained. A second paper, by Li and Lin,\(^{14}\) also looking at a (different) model potential for the same three species, concluded that the binding energies for He–H\(^{-}\), Ne–H\(^{-}\), and Ar–H\(^{-}\) were 4.99 cm\(^{-1}\), 613 cm\(^{-1}\), and 1034 cm\(^{-1}\). The latter two values are far in excess of the reported values of Ref. 12, although the He–H\(^{-}\) one is in reasonable agreement.

II. COMPUTATIONAL METHODOLOGY

Potential energy curves were calculated for BeH\(^{-}\), MgH\(^{-}\), CaH\(^{-}\), SrH\(^{-}\), BaH\(^{-}\), and RaH\(^{-}\) using CCSD(T) theory as implemented in the MOLPRO software package,\(^{15}\) the basis sets employed were as follows. For hydrogen,
aug-cc-pVXZ (X = Q, 5) basis sets were used, while for the two lighter metals, Be and Mg, all-electron aug-cc-pwCVXZ (X = Q, 5) basis sets were used. For the heavier metals, Ca, Sr, Ba, and Ra, aug–cc-pwCVXZ-PP (X = Q, 5) valence basis sets were used along with the small-core ECP10MDF, ECP28MDF, and ECP60MDF relativistic effective core potentials, respectively. Using these two different quality basis sets allows for the extrapolation of the interaction energy to the basis set limit at each internuclear separation (here designated extrapolated basis set, EBS, limit), employing the methodology of Halkier et al. In each case, all electrons not described by an ECP were included in the correlation treatment, although the work of Verdicchio et al. reported that for BeH inclusion of the Be 1s core electrons in the correlation made a negligible contribution to the energy.

We also calculate potential energy curves for RG–H using the CCSD(T) approach. For H and He we employed the aug-cc-pVQZ and aug-cc-pV5Z basis sets, while for Ne and Ar we employed the aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets. For Kr, Xe, and Rn, we employed the ECP10MDF, ECP28MDF, and ECP60MDF effective core potentials, with aug-cc-pwCVQZ-PP and aug-cc-pwCV5Z-PP valence basis sets. In all cases, we correlate only the valence electrons. Again, these curves were pointwise extrapolated to the basis set limit.

Potential energy curves were used as input to LEVEL 8.0 (Ref. 27) which was used both to interpolate the potential energy curves and calculate rovibrational energies. Correction for basis set superposition error (BSSE) was not made for either set of species. For the MgH species there is expected to be significant changes away from atomic electron density distribution, and possible overlap between the atomic orbitals making application of the counterpoise correction not possible. In any case, with such large basis sets, the percentage error from BSSE is expected to be small in all cases. The equilibrium bond length, $R_e$, and equilibrium dissociation energy, $D_e$, were each extracted directly from the LEVEL output. The lowest two vibrational ($J = 0$ and 1) rotational levels were employed in standard Morse expressions to allow the various standard spectroscopic constants to be determined.

Atomic charges were calculated using Mulliken population analysis, natural population analysis (NPA), and atoms in molecules (AIM) methodologies. The Mulliken and NPA analyses were performed with routines integrated into Gaussian, while the AIM analysis employed the AIMAll program using the WFX file produced by Gaussian, which allowed ECP-based basis sets to be employed (see Ref. 33 for details). In each case, the calculations were conducted at the CCSD level of theory with basis sets of triple zeta quality corresponding to those given above, using the CCSD(T)/EBS equilibrium bond length. We have compared the calculated interaction energy at the $R_e$ value obtained at the CCSD(T)/EBS level with those obtained at the QCISD and CCSD levels of theory.

In addition to the above, natural orbital contour plots were produced, again using MOLPRO, to generate the wavefunctions at the QCISD/aug-cc-pwCVTZ-PP of theory, and using the MOLDEN visualisation package to produce the plots.

Finally, we also performed CASSCF+MRCI+Q/aug-cc-pwCVTZ-PP single-point interaction energy calculations using the supermolecule approach, to ascertain the effect of any multireference behaviour on $D_e$; all valence electrons were correlated.

## III. RESULTS AND DISCUSSION

Potential curves for all species and using all basis sets are provided as supplementary material.
A. Spectroscopic parameters of M_{II}aH^−

The spectroscopic constants for the entire M_{II}aH^− series are presented in Table I. As can be seen from the values for \( R_e \) and \( D_e \) for BeH^− and other constants, the present results are in excellent agreement with the very recent MR-ACPF results from Koput.\(^7\) The conclusion is that multireference effects are not significant in determining these parameters. Separately we reached similar conclusions using the CASSCF + MRCI + Q method with smaller basis sets (results not presented herein). Further, Koput\(^7\) also explored corrections for full-CI, relativistic and diagonal Born-Oppenheimer effects, which were all found to be relatively small, although inclusion of these would be required to gain spectroscopic accuracy, which was the aim of that work. On the other hand, the best results from Koput\(^7\) and ourselves do not agree with the FCI/cc-pV6Z results of Verdicchio et al.\(^1\) Tests by ourselves, using CCSD(T)/cc-pCVQZ and CCSD(T)/cc-pwCVQZ interaction curves, extrapolated to the basis set limit, and also the MR-ACPF/cc-pV6Z results of Koput, each compared to the corresponding results using the augmented forms of the basis set, show that this difference is essentially almost completely due to the lack of diffuse functions in the study of Verdicchio et al.\(^1\) Further, Koput showed that addition of further diffuse functions, over and above the singly-augmented (aug-), did not affect the results significantly. We thus conclude that our level of calculation, employing large, singly augmented basis sets and extrapolating to the basis set limit, is wholly sufficient for BeH^−. We can also note the very close agreement for MgH^− between our values and those of the PNO-CI and CEPA calculations of Ref. 3; however, this would not take into account multireference effects, if these were more pronounced for the heavier species. To examine this, we looked at the \( T_1 \) diagnostic\(^36\) values from the CCSD(T)/aug-cc-pwCV5Z calculations, which are collected in Table III. The value for BeH^− is below the commonly accepted critical value of 0.02, suggesting it is little affected by multireference behaviour, while MgH^− has a value on the cusp; the other species have values significantly above this. Hence, we tested for the possible effect of multireference behaviour on our values. First, we note that the highest \( T_1 \) diagnostic value was for BaH^− at 0.049, and so we calculated an interaction energy curve at the CASSCF + MRCI + Q/aug-cc-pwCV5Z level. The \( R_e \) value obtained was 2.349 Å, which compares very favourably with the CCSD(T)/aug-cc-pwCV5Z value of 2.341 Å; in a similar vein, the corresponding \( \omega_e \) values are 976.4 cm\(^−1\) and 985.6 cm\(^−1\). These values suggest that multireference behaviour is not affecting the spectroscopic values at the minimum of the curves. We have also calculated the \( D_e \) values, and collect these in Table III also. As may be seen, there is a difference in the calculated \( D_e \) values between CASSCF + MRCI + Q and CCSD(T), but it is small and the differences are variable across the series. The small differences suggest that the CCSD(T) values are, for the most part, reliable for these species; additionally, there is consistency between these values and the CCSD(T)/EBS values in Table I. It is expected that the latter should be the most reliable, and expected to be close to CASSCF + MRCI + Q/EBS values, were these to be calculated.

For completeness, we also calculated \( D_e \) values employing the CCSD and QCISD methods with both aug-cc-pwCVTZ and aug-cc-pwCV5Z basis sets. The values in Table III suggest that the differences between the methods used for the population analysis and the contour plots, to be discussed below, is minimal, and so these are representative of the picture that would be seen at the full CCSD(T)/EBS level.

If we now consider the spectroscopic parameters in Table I, we can note various trends. First, we see that the binding energies, \( D_e \), are considerable, with BaH^− having the largest binding energy and MgH^− having the lowest; the trend with atomic number of M_{II}a is oscillatory and we shall discuss this further below. The trend in force constants also follows this oscillatory trend, albeit not so markedly. We have already noted the excellent agreement of our calculated \( D_e \) value with the best available for BeH^−. We also note the good agreement of the corresponding value for MgH^− with the previously reported values, obtained from both PNO-CI and CEPA calculations.\(^3\) As far as we are aware, the present results for the other species are the only such values that have been reported.

We also note that the \( R_e \) values are monotonically increasing (see Figure 1), which is in line with the expected increasing size of the M_{II}a atom; again, further comment is provided below. Excellent agreement of the \( R_e \) values with the recent MR-ACPF results\(^7\) has been noted for BeH^−, and this is also true of the comparison with the PNO-CI and CEPA calculations for MgH^−.\(^3\) Similar to the \( D_e \) values, the results for the other species are the only such values that appear to have been reported.

Results for the vibrational and rotational constants are also in excellent agreement with the MR-ACPF study\(^7\) for BeH^−, as are the MgH^− results from the PNO-CI and CEPA study.\(^3\) Indeed the good agreement for these species gives

### Table III. Interaction energies (cm\(^−1\)) calculated using QCISD, CCSD, CCSD(T), and CASSCF + MRCI + Q methods at the “best” CCSD(T) \( R_e \) with the quintuple-\( \xi \) and triple-\( \xi \) basis sets outlined in the text. \( \Delta \)MRCI + Q is the difference between the MRCI + Q and CCSD(T) interaction energies, expressed as a percentage of the CCSD(T) energy. \( \omega_e \) and \( \omega_V \) refer to the corresponding basis sets as described in the text.

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<td>15 010</td>
<td>15 290</td>
<td>14 938</td>
<td>15 196</td>
<td>15 368</td>
<td>0.041</td>
<td>15 197</td>
<td>1.11</td>
</tr>
<tr>
<td>BaH^−</td>
<td>16 771</td>
<td>17 323</td>
<td>16 649</td>
<td>17 165</td>
<td>17 377</td>
<td>0.049</td>
<td>17 295</td>
<td>0.47</td>
</tr>
<tr>
<td>RaH^−</td>
<td>13 858</td>
<td>14 271</td>
<td>13 750</td>
<td>14 136</td>
<td>14 309</td>
<td>0.046</td>
<td>14 175</td>
<td>0.94</td>
</tr>
</tbody>
</table>
confidence to the reliability of the calculated values for the other constants, and those for the heavier species reported herein.

The number of bound levels for the MIIaH\(^-\) species is 27, 31, 40, 42, 48, and 44 for RG = He–Rn, respectively. We provide lists of all of the calculated bound levels as supplementary material. In addition, we use these to produce Birge-Sponer plots, which are presented in Figure 2 and discussed below.

**B. Spectroscopic parameters of RG–H\(^-\)**

The calculated spectroscopic parameters are presented in Table II. Considering first the values for He–H\(^-\), it may be seen that the species is very weakly bound. Our best values are \( R_e = 6.87 \) Å and \( D_e \) value of 3.9 cm\(^{-1}\), with just a single vibrational level supported by the well; as a consequence, we did not derive a harmonic vibrational wavenumber. Our values are in reasonable agreement with the other reported values, except for those of Shalabi \textit{et al.} \cite{11} There is a small disagreement with the \( R_e \) value from Vallet \textit{et al.} \cite{12} as we obtain a slightly larger value, although our \( D_e \) value is actually very slightly greater. Both the latter study and our own predict a single bound vibrational level for this system. There is reasonable agreement with one of the model potential results for He–H\(^-\) \cite{14} with the results from the other study \cite{13} being too sensitive to one of the parameters for us to be conclusive of its reliability.

For Ne–H\(^-\) and Ar–H\(^-\) there only appears to be a single quantum chemical study, that by Vallet \textit{et al.} \cite{12} to which to compare. As with He–H\(^-\) we find our \( R_e \) value is slightly different (although in the opposite direction) and again our \( D_e \) value is greater. Interestingly, despite the direction of the differences, we only find a single bound level for NeH\(^-\), while Vallet \textit{et al.} \cite{12} found two. For ArH\(^-\) the agreement is much better between our results and those of Vallet \textit{et al.} \cite{12} and we note that both potentials support six bound vibrational levels.

The two dissociation energies obtained from the model potential study (613 cm\(^{-1}\) and 1034 cm\(^{-1}\) for Ne–H\(^-\) and Ar–H\(^-\)) \cite{14} are far too high when compared to the values here and in Ref. 12, and suggest that the model or its parameters are in need of attention. As far as we are aware, there have been no published studies on the heavier RG–H\(^-\) species.

As can be seen from Figure 1 and Table II, and as expected, \( D_e \) increases as the atomic number of the RG atom increases. It is particularly interesting to note, however, that \( R_e \) decreases monotonically as the atomic number of RG increases, contrary to the usual trend, such as seen for the MIIaH\(^-\) species. The number of bound levels for the RG–H\(^-\) species is 1, 1, 6, 7, 10, and 11 for RG = He–Rn, respectively, and are provided as supplementary material. \cite{35}

**C. Interactions**

1. **RG–H\(^-\)**

We first discuss the interactions in the RG–H\(^-\) species, which are expected to be physical in nature, with the approach of H\(^-\) resulting in a charge/induced-dipole interaction, as well as higher terms. In addition, there will be repulsion between the electrons of H\(^-\) and those of the RG atom. The balance between these terms will decide the resultant \( R_e \) and \( D_e \)
values. In Figure 3, we show contour plots of the electron density at the equilibrium separation for a selection of the RG–H− species. As may be seen, for He–H− the HOMO and HOMO−1 correspond to the 1s orbitals on the different atoms; this is to be expected owing to the large value of the equilibrium separation. For the other species, the HOMO is largely the H 1s orbital with the HOMO−1 being largely the RG outermost occupied p_z orbital. As the atomic number of the RG atom increases, the H− atom approaches closer and distortion of the H− 1s orbital occurs. It is only for the heaviest species that the orbitals have contributions from both atomic centres, and even then this is rather minimal. In Table IV we present the calculated charges on the RG atom using the Mulliken, NPA, and AIM methods. As can be seen, the charges are all very small, particularly for the first two approaches. It appears that the AIM approach gives the most reliable results when compared to the contour plots, with a gradual increase of the outermost occupied p_z orbital into the HOMO. This result is somewhat surprising, given the monotonically decreasing trend in R_e with atomic number, which might be taken as suggesting a reasonable interaction between the centres. It is interesting that a similar trend was found for the neutral coinage metal CM-RG complexes, although the binding energy in those species was less, owing to their being neutral species.

In Table V we present the calculated charge/induced-dipole term, using the dipole polarizabilities presented in Table VI obtained from Refs. 2, 38, and 39, and the ratio of this to our calculated D_e value. All of the ratios are very close to each other, except for He–H− which is somewhat lower; the values indicate that there is a significant repulsion term for all species, as expected for H− interacting with a closed-shell RG atom. The increasing polarizability of RG with atomic number (see Table VI) leads to the charge/induced-dipole interaction increasing, and this will cause a greater interaction between RG and H−, but of course there are more electrons on RG, leading to greater repulsion. Except for the 1s^2 He atom, the ratios of D_e to the charge/induced-dipole term is rather constant, indicating that these two opposing effects are similar in magnitude. However, the unexpected monotonically decreasing R_e values, and the contour plots, suggest that this balance occurs only when the RG atom has approached relatively close to H−, deforming the 1s electron density. That
this is possible suggests that H$^-$ is rather “soft,” which can be attributed to its having two electrons in the 1s orbital, one of which is “extra,” causing repulsion between these, and a rather diffuse electron cloud. Indeed, if our recent definition of an ion’s effective radius in a physically bonded system (denoted $R^e$)\cite{10} is considered, then $R^e$ for H$^-$ is deduced from the $R_e$ value of He–H$^-$ to be very large at $\sim$5 Å. In solids the derived radius for H$^-$ is much smaller at 1.56 Å,\cite{41} suggesting a very compressed electron distribution, explainable from the soft nature of H$^-$ and the interaction with the surrounding lattice.

### 2. BeH$^-$ and Be–He

The description of the bonding for BeH$^-$ given by Verdicchio et al.\cite{1} notes that the beryllium atom can form two $sp$ hybrid orbitals. One hybrid will be oriented away from the incoming H$^-$ and the other will be oriented toward the oncoming hydride. In the picture of the bonding given by Verdicchio et al.,\cite{1} the hybrid orbital oriented away from the incoming H$^-$ forms a lone pair, with the other overlapping with the H 1s orbital, forming a $\sigma$ bond. This conclusion was based upon a calculation of the charge shift, which was interpreted in terms of negative charge becoming localized on the Be atom, on the opposite side to the direction of approach of H$^-$ as $R$ decreased. This was supported by contour plots of the FCI natural orbitals.

We show contour plots of the QCISD natural orbitals in Figure 4 as a function of the intermolecular separation. It may be seen that, at long range, the HOMO and HOMO-1 are the Be 2$s$ and H 1$s$ orbitals, respectively. As the H$^-$ approaches the metal centre we see that the H 1$s$ orbital starts to elongate, owing to interaction with the Be 2$p_z$ orbital; this may also be viewed as a bonding overlap of the H 1$s$ orbital with an $sp$ hybrid orbital on Be, formed from the 2$s$ and 2$p_z$ orbitals. Concurrently, the Be 2$s$ orbital may be seen to distort on the side opposite to the incoming H$^-$, consistent with the formation of the other Be $sp$ hybrid orbital. The drivers for this distortion are threefold. First, the reduction in electron repulsion: the incoming, closed-shell, H$^-$ will experience significant repulsion with the electrons of the closed-shell Be atom; since the Be 2$p$ orbitals lie lower than those of the H 2$p$ ones then a reduction in the repulsion energy can be achieved by formation of the $sp$ hybrid and movement of the Be electron density away from the incoming H$^-$ . Second, the formation of the $sp$ hybrid also allows for the possibility of a bonding interaction with the H 1$s$ orbital to occur, enhancing the interaction between the species. Third, the reduction in the repulsion allows the H$^-$ to approach more closely, as electron density continues to move into the $sp$ hybrid orbital; the closer the approach, the higher the electrostatic attraction terms, such as the charge/induced-dipole interaction. The approach of H$^-$ is favourable until the cost of promotion of electron density into the higher 2$p$ orbital and the repulsion terms of the interaction potential are balanced by the attractive electrostatic and covalent terms.
As may be seen, at $R_e$ a rather extreme situation has developed, with a significant amount of electron density localized on the Be centre, on the side opposite to the incoming H$^-$, giving a very asymmetric density. We suggest that this leads to a small, additional attractive term in the potential of a Coulomb interaction between the H$^-$ and the partially exposed beryllium core. We also note that the electron density on the hydrogen atom is largely located centrosymmetrically, but with the Be atom apparently burrowing into the outer reaches of the H$^-$ 1s orbital. The NPA data calculated at $R_e$, shown in Table VII, supports the latter picture.

The HOMO appears to be almost entirely composed of Be orbitals, with 65.2% Be 2$s$ character and 34.6% Be 2$p_z$ character, with the remaining character coming from small contributions from Be orbitals of higher angular momentum and very small amounts of H 1$s$ character. Thus the HOMO can be viewed as a lone pair on the Be atom, formed as an $sp$ hybrid. It has a natural orbital occupancy of 1.735 at the CCSD level, using triple-zeta basis sets. The HOMO-1 orbital is largely composed of the H 1$s$ orbital (81.5%), but there is an 18.5% contribution from the Be orbitals, which can be well described as an $sp$ hybrid. Overall, this looks like a movement of the electron density on Be away from the incoming H$^-$, and then the partial donation of electron density from H$^-$ to the Be $sp$ hybrid orbital, in a dative covalent manner, but with both atoms retaining the majority of their electron density and very little being shared. We examine this further by considering the atomic charges.

The calculated natural orbital atomic charges are presented in Table VIII. In the case of BeH$^-$, the three methodologies employed produce very different results. Mulliken population analysis suggests a charge of almost $-1e$, corresponding to the total excess negative charge being transferred from the hydrogen anion to the metal, which would only be in agreement with the picture at short $R$, presented by Verdicchio et al. However, Mulliken population analysis is known to give unreliable results in many cases, and so we look now at the NPA results. This gives a very different picture, ascribing a charge of $-0.345$ to the beryllium atom. In our recent work on M$^+$–RG$_2$ (M = Li, Na, Be, and Mg), we confirmed that NPA analyses can lead to too-high a charge on the metal centre, while AIM gave results more in line with expectations. The results of the AIM analysis suggest that the negative charge remains localized to the hydrogen centre, with a charge of only $-0.060$ located on the beryllium; a result much more in line with the contour plots of Figure 4 and with expectations based upon the relative electronegativities and anion stabilities as discussed earlier. In addition, we note that these conclusions are in line with the “charge shift” plot in Figure 6 of Ref. 1, where we estimate a value of about $+0.6$ at $R_e$. This value is consistent with the excess negative charge being located between the H and Be centres. We also note

![FIG. 4. Natural orbital contour plots of the antibonding HOMO and bonding HOMO-1 natural orbitals for the M$_{IIa}$H$^-$ complexes calculated from the CCSD(T)/EBS electron density, at various internuclear separations; $R_e$ is the CCSD(T)/EBS value in each case (Table I).](image-url)
that the trend in the contour plots shown in Figure 4 of the present work suggest that at very short $R$, the electron density on Be may be repelled enough for significant electron density to appear on the “other” side, and for there to be more significant donation from H−. However, overall, we conclude that at $R_e$, the charge transfer in this system is minimal and that the AIM method is more reliable than the Mulliken and NPA ones. Note that we also concluded that the AIM charges were more in line with the contour plots for the RG−H+ species (see above).

We have also investigated the role of the negative charge in these systems by performing calculations on neutral beryllium in the presence of a negative point charge. From these it was seen that the point charge drives the perturbation of electronic structure of the beryllium atom, as the electron density localizes away from the incoming charge in order to minimize repulsive effects by formation of the $sp$ hybrid orbitals, exactly as observed for BeH−.

On the other hand, the neutral Be−He complex, although having the same electronic structure for its individual moieties, is very different in character at its equilibrium separation compared to the strongly bound BeH−. For Be−He, potential energy curves (provided as supplementary material) were calculated in the same way as described above, again using CCSD(T) theory, and aug-cc-pCVXZ ($X = Q, 5$) basis sets for Be and aug-cc-pVXZ ($X = Q, 5$) for He, with a final extrapolated basis set potential energy curve being produced. From this, $D_e$ was found to be 5.62 cm−1, which is in excellent agreement with the value of 5.7 cm−1 reported previously by one of us. Along with a significantly longer $R_e$ of 4.511 Å, this demonstrates how the strength of this interaction is considerably weaker for Be−He than for the BeH− system, and more like the He−H− interaction. Furthermore, molecular orbital contour plots of Be−He at $R_e$ (not shown) indicate that no delocalization of electrons between atoms occurs, and that the interaction is largely physical in nature, also similar to He−H− (see contour plot in Figure 3).

We conclude that in BeH− the interaction is initially driven by the charge/induced-dipole interaction, which causes the moieties to move together. At about 2.5$R_e$ the $sp$ hybrids start to be clearly formed (see Figure 4), which both serve to produce a small amount of incipient chemical bond formation, as well as reducing the repulsion by allowing electron density on the Be atom to move away from the incoming H−. Concomitantly, this movement of electron density allows the H− a partial view of the Be+ core, leading to some Coulomb interaction. The small size of Be leads to these being able to move close together, enhancing the attractive terms in the interaction. A balance is reached when the cost of moving electron density into the $sp$ hybrid together with the rising electron repulsion, matches the increased attraction terms arising from both the closer proximity of the two centres together with the Coulomb attraction between H− and the partially exposed Be+ centre.

It is interesting to note that the BeH− potential energy curve shows no obvious sign of an avoided crossing, which might be expected if the charge from H− moved to the Be centre, in line with the $T_1$ values, and close agreement between the CCSD(T) and CASSCF + MRCI + Q results. Further, the Birge-Sponer plot for BeH− in Figure 2 shows no sign of such an effect, with the expected linear region, and the long-range curvature.

3. Other MIIaH+ species

For MgH−, a similar picture emerges, but the greater size of Mg leads to a larger $R_e$ value and so smaller attractive terms, such as the Coulomb and charge/induced-dipole terms. This is despite the expected slightly lower cost of $sp$ hybridization, as judged by the smaller $^1P ← ^1S$ transition (see Table VI). The $D_e$ value is still significant, though, being calculated to be just under 12 000 cm−1. Looking at Table VII, we see that the NPA composition of the orbitals of MgH− and BeH− is quite similar, but for MgH− there is less $sp$ hybridization in the (bonding) HOMO-1 orbital and more in the (antibonding) HOMO orbital, also adding to the weaker bonding overall.

With the expected increasing atomic size, we might then anticipate a further fall in interaction energy as we continue to descend Group 2, but it can be seen that the $D_e$ values for the heavier Group 2 hydride anions are higher than that of MgH−. This is not a continuous increase (see Figure 1 and Table I), as the value seen for SrH− is somewhat higher than that of CaH−, and the value for RaH− is notably smaller than that of BaH−.

Table VI shows the excitation energies for the first $^1P$ and $^1D$ states of the Group 2 metals. These energies correspond to the movement of an $ns$ valence electron into an $np$ or $nd$ orbital, and are therefore indicative of the energetic cost associated with the orbital hybridization process. For Be and Mg, the $^1P$ state is notably lower in energy than the $^1D$ one and consequently, $sp$ hybrid orbitals form for these elements; for Ca, Sr, Ba, and Ra, however, the $^1D$ state is the lower lying. The heavier complexes would thus be expected to undergo $sd$ hybridization preferentially, and if the gap between the two excited states is small enough then $spd$ hybrids can form. Both $^1P$ and $^1D$ excitation energies are seen generally to decrease descending the group, implying that, regardless of which orbitals are involved, the hybridization becomes more energetically favourable for the heavier metals. This is seen to be in agreement with the trend seen in $D_e$, with the heavier complexes being more strongly bound. The source of this difference can be understood by reference to Table VII and to the contour plots in Figure 4. Table VII shows that for the heavier MH− species, significant $d$ character is now present in the HOMO and HOMO-1 orbitals, although more so in the HOMO-1. In particular, the $d$ orbital that is of the correct symmetry to interact is $(n−1)d_z$. We see that the contour plots shown for CaH− and BaH−, particularly for the latter, each show electron density “off-axis” as well as being positioned behind the metal centre on the side away from the incoming H−. Hence, we have the same loss of electron density between the approaching partners as we did in the cases of BeH− and MgH−, decreasing repulsion, and increasing the attractive terms, and allowing a Coulomb attraction between the H− and the partially revealed M+ core. However, this time we have the additional “bonus” of being able to move electron density off-axis, reducing the electron density...
repulsion effects further, and so allowing closer approach of H\(^-\) and increases in the attractive terms, leading to a higher \(D_e\) overall.

A very similar effect was seen in our work on the M\(_{\text{IIa}}\)\(^+\)-RG complexes.\(^{45}\) It is interesting to note that the overall populations of the metal valence ns orbitals are very similar for all MH\(^-\) species, indeed the population is slightly higher for the heavier species than it is for MgH\(^-\), but the ability to make use of the 3d\(_{z^2}\) orbital allows electron repulsion effects to be reduced more than in the two lightest species. This is particularly marked in the case of the HOMO-1 for BaH\(^-\) where almost 2/3 of the electron density that resides on Ba is located in the 5d\(_{z^2}\) orbital, leading to this species having the largest \(D_e\) value. This can be attributed to the very small s-d gap for Ba (see Table VI), in line with our observation on Ba\(^-\)RG complexes;\(^{45}\) we highlight that even though \(R_e\) for BaH\(^-\) than BeH\(^-\), in line with the larger atomic number of Ba, it is remarkable that the BaH\(^-\) \(D_e\) value is the highest of the M\(_{\text{IIa}}\)H\(^-\) species.

The greater interaction terms are also caused by the fact that the electrostatic attraction terms are expected to be greater for the heavier M\(_{\text{IIa}}\) atoms. In Table VI we give the \(\alpha_d\) values of the neutral M\(_{\text{IIa}}\) and M\(_{\text{IIa}}\)\(^+\) species. Both of these may be seen to have significant values, so that in the interacting MH\(^-\) species, even when there is significant lowering of the electron density between the two approaching atoms, there will still be a large charge/induced-dipole interaction term. Further, this term will be increasing as the atomic number of M\(_{\text{IIa}}\) is increasing. In Table V we show the calculated charge/induced-dipole terms, and compare these to \(D_e\). Additionally, in Figure 1 we show the variation of both of these terms with M\(_{\text{IIa}}\). As may be seen, the trend in the former closely follows the trend in the latter. Thus, although there are large repulsion terms and other higher-order attraction terms to consider, the main variation in \(D_e\) is carried by the variation in the charge/induced-dipole term. The smooth trends in \(R_e\) (see Figure 1) and \(\alpha_d\) (see Table VI) indicate that it is a subtle balance that produces this oscillatory variation in \(D_e\).

It is interesting to note the great similarity in the atomic charges between all three population methods for the heavier species (see Table VIII), in contrast to the two lightest species. While it is true that the Mulliken charges are still overestimated, they are much closer to the NPA and AIM values; and the latter two are very close to each other. This suggests that it is the short bond lengths, and distortion of the atomic densities which are causing the Mulliken population method, in particular, but also NPA to fail; the AIM method, on the other hand, seems more robust. We also note that the generally increasing negative atomic charges on the metal centres are in line with the increasing electron affinities of the species (see Table VI).

Another way of viewing the trends in \(D_e\) is that BeH\(^-\) has a value that is “too high.” This deviation could be rationalized both by the small size of the Be atom, allowing the atoms to move close together, as mentioned above, but also by recalling that the outermost valence electrons on the metal centres are not found in pure ns atomic orbitals in the M\(_{\text{IIa}}\)H\(^-\) species. Instead they are found in hybrid orbitals that facilitate the movement of electron density away from the internuclear region. In this way, the incoming H\(^-\) has a clearer “view” of the metal cation and will experience a stronger Coulombic interaction. For all Group 2 metals except beryllium, the HOMO of M\(_{\text{IIa}}\)\(^+\) is a filled (\(n-1\))p orbital, while beryllium possesses no such filled p-orbital, and instead presents its core 1s orbital to the hydride anion. The repulsive interaction with this s orbital is expected to be less compared to the repulsive interaction experienced by the rest of the series on account of the more directional occupied p\(_{z}\) orbitals. Consequently, the overall strength of interaction for BeH\(^-\) may be viewed as being higher than might be anticipated from the other complexes.

Finally, we note that RaH\(^-\) also deviates from the observed trends, but this is easily explained by the lanthanide contraction and relativistic effects. Thus, we expect Ra not to be as large as expected based on the trend Be–Ba, and also we expect the (\(n-1\))d orbital to be comparatively both less contracted and of higher energy than it is for Ba. Thus, overall, the comparatively lower \(D_e\) value for RaH\(^-\) and the smaller contribution of the 6d\(_{z^2}\) orbital to the HOMO-1 bonding orbital is not that surprising.

Looking at the Birge-Sponer plots in Figure 2, as for BeH\(^-\) we see that these are highly linear early on, with the expected tail to higher energy. This, and the close agreement of the present CCSD(T) results with the MR-ACPF approach for BeH\(^-\) as well as the multireference results described above, suggests that there are no significant avoided crossings. The picture thus seems to be of H\(^-\) approaching the M\(_{\text{IIa}}\) atom and then hybridization, followed by some dative covalent bonding of H\(^-\) into the empty sp (or sp\(_d\)) hybrid orbital.

### IV. CONCLUSIONS

Potential energy curves for the RG–H\(^-\) and M\(_{\text{IIa}}\)H\(^-\) series have been calculated using CCSD(T) theory and large basis sets, and extrapolated to the basis set limit. The results for RG–H\(^-\) show that these are physically bound, with a significant charge/induced-dipole interaction, but also a significant repulsion term. The balance of these, with the “soft”

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**TABLE VIII.** Mulliken, NPA, and AIM charges (CCSD/aug-cc-pVTZ) on the metal centre for each member of the M\(_{\text{IIa}}\)H\(^-\) series, along with the Cremer-Kraka bonding parameter,\(^{46}\) \(H(R)\), obtained from an AIM analysis.

<table>
<thead>
<tr>
<th></th>
<th>BeH(^-)</th>
<th>MgH(^-)</th>
<th>CaH(^-)</th>
<th>SrH(^-)</th>
<th>BaH(^-)</th>
<th>RaH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mulliken</td>
<td>-0.990</td>
<td>-0.711</td>
<td>-0.355</td>
<td>-0.266</td>
<td>-0.205</td>
<td>-0.202</td>
</tr>
<tr>
<td>NPA</td>
<td>-0.345</td>
<td>-0.219</td>
<td>-0.180</td>
<td>-0.160</td>
<td>-0.178</td>
<td>-0.153</td>
</tr>
<tr>
<td>AIM</td>
<td>-0.060</td>
<td>-0.104</td>
<td>-0.117</td>
<td>-0.113</td>
<td>-0.178</td>
<td>-0.109</td>
</tr>
<tr>
<td>(H(R))</td>
<td>-3.76 \times 10^{-2}</td>
<td>-3.44 \times 10^{-3}</td>
<td>-6.05 \times 10^{-3}</td>
<td>-5.66 \times 10^{-3}</td>
<td>-8.71 \times 10^{-3}</td>
<td>-6.23 \times 10^{-3}</td>
</tr>
</tbody>
</table>
nature of the $H^-$, leads to an increasing distortion of the “soft” $H^-$ 1s density as the atomic number of RG increases; interestingly, this also leads to a monotonic decrease in the $R_e$ values with increasing atomic number of RG, contrary to usual expectations. Agreement of spectroscopic constants for the three lighter complexes was seen with the study of Vallet et al., but significant disagreements were seen with other studies, particularly with the Ne–$H^-$ and Ar–$H^-$ results from the model potential study by Li and Lin. Finally, the lack of covalency in these systems is confirmed by the calculated values of the Cremer-Kraka parameter, $H(R)$, given in Table IV, which are all positive, whereas negative values indicate covalency.

Results for Be$H^-$ and Mg$H^-$ are in good agreement with previous results, but only if the basis set includes diffuse functions. We particularly note the good agreement with the recent multireference results of Koput for Be$H^-$. The entire M$_{II}$a$H^-$ group is found to be strongly bound as a result of $sp$ or $spd$ hybridization of the metal, reducing electron repulsion terms. Be$H^-$ appears to have an anomalously high $D_e$, which is attributed to the absence of filled $p_z$ orbitals giving a weaker repulsive interaction with $H^-$ when compared to the rest of the series.

In both sets of species studied the charge-induced-dipole interaction is significant and it appears to set the trend for the interaction, even though it is much greater than $D_e$ in all cases, particularly for M$_{II}$a$H^-$.

The large repulsion term is as expected for interactions between closed-shell species, but it is highly interesting to see that for the M$_{II}$a$H^-$ species the ability to displace electron density away from the incoming $H^-$ leads to a very strong interaction. Despite this, the amount of charge transfer for the lighter species is rather low, although the charge transfer is higher for the heavier species, in line with the increasing electron affinities of the M$_{II}$a atoms. Finally, the calculated values of the Cremer-Kraka parameter, $H(R)$, presented in Table VIII do indicate a small amount of covalency in all of these systems, with the values all being slightly negative, but far away from values for truly covalent species. It is interesting to note that the most negative value is for Be$H^-$ which would indicate it is the most covalent (although the amount of covalency is still small). We reiterate that overall, it seems that the AIM charges are more in line with the contour plots than are the NPA, but the Mulliken charges are significantly too high in most cases.

In summary, the RG–$H^-$ and M$_{II}$a$H^-$ species are two contrasting series, despite both arising from the interaction between a closed-shell atom and a closed-shell anion. The strong binding of the M$_{II}$a$H^-$ species arises from the ability of M$_{II}$a to undergo hybridization, which is not possible for the RG atoms, whose excited states lie very high in energy. The weak binding in Be–He confirms that it is the initial repulsion from the incoming $H^-$ that induces the hybridization in the M$_{II}$a$H^-$ species, which is “paid for” by the increased attractive terms, and the reduction in the electron repulsion terms.

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44 http://physics.nist.gov/PhysRefData/ASD/levels_form.html