Ab initio studies of the ground and first excited states of the Sr–H₂ and Yb–H₂ complexes

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Accurate intermolecular potential-energy surfaces (IPESs) for the ground and first excited states of the Sr–H₂ and Yb–H₂ complexes were calculated by means of the CCSD(T) method with the Douglas-Kroll-Hess Hamiltonian and modified Dunning’s basis sets of triple-$\zeta$ quality extended with 2 sets of diffuse functions and a set of midbond functions. The ground-state IPESs are similar in both complexes, being relatively isotropic with two minima and two transition states (equivalent by symmetry). The global minima correspond to the collinear geometries with $R = 5.45$ and 5.10 Å and energies of $-27.7$ and $-31.7$ cm$^{-1}$ for the Sr–H₂ and Yb–H₂ systems, respectively. The calculated surfaces for the Sr($^3P$)-H₂ and Yb($^3P$)-H₂ states are deeper and more anisotropic and they exhibit similar patterns within both complexes. The deepest surfaces are characterised by the global minima of ca. $-2553$ and $-2260$ cm$^{-1}$ in the T-shape geometries at $R = 2.41$ and 2.29 Å for Sr–H₂ and Yb–H₂, respectively. Additional calculations for the complexes of Sr and Yb with the He atom revealed a similar, strong dependence of the interaction energy on the orientation of the $p$-orbital in the the Sr($^3P$)-He and Yb($^3P$)-He states.

I. INTRODUCTION

Strontium (Sr) is an alkaline-earth metal with atomic number $Z = 38$, while ytterbium (Yb) is a rare-earth metal with $Z = 70$. However, because of its electronic configuration, Yb resembles the alkaline-earth elements. In both Sr and Yb the ground states of [Kr]$5s^2$ or [Xe]$4f^{14}6s^2$ configurations, respectively, correspond to $^1S_0$ terms. This resemblance between Sr and Yb also implies similar schemes in their lowest excited states. The first excited triplet configurations for the Sr atom and the corresponding energies of the states are $^3$S$_0$: [Kr]$5s5p$ $\rightarrow$ $^3P_0$ (14 317.520 cm$^{-1}$), $^3P_1$ (14 504.351 cm$^{-1}$), and $^3P_2$ (14 898.653 cm$^{-1}$), while for the Yb atom we have: [Xe] $4f^{14}6s6p$ $\rightarrow$ $^3P_0$ (17 288.439 cm$^{-1}$), $^3P_1$ (17 992.007 cm$^{-1}$), and $^3P_2$ (19 710.388 cm$^{-1}$). The spin-orbit coupling (SOC) splittings in Sr (186.831 and 394.212 cm$^{-1}$) and in Yb (703.568 and 1 718.381 cm$^{-1}$) demonstrate violation of the Landé interval rule.

Simple forms of the ground-state interaction potentials with no hyperfine structure, availability of many stable isotopes, the long-lived metastable $^3P_0$ states resulting in the ultranarrow intercombination transitions of $^1S_0 \rightarrow ^3P_0$ at experimentally convenient wavelengths are the most important advantages of these two-electron elements, which made them attractive objects for research studies. They have been successfully used in the fields of trapping ultracold quantum gas and Bose-Einstein condensation, quantum information processing, Fermi degeneracy, studies of fundamental symmetries or photoassociation spectroscopy.

However, it seems that it is the optical atomic clock (see e.g. Refs. [12] and [17]) that receives the most attention, and thus quickly became a hot research topic. Driven by progress in the fields of atomic, optical and quantum science, vast improvements in atomic clocks was made and they soon surpassed the accuracy of caesium microwave clocks [18–21]. Optical atomic clocks are already being used to test fundamental theories and in development of new definitions of time and frequency standards [22, 23], heralding a revision of the International System of Units (SI) [24]. They are also crucial for a rapid development in technologies that support broadband communication networks, navigation with global positioning systems (GPS) or clock-based geodesy [25].

In each of the standards, the concept of the reference frequency we tightly relate to the resonance frequency of the unperturbed atom or ion. However, in practise such a situation is impossible to attain and often, instead of being eliminated, the influence of external factors are usually best minimised and meticulously included in the systematic error budget. Thus, the actual accuracy depends on the control we have over the perturbations that the system experiences. One of these factors are collisions of residual-gas atoms or molecules with the clock atom resulting in a frequency shift of the transition-line center. Recent improvements in the control of the systematic corrections in optical atomic clocks towards the $10^{-18}$ level and beyond, make the collisional frequency shift [26, 27] an important contribution to the error budget [28]. The measurements of the partial pressures of the background gases in the vacuum chamber showed [29] that the most abundant gas is molecular hydrogen (approx. 60% of the pressure).

Therefore, in this study we focus on the interactions of the Sr and Yb atoms in their ground and first excited states with the ground-state H₂ molecule. The intermolecular potential-energy surfaces (IPESs) are ab initio calculated using highly accurate methods and large basis sets. The knowledge of the IPESs is crucial for estimations of the collisional frequency shifts, which are essen-
tial for ultimate clock performance.

The manuscript is organized as follows: In Sec. II the details of the quantum-chemical calculations are given. Then, in Sec. III the results of the studies are presented: In Sec. III A we describe methodological aspects and the results of the basis set studies, while in Sec. III B the details of the IPESs are reported. Finally, in Sec. IV we summarize and conclude.

II. COMPUTATIONAL DETAILS

The geometries of the systems were characterised by three variables: the H–H bond length \( r_{\text{HH}} \), the distance \( R \) from the Sr (or Yb) atom to the center of the \( \text{H}_2 \) molecule, and the angle \( \theta \) between the \( \text{H}_2 \) molecular axis and the line connecting the Sr (or Yb) atom with the center of \( \text{H}_2 \). \( \theta = 0 \) corresponds to the Sr-H\( _2 \) (or Yb-H\( _2 \)) collinear orientation, while \( \theta = 90^\circ \) denotes the T-shape geometry of the complex. Because of the symmetry of the system, only the values \( 0 \leq \theta \leq 90^\circ \) needed to be considered. In all calculations the value of \( (r_{\text{HH}}) = 0.7666393 \) \( \text{Å} \) representing the H–H distance averaged over the ground vibrational state of \( \text{H}_2 \) \cite{30, 31} was used.

The quantum chemical calculations for systems containing heavier atoms are usually very challenging. Not only because of a large number of electrons to correlate making the studies time- and resource-consuming, but also because of partially multiconfigurational character resulting from mixing of several close-lying states, non-negligible relativistic contributions and a lack of families of basis sets allowing for estimation of the complete basis set limit.

In this study we have employed the spin-restricted coupled cluster with single, double and non-iterative triple excitation [R-CCSD(T)] method as implemented in MOLPRO (2012.1 \cite{32} version). At the moment, this method \cite{40} is the most efficient way to handle multi-electron systems, the angle \( \theta \) and third order Douglas-Kroll-Hess (DKH) Hamiltonian \cite{33–35} in the case of the Sr-H\( _2 \) complex.

In the calculations with the ECP28MB pseudopotential, the ECP28MB-ANO \cite{48} basis set was employed for the Yb atom and Dunning’s augmented standard aug-cc-pVXZ (X=D, T, Q) basis set \cite{12, 17} (denoted as aXZ) for the H atoms. This set was also extended by adding respectively 4 and 2 \( h \) - and \( i \)-type functions using the 4 and 2 lowest exponents of the \( g \)-type functions.

In the calculations for the Sr-H\( _2 \) system, the aug-cc-pVTZ-DK2 basis set \cite{15} for the Sr atom and the aug-cc-pVXZ-DK basis set \cite{10, 11} for the H atom, further denoted as aTZ-DK.

In some cases we increased the number of diffuse functions using the even-tempered scheme implemented in MOLPRO \cite{32} (since denoted as “even”). All the basis sets were further extended by a set of the 3s3p2d2f1g1h midbond functions denoted as 33211.

In the calculations for the complexes with helium, the cc-pVTZ-DK and aug-cc-pVTZ-DK bases \cite{15, 12} for the \( \text{He} \) atom were used (see Sec. III B 2).

III. RESULTS

A. Methodological aspects and basis set study

As the first step in our study, we decided to test the PP approximation. The CCSD(T) interaction energies calculated with the ECP28MB PP for the Yb-H\( _2 \) collinear geometry are collected in Table I. As a reference, in the last column we have added the CCSD(T)-DKH3 results obtained with the uncontracted ANO-RCC (\( \text{iANO-RCC} \)) basis set extended with the 33211 midbond set.

The results in Table I indicate that the minimum of the interaction energy corresponds approximately to \( R = 5.20 \) \( \text{Å} \) and its position seems to be independent of the used basis set. An addition of more diffused functions (1 or 2 even-tempered) decreases slightly the absolute value of the interaction energy (from \(-28.00 \) to \(-27.80 \text{ cm}^{-1} \)), while an extension of the basis set with functions with greater angular momentum (\( h \), \( i \))

The interaction energies were corrected for the basis set superposition error using the counterpoise (CP) method \cite{10}.

To find the optimal basis set for the IPES calculations, we have started our study with an analysis of the performance of several available basis sets. The tests were carried out for the computationally more demanding Yb atom. We mainly focused on correlation-consistent family of basis sets developed for scalar relativistic calculations. The cc-pVXZ-DK3 \((X=D, T, Q)\) basis set \cite{41} for the Yb atom and the cc-pVXZ-DK \((X=D, T, Q)\) basis set (original exponents taken from Ref. \cite{42} and recontracted in Ref. \cite{43}) for the H atoms were used. A combination of the two bases equal in \( X \) in this study we denote as XZ-DK.

Further, the large ANO-RCC basis set \cite{44, 45} was also employed.

In the calculations with the ECP28MB pseudopotential, the ECP28MB-ANO \cite{48} basis set was employed for the Yb atom and Dunning’s augmented standard aug-cc-pVXZ \((X=D, T, Q)\) basis set \cite{12, 17} (denoted as aXZ) for the H atoms. This set was also extended by adding respectively 4 and 2 \( h \) - and \( i \)-type functions using the 4 and 2 lowest exponents of the \( g \)-type functions.

In the calculations for the complexes with helium, the cc-pVTZ-DK and aug-cc-pVTZ-DK bases \cite{15, 12} for the \( \text{He} \) atom were used (see Sec. III B 2).
TABLE I: The CCSD(T) interaction energy values (in cm$^{-1}$) for the ground state of the Yb-H$_2$ complex in the collinear geometry. The intermolecular distance values $R$ are given in angstroms. In all the calculations the 332211 midbond function set was used. See Sec. III A for more details regarding the used basis functions (bs).

| Yb | Basis set | Additional bs | $R$ | Interaction energy |
|----|-----------|---------------|----|-------------------|
| ECP28MWB | ECP28MWB-ANO | 1 even | 4.80 | -21.17 |
| ECP28MWB | ECP28MWB-ANO | $h_{1} + 1$ even | 5.00 | -24.01 |
| ECP28MWB | ECP28MWB-ANO | 2 even | 5.60 | -24.61 |

As the next step we performed frozen-core CCSD(T) calculations using the DKH3 Hamiltonian. In the calculations we employed the XZ-DK basis sets extended by the 332211 midbond function set and the resulting interaction energies are shown in Table II. For most of the bases the minimum is located in the proximity of $R = 5.20$ Å. However, for some of them, the position of the minimum shifts to shorter intermolecular distances. As one can expect, the interaction energy increases (in absolute value) with the increasing size of the basis set ($-23.92$ and $-29.72$ cm$^{-1}$ for the DZ-DK and QZ-DK bases, respectively), and a greater change is observed for the DZ-DK to TZ-DK transition ($-23.92$ vs. $-27.66$ cm$^{-1}$) than for the TZ-DK to QZ-DK one ($-27.66$ cm$^{-1}$ and $-29.72$ cm$^{-1}$, respectively). We have also tested the effect of an addition of diffuse functions on the interaction energy of the complex. The effect is largest for the smallest, DZ-DK basis set. After the addition of two sets of diffuse functions ("DZ-DK+2 even" in Table II), the obtained value of $-33.04$ cm$^{-1}$ seems to be overestimated in comparison with the reference, uncontracted ANO-RCC basis set result of $-31.45$ cm$^{-1}$. A similar extension of a basis set for TZ-DK and QZ-DK causes a much smaller change ($-3.75$ and $-1.90$ cm$^{-1}$, respectively). It indicates that these bases are more balanced than the DZ-DK one. An addition of the third set of diffuse functions in the case of the TZ-DK basis set lowers the interaction energy only by 0.02 cm$^{-1}$. It means that this basis set is already saturated with diffuse functions.

Since the CCSD(T) results obtained with the DKH Hamiltonian seem to be more reliable than the PP ones, we have decided to perform the calculations employing the former approximation. Because of its medium size and the results close to the uANO-RCC+332211 ones, the TZ-DK basis set extended with 2 sets of diffuse functions and the 332211 midbond set (denoted as TZ-DK+2 even+332211) will be used in the following studies. Some additional tests (not presented here) showed that the difference between the TZ-DK+2 even+332211 and uANO-RCC+332211 results in the lowest excited Yb($^3P$)-H$_2$ state are also small. For consistency’s sake, the aug-cc-pVTZ-DK2 basis set [48] for the Sr atom and the aug-cc-pVXZ-DK basis set [42,43] for the H atom both extended with 2 sets of diffuse functions were used in the case of Sr-H$_2$. 

Increases (in absolute value) the calculated interaction energy ($-27.99$ vs. $-28.40$ cm$^{-1}$). A more pronounced difference corresponds to the change of the hydrogen basis set from aDZ to aTZ (from $-27.99$ to $-29.81$ cm$^{-1}$).

However, it is clear that the interaction energy is still underestimated (in absolute value) by ca. 1.64 cm$^{-1}$ in comparison with the best CCSD(T)-DKH3/uANO-RCC+332211 result.
TABLE II: The CCSD(T) interaction energy values \((\text{in cm}^{-1})\) for the ground state of the \(\text{Yb-H}_2\) complex in the collinear geometry. The intermolecular distance values \(R\) are given in angstroms. In all the calculations the 332211 mdmb function set was used. See Sec. III A for more details regarding the used basis functions (bfs).

| Basis set          | DZ-DK | DZ-DK | DZ-DK | TZ-DK | uTZ-DK | TZ-DK | TZ-DK | TZ-DK | QZ-DK | QZ-DK | QZ-DK |
|--------------------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|
| Additional bfs     |       |       |       |       |        |       |       |       |       |       |       |
| Number of bfs      | 150   | 183   | 216   | 229   | 385    | 283   | 337   | 391   | 330   | 411   | 492   |
| Interaction energy |       |       |       |       |        |       |       |       |       |       |       |
| \(R\)              |       |       |       |       |        |       |       |       |       |       |       |
| 5.00               | 229.1 | 227.2 | 226.9 | 228.6 | 227.0 | 227.0 | 227.0 | 227.0 |
| 5.20               | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 |
| 5.40               | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 | 227.0 |

B. IPESs

1. \(\text{Sr-H}_2\) and \(\text{Yb-H}_2\)

The calculations for the first excited \(\text{Sr}^{(3P)}\)-\(\text{H}_2\) and \(\text{Yb}^{(3P)}\)-\(\text{H}_2\) states involve considering three states corresponding to three possible spatial orientations of the singly occupied \(p\)-orbital and they can be classified according to their symmetry. Simplistic representations of the singly occupied \(p\)-orbital orientation in the first excited state are shown in Fig. [Fig. 1]. As the \(\text{H}_2\) molecule approaches the \(\text{Sr}\) (\(\text{Yb}\)) atom collinearly (\(C_\infty\) symmetry), the degeneracy of the \(3P\) state is lifted and gives rise to one state of \(3A_1\) symmetry and one doubly degenerate state of \(3B_1\) (= \(3B_2\)) symmetry. In arrangements of lower symmetry, the latter state further splits into two states. In the collinear geometry (\(C_\infty\)) the states can be labelled as \(3A_1\) and \(3B_1\) (= \(3B_2\)) – see Figs. [Fig. 1]-c. In the T-shape geometry (\(C_{2v}\)) we have the \(3A_1\), \(3B_1\) and \(3B_2\) states (cf. Figs. [Fig. 1]-f), whereas in bent symmetry (\(C_s\)) the states become \(1A_1\), \(2A_1\)' and \(3A_1''\).

FIG. 1: Schematics of the singly occupied \(p\)-orbital orientation in the first excited state of the \(\text{Me-H}_2\) (\(\text{Me = Sr,Yb}\)) complexes for the collinear (a-c) and T-shape (d-f) configurations.

To ease the analysis, here we employ a nomenclature similar to that corresponding for the T-shape geometry, that is \(A_1\), \(B_1\) and \(B_2\). This approximately describes the orientation of the singly occupied \(p\)-orbital. In the case of the \(A_1\) surface the \(p\)-orbital is directed towards the hydrogen molecule (Figs. [Fig. 1]a and d), whilst in the case of the \(B_1\) surface the \(p\)-orbital is perpendicular to the complex symmetry plane (Figs. [Fig. 1]b and e). The \(B_2\)
surface corresponds to the third situation, where the $p$-orbital is neither perpendicular to the complex symmetry plane nor directed towards $H_2$ (Figs. 1 and f).

The calculated potential-energy curves for the ground and the first excited state of the Sr-H$_2$ and Yb-H$_2$ complexes are depicted in Figs. 2 and 3 respectively. The values of the $\theta$ angle were chosen that they correspond to the abscissas of 9-points Lobatto-Gauss quadrature. In fact, because of the symmetry of the system, we needed to run the calculations only for 5 different angles.

FIG. 2: The calculated intermolecular potential-energy curves for the ground (a) and the first excited (b–d) states of the Sr-H$_2$ complex.

Two minima and two transition states (equivalent by symmetry) are found on the ground-state IPES. The global minimum is characterised by the collinear geometry, $R = 5.45$ Å ($5.10$ Å) and an energy of $-27.68$ cm$^{-1}$ ($-31.72$ cm$^{-1}$), while the transition state corresponds to the T-shape geometry with $R = 5.62$ Å ($5.26$ Å) and an energy of $-18.37$ cm$^{-1}$ ($-21.65$ cm$^{-1}$) in the case of the Sr-H$_2$ (Yb-H$_2$) complex.

The calculated excited-state surfaces (Figs. 2b-d and 3b–d) are deeper and more anisotropic than the respective ground-state one and they exhibit a similar pattern within both complexes. In the following description the given value refers to the Sr-H$_2$ complex, while the value in parentheses to Yb-H$_2$.

The $A_1$ surfaces (see Figs. 2b and 3b) are the shallowest ones with the global minimum of $-47.83$ cm$^{-1}$ ($-47.84$ cm$^{-1}$) for $\theta = 0^\circ$ and $R = 6.22$ Å ($6.08$ Å), but are still deeper than those of the ground state (cf. Figs. 2a and 3a). As $\theta$ increases, the minima on the curves become shallower and for $\theta = 90^\circ$ the potential energy curves have mainly repulsive character. Only a very shallow (less than 0.03 cm$^{-1}$ in absolute value) minimum (a transition state on the IPES) appears in the vicinity of $R = 8.02$ Å for Yb-H$_2$ (no minimum in the case of the Sr-H$_2$ system).

The $B_1$ IPESs are much deeper than the $A_1$ ones. The global minimum has an energy of $-213.24$ cm$^{-1}$ ($-299.50$ cm$^{-1}$) and corresponds to the T-shape geometry with $R = 3.13$ Å ($2.99$ Å). The transition state at the collinear arrangement with an energy of $-2.88$ cm$^{-1}$ ($-12.00$ cm$^{-1}$) lies at $R = 5.05$ Å ($4.44$ Å).

A similar pattern to the $B_1$ IPESs present the $B_2$ surfaces. However, these surfaces are the deepest one with the global minimum of ca. $-2052.8$ cm$^{-1}$ ($-2260.1$ cm$^{-1}$) in the T-shape geometry at $R = 2.41$ Å ($2.29$ Å). The transition states are exactly the same as for the $B_1$ surfaces, since both IPESs at the collinear arrangement correlate to the same state.

2. Sr-He and Yb-He

To check whether the above observed patterns in the calculated interaction energies reflect a more general trend, we compare our results with isoelectronic, but simpler complexes of Sr and Yb with He. Using the same methodology as above and analogous basis sets, we have calculated the potential-energy curves for both dimers. The aug-cc-pVTZ-DK and cc-pVTZ-DK bases for the He atom were used in the case of the Sr-He and Yb-He complexes, respectively.

The excited states are labelled similarly as for the complexes with H$_2$: $A_1$ (the $^3A_1$ state) with the $p$-orbital along the (Sr(Yb))-He interatomic axis and $B_1$ (= $B_2$) (the $^3B_1$ (= $^3B_2$) states) with the $p$-orbital is perpendicular to the (Sr(Yb))-He axis (compare Fig. 1).

The results, depicted in Fig. 4 are similar in both systems with the Yb-He curves being usually deeper than the Sr-He ones. The exception is the $A_1$ state where the (weak) interaction (slightly exceeding 1 cm$^{-1}$ in absolute value) is comparable in both complexes.

In the ground state the interaction-energy minimum is
The calculated intermolecular potential-energy curves for the ground (a) and the first excited (b) states of the Sr-He and Yb-He complexes.

FIG. 4: The calculated intermolecular potential-energy curves for the ground (a) and the first excited (b) states of the Sr-He and Yb-He complexes.

\(-3.11 \text{ cm}^{-1}\) at 6.23 Å for Sr-He and \(-3.87 \text{ cm}^{-1}\) at 5.82 Å for Yb-He, while in the exited B1 state the minima are much deeper with energies of \(-10.54 \text{ cm}^{-1}\) (at 4.99 Å) and \(-16.59 \text{ cm}^{-1}\) (at 4.50 Å) in the Sr-He and Yb-He complexes, respectively.

The results reveal a similar trend as for the complexes with the hydrogen molecule and confirm a strong dependence of the interaction energy on the orientation of the singly occupied p-orbital: the interaction is attractive and much stronger when the p-orbital is perpendicular to the interatomic axis and is almost repulsive if the p-orbital is oriented towards the He atom.

IV. SUMMARY

Accurate IPESs for the ground and first excited states of Sr-H\(_2\) and Yb-H\(_2\) were constructed using a high-level ab initio method and extensive basis sets. Methodological and basis-set studies were performed in order to ensure the proper choice of the approximation. In the calculations of the IPESs, the CCSD(T) method with the DKH Hamiltonian and the modified Dunning’s basis sets of triple-ζ quality extended with 2 sets of diffuse functions and the 332211 midbond set were used.

The shapes of the ground-state IPESs are similar in both complexes, being relatively isotropic with two minima and two transition states (equivalent by symmetry). The global minima correspond to the collinear geometries with \(R = 5.45\) and 5.10 Å and energies of \(-27.68\) and \(-31.72 \text{ cm}^{-1}\) for the Sr-H\(_2\) and Yb-H\(_2\) systems, respectively.

The calculated excited-state surfaces for Sr\((3P)\)-H\(_2\) and Yb\((3P)\)-H\(_2\) are deeper and more anisotropic and, again, they exhibit a similar pattern within both complexes. The A1 surfaces are the shallowest ones with the global minimum of \(-47.83 \text{ cm}^{-1}\) (at \(R = 2.41\) and 2.29 Å) in the T-shape geometries for Sr-H\(_2\) (Yb-H\(_2\)). The B1 IPESs are much deeper than the A1 ones, but the B2 surfaces are the deepest ones with the global minimum of ca. \(-2052.8\) and \(-2260.1 \text{ cm}^{-1}\) in the T-shape geometries at \(R = 2.41\) and 2.29 Å for Sr-H\(_2\) and Yb-H\(_2\), respectively.

Additional calculations for the isoelectronic complexes of Sr and Yb with the He atom revealed a similar, strong dependence of the interaction on the orientation of the p-orbital in the Sr\((3P)\)-He and Yb\((3P)\)-He states.

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