Rydberg states of ZnAr complex

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ABSTRACT

Ab initio potential energy curves (PECs) of electronic states of ZnAr complex are calculated up to Rydberg state correlating with the \((4s6s)^1S_0\) asymptote of Zn atom. Analysis of various sources of errors of presented calculations is performed including finite basis set size, deficiencies in inclusion of the electron correlation and relativistic effects, and size-inconsistency errors of the multireference second-order perturbation theory. In particular, it is emphasised that the inclusion of the midbond bases substantially improves the convergence rate of the binding energies with respect to the basis set size not only for the van der Waals ground state of ZnAr complex, but also it is the case for the excited states including the Rydberg ones. Wherever it is possible, the comparison with the experimental data and other theoretical results is presented. Properties of the double-well PECs of the \(\Sigma\) Rydberg states are interpreted within the simplified theory, in which, the appearance of the energy barrier and, partially, of the outer well originates from the low-energy scattering of the Rydberg electron on the Ar atom.

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1. Introduction

Usually peculiar shapes of potential energy curves (PECs) of diatomic molecules result from the avoided crossings of two or more states of the same symmetry. Another source of the non-standard properties of PECs may be the change of the relative importance of spin–orbit interaction along the internuclear distance resulting in change of the physical character of the electronic state. An additional origin of special properties of PECs arises when at least one of the constituent atoms is excited into...
the Rydberg state with spatial extent beyond the range of internuclear distance at which attractive internuclear forces dominate, i.e. outside the (inner) well of the potential energy. In such a case, PECs of the Rydberg \( \Sigma \) states exhibit undulations reproducing the oscillations of the atomic Rydberg electron density along the molecular axis \([1]\). An extreme consequence of PEC undulations is the formation of the ultra-long Rydberg molecule, e.g. \( \text{Rb}(5s) - \text{Rb}(ns) \) \( ^3\Sigma \), \( n = 34 - 40 \), within one of the outer wells \([2-4]\) exhibiting macroscopic bond length \((\sim 0.1 \mu \text{m})\), homonuclear molecules possessing permanent electric dipole moment \([5]\) reaching values of kilo-Debye \([6]\) and having exotic electronic densities of trilobite \([6]\) or butterfly \([7]\) shape.

In 1980s, spectra of 12-group metal atom – rare gas (Me-Rg) van der Waals (vdW) complexes provided early experimental indication of the undulations of PECs \([5-7]\). \( (6s7s) ^3\Sigma \) of HgAr \([8]\). It is interesting to note that in that place, this PEC was considered as two distinct ones, possibly realised by \( \Omega = 1 \) and \( 0^- \) states \([9, 10]\) strongly bound state with minimum reflecting the energy well of the Hg\(^+\)Ar cation ground state and the ‘unexplained’ weakly bound state possessing energy minimum at longer internuclear distance.\(^1\) Correct double-well character of \( (6s7s) ^3\Sigma \) states of HgAr was suggested by Kraus and Mies \([11]\). Further experimental explorations of the lowest \( ^3\Sigma \) Rydberg states of other Me–Rg vDW complexes have shown that these states exhibit the double-well character: CdAr \([12-16]\), CdKr \([14, 17, 18]\) or they just possess an energy barrier without the outer well: \( E(3\Sigma^+)\ \text{Hg}(7\ ^3S_1)\text{Ne} \) \([19]\) or CdNe \([20]\), where the inner energy minimum is above the corresponding atomic asymptote. Also, higher Rydberg states were experimentally observed: \( \text{Hg}(n\ ^3S_1)\text{Ne} \) \((n = 8 - 10)\) and \( \text{Hg}(8\ ^3S_1)\text{Ar} \) \([21]\); \( \text{Hg}(n\ ^1S_0)\text{Ne} \) \((n = 7 - 9)\) \([22]\); in this case, clear experimental evidence of the energy barrier was reported only for the lowest singlet Rydberg state, i.e. \( \text{Hg}(7\ ^1S_0)\text{Ne} \) \([22]\). At the same time, recent \textit{ab initio} calculations \([23]\) performed for CdAr complex up to the Rydberg state \( 2S+1\Omega(\pm) = 1\Omega^+ \) correlating with the \( (5s5s) ^1S_0 \) asymptote have supported the expectation that all the Rydberg states of predominant \( \Sigma \) symmetry considered there possess two energy minima separated by energy barrier with the top above the atomic asymptote; it is noted that spin–orbit interaction (SO) was included in calculations in Ref. \([23]\) and, as a consequence, \( \Lambda = |M_\Lambda| \) is no longer a good quantum number in a strict sense. Similarly, double-well PECs are obtained in present \textit{ab initio} calculations of the \( (\Sigma) \) Rydberg states of ZnAr. As an example of the double-well Rydberg state, Figure 1 presents \textit{ab initio} PEC of \( ^3\Sigma \) state of ZnAr correlating with the \( (4s4d) ^3D \) asymptote. In addition,

\[ E = E_b + \frac{1}{2} D_e (R - R_{\text{in}})^2 + \frac{1}{2} D_{\text{ex}} (R - R_{\text{out}})^2 \]

Figure 1 introduces some characteristics of PECs that are defined later. Also, almost all the \textit{ab initio} PECs of the two lowest Rydberg states \( E(0^-)(n\ ^3S_1) \) and \( 1\Omega^+(n\ ^1S_0) \) obtained by Czuchaj et al., i.e. for \( \text{Zn}(n = 5)\text{Rg} \) \([24]\), \( \text{Cd}(n = 6)\text{Rg} \) \([25, 26]\) and \( \text{Hg}(n = 7)\text{Rg} \) \([27]\) complexes, possess two wells (Rg = Ar, Kr, Xe) or at least energy barrier (Rg = Ne); the exceptions are Me–He complexes, where these Rydberg states are purely repulsive.

Before we proceed further, it is worth to mention that 12–group metal atoms have attracted an attention as the possible candidates for optical lattice clocks \([28–34]\) due to very small black-body radiation shift of the \( 1\ ^1S_0 - 3\ ^3P_0 \) clock transition. Also, just recently, vDW diatomic complexes containing Zn or Cd and an alkali–metal or alkaline–earth–metal atoms were considered within \textit{ab initio} approach \([35]\) for the potential use in the ultracold physics and chemistry.

This work presents results of \textit{ab initio} relativistic all-electron calculations performed for electronic states of ZnAr complex up to the \( 1\ ^1S_0 \) \((6s\ ^3S_0)\) Rydberg state. These electronic states correlate with the following valence and Rydberg states of Zn atom \([36]\),

\[
(4s^2\ ^1S_0), (4p^3\ ^1P_{0,1,2}), (4p^1\ ^1P_1)
\]
and

\[(5s^3 S_1), (5s^1 S_0)\]  
\[(5p^3 P_{0,1,2}), (4d^1 D_2), (4d^3 D_{1,2,3})\],
\[(5p^1 P_1), (6s^3 S_1), (6s^1 S_0)\]  

respectively (see also Figure 2). In the above atomic asymptotes, we omit in the electronic configurations the set of \([Ar]3d^{10}\) closed shells as well as the 4s orbital in the case of 4s n'\(n'\) excited states, thus 4sn'\(n'\) \(\equiv n'\)\(n'\).

Rydberg states of ZnAr studied here can be considered as the intermediate between the low-lying valence states of traditional physical chemistry and the highly excited long-range Rydberg molecules obtained within ultracold regime. In particular, present \textit{ab initio} PECs of all the considered Rydberg states of predominant \(\Sigma\) character possess two-well shape. It is also shown that, as in the case of the long-range Rydberg molecules, the undulations of the PECs of the \(\Sigma\) Rydberg states may be attributed to the scattering of the Rydberg electron on the ground-state (Ar) atom.

The existing experimental results for ZnAr complex are rather far from being exhaustive; they cover the data for ground state [37, 38], \(a^3\Pi^- (4p^2 P_0)\) and \(b^3\Pi (4p^3 P_2)\) [39], \(C^1\Pi (4p^1 P_1)\) [37, 40], \(D^1\Pi^+ (4p^1 P_1)\) [41] and \(E^3\Sigma (5s^3 S_1)\) [39]. There were also previous theoretical studies of ZnAr complex based on \textit{ab initio} calculations performed up to the \(1\)\(^1\)\(^0\) (5s\(^1\)\(S_0\)) Rydberg state by Czuchaj et al. [24, 42, 43] and later by Krosnicki [41, 44, 45]. Other theoretical works were devoted to the repulsive part of PEC of the \(3\Sigma^+_1\) state of ZnRg (Rg = Ar, Kr, Xe) complexes correlating with the Zn(4p\(^3\)P) asymptote [46] or to the ground state of ZnAr complex [47–49]. As it is seen, the available literature data cover the states of ZnAr complex correlating with (1) and (2) asymptotes.

Table 1. Contraction schemes of basis sets used in present calculations of the ground and excited states of ZnAr complex, where standard specification (primitive functions)/(contraction scheme) is used. Exponents and contraction coefficients of Zn ANO-R basis set are collected in SM.

|            | Zn ANO-R [73]   | Ar ANO-RCC [74] | Midbond | Size          |
|------------|-----------------|-----------------|---------|--------------|
| I          | [8s7p4d3f]      | [6s5p3d2f1g]    | 129     |              |
| I'         | "              | "              |         |              |
| II         | [10s8p6d4f2g]   | [7s6p4d3f2g]    | 194     |              |
| II'        | "              | "              | 233     |              |
| III        | [11s9p7d4f2g]   | [8s7p5d4f2g]    | 219     |              |
| III'       | "              | "              | 259     |              |
| III-332    | "              | "              | 241     |              |
| III-33211  | "              | "              | 257     |              |
| III-a5Z    | "              | "              | 299     |              |

\(^a\)ANO-RC H basis \((8s4p3df1f)\) [75].
\(^b\)Tao-Pan midbond functions [53]; exponents for \(s\) functions \((0.90.30.1), p\) \((0.90.30.1), d\) \((0.60.2), f\) \((0.3)\).
\(^c\)H (9s5p4d3f2g)/(16s5p4d3f2g) [77].

![Figure 2](image_url)  
**Figure 2.** Valence states (green lines) and Rydberg states (red lines) of Zn atom considered in this work. Horizontal lines represent estimations of the classically accessible region for the valence/Rydberg electron. \(V_{\text{Zn}^+}\) potential is evaluated here as the interaction energy between \(\text{Zn}^+\) and classical point charge \(-|e|\). Graph is based on results of (DKH2)MS-CASPT2 calculations performed for Zn, Zn\(^+\) and Zn\(^+\) \(-|e|\) with III basis (see Table 1).
To validate our results of ab initio calculations for further use in planning and interpretation of the experimental spectra, we provide twofold evaluation of the quality of the results. Namely, wherever it is possible our results are compared with the experimental data [37–41] and other ab initio calculations [24, 41–49]. This comparison concerns only the low-lying states correlating with (1) and (2) asymptotes, as there is no available data for the states of \( \text{ZnAr} \) correlating with (3) asymptotes. Furthermore, part of the experimental and theoretical results existing in the literature cannot be treated as the reference data as it is discussed in Section 3. Thus we attempt to evaluate the accuracy of present ab initio calculations in an independent way. Such evaluation is possible thanks to the comprehensive character of the numerical results presented here. The analysis of errors includes the effect of the incompleteness of the basis set, deficiencies in description of the electron correlation and size-inconsistency errors of the multi-reference perturbation theory and level of the description of the relativistic effects. Combining these two approaches, we provide the estimates of the accuracy of the ab initio PECs of the high-lying Rydberg states of \( \text{ZnAr} \) complex.

In the context of the convergence of the ab initio results with the basis set size, the additional ghost-atom basis functions located between the interacting atoms are often in use. Namely, these so-called midbond functions, in connection with the counterpoise method of the elimination of basis set superposition error (BSSE) [52], are known to speed up the convergence of the binding energy with respect to the basis set size [53–60] and it is especially pronounced in the case of theoretical description of the weak interatomic interactions, e.g. of the ground state of vdW complexes. Similar conclusions were derived from the symmetry-adapted perturbation theory (SAPT) [61–63], where the special emphasis is put on the convergence of the dispersion interaction energy with basis-set size. These comprehensive analyses have shown the ability to obtain very accurate results for weakly bound ground states with midbond functions. Although the midbond functions were also used for the calculations of the low excited states of vdW complexes, e.g. \( \text{KrXe} \) [64], benzene–Ar [65], p-difluorobenzene–Ar [66], fluorobenzene–Ar [67], H-BF [68], NO–Ne and NO–Ar [69], \( \text{Ar–CS}_2 \) [70], \( \text{Sr–H}_2 \) and \( \text{Yb–H}_2 \) [71], ErYb [72], to the best of authors’ knowledge there is no comprehensive analysis of the effect of inclusion of midbond functions on the description of the excited states. This work provides series of calculations performed with various basis sizes with and without midbond functions for the calculations of the excited valence and Rydberg states of \( \text{ZnAr} \) complex. This allows to show the considerable effect of use of the midbond functions especially for the description of the (inner) wells of the electronic excited states.

Next sections of this paper cover the following subjects: computational details (Section 2), evaluation of accuracy of present ab initio calculations (Section 3.1), presentation of the complete results for the valence (Section 3.2) and Rydberg states (Section 3.3) of \( \text{ZnAr} \) complex along with comparison with the experiment and the results of other calculations, discussion on physical origins of the undulations of PECs of the \( \Sigma \) Rydberg states (Section 4), and finally, summary and conclusions with special focus on discussion on errors of present ab initio calculations are presented in Section 5.

2. Computational details

New relativistic all-electron atomic-natural-orbital-type (ANO-R) basis was devised for Zn atom allowing for the description of excited states up to the (4s6s) \(^1\)S; construction of spectroscopic basis functions for this basis set is described in Ref. [73], whereas the parameters of this basis, i.e. exponents and contraction coefficients, are collected in Supplemental Material (SM) of present work. Ar centre was represented by all-electron ANO-RCC basis [74], where RCC stands for relativistic basis with semi-core correlation. To obtain rather highly converged results with the basis set size, we used the midbond basis localised in the geometric centre of the molecule. We have chosen rather non-standard, in this context, hydrogen ANO-RCC basis set [75] having similar character as the above-mentioned nucleus-centred atomic bases. This choice was indirectly inspired by the approach of Patkowski et al. [56–60], where in addition to the nucleus-centred aug-cc-pVXZ bases the hydrogen bases of the same kind and quality were used as the midbond functions. Such an approach has led to results highly converged with basis set size. In particular, such midbond functions have allowed to obtain high-quality ground state of \( \text{Cd}_2 \) [76]. For comparison purposes, we also use midbond hydrogen aug-cc-pV5Z functions as well as standard midbond Tao-Pan functions [53–55]. Contractions schemes of basis sets used throughout this work are presented in Table 1, where the number of contracted basis functions increases from I to III basis; primed bases, e.g. III’, contain hydrogen ANO-RCC midbond functions. Tao-Pan midbond functions (332) and (33211) [53–55] as well as aug-cc-pV5Z hydrogen basis [58, 76, 77] along with the largest contraction nucleus centred basis III are denoted as III-332, III-33211 and III-a5Z bases, respectively.

For the calculation of PECs of \( \text{ZnAr} \) complex, the following grid of points \( R \) was used (internuclear distances in bohr): from 3.4 to 9.6 with step 0.2; from 9.6 to 24.0
with step 0.4; from 24 to 30 with step 1; from 30 to 40 with step 2; from 40 to 60 with step 4; from 60 to 100 with step 10.

Scalar relativistic effects were included by means of second-order Douglas–Kroll–Hess Hamiltonian (DKH2) [78, 79]; for comparison purposes, part of the calculations was also performed with exact two-component Hamiltonian X2C [80].

The ground and excited states of ZnAr complex, up to state correlating with the (4s6s) 1S asymptote, were obtained within state-average-complete active space self-consistent field method (SA-CASSCF) [81, 82] for the active space obtained by distributing two electrons on molecular orbitals of predominant Zn 4s, 4p, 5s, 5p, 4d, 6s character. State-averaging procedure was performed over the following sets of states of C_{2v} symmetry (superscript denotes spin multiplicity): seven singlet 1A_1 states, six triplet 3A_1 states, three 1B_1 states, three 3B_1 states, three 1B_2 states, three 3B_2 states; single state of 1A_2 and 3A_2 symmetries. Since the results of the multi-configurational SCF calculations are known to be dependent on the input orbitals, present SA-CASSCF calculations were carried out along the grid with the input orbitals taken from the previous SA-CASSCF calculation performed for the adjacent grid point starting from R = 8.4 bohr in both directions; this approach has allowed to obtain smooth PECs. Dynamic correlation effects were accounted for via multi-state second-order CAS perturbation theory (MS-CASPT2) [83–85], in which Zn 3d and Ar 3s3p closed shells were also correlated. Multi-state step of MS-CASPT2 method was employed over the same sets of states as in the state-averaging procedure of SA-CASSCF method. To diminish the effect of the so-called weak intruder states, the imaginary shift 0.1 a.u. was applied for the zero-order Hamiltonian [86]. Following the approach used for the construction of ANO-R basis set [73], no IPEA shift [87] was used. SO interaction was included via restricted active space state interaction method (RASSI-SO) [88], in which the matrix of SO operator within atomic mean field integrals approximation (AMFI) was evaluated for the perturbatively-modified CASSCF wave functions resulting from MS-CASPT2 method. Diagonal matrix elements of SO matrix were shifted by the corrected eigenvalues of the second-order effective Hamiltonian of MS-CASPT2 method; for more details see description of the procedure of elimination of BSSE error presented below.

For the ground and the excited spin triplet states that are the lowest ones in each of irreducible representations of C_{2v} point group, correlating with the (4s4p) 3P and (4s4d) 3D asymptotes of Zn (only the 3Δ state for the latter one) were calculated within coupled-clusters theory CCSD(T) with non-iterative triples correction [89].

As in the case of CdAr [23], the iterative procedure of the solution of CCSD equations for the corresponding lowest excited singlet states of ZnAr did not converge. For the largest basis III-a5Z we have also performed the RASSI-SO calculations, in which the spin-free energies for the ground state and the lowest excited states correlating with the (4s4p) 3P asymptote were substituted with CCSD(T) energies. In this way, we have obtained benchmark results for the lowest triplet states denoted hereafter as CCSD(T)/RASSI-SO.

Additionally, PEC of the ground state 2Σ of the ZnAr\(^{+}\) cation was calculated within CAS-CI/CASPT2 and CCSD(T) methods, where in the former case, the zero-order CAS-CI wavefunction was constructed from the pseudo-natural orbitals of SA-CASSCF calculation performed for the neutral ZnAr complex for a set of states of a given irreducible representation of C_{2v} point group. Such an approach allows to evaluate averaged Zn\(^{+}\)-Ar interaction that is taken into account within the corresponding SA-CASSCF/MS-CASPT2 calculations of the electronic states of ZnAr. This interaction energy is used in Section 4 for the calculation of valence electron PECs as defined in Equation (9). All the considered PECs were corrected due to BSSE by means of the counterpoise method [52]. In the case of PECs obtained within MS-CASPT2/RASSI-SO approach, the BSSE correction was performed at the MS-CASPT2 step. To perform BSSE correction properly, some reorderings of the energy states had to be done by tracking the physical character of a given PEC leading to quasi-diabatic PECs at MS-CASPT2 level of calculations. Then, PEC of each excited state was shifted (at R = 100 bohr) to the experimental atomic asymptote and such corrected eigenvalues of effective MS-CASPT2 Hamiltonian were added to the diagonal elements of SO matrix within RASSI-SO method.

All the above-mentioned calculations were performed with Molcas 8.2 [90]. Vibrational frequencies were obtained with the OpenMolcas 18.09 [91, 92] VibRot program using Numerov’s method for the solution of nuclear Schrödinger equation for the 999 grid points obtained with cubic splines fitted to numerical representation of the ab initio PECs within the range of internuclear distance from 3.4 to 20 bohr; in the case of few PECs (one or two PECs, depending on the basis set) the internuclear distance range and number of grid points had to be increased in order to obtain numerically correct results.

### 2.1. Relations obeyed by a Morse potential

There is some confusion in the literature in the context of vibrational frequencies, e.g. the ab initio fundamental frequencies calculated in Ref. [24] are directly compared
with the values of harmonic frequencies \([48, 49]\), probably due to the use of the same symbol \(\omega_e\) in both cases. In this context, we use distinct denotations, \(\omega_e^{[f]}\) and \(\omega_e^{[h]}\) for fundamental and harmonic frequencies, respectively, recalling also the approximate relation between these two quantities

\[
\omega_e^{[f]} \approx \omega_e^{[h]} - 2 \omega_e x_e, \tag{4}
\]

where \(\omega_e x_e\) is the anharmonicity corresponding to \(\omega_e^{[h]}\). Due to the frequent use of a Morse potential as the representation of the electronic states for the interpretation of the experimental spectra of ZnAr complex [37–41, 45], we will also make some estimations applying relations strictly obeyed by Morse potentials, i.e. Equation (4) and the following expression for well depth

\[
D_e = \frac{(\omega_e^{[h]})^2}{4 \omega_e x_e}. \tag{5}
\]

It should be noted that also the Birge–Sponer (B–S) extrapolation used in the analysis of the experimental spectra [37–40] is strictly valid for a Morse potential.

### 3. Results and discussion

#### 3.1. Estimates of accuracy

First, we consider the finite basis effects at the level of spin-free calculations, i.e. before inclusion of SO interaction. Ground state \((4s)^2S\) \(^2\Sigma\) of ZnAr\(^{+}\) cation may be treated as a parent state of ZnAr states. Thus it is informative to examine trends of changes of its PEC with respect to the basis set size as it is presented in Figure 3.\(^3\) In this figure, one can observe the deepening of the potential well across the series of basis functions I–III–I’–III’, which confirms the importance of the midbond functions of primed bases around the equilibrium distance \(R_e\). Interchanges of the ordering of PECs in the insets of Figure 3 illustrate the gradual decrease of the effect of midbond functions on the interaction energy at larger internuclear distances \(R\). Namely, in the limit of \(R \to \infty\) the PECs obtained with basis containing midbond functions, e.g. II’, approach the counterparts obtained with basis without midbond functions, in particular II’\(\to\)II. Figure 3 and Table S8 in SM show the monotonic increase of well depth \(D_e\) across the basis series I–III–I’–III’ and it is accompanied with the decrease of \(R_e\). According to approximate relations expressed using Equations (4) and (5), it is not surprising to find in Table S8 of SM that fundamental frequency \(\omega_e^{[f]}\) follows the increase of \(D_e\) values.

States of ZnAr complex inherit the properties of ground state of ZnAr\(^{+}\) cation. In particular, their inner well spectroscopic characteristics, i.e. equilibrium distance \(R_e\), potential well depth \(D_e\) and fundamental frequency \(\omega_e^{[f]}\), obey in general the same trends of changes with respect to basis set size as the corresponding characteristics of ZnAr\(^{+}\) ground state. This can be seen in Figure 4, where the considered characteristics are plotted against the number of basis set functions for the selected states of ZnAr.\(^4\)

For the \(\Sigma\) Rydberg states the position of the top of energy barrier \(R_b\), \(E_b\) along with outer well characteristics \(R_{out}\), \(D_{out}\) obtained with MS-CASPT2 method and DKH2 Hamiltonian are collected in SM (Tables S11–S14 and Figures S13–S14). The position of the top of the energy barrier on energy scale \(E_b\) is evaluated in this work as the difference between the local energy maximum and the energy at \(R = 100\) bohr. Figure 1 illustrates definitions of the considered characteristics. In spite of the changes in the ordering of PECs of the ground state \(^2\Sigma\) of ZnAr\(^{+}\) calculated with different basis sets at the larger distances (insets in Figure 3), one can observe the general tendency of underestimation of \(R_b\) and \(D_b\) values and the overestimation of \(E_b\) and \(R_e\) values obtained for relatively small basis sets (SM, Figures S13–S14). Deviations from these trends may be attributed to the presence of avoided crossings of adiabatic MS-CASPT2 PECs of the \(\Sigma\) Rydberg states (SM, Figure S15).

To show in a concise form the aspects of the convergence of the \(ab\) \textit{initio} results with the basis set size, the following mean absolute error (MAE) is introduced

\[
\text{MAE}(X)_{\text{(basis)}} = \frac{1}{N_s} \sum_{i=1}^{N_s} \left| X_{\text{(basis)}} - X_{\text{III–a5Z}} \right|, \tag{6}
\]

\[\text{Figure 3. PECs of the ground state } (4s)^2S \, ^2\Sigma \text{ of ZnAr}^{+} \text{ cation obtained for series of I–III and I’–III’ basis sets, where the primed bases contain midbond functions. Samples of PECs in the insets show the changes of the ordering of PECs at increasing internuclear distances. PECs were obtained with CCSD(T) method and DKH2 Hamiltonian. For the information on basis sets, see Table 1.}\]
Figure 4. MS-CASPT2 (solid line) and CCSD(T) (dotted line) values of $R_e$, $D_e$ and $\omega^f_\ell$ spectroscopic characteristics of states $X ((4s^2)^1S)^1\Sigma$, $((4s4p)^3P)^3\Sigma$, $3\Pi$ and $((4s4d)^3D)^3\Delta$, as a function of the basis set size. Single asterisk around 300 functions represents CCSD(T) value for III-a5Z basis. All results were obtained with DKH2 Hamiltonian.

where $X$ represents the characteristics of PECs obtained with MS-CASPT2 method, e.g. $R_e$, $D_e$, $\omega^f_\ell$, and the MAE is defined with respect to the results obtained with the largest basis set III-a5Z. Averaging in Equation (6) is performed over a given group of $N_s$ states. In particular, we will consider group of valence states correlating with (1) asymptotes, group of Rydberg states correlating with (2) and (3) asymptotes, and finally, group of the $\Sigma$ Rydberg states. In analogy to $\text{MAE}(X)^{\text{basis}}$, we also define mean relative error (MRE)
as follows:

\[
\text{MRE}(X)^{\text{(basis)}} = \frac{1}{N_i} \sum_{i=1}^{N_i} \frac{|X^{(\text{basis})} - X^{(\text{III-\text{aSZ}})}|}{X^{(\text{III-\text{aSZ}})}} \times 100\%.
\]  

(7)

In Figure 5, the MAE\((X)^{\text{(basis)}}\) along with MRE\((X)^{\text{(basis)}}\) errors are presented for inner-well spectroscopic characteristics, i.e. \(X = R_e, D_e, \omega_e^{[f]}\), separately for the valence and Rydberg states. It is seen in Figure 5 that the overall convergence schemes with basis set size for these two distinct groups of states are essentially the same. The MAEs

\[\text{Figure 5.} \text{ (Top) MAE}(X)^{\text{(basis)}} \text{ (Equation 6) and (bottom) MRE}(X)^{\text{(basis)}} \text{ (Equation 7) errors of } X = R_e, D_e, \omega_e^{[f]} \text{ spectroscopic characteristics of the inner well are presented separately for (left) valence and (right) Rydberg states. Results of MS-CASPT2 calculations with DKH2 Hamiltonian are presented.}\]
of (inner-well) $R_e$ are larger for the valence states, whereas the corresponding errors for $D_e$ and $\omega_e^{[f]}$ are larger for Rydberg states, which means that in this case the larger absolute values are accompanied with larger errors. However, all the MREs are larger for the valence states. It is noted that the inclusion of the midbond functions is as much important for the description of the inner well of the Rydberg states as in the case of the valence states.

Energy barriers as well as the outer wells of the Rydberg states of $\Sigma$ symmetry appear at larger internuclear distances. Namely, positions of the top of energy barrier $R_b$ range from 9 to 17 bohr for the considered states, whereas the equilibrium distances for the outer well $R_e^{\text{out}}$ appear at roughly 13–26 bohr. Thus the effect of inclusion of midbond functions in this case should not be as large as in the case of the inner well. In Figure 6, MAE($X$) for $X = R_b, E_b, R_e^{\text{out}}, D_e^{\text{out}}$ are presented. It is seen in Figure 6 that the results obtained with the largest basis without midbond functions (III) surpass counterparts obtained with medium-size basis II’ with midbond functions, whereas in the case of inner well results of calculations with III basis were already recovered with the smallest basis containing midbond functions (I’).

We estimate errors due to basis set incompleteness with difference between MS-CASPT2 results obtained with basis II’ and the largest one, III-a5Z, i.e. with MAE($X$)$_{II'}$ defined in Equation (6) separately for valence and Rydberg states. Somewhat arbitrary choice of basis II’ in this context is expected to be rather conservative. To provide slightly more general point of view, we also consider mean relative error MRE($X$)$_{II'}$ (in %) defined in Equation (7). The values of errors discussed below may be consulted in Figures 5 and 6. We have considered three distinctive points of PECs: energy minimum of inner well characterised by $R_e^{\text{in}}, D_e^{\text{in}}$ and $\omega_e^{[f]}$ for all the states and, additionally, the top of energy barrier ($R_b$ and $E_b$) and energy minimum of outer well ($R_e^{\text{out}}$ and $D_e^{\text{out}}$) for the Rydberg states of $\Sigma$ symmetry. Within such an approach, equilibrium distances $R_e^{\text{in}}$ tend to be overestimated due to the incompleteness of basis set in average by 0.05 bohr (0.5%) and 0.02 bohr (0.4%) in the case of valence and Rydberg states, respectively. Inner-well

![Figure 6](image-url). Mean errors (left) MAE($X$)$_{\text{basis}}$ (Equation 6) and (right) MRE($X$)$_{\text{basis}}$ (Equation 7) of $R_b, E_b, R_e^{\text{out}}, D_e^{\text{out}}$ with respect to the ab initio results obtained with the largest basis set III-a5Z for the Rydberg states of $\Sigma$ symmetry. Results of MS-CASPT2 calculations with DKH2 Hamiltonian are presented.
depths $D_{e}^{in}$ are underestimated in average by 15 cm$^{-1}$
(7%) and 55 cm$^{-1}$ (6.5%) in the case of valence and Rydberg states, respectively. Similarly, fundamental frequencies $\omega_{e}^{[f]}$ are underestimated in average by 1 cm$^{-1}$ (4%) in the case of valence states and by 5 cm$^{-1}$ (6%) in the case of Rydberg states. The positions of the top of energy barrier $R_{e}$ of the $\Sigma$ Rydberg states are underestimated in average by 0.2 bohr (0.35%), whereas the heights of the energy barrier $E_{e}$ are overestimated in average by 20 cm$^{-1}$ (30%). Finally, the equilibrium distances $R_{e}^{out}$ of the $\Sigma$ Rydberg states are overestimated in average by 0.92 bohr (5%), whereas outer-well depths $D_{e}^{out}$ are underestimated in average by 2.5 cm$^{-1}$ (31%). The sudden increase of relative errors of the considered energies from the inner to the outer well is due to the fact that midbond functions primarily enhance description of the area of inner wells. In this context, it is interesting to compare the above-mentioned relative errors with the corresponding errors estimated with basis set without midbond function, i.e. by comparing MRE($X$)$^{II}$ with MRE($X$)$^{II}$, 6.5% vs 25% ($D_{e}^{in}$), 30% vs 44% ($E_{e}$) and 31% vs 63% ($D_{e}^{out}$). This means that the effect of midbond functions on relative errors of interaction energy is rather substantial, even for quite large internuclear distances.

Deficiency of MS-CASPT2 method in description of the interaction energy is estimated with respect to the results of CCSD(T) method. Since it was impossible to perform CCSD(T) calculations for the $\Sigma$ Rydberg states within present approach, the comparison of the results of these two methods may be performed only for the inner well characteristics; spin-free results for all the states for which CCSD(T) calculations were performed are collected in SM (Tables S6–S8). It is seen that MS-CASPT2 method tends to underestimate equilibrium distances $R_{e}$, whereas this method overestimates potential well depths $D_{e}$ and vibrational frequencies $\omega_{e}^{[f]}$. As it is discussed in Section 3.2, in the case of ground state of ZnAr complex (Table 2), the consequences of state-average procedure of SA-CASSCF and second-order couplings of multi-state step of MS-CASPT2 seem to diminish these discrepancies with respect to CCSD(T) results. Inspection of Figure 47 allows to note a slight tendency in decrease of differences between the results of MS-CASPT2 and CCSD(T) methods with the increase of basis-set size. Considering description of Rydberg states, we can only provide estimates of errors due to incomplete treatment of the correlation effects based on results obtained for the (4s4d)$^{3}$D$^{3}\Delta$ state (SM, Table S7), where for the largest basis set III-a5Z well depth $D_{e}$ obtained with MS-CASPT2 method is larger by 66 cm$^{-1}$ than CCSD(T) counterpart (4% relative error), whereas MS-CASPT2 value of the $R_{e}$ is smaller by only 0.01 bohr than CCSD(T) one. The overestimation of the well depth of the same order, i.e. by 35 cm$^{-1}$ (3% relative error), was obtained with CASPT2 method in the case of the (5s5d)$^{3}$D$^{3}\Delta$ state of CdAr complex [23]. It is also noted that MS-CASPT2 method with the present choice of active space outperforms the CCSD one in description of the states of ZnAr complex.

It is interesting to note that in the case of MS-CASPT2 method the errors due to incompleteness of the basis set and deficiencies in description of the interaction energy tend to cancel out each other. In particular, this cancellation of errors seem to be very effective in present ab initio MS-CASPT2 calculations with basis III-a5Z, especially within the inner wells of Rydberg states of ZnAr complex. This issue is also discussed in Section 3.3 in the case of the Rydberg state $E^{3}1 (5s^{3}S_{1})$.

Performance in description of intra-atomic correlation effects is illustrated here (SM, Table S2) by the accuracy of the Zn excitation energies with respect to the experimental data [36]. In this context, MS-CASPT2 method reaches mean absolute error (MAE) below 600 cm$^{-1}$ (being at most few-percent relative error) for the largest atomic basis III and outperforms CCSD and CASPT2 methods exhibiting MAE of 1200 cm$^{-1}$ and 900 cm$^{-1}$, respectively, for the same basis; MAE obtained with CCSD(T) equals to 140 cm$^{-1}$.

Concerning the level of treatment of the scalar relativistic effects, i.e. comparison of results obtained with DKh2 and X2C Hamiltonians, the situation is not clear; see the results of MS-CASPT2/RASSI-SO method obtained with basis III’ collected in Tables 2–8. For all the states of predominant $^{1}\Sigma$ character, the spectroscopic characteristics obtained with DKh2 and X2C are almost the same. At the same time, in the case of the remaining states, the results differ more noticeably. In particular, the (inner) well depths obtained within X2C are smaller by few percent (and not more than 40 cm$^{-1}$) than the DKh2 counterparts, and these differences are of the same order, though, of the opposite sign, as the corresponding differences between the $D_{e}$ values obtained with III’ and III-a5Z bases. Such ambivalent behaviour of these differences depending on symmetry of states is not understood. It is possible that it could be partly the result of the relatively high sensitivity of the SA-CASSCF procedure on the starting orbitals. It is also noted that the above-mentioned differences are reflected in the results of MS-CASPT2 calculations (without SO interaction), thus the effect of SO coupling on the differences between DKh2 and X2C is rather of a minor importance.

Finally, size-inconsistency errors of MS-CASPT2 method, see Section 2 in SM, do not exceed 5.5 cm$^{-1}$ and, in the majority of cases, they are below 1 cm$^{-1}$.
Atomic calculations for Zn indicate that SO splittings are underestimated within AMFI approach by roughly 20%.9

### 3.1.1. Discussion on present benchmark results

In this section, we attempt to estimate the accuracy of our benchmark DKH2 CCSD(T) calculations performed with the largest basis set III-a5Z considering the incompleteness of the basis and deficiencies in description of the electron correlation. We discuss our results in the context of recent very precise calculations [35] performed for the ground state of the closed-shell vdW complexes SrZn, Zn2 and ZnCd. In that work, the CBS limit at the level of CCSD(T) calculations was achieved for aug-cc-pwCVSZ-PP basis with midbond functions. Furthermore, in Ref. [35] the full iterative triple- and quadrupole excitation corrections $\Delta T$ and $\Delta Q$, respectively, were obtained with consecutively smaller basis sets.

First, we compare the quality of Zn atomic properties obtained at the level of CCSD(T) method with aug-cc-pwCVSZ-PP basis in Ref. [35] and with III basis in this work. It is noted that the scalar relativistic effects in Ref. [35] are taken into account by means of small-core energy-consistent potentials ECPMDF [93], which are compared with results of present work obtained with all-electron approach, where the scalar relativistic effects are included via DKH2 Hamiltonian. Calculated ionisation potential of Zn atom take the values 75 848 cm$^{-1}$ [35] and 75 426 cm$^{-1}$ (this work) with the corresponding errors 79 cm$^{-1}$ (0.1%) and $-343$ cm$^{-1}$ ($-0.5\%$) with respect to the experimental value 75 769 cm$^{-1}$ [36]. Static dipole polarisability of Zn atom calculated with III basis 38.2 a.u. is slightly closer to the recommended value 38.7 ± 0.3 a.u. [94] than the counterpart 37.7 a.u. [35] obtained with aug-cc-pCVS5Z-PP basis. In addition, the calculated with basis III (Table 1) ionisation potential of Ar atom, 126 848 cm$^{-1}$ differ from the experimental counterpart, 127 110 cm$^{-1}$ [36] only by $-262$ cm$^{-1}$ ($-0.2\%$). Also, the value of polarisability of Ar atom obtained with III basis, 11.06 a.u., is very close to the recommended one, i.e. 11.083 ± 0.007 a.u. [94]. Thus the basis III-a5Z used in this work is expected to provide the results of similar quality as aug-cc-pwCVS5Z-PP basis with midbond functions in Ref. [35], i.e. being close to the CBS limit for the ground state. This is in agreement with our estimate of the $D_0$ error, $-3$ cm$^{-1}$, due to the incompleteness of the basis being the difference between $D_0$ values obtained with II’ and III-a5Z bases for $X^1\Omega^+$ state of ZnAr.10

Second, the $\Delta T$ and $\Delta Q$ corrections calculated for the SrZn molecule in Ref. [35] are of the amount of

### Table 2. Spectroscopic characteristics of the ground state $X^1\Omega^+$ of ZnAr: equilibrium internuclear distances $R_e$ (bohr), potential well depths $D_e$ (cm$^{-1}$), fundamental frequencies $\omega_{01}^{(l)}$ (cm$^{-1}$), harmonic frequencies $\omega_{01}^{(h)}$ (cm$^{-1}$) and anharmonicities $\omega_{01}\chi_p$ (cm$^{-1}$) derived from ab initio PECs. For comparison purposes, the experimental and other theoretical values are also collected.

| $R_e$ | $D_e$ | $\omega_{01}^{(l)}$ | $\omega_{01}^{(h)}$ | $\omega_{01}\chi_p$ | Method | Ref. |
|------|------|-----------------|-----------------|-----------------|--------|------|
| 7.99 | 80.9 | 17.0            | 19.6            | 1.21            | CCSD(T), QRel. ECP$^a$ | [42]  |
| 7.97 | 78.3 | DFT(B97-1), NRel., AE$^b$ | [47]  |
| 8.05 | 86.0 | DFT(PW86), NRel., AE$^b$ | [48]  |
| 8.01 | 97   | 17.9$^c$        | 21.6$^c$        | 1.59            | CCSD(T), NRel., AE$^b$ | [48]  |
| 7.98 | 78.2 | 16.9            | 19.2            | 1.02            | CCSD(T), QRel. ECP$^e$ | [41, 44, 45]  |
| 7.72 | 101.3| 19.75$^c$       | 22.45           | 1.358           | Tang-Toennies potential model | [49]  |
| 8.08 | 82   | 18.0            | 20.2            | 1.08            | MS-CASPT2/RASSI-SO, DKH2, III | This work |
| 8.00 | 91   | 18.8            | 20.9            | 0.92            | MS-CASPT2/RASSI-SO, DKH2, III' | |
| 7.99 | 91   | 18.8            | 20.9            | 1.04            | MS-CASPT2/RASSI-SO, X2C, III' | |
| 7.97 | 94   | 19.1            | 21.3            | 1.10            | SA-CASSCF/MS-CASPT2, DKH2, III-a5Z | |
| 8.03 | 101  | 19.5            | 21.6            | 1.03            | SA-CASSCF/CASPT2, DKH2, III-a5Z | |
| 7.73 | 110  | 20.9            | 23.5            | 1.32            | SS-CASSCF/CASPT2, DKH2, III-a5Z | |
| 8.02 | 77   | 16.9            | 19.5            | 1.35            | CCSD(T), DKH2, III | |
| 8.01 | 86   | 18.0            | 20.5            | 1.35            | CCSD(T), DKH2, III' | |
| 7.90 | 88   | 18.2            | 21.1            | 1.57            | CCSD(T), DKH2, III-a5Z$^d$ | |
| 7.90 ± 0.13 | 95.9 | 18.34           | 20.5            | 1.1             | Expt.$^f$ | [37]  |
| 57.1 ± 0.5$^h$ | 18.34 | 23.1 ± 1        | 2.3 ± 0.5       | 1.2             | Expt.$^f$ | [38]  |
| 8.28 ± 0.04 | 81.7 | 17.4$^i$        | 19.8            | 1.2             | Expt.$^f$ | |

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$^{a}$Quasirelativistic effective-core potentials (ECPs) for Zn$^{2+}$ and Ar$^{+}$ along with (9s9p8d4f2g),(8s8p7d4f2g) and (9s8p4d3f)/(18s7p4d3f) basis sets, respectively. Value $D_e = 89.9 \text{cm}^{-1}$ in Table 3 in Ref. [42] seems to be a mistake; compare with numerical data in Table 1 [42].

$^{b}$All-electron, non-relativistic approach; aug-cc-pVTZ basis set for Zn (21s17p10d5f2g)/(8s7p5d3f2g) and Ar (16s10p3d2f)/(6s5p3d2f) [107].

$^{c}$Approximate value of the fundamental frequency, Equation (4).

$^{d}$All-electron, non-relativistic approach, Zn (17s12p7d3f)/(16s6p4d3f), Ar aug-cc-pV anchors, (6s5p3d2f).

$^{e}$Quasirelativistic ECPs for Zn$^{2+}$ and Ar$^{+}$ along with (18s14p14d8f4g2h)/(10s9p8s6d4f4g2h) and (9s8p4d3f2g)/(7s6p4d3f2g), respectively, being the even-tempered continuations of the corresponding aug-cc-pV anchors bases from Refs. [107, 108].

$^{f}$Present ab initio benchmark values.

$^{g}$Assuming $\omega_{01}\chi_p = 1.1 \text{cm}^{-1}$ to follow the corresponding values for CdAr and HgAr complexes [37].

$^{h}$Estimated with Equation (3) assuming Morse potential.

$^{i}$Extracted from Birge–Sponer extrapolation of the $C^1\Omega^+(1p^1 P_1) \rightarrow X^1\Omega^+$ spectrum data [37]; see also Table 4.

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$\Delta T$ and $\Delta Q$ corrections calculated for the SrZn molecule in Ref. [35] are of the amount of
5% and 6% of $D_e$, respectively, resulting in PEC deepening. It is noted in Ref. [35] that since these corrections were obtained with relatively small bases, they are expected to be slightly overestimated. Assuming proportional $\Delta T$ and $\Delta Q$ corrections for ZnAr complex, they would enlarge $D_e$ of $X^{1\Sigma}$ state by less than 10 cm$^{-1}$. It means that corrections due to higher-order correlation effects as well as the enlargement of the basis set should lead to PEC deepening. At the same time, the present benchmark CCSD(T) value of $D_e$ of $X^{1\Sigma}$ state of ZnAr, 88 cm$^{-1}$, is already larger than the experimental counterpart 81.7 cm$^{-1}$ [38]. It means that the considered corrections would increase the difference between present theoretical and experimental values of the ground state well depth. The solution of this problem needs further work that is beyond the scope of this paper.

Just recently, the new explicitly-correlated bases for 12-group metals were developed [95]. The rapid convergence of the results of CCSD(T)-F12 method was obtained there, reaching the quality of the results of CCSD(T) method with conventional five-zeta basis already with double-zeta F12 counterpart. However, the new explicitly-correlated bases along with auxiliary ones were optimised for the calculations of the ground state of 12-group metals and their molecules [95] putting in question the use of such specialised bases for the highly excited states. Furthermore, it was concluded in [95] that fully converged results for the vdW complexes require midbond functions developed for F12 methods. Nevertheless, the use of explicitly-correlated methods of the F12 kind [97, 98] provides a way of reaching highly converged results. Furthermore, in the context of the calculation of the highly excited states, the development of

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**Table 3.** Spectroscopic characteristics of the valence excited states of ZnAr complex correlating with the $(4s4p)^3P_{j=0,1,2}$ asymptote: equilibrium internuclear distances $R_e$ (bohr), potential well depths $D_e$ (cm$^{-1}$), fundamental frequencies $\omega_0$ (cm$^{-1}$), harmonic frequencies $\omega_{h}$ (cm$^{-1}$) and anharmonicities $\omega_{h} \delta$ (cm$^{-1}$) derived from ab initio PECs. For comparison purposes, the experimental and other ab initio values are also collected wherever they are available.

| State | $R_e$ | $D_e$ | $\omega_0$ | $\omega_{h}$ | $\omega_{h} \delta$ | Method | Ref. |
|-------|-------|-------|-----------|-------------|-----------------|--------|-----|
| $a^2\Pi_{3/2}$ (4p$^3P_2$) | 6.27 | 124 | 28.6 | 33.0 | 1.55 | CASPT2/SO, QRel. ECP$^a$ | [24] |
| | 6.28 | 152 | 29.7 | 33.6 | 1.58 | MS-CASPT2/RASSI-SO, DKH2, III | This work |
| | 6.09 | 210 | 36.1 | 39.9 | 1.73 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 6.12 | 202 | 35.6 | 39.5 | 1.75 | MS-CASPT2/RASSI-SO, X2C, III | |
| | 6.22 | 175 | 32.0 | 35.7 | 1.60 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |
| | 6.24 | 330 | 38.4$^b$ | 41 | 1.3 | Expt.$^c$ | [39] |
| $A^2\Pi_{3/2}$ (4p$^3P_1$) | 6.20 | 279 | 35.5 | 38.5 | 1.45 | CASPT2/SO, QRel. ECP$^a$ | [24] |
| | 6.18 | 287 | 35.6 | 38.1 | 1.24 | MS-CASPT2/RASSI-SO, DKH2, III | This work |
| | 6.04 | 348 | 40.5 | 43.3 | 1.41 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 6.07 | 341 | 40.2 | 42.9 | 1.33 | MS-CASPT2/RASSI-SO, X2C, III | |
| | 6.15 | 312 | 37.4 | 39.8 | 1.21 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |
| $B^2\Pi_{1/2}$ (4p$^3P_1$) | 6.25 | 107 | 30.7 | 34.7 | 1.31 | CASPT2/SO, QRel. ECP$^a$ | [24] |
| | 6.24 | 141 | 32.1 | 35.4 | 1.39 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 6.19 | 165 | 34.2 | 37.4 | 1.40 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |
| $b^2\Pi_{1/2}$ (4p$^3P_2$) | 6.18 | 278 | 35.5 | 38.2 | 1.32 | CASPT2/SO, QRel. ECP$^a$ | [24] |
| | 6.20 | 287 | 35.6 | 38.1 | 1.24 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 6.04 | 348 | 40.5 | 43.3 | 1.42 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 6.07 | 341 | 40.2 | 42.9 | 1.34 | MS-CASPT2/RASSI-SO, X2C, III | |
| | 6.15 | 312 | 37.4 | 39.8 | 1.21 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |
| $c^2\Pi_{3/2}$ (4p$^3P_2$) | 9.82 | 33 | 8.5 | 10.4 | 1.11 | MS-CASPT2/RASSI-SO, X2C, III' | [39] |
| | 9.40 | 45 | 10.9 | 13.3 | 1.23 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |
| $d^2\Pi_{3/2}$ (4p$^3P_2$) | 9.97 | 36 | 11.8 | 15.2 | 1.50 | CASPT2/SO, QRel. ECP$^a$ | [24] |
| | 9.75 | 35 | 9.4 | 11.6 | 1.08 | MS-CASPT2/RASSI-SO, DKH2, III | This work |
| | 9.61 | 43 | 10.6 | 12.7 | 1.11 | MS-CASPT2/RASSI-SO, DKH2, III | |
| | 9.61 | 43 | 10.6 | 12.8 | 1.11 | MS-CASPT2/RASSI-SO, X2C, III | |
| | 9.68 | 42 | 10.1 | 11.8 | 0.92 | CCSD(T)/RASSI-SO, DKH2, III-a5Z | |

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$^a$Quasirelativistic ECPs for Zn$^{10+}$ and Ar$^{8+}$ along with (9s9p8d4f2g) /[8s8p7d4f2g] and (9s8p4d3f) /[8s7p4d3f] basis sets, respectively. CASPT2/SO calculations performed for SA-CASSCF wavefunctions of CAS=(4p4s5p)$^2$.

$^b$Approximate value of the fundamental frequency, Equation (4).

$^c$Ajustment $\omega_{h} \delta$ was assumed in Ref. [39]; the overestimation of $D_e$ of the Rydberg state $E\ ^{1}(5\ ^{1}S)$ in Ref. [39] results in the similar overestimation of $D_e$ of the $a^2\Pi_{3/2}$ state; see also Table 5.

$^d$Energy barrier at $R_e = 8.2$ bohr, $E_b = -24.8$ cm$^{-1}$ (below the atomic asymptote), outer well at $R_{out} = 9.61$ bohr, $D_{out} = 35$ cm$^{-1}$.

$^e$Energy barrier at $R_e = 8.51$ bohr, $E_b = -41.8$ cm$^{-1}$ (below the atomic asymptote), outer well at $R_{out} = 8.95$ bohr, $D_{out} = 42.7$ cm$^{-1}$.

$^f$Outer well not observed.
Table 4. Spectroscopic characteristics of the valence excited states of ZnAr complex correlating with the $^1P_1$ asymptote: equilibrium internuclear distances $R_e$ (bohr), potential well depths $D_e$ (cm$^{-1}$), fundamental frequencies $\omega_{0e}^{(f)}$ (cm$^{-1}$), harmonic frequencies $\omega_{0e}^{(h)}$ (cm$^{-1}$) and anharmonicities $\omega_{0e}^{(h)}$ (cm$^{-1}$) derived from ab initio PECs. Values in parentheses obtained by fitting to vibrational levels up to $v = 14$; otherwise, only the three lowest vibrational levels were taken into account in the fitting procedure. For comparison purposes, the experimental and other ab initio values are also collected wherever they are available.

| State       | $R_e$   | $D_e$     | $\omega_{0e}^{(f)}$ | $\omega_{0e}^{(h)}$ | $\omega_{0e}^{(h)}$ | Method                        | Ref. |
|-------------|---------|-----------|---------------------|---------------------|---------------------|--------------------------------|------|
| $^3\Sigma$  | 5.75    | 509       | 40.7                | 50.1                | 50.1                | 1.40                          |      |
|             | 5.59    | 560       | 51.0                | 54.8(54.0)          | 54.8(54.0)          | 2.08(1.54)                    | [24] |
|             | 5.49    | 658       | 57.6                | 61.8(60.9)          | 61.8(60.9)          | 2.24(1.72)                    |      |
|             | 5.52    | 642       | 56.5                | 60.4(59.8)          | 60.4(59.8)          | 2.16(1.69)                    |      |
|             | 5.48    | 677       | 58.4                | 62.5(61.6)          | 62.5(61.6)          | 2.10(1.73)                    |      |
| 5.61±0.07   | 706     | 58.7±5    | 61.57±0.07          | 1.42±0.003          | 60.1±0.07           | 690 59.2±62                  |      |
|             | Exppt.  | 1.4       |                      |                     | Exppt.              | [37] |
| 5.75±0.07   | 667     | 58.7±5    | 61.57±0.07          | 1.42±0.003          | 60.1±0.07           | 690 59.2±62                  |      |
|             | Exppt.  | 1.4       |                      |                     | Exppt.              | [40] |
| $^1P_1$     | 12.28   | 43        | 7.9                 | 8.9                 | 8.9                 | 0.44                          | [24] |
|             | 11.54   | 61        | 9.0                 | 9.7                 | 9.7                 | 0.36                          |      |
|             | 11.43   | 68        | 9.4                 | 10.2                | 10.2                | 0.47                          |      |
|             | 11.39   | 68        | 9.4                 | 10.5                | 10.5                | 0.62                          |      |
|             | 11.40   | 67        | 9.3                 | 9.9                 | 9.9                 | 0.26                          |      |
|             | 13.00   | 48        |                      |                     |                     | Exppt. 1 (ab initio)          | [41] |

$^a$Quasirelativistic ECPS for Zn$^{20+}$ and Ar$^{8+}$ along with (9S$p$8d4f2g)/[8S$p$7d4f2g] and (9S$8p$4f3d)/[8S7p4d3f] basis sets, respectively. CASPT2/SO calculations performed for SA-CASSCF wavefunctions of CASS= (4S,pS5S,p)^2.

$^b$Assuming $\omega_{0e}^{(h)} = 1.1 \text{ cm}^{-1}$ for the X$^1\Sigma^+$ ground state of ZnAr to follow the corresponding values for CdAr and HgAr complexes [37]; see also Table 2.

$^c$Approximate value of the fundamental frequency, Equation (4).

$^d$Extracted from Birge-Sponer extrapolation of the C$^3$ (4p$^1P_1$) ← X$^1\Sigma^+$ spectrum data [37]; see also Table 2.

$^e$Repulsive part of PEC was investigated experimentally; values of $R_e$ and $D_e$ strongly depend on input ab initio data – compare with results from Ref. [24].

Table 5. MS-CASPT2/RASSI-SO spectroscopic characteristics of the Rydberg states of ZnAr complex correlating with the (4s5s) $^3\Sigma$ and $^1\Sigma$ asymptotes: equilibrium distances $R_e$ (bohr), potential well depths $D_e$ (cm$^{-1}$), fundamental frequencies $\omega_{0e}^{(f)}$ (cm$^{-1}$), fundamental frequencies $\omega_{0e}^{(h)}$ (cm$^{-1}$), harmonic frequencies $\omega_{0e}^{(h)}$ (cm$^{-1}$), positions of the top of energy barrier $R_0$ (bohr) and $E_0$ (cm$^{-1}$); in and out superscripts correspond to the inner and outer wells of the PECs, respectively. Values in parentheses obtained by fitting to vibrational levels up to $v = 14$; otherwise, only the three lowest vibrational levels were taken into account in the fitting procedure. Results obtained with $\text{III}'$ and $\text{III}-\text{aSZ}$ basis sets.

| State       | $R_e^0$ | $D_e^0$ | $\omega_{0e}^{(f)}$ | $\omega_{0e}^{(h)}$ | $\omega_{0e}^{(h)}$ | $R_0$ | $E_0$ | $R_0^{\text{out}}$ | $D_e^{\text{out}}$ | Method   |
|-------------|---------|---------|---------------------|---------------------|---------------------|-------|-------|-------------------|-------------------|----------|
| $^3\Sigma$  | 4.96    | 1440    | 126.9               | 132.4               | 2.79                | 8.85  | 66    | 13.8              | 14               | DKH2, III |
| $^1\Sigma$  | 4.93    | 1590    | 131.8               | 137.5               | 2.87                | 8.90  | 61    | 13.7              | 18               | DKH2, III' |
| $^1\Sigma$  | 4.94    | 1556    | 129.9               | 135.5               | 2.88                | 8.89  | 62    | 13.7              | 17               | X2C, III' |
| $^1\Sigma$  | 4.92    | 1618    | 132.7               | 138.2               | 2.78                | 8.90  | 59    | 13.6              | 19               | DKH2, III-aSZ |
| $^3\Sigma$  | 5.03    | 1115    | 118.2               | 114.8               | 0.17                | 8.50  | 127   | 14.3              | 15               | Ref. [24] |
| $^1\Sigma$  | 4.96    | 1440    | 126.9               | 132.4               | 2.79                | 8.85  | 66    | 13.8              | 14               | DKH2, III' |
| $^1\Sigma$  | 1450    | 131.8   | 137.5               | 136.9               | 2.87(2.58)          | 8.90  | 61    | 13.7              | 18               | DKH2, III' |
| $^1\Sigma$  | 4.94    | 1556    | 129.9               | 135.5               | 2.89(2.54)          | 8.90  | 62    | 13.7              | 17               | X2C, III' |
| $^1\Sigma$  | 4.92    | 1618    | 132.7               | 138.2               | 2.78(2.61)          | 8.92  | 59    | 13.6              | 19               | DKH2, III-aSZ |

$^a$Quasirelativistic ECPS for Zn$^{20+}$ and Ar$^{8+}$ along with (9S$p$8d4f2g)/[8S$p$7d4f2g] and (9S$8p$4f3d)/[8S7p4d3f] basis sets, respectively. CASPT2/SO calculations performed for SA-CASSCF wavefunctions of CASS= (4S,pS5S,p)^2.

$^b$Estimated with Equation (5) assuming a Morse potential.

the multireference F12 methods can be very promising [99–101] once the appropriate bases feasible for description of such states are available [102].

### 3.2. Valence states of ZnAr complex

The inspection of valence states of ZnAr complex allows to perform comparison of the results of present ab initio calculations with the experimental data [37–41] and the results of other calculations [24, 42, 43, 46–49], as most of previous work was done for the ground state and electronic excited states correlating with the (4s4p) $^3P_1$ and $^1P_1$ asymptotes. Here, we will not consider previous ab initio PECs of ZnAr [41, 44, 45] obtained with internally contracted multireference configuration interaction method (ICMRCI) [103–106] as these studies were
mainly focused on the calculation of accurate values of TDMs, whereas the values of well depths $D_e$ obtained in that work are substantially underestimated.

In Table 2, the results of present ab initio calculations are collected along with other theoretical values and available experimental data for the ground state $X^1\Sigma^+$ of ZnAr. First, by considering only present ab initio results for the ground state, it can be seen that the inclusion of midbond functions in the case of basis III (i.e. III vs III' and III-a5Z) leads to increase of the value of well depth $D_e$ by roughly 10 cm$^{-1}$, which still exceeds 10%. MS-CASPT2 method gives surprisingly close values of $D_e$ to the CCSD(T) counterparts, where the former values are larger by ~5 cm$^{-1}$ than the latter ones. There are three possible reasons for this agreement. On one hand, relatively large active space allows within SA-CASSCF/CASPT2 method to include, in addition to single and double excitations, the selected higher-order excitations (up to quadrupole ones) leading to relatively good description of the dispersion interaction energy. On the other hand, the fact that active orbitals were optimised to minimise the average energy of seven states of $^1A_1$ symmetry, which means that they are not optimal for the ground state, prevents from expected larger overestimation of $D_e$ within CASPT2 method. For example, the single-state (SS) CASSCF/CASPT2 method has led to 126 cm$^{-1}$ potential well depth of the ground state of CdAr complex, which is larger roughly by 30 cm$^{-1}$ than the corresponding CCSD(T) value obtained with the same atomic basis [23]. Indeed, similar SS-CASSCF/CASPT2 calculation with CAS= (4s4p5s5p4d6s)$^2$ for the ground state of ZnAr complex gives 22 cm$^{-1}$ deeper PEC than CCSD(T) with $R_e$ shorter by 0.17 bohr (see Table 2). Furthermore, as it was obtained in the case of CdAr [23], it is expected that MP2 method (second-order Möller-Plesset perturbation theory) would overestimate the interaction energy of ZnAr in its ground state to a larger extent than SS-CASSCF/CASPT2. The inclusion of the second-order couplings at multi-state step of SA-CASSCF/MS-CASPT2 method leads to slightly smaller well depth, by 9 cm$^{-1}$, in comparison to the result of SA-CASSCF/CASPT2 method. It is noted that SO interaction has no observable effect on PEC of the ZnAr ground state. At the same time, some rather minor effects of different level of introduction of the scalar-relativistic effects can be observed by comparing results obtained for DKH2 and X2C Hamiltonian in Table 2. Finally, considering the level of theory and basis set size, the present CCSD(T) calculations with III-a5Z basis may be considered as present ab initio benchmark.

Second, it is seen in Table 2 that present benchmark ab initio values of $R_e$ and $\omega_e$ are very close to the experimental counterparts taken from Ref. [37]. It should be
noted that the fundamental frequency $\omega_{ej}$ was measured directly in Ref. [37]. Furthermore, the rotational frequencies $\omega_{ej}$, $\omega_{ej}$, positions of the top of energy barrier $R_b$, and $E_b$ in (cm$^{-1}$); in and out superscripts correspond to the inner and outer wells of the PECs, respectively. Results obtained with III, III' and III-a5Z basis sets.

Table 7. MS-CASPT2/RASSI-SO spectroscopic characteristics of the Rydberg states of ZnAr complex correlating with the (4s4d)$^1D_2$ and $^3D_{2,3}$ asymptotes: equilibrium distances $R_e$ (bohr), potential well depths $D_e$ (cm$^{-1}$), fundamental frequencies $\omega_{ej}$ (cm$^{-1}$), first harmonic frequencies $\omega_{ej}$, anharmonicities $\omega_{ej}$, and in and out of equilibrium state. Larger experimental value of equilibrium distance was determined directly rather than the absolute distance $R_e$ [38]. However, as one can see in Tables 2 and 4, there were problems in Ref. [37] with the preliminary phenomenological value of $R_e$. Moreover, the rotational spectrum of the $^1\Sigma^+$ was partially measured in Ref. [37] allowing for direct evaluation of the experimental value $R_e = 7.90 \pm 0.13$ bohr for the ground state. Larger experimental value of equilibrium distance of $X^10^+$ state reported in Ref. [38] is probably affected by the preliminary phenomenological value of $R_e$ taken as an input for the further analysis of experimental spectra, where $\Delta R_e$ was determined directly rather than the absolute distance $R_e$ [38]. However, as one can see in Tables 2 and 4, there were problems in Ref. [37] with unambiguous evaluation of the well depths $D_e$ of the ground $X^10^+$ and the excited $^1\Sigma^+$ states of ZnAr additionally affected by the approximation Equation (5) based on a Morse model potential. In particular, the value of
the anharmonicity for the ground state, i.e. 1.1 cm\(^{-1}\) assumed in Ref. [37], is much closer to the theoretical and other experimental counterparts collected in Table 2 than that of 2.3 \(\pm 0.5\) cm\(^{-1}\) extracted from B–S extrapolation of the C\(^{-1}\)(4\(s^1 P_1) \rightarrow X\(^0\) 1\(^1\)S\(^0\)) spectrum [37], leading to the conclusion that the larger value of \(D_e\) from [37], i.e. 95.9 cm\(^{-1}\), is probably the more accurate one. At the same time, present benchmark \emph{ab initio} value of the \(D_e\) for the ground state differs from the experimental value from Ref. [38] by less than 7 cm\(^{-1}\), which can be considered as very good result. Similar level of accuracy was achieved in recent CCSD(T) calculations performed for the ground state of CdAr [23] and Cd\(_2\) [76] vdW complexes.

Third, comparing the results of various CCSD(T) calculations performed for the ZnAr ground state collected in Table 2, one can see that the use of nucleus-only centred basis sets, i.e. present results obtained with basis III and those taken from Refs. [24, 41–45] lead to very similar values of the spectroscopic characteristics. However, it is also seen that the non-relativistic CCSD(T) calculations [48] of ZnAr ground state resulted in the largest value of the well depth (97 cm\(^{-1}\)) among the coupled-cluster results, despite of the use of rather moderate all-electron basis Zn (17s12p7d3f)/[6s5p4d3f] and Ar aug-cc-pVTZ (16s10p3d2f)/[6s5p3d2f]. At the same time, present CCSD(T) calculations performed with the larger basis, e.g. III-a5Z (see Table 1 for the basis specification), that account for relativistic effects via DKH2 Hamiltonian lead to smaller well depth \(D_e\). Furthermore, it is evident from Figure 4 that the increase of the basis size leads to the increase of \(D_e\) of the ground state. Thus we conclude that the ZnAr ground state well depth \(D_e\) calculated within non-relativistic approach [48] is overestimated and it may be directly ascribed to the lack of the relativistic effects. In this context, the results of non-relativistic DFT calculations [47] presented in Table 2 should be compared rather with the non-relativistic CCSD(T) calculations [48] than with the experimental data to assess the quality of the exchange-correlation functionals of Ref. [47]. It can be also noted that the results of recent modelling of the ground state of ZnAr based on Tang–Toennies potential [49] are close to the non-relativistic CCSD(T) counterparts [48].
**Ab initio** results for all the valence excited states of ZnAr complex, i.e. the ones correlating with the \((4s4p)^3P_j=0,1,2\) and \(^1P_1\) asymptotes, along with the available experimental data, are collected in Tables 3–4 and their PECs are presented in Figure S16 in SM. Inspecting Tables 3–4, one can derive similar conclusion about the important role of midbond functions as in the case of the ground state. However, the differences between the results of MS-CASPT2 and CCSD(T) methods obtained for the majority of the valence excited triplet states (Table 3) are more significant than in the case of the ground state, as the MS-CASPT2 potential well depths are larger by roughly 35 cm\(^{-1}\) than the CCSD(T) counterparts and they are accompanied with smaller equilibrium distances (by more than 0.1 bohr in the majority of cases). The effect of scalar relativistic energy terms missing in DKH2 approach (in comparison to X2C) is much smaller than the error in correlation energy of CASPT2 method. Once again, the results of \textit{ab initio} CASPT2/SO calculations of Czuchaj et al. [24] are closest to present MS-CASPT2/RASSI-SO ones obtained with basis III without midbond functions.

It is interesting to note that the two-well character of the \(B^31\ (4p^3P_1)\) state driven by the SO interaction reported by Czuchaj et al. [24] is lost in present \textit{ab initio} calculations including midbond functions; only, the peculiar shape of the corresponding PEC remains.\(^{12}\)

The comparison of present \textit{ab initio} results obtained for the valence excited states with the experimental counterparts needs extended discussion. First, we will consider the \(C^11\ (4p^1P_1)\) state that may be observed experimentally via direct excitation from the ground state [37, 40]. Experimental values of \(R_e\) in Table 4 differ quite significantly from each other and cannot be considered to be in agreement. As it was mentioned above, in Ref. [37] the rotational spectrum of the \(C^11, \nu' \leftarrow X^01^+, \nu'' = 0\) transitions was partially resolved, thus the experimental values of equilibrium distance 5.61 ± 0.07 bohr of the \(C^11\) state is probably the closest to the real one. It is seen that the \textit{ab initio} \(R_e\) values of present MS-CASPT2/RASSI-SO calculations are smaller by roughly 0.1 bohr, which is expected, e.g. by examination of difference between the present results of MS-CASPT2 and CCSD(T) methods (Table 3). At the same time, experimental value of \(D_e\) from Ref. [40] falls in between the two values proposed in other experimental work [37]. Potential well depths of this state obtained in MS-CASPT2 method, increasing the basis set size, reach the region of the experimental counterparts. Taking into account the trend of changes of \textit{ab initio} value of \(D_e\) with basis set size,\(^{13}\) it seems that in the complete basis set limit (CBS) the MS-CASPT2 binding energy will probably exceed the experimental values, which is, once again, expected in the case of MS-CASPT2 method. \textit{Ab initio} values of harmonic frequencies obtained for the largest basis sets with midbond functions are very close to the experimental one. The overestimation of the theoretical anharmonicity \(\omega_{2\nu e}\) is partially diminished if this parameter is fitted to vibrational levels up to \(\nu' = 14\) as in Ref. [37] (see the values of \(\omega_{2\nu e}\) in parentheses in Table 4). The remaining discrepancy is at least partially removed with the inclusion of the higher-order anharmonicity \(\omega_{\nu'ke} = 0.014\) cm\(^{-1}\) (this value was obtained with III-a5Z basis), which, for high vibronic excitations, i.e. \(\nu' \geq 10\), exceeds 10% of the energy correction due to \(\omega_{\nu'ke}\). Interestingly, the \textit{ab initio} value of the \(\omega_{\nu'ke}\) obtained in Ref. [24] is practically the same as the experimental one; however, it is accompanied with highly underestimated well depth and vibrational frequencies.

Position of the energy minimum of the \(D^110^+\ (4p^1P_1)\) state reported in Ref. [41] was modelled using data obtained for the repulsive part of the PEC and is strongly affected by the input parameters taken from previous \textit{ab initio} calculations [41]. The actual well depth is expected to be slightly smaller (probably by less than 10 cm\(^{-1}\))\(^{14}\) than present MS-CASPT2/RASSI-SO results in Table 4 obtained for largest basis set III-a5Z.

Experimental values of spectroscopic characteristics obtained for the \(a^30^0\ (4p^3P_0)\) and \(b^32\ (4d^3P_2)\) states were obtained from the excitation spectra using the \(E^{31} (5s^3S_1) \leftarrow a^30^0\ (4p^3P_0), b^32\ (4d^3P_2)\) transitions [39], where the rotational structure was partially resolved allowing for the evaluation of the equilibrium distances of the corresponding electronic states. It is seen in Table 3 that the CCSD(T)/RASSI-SO values of the \(R_e\) are very close to the experimental counterparts for the \(a^30^+\) and \(b^32\) states (as well as for the \(E^{31}\) state in Table 5). Experimental values of other spectroscopic characteristics taken from Ref. [39] are affected by the assumed value of the \(\omega_{2\nu e} = 1.3\) cm\(^{-1}\) of the considered lower states and by the evaluation of the inner-well depth of the Rydberg state \(E^{31} (5s^3S_1)\) using approximate relation Equation (5) in Ref. [39]. On one hand, the assumed value of the anharmonicity seems to be rational in the light of the present \textit{ab initio} calculations, especially in the case of the \(b^32\) state. On the other hand, it is seen in Table 3 that the CCSD(T)/RASSI-SO values of the \(D_e\) and \(\omega_e\) for the \(a^30^+\) and \(b^32\) states are much smaller (\(D_e\) by more than 100 cm\(^{-1}\)) than the corresponding values evaluated from the experiment [39]. Such large discrepancies are rather not due to deficiencies of present CCSD(T)/RASSI-SO approach. They are most probably the consequences of the overestimation of the inner-well depth of the Rydberg \(E^{31}\) state; the discussion is postponed to next subsection, where results for the Rydberg states of ZnAr complex are presented.
3.3. Rydberg states

Spectroscopic characteristics of the Rydberg states of ZnAr complex up to the $^1\Lambda^+$ state are collected in Tables 5–8. PECs of the Rydberg states obtained within the ab initio MS-CASPT2/RASSI-SO calculations are plotted in Figures 7–9. For the selected lowest Rydberg states correlating with the $(4s5s)^3\Sigma^+_1$ and $^1\Sigma_0$ asymptotes, the experimental as well as previous ab initio results are available [24, 39]; they are also included in Table 5. It is seen that the ab initio value of the equilibrium distance $R_e$ of the inner well of the $E^31$ state is almost the same as the experimental counterpart derived from the rotational spectra [39]. At the same time, the value of $D_e$ of the $E^31$ state reported in experimental work [39] is larger than the ab initio counterparts by more than 200 cm$^{-1}$, which is rather large discrepancy. This requires extended discussion.

From the point of view of present ab initio results, it can be expected that the actual inner-well depth of the $E^31$ state is around the value obtained within the MS-CASPT2/RASSI-SO approach with the largest basis III-a5Z, i.e. $D_e^{in} \sim 1600$ cm$^{-1}$. This expectation is due to the observation that the two most important factors that affect the accuracy of the present ab initio calculations, i.e. incompleteness of the basis and the deficiencies in description of the electron correlation effects, cancel each other (probably quite large extent). Namely, it can be derived from Table S11 in SM that in the CBS limit the MS-CASPT2 value of the $D_e^{in}$ of the $(4s5s)^3\Sigma$ state should be larger than 1618 cm$^{-1}$ value obtained with III-a5Z basis and DKH2 Hamiltonian. Here, we estimate energy error due to incompleteness of the basis set by the difference between $D_e^{in}$ values obtained with II' and III-a5Z bases, which is roughly equal to 60 cm$^{-1}$. By comparing the results of the MS-CASPT2 method with the CCSD(T) counterparts (see, e.g. Table S7 in SM), it is seen that the inclusion of the higher-order correlation effects leads to the decrease of the potential well depth; here, we estimate this error by the difference between MS-CASPT2 and CCSD(T) values of the $D_e$ obtained with basis III-a5Z for the $(4s4d)^3\Delta$ Rydberg state (Table S7 in SM),
which is also roughly equal to $60 \text{ cm}^{-1}$. Thus the above-mentioned two dominating errors seem to cancel each other quite effectively. Finally, taking into account the tendency of the lowering of the $D_{e}^{in}$ value by inclusion of some remaining scalar-relativistic effects within X2C approach in comparison to the DKH2 one (Table 5), the actual value of the inner-well depth of the $E^3{1}$ is most likely close to the $D_{e}^{in} \sim 1600 \text{ cm}^{-1}$.

At the beginning of discussion of experimental results it is noted that present $ab \text{ initio}$ results support the assignment of the vibrational levels performed in Ref. [39] and based on the analysis of the isotope shifts observed in vibrational laser-induced fluorescence (LIF) excitation spectra. Thus the above-mentioned discrepancy between the $ab \text{ initio}$ and experimentally estimated values of the inner-well depth of the $E^3{1}$ is rather not due to wrong assignment of the vibrational levels that would explain it in the most simple way. Once the assignment had been made in Ref. [39], the anharmonicity $\omega_{ex}^{[h]}$ of the $E^3{1}$ state was directly extracted from the experimental data. At the same time, the experimental value of the harmonic frequency $\omega_{e}^{[h]}$ is obtained from the B–S extrapolation [39], i.e. assuming a Morse potential. Furthermore, the inner-well depth was estimated using Equation (5) in Ref. [39], which once again assumes a Morse potential and it is already affected by the just mentioned approximate evaluation of $\omega_{e}^{[h]}$. On one hand, if one takes into account the double-well character of the $E^3{1}$ state, then it is obvious that a Morse potential cannot represent correctly the total PEC of this state, even qualitatively. Thus estimates in Ref. [39] that use atomic asymptotes may suffer here from the incorrect (exponential) behaviour of a Morse potential at large distances, but in addition, such model potential cannot also take into account the existence of the outer well of the considered Rydberg state. On the other hand, in Ref. [39] only the inner well of $E^3{1}$ state was explored experimentally up to $v' = 14$ level, which at first sight could be represented with caution by a Morse potential. Interestingly, the low $ab \text{ initio}$ value of the higher-order anharmonicity $\omega_{ex} \approx -8 \cdot 10^{-4} \text{ cm}^{-1}$ (basis III-a5Z, fitting for levels up to $v' = 14$) seems to support the latter statement. However, the existence of the energy barrier makes the outside wall of the inner well steeper affecting the distribution of the higher vibrational levels and, as a consequence, the values of $\omega_{ex}^{[h]}$ and $\omega_{e}^{[h]}$ characteristics. Finally, we estimate inner-well depth $D_{e}^{in}$ of the $E^3{1}$ state with Equation (5) using $\omega_{e}^{[h]}$ and $\omega_{ex}^{[h]}$ extracted from $ab \text{ initio}$ results to be $1822 \text{ cm}^{-1}$ (Table 5), which is close to the corresponding value based on experimental data [39]. Thus we conclude that the $1829 \text{ cm}^{-1}$ value of inner-well depth of the $E^3{1}$ state taken from Ref. [39] is overestimated by roughly $200 \text{ cm}^{-1}$ and it is caused mainly by the use of a Morse potential representation of PEC of the inner well of the considered Rydberg state of ZnAr complex.

In the light of the above discussion, the discrepancies between well depths of the valence $a^30^{-}$ and $b^32^{-}$ states taken from experimental paper [39] and present CCSD(T)/RASSI-SO counterparts from Table 3 become more clear. Namely, well depths $D_{e}$ were evaluated in Ref. [39] using the experimental atomic asymptotes and the overestimated by $200 \text{ cm}^{-1}$ value of $D_{e}^{in}$ for the $E^3{1}$ state (and assuming the value of the anharmonicity $\omega_{ex} = 1.3 \text{ cm}^{-1}$ for the considered valence states). Thus, taking into account the error of present CCSD(T)/RASSI-SO calculations due to the incompleteness of the basis set, i.e. underestimation of $D_{e}$ by roughly $20 \text{ cm}^{-1}$ (see below), it is expected that the $D_{e}$ values of the $a^30^{-}$ and $b^32^{-}$ states are overestimated in Ref. [39] by more than $100 \text{ cm}^{-1}$. Concerning underestimation of CCSD(T)/RASSI-SO values of $D_{e}$, CBS error of the binding energies of the valence $a^30^{-}$ and $b^32^{-}$ states is
estimated here with the difference between CCSD(T) values of \( D_e \) obtained with II' and III'-a5Z bases, i.e. 291 and 312 \( \text{cm}^{-1} \), respectively; see results for \((4s4p)^3\Pi\) state in SM, Table S7.

Other \textit{ab initio} calculations were performed only for the two lowest Rydberg states correlating with the \((4s5s)\,^5S_1\) and \(^1S_0\) asymptotes \([24, 44]\). As it can be seen in Table 5, the inner-well depth \( D_e^{\text{int}} \) of the \(^5\)\(^1\) \((5s\,^1S_0)\) state reaches the result of present calculations with the largest basis III-a5Z. The latter observation is not understood in the context of all the other results of Czuchaj et al. \([24]\), where almost all potential well depths are smaller than the context of all the other results of Czuchaj et al. \([24]\).

Within CASPT2/SO approach in Ref. \([24]\) is significantly smaller than the present results, whereas the corresponding CASPT2/SO value of \( D_e^{\text{int}} \) of the \(^1\)\(^0\) \((5s\,^1S_0)\) state reaches the result of present calculations with the largest basis III-a5Z. The latter observation is not understood in the context of all the other results of Czuchaj et al. \([24]\), where almost all potential well depths are smaller than present \textit{ab initio} results obtained with basis sets large enough (see Tables 2–5).

4. Undulations of PECs of \( \Sigma \) Rydberg states of ZnAr complex

The energy barriers of PECs of Rydberg \( \Sigma \) states correlate with the distance from the Zn nucleus at which the electron charge density of the corresponding atomic Rydberg orbital possesses outer maximum. At such distance, the local maximum of the positive Coulomb and exchange interaction energies between the Zn and Ar atoms appears. If these positive contributions to the interaction energy dominate in such a region over the negative induction and dispersion interaction energies, the energy barrier with the top over the atomic asymptote is formed.

For the interpretation purposes, in the discussion below we will use the approximate model of the Rydberg complex consisting of three distinct subsystems: Zn\(^{+}\) cation, Rydberg electron and Ar atom. Following Fermi and Omont \([112, 113]\), the interaction between Rydberg electron and the Ar atom may be considered as the low-energy \( s \)-wave scattering of the electron on Ar atom leading to the following energy shift depending on the internuclear distance \( R \)

\[
\Delta E_s(R) = 2\pi A_s(k_R)|\Psi_{nl0}(R, 0, 0)|^2 ,
\]

where \( A_s(k_R) = -\frac{\tan(\delta(k_R))}{k_R} \) is the \( s \)-wave scattering length, \( k_R \) is the (classical) momentum of the Rydberg electron \([4, 113]\), \( \delta(k_R) \) is the scattering phase shift and \( \Psi_{nlm}(r, \theta, \phi) \) is the atomic Rydberg wavefunction; here the internuclear axis plays the role of the quantisation axis, where the angular coordinates \( \theta \) and \( \phi \) are zero. It is important to note that \( e^-\text{Ar} \) scattering length \( A_s(k_R) \) is negative in the \( k_R \rightarrow 0 \) limit and becomes positive for relatively small values of momentum \( k_R \) \([114]\) classically accessible for the Rydberg electron. \(^{15}\) It is noted that this approximate model of interaction between the Rydberg electron and the ground state (Ar) atom is more accurate for highly excited molecules such as the Rydberg ones \([4]\). Thus in this work we show the approximate interaction energies evaluated from this model only for the highest considered Rydberg states correlating with the \((4s6s)^3\Sigma\) and \(^1\)\(^S\) \((5s\,^1S_0)\) asymptotes (Figure 13).

To uncover the Rydberg \( e^-\text{Ar} \) interaction from present \textit{ab initio} calculations, we define valence electron PEC \([1]\)

\[
\Delta E(R) = E_{ZnAr}(R) - E_{ZnAr^+}(R) - E_{\text{atom}}
\]

as the difference between the total energy of the ZnAr complex in a given Rydberg state and the ground state energy of the \( \text{ZnAr}^+ \) cation \([1]\) for each internuclear distance \( R \). In Equation (9), the atomic Rydberg state energy \( E_{\text{atom}} \) with respect to ionisation limit is also subtracted shifting \( \Delta E(R) \) to zero at \( R \rightarrow \infty \). In this

\[\text{Figure 10. } |\Psi_{nl0}(r, 0, 0)|^2 \text{ charge density of Zn 5s atomic orbital on } z \text{-axis, } \Delta E \text{ valence electron PEC and interaction energy } E \text{ for the } \Sigma \text{ and } \Sigma \text{ Rydberg states of ZnAr correlating with the } (4s5s)\,^5\Sigma \text{ and } (4s5s)\,^3\Sigma \text{ asymptotes, respectively. All results obtained with } (MS\text{-})\text{CASPT2 method for DKH2 Hamiltonian and III'} \text{ basis. Inset represents extension of the curves of the respective panel for the larger distances.}\]
work, all the quantities in Equation (9) are calculated with MS-CASPT2 method. In the middle plots of Figures 10–13, the valence electron PECs are presented. In the top and bottom plots of these figures, the electron density $|\psi_{nl}(r, 0, 0)|^2$ of the Rydberg atomic orbitals and the corresponding interaction energy curves (IECs) are presented, respectively; here IEC is defined as PEC, in which the atomic asymptote is shifted to zero. Rydberg orbitals $\psi_{nl}$ of Zn are here obtained as the atomic natural orbitals being the eigenfunctions of the corresponding one-particle CASPT2 density matrices. Similarity between Rydberg electron density and $\Delta E(R)$ for $R$ large enough is evident in these plots (Figures 10–13). It supports the fact that the valence electron PEC (9) is in first approximation determined by $e^-Ar$ interaction and its shape reflects the $R$-dependence of the energy shift $\Delta E_s$ defined in Equation (8).\(^{16}\)

Further energy terms originating from simplified model of Rydberg complex that contribute to the $\Delta E(R)$ are the three-body induction term $\Delta E_{3b}(R)$ [115] and the energy shift $\Delta E_{p}(R)$ corresponding to $p$-wave $e^-Ar$ scattering [4,113]. The $\Delta E_{3b}(R)$ energy term corresponds to the interaction between Zn$^+$ cation and the electric dipole moment induced on Ar atom by Rydberg electron as well as the interaction between Rydberg electron and the electric dipole moment induced on Ar atom by Zn$^+$ cation. Three-body energy correction $\Delta E_{3b}(R)$ is positive and for $R$ large enough it reflects the shape of electron density $|\psi_{nl}(R, 0, 0)|^2$ (Figure S18 in SM); thus $V_{3b}$ also contributes to the energy barrier of $\Sigma$ Rydberg states. $\Delta E_{p}$ correction seems to play a role in the appearance.
of energy barrier in ab initio PECs of $\Pi$ Rydberg states correlating with the $(4s4d)^1D$ and $^3D$ asymptotes, where for small atomic bases such energy barriers are obtained (SM, Section S4).

As it can be seen in Figures 10–13, the distance $R_p$ at which the energy barriers appear in the case of Rydberg $^2\Sigma^+\Sigma$ states is slightly larger than the position of the outer maximum of square of the corresponding atomic orbitals of Zn. Shift of the top of the energy barrier outwards the Zn nucleus as well as the lowering of the height of the energy barrier is the result of attraction interactions between Zn$^+$ cation and Ar atom. It is also noted that the number of maxima of the charge density of atomic Rydberg orbitals increases with the principal quantum number leading to the possibility of formation of the larger number of energy barriers. However, these maxima of electron charge density appear at relatively short distances from the Zn nucleus and, as a consequence, the corresponding inner maxima of Coulomb and exchange Zn–Ar interactions ‘sink’ in the inner well of PEC, where the attractive interatomic forces dominate. Such hidden inner maximum was evidenced [23] in the case of the $(5s7s)^3\Sigma$ and $^1\Sigma$ states of CdAr at roughly 7 bohr by inspection of the valence electron PECs. Similar situation is observed in Figure 13, where two maxima appear in the valence electron PECs of $\Sigma$ states of ZnAr correlating with the $(5s6s)^3S$ and $^1S$ asymptotes; also, a substantial change in curvature of the corresponding PECs at roughly 7.5 bohr may be noted (Figure 9).

The shallow outer wells are formed on the longer-distance-side of the energy barrier as the result of the domination of attractive induction and dispersive forces over the minor Coulomb and exchange interactions. Taking into account the fact that valence electron PECs represent primarily the interaction of the Rydberg electron with the ZnAr$^+$ cation, it is interesting to note that there are very shallow minima of the valence electron PECs located in the range, where the outer wells of the $\Sigma$ Rydberg states appear (see the insets in the middle panels of Figures 10–13). Though the minima of valence electron PECs are rather small, their depths are still substantial in comparison to the total depths of the outer wells (insets in the bottom panels of Figures 10–13). The
appearance of the considered minima may be due to the attractive character of the interaction of the Rydberg electron and Ar atom slightly outside the border of the classically allowed region of the electron; at this border, the electron momentum $k_R$ approaches zero, the $e-$Ar scattering length $A_e(k_R)$ of Equation (8) takes the negative values (SM, Figure S17) and, as a consequence, $\Delta E_i$ is also negative (Figure 13). It is noted that $\Delta E_p$ term (SM, Figure S18) also contributes negatively in this region, whereas three-body polarisation term $V_{3b}$ may completely diminish the minimum of valence electron PECs as it can be seen in the case of ZnAr states correlating with the $(4s5s)\,^3S$ and $^1S$ asymptotes (Figure 10). Finally, both terms, $\Delta E_p$ and $\Delta E_{3b}$, partly diminish the $\Delta E_i = 0$ minimum appearing at the outer node of the atomic Rydberg state; it is seen, e.g. at $R \sim 10$ bohr in the case of $\Sigma$ states correlating with the $(4s6s)\,^3S$ and $^1S$ asymptotes by comparing the values of $|\Psi|^2$, $\Delta E$ with approximate interaction energies $\Delta E_i = \Delta E_i + \Delta E_p + \Delta E_{3b}$ in Figure 13; see also $\Delta E_p$, $\Delta E_{3b}$ in Figure S18 in SM. It is also noted (Figure 13) that the approximate interaction energies estimated using atomic Rydberg wavefunctions overestimate the valence electron PECs extracted from molecular calculations.

The ‘amplitudes’ of PEC undulations decrease with principal quantum number, which is seen by comparing the values of $E_b$ and $D_{out}$ for the $2S^{+1}\Sigma$ states correlating with the $(4sns)\,^{2S+1}\Sigma$ asymptotes and $n = 5, 6$ (Tables 5 and 8). This supports the expectation that the shape of PECs of Rydberg states converge to the one of ZnAr $^+$ cation.

The larger number of energy barriers may be observed for highly excited Rydberg states [1] leading to the possibility of formation of the so-called Rydberg molecules [4], where the bond length reaches $\mu$m and corresponds to one of the outer wells. In such a case, the negative value of the electron-atom scattering length $A_e(k_R)$ at momentum approaching zero limit is crucial (see Equation 8). Otherwise, the positive value of Fermi potential $\Delta E_i(R)$ at the border of the classically accessible region prevents the formation of the outer well in the case of very high Rydberg states [4]. From this point of view, it is interesting to note that the conditions, at which the outer well in low $\Sigma$ Rydberg states of MeRg ($Me = Zn$, Cd, Hg) complexes are formed, seem to be the same as in the case of Rydberg molecules. Czuchaj et al. performed ab initio calculations for ZnRg [24], CdRg [25, 26] and HgRg [27] complexes reaching the lowest two Rydberg states of $\Sigma$ symmetry correlating with Zn$(4s5s)$, Cd$(5s6s)$, Hg$(7s8s)$ $^3S_1, ^1S_0$ asymptotes. These ab initio PECs possess outer well in the case of MeAr, MeKr and MeXe complexes, whereas there are no such outer wells in MeHe and MeNe complexes. Needless to say that in the limit $k_R \to 0$ the scattering lengths of electron with Ar, Kr and Xe atoms are negative, whereas in the case of He and Ne atoms – the corresponding scattering lengths are positive [113]. This is accompanied with the monotonic increase of the atomic dipole polarisabilities $\alpha_{Rg}$ from He to Xe [94, 113]. Thus relatively weak induction and dispersion attractive Me$^+ – Rg$ interactions (Rg = He, Ne) due to small $\alpha_{Rg}$ values are accompanied with a positive contribution of $\Delta E_i(R)$ outside the region of the outer lobe of the Rydberg electron orbital preventing from a formation of the outer well. The opposite situation is found in the case of MeAr, MeKr and MeXe complexes, where the relatively strong Me$^+ – Rg$ attractive interactions are supported with the negative $\Delta E_i(R)$ correction within that region resulting in the formation of the outer wells. These statements are in line with experimental observations of the lowest Rydberg states of MeRg complexes, i.e. HgAr [8], CdAr [12–16], CdKr [14, 17, 18], HgNe [19], CdNe [20] described in Introduction.

5. Summary and conclusion

This work presents the results of all-electron ab initio calculations of the ground and excites states of ZnAr up to the $(4s6s)\,^1S_0$ atomic asymptote. In particular, we present first ab initio calculations of the Rydberg states of ZnAr correlating with the $(4s5p)^3P_{0,1,2}$, $(4s4d)^1D_2$, $(4s4d)^3D_{1,2,3}$, $(4s5p)^1P_1$, $(4s6s)^3S_1$ and $^1S_0$ atomic asymptotes. Calculations were performed within MS-CASPT2/RASSI-SO approach including scalar relativistic effects by means of DKH2 and X2C Hamiltonians; for the ground and the particular excited states the CCSD(T) calculations were performed. Various basis sets differing in size were used and the effect of inclusion of the midbond functions was also analysed.

Concerning Rydberg states, it is observed that all these states of ZnAr of predominant $\Sigma$ symmetry exhibit double-well character. Similarly, as in the case of the ultra-long Rydberg molecules, the appearance of the energy barrier between these wells is ascribed mainly to the $s$-wave scattering of the Rydberg electron on the ground-state atom (here, Ar atom). Outer wells of the $\Sigma$ Rydberg states are also the partial result of this scattering as well as of the attractive induction and dispersion interactions between Zn$^+$ and Ar. Furthermore, experimental observations, ab initio calculations and the above-mentioned scattering picture, they all seem to support the general rule stating that the appearance of the outer well in $\Sigma$ Rydberg states of MeRg complexes ($Me = Zn$, Cd, Hg) may be mainly attributed to the properties of the ground-state Rg atom. Namely, MeRg complexes, where
Rg = Ar, Xe, Kr atoms are characterised by the relatively large \( \alpha_{Rg} \) dipole polarisabilities and negative \( s \)-wave e-Rg scattering lengths \( A_s(k_{Rg}) \) in the \( k_{Rg} \rightarrow 0 \) limit, exhibit outer well in the \( \Sigma \) Rydberg states. At the same time, the \( \Sigma \) Rydberg states of MeHe and MeNe complexes do not form outer wells. In this case, He and Ne exhibit relatively low \( \alpha_{Rg} \) dipole polarisabilities and positive values of \( s \)-wave scattering length \( A_s(k_{Rg}) \) in the limit \( k_{Rg} \rightarrow 0 \).

Various sources of the errors of present ab initio calculations are summarised and discussed below. These errors depend on each other in a non-trivial way. Nevertheless, here we have performed their independent estimates.

First of all, it is concluded that the use of the mid-bond functions has significant impact on the description of the (inner) well of valence as well as the Rydberg states of ZnAr complex. However, in spite of the use of midbond functions, it is also concluded that the incompleteness of the basis set is the source of the one of major errors. In the CBS limit, the potential wells are expected to be deeper. Another major source of errors is due to the deficiency in description of electron correlation in MS-CASPT2 method. This method tends to overestimate the interaction energy in comparison with the results of CCSD(T) calculations. Interestingly, these two major errors in the case of the MS-CASPT2 method seem to cancel each other in the region of the inner well of Rydberg states of ZnAr complex. Such cancellation of errors may be the underlying reason for the general success of CASPT2 method in reproduction of experimental results. Furthermore, the MS-CASPT2 method outperforms the CCSD that has the opposite tendency of the underestimation of interaction energy. Sources of some of the remaining errors, including inaccuracy in description of the relativistic effects and in description of the atomic asymptotes, and lack of size consistency of MS-CASPT2 method, were also analysed. Concerning the level of treatment of the scalar relativistic effects, the situation is not clear. For all the states of predominant \( ^1\Sigma \) character, the spectroscopic characteristics obtained with DKH2 and X2C are almost the same. At the same time, in the case of the remaining states, the results differ more noticeably. All the considered ab initio methods tend to underestimate the Zn excitation energies. Mean average error with respect to experimental excitation energies decreases in the following order: CCSD, CASPT2, MS-CASPT2, CCSD(T) reaching 600 and 140 cm\(^{-1}\) in the case of the last two methods. Size-inconsistency errors of MS-CASPT2 method do not exceed 5.5 cm\(^{-1}\) and, in the majority of cases, they are below 1 cm\(^{-1}\). Atomic calculations for Zn indicate that SO splittings are underestimated within AMFI approach by roughly 20%.

Present results of ab initio calculations are in very good agreement with the experimental counterparts, wherever reliable experimental values are available. Some serious discrepancies from the values extracted from experimental data are tentatively ascribed to the frequent use of the relations valid for a Morse potential representation in the evaluation of the spectroscopic characteristics based on the observed spectra.

Taking into account all the above discussion, it is expected that the Rydberg states obtained within present ab initio approach, i.e. MS-CASPT2/RASSI-SO with the largest basis set III-a5Z, provide reliable data for further experimental spectroscopic exploration of ZnAr complex.

Notes

1. Quantum number \( \Omega = |M_S + M_L| \) corresponds to the projection of the total electronic angular momentum on the molecular axis and the superscripts \( o^{\pm} \) identify the \( \Omega = 0 \) states that do not change (+) or invert (−) their sign under the reflection with respect to the plane containing molecular axis.

2. This 'diabatisation' led to irregularities of PEC within inner well of \( (4d6s)^1\Sigma \) state in the case of calculations with I-III and \( ^{1}\Gamma^{−}^{−}I′ \) bases. Therefore, we have not performed such reordering in the case of \( (4s5p)^1\Sigma \) and \( (4s6s)^1\Sigma \) states obtained with III-332, III-33211 and III-a5Z bases.

3. The spin-free PECs of ZnAr complex obtained with I-III and \( ^{1}\Gamma^{−}^{−}I′ \) basis sets can be found in SM (Figures S1–S8).

4. Spectroscopic characteristics, i.e. \( R_e, D_e \) and \( \omega^j_{e} \), obtained with MS-CASPT2 and CCSD(T) methods for all the considered states of ZnAr complex and with all the basis sets of Table 1 are collected in SM (Tables S6–S14 and Figures S9–S12). Deviations from the general trends of changes of the values of \( R_e, D_e \) and \( \omega^j_{e} \) obtained with different basis sets may be attributed to the avoided crossings (SM, Figure S15).

5. Figure 4 in main text and the Figures S9–S12 in SM present the patterns of convergence of the inner-well spectroscopic characteristics \( R_e, D_e, \omega^j_{e} \) of the individual states.

6. Figures S13–S14 in SM present the patterns of convergence of \( R_b, E_b, R^o_{c}, D^o_{c} \) for the individual \( \Sigma \) Rydberg states.

7. Tables S6–S8 in SM collect the values of \( R_e, D_e, \omega^j_{e} \) plotted in Figure 4.

8. Consult Figures S1–S4 and Table S9 in SM.

9. Tables S4 and S5 in SM present results of atomic MS-CASPT2/RASSI-SO calculations.

10. Consult Table S6 in SM.

11. See also Ref. [96].

12. PEC of \( B^{3}\Sigma (4p^3P_{1}) \) state is presented in Figure S16 in SM.

13. In particular, the values of well depth \( D_e \) of \( (4s4p)^1\Pi \) state are 644 cm\(^{-1}\) and 677 cm\(^{-1}\) for \( ^{2}\Pi^{−} \) and \( ^{3}\Pi^{−}a5Z \) bases, respectively (Table S10 in SM).

14. This is estimated by the difference of 7 cm\(^{-1}\) between well-depth \( D_e \) values obtained with MS-CASPT2 method for \( ^{2}\Pi^{−} \) and III-a5Z bases (Table S10 in SM).
15. Figure 2 and Figure S17 in SM present classically accessible regions for Rydberg electrons and $e-\text{Ar}$ scattering length $A_e(R)$, respectively.
16. Compare also with $\Delta E_e(R)$ presented in Figure 13 (and in Figure S18 of SM) calculated for the highest Rydberg states of ZnAr complex considered here.

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The authors report there are no competing interests to declare.

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