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Interactions of transition metal atoms with He

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Abstract. The adiabatic interaction potentials were obtained for the paradigm transition metal-rare gas interactions: Sc(^{2}D)–He and Ti(^{3}F)–He and their di-cations. The ab initio approach included the coupled cluster and multireference configuration interaction methods. He atoms form very weak van der Waals complexes with Sc and Ti with well-depths of ca. 4–5 cm^{-1}. The interactions are characterized by the nearly-degenerate manifolds of adiabatic states with splittings of the order of 0.1 cm^{-1} or less. The anisotropy of the Ti–He interaction is smaller than that for the Sc–He interaction. The origin of the weak anisotropy of these interactions was analyzed. The exchange repulsion was found to be nearly the same in the Σ, Π and Δ states due to the valence *d*-electrons being submerged under the doubly filled 4*s* electron sub-shell. The anisotropy of the total potential is controlled by the weakly-anisotropic dispersion interaction.

PACS. 34.20.-b Interatomic and intermolecular potentials and forces, potential energy surfaces for collisions – 31.50.Df Potential energy surfaces for excited electronic states – 31.15.Ar Ab initio calculations

1 Introduction

Open-shell atoms are very interesting and still relatively poorly understood chemical species. Their chemical reactions and inelastic processes make them of key importance in the chemistry of atmospheres, plasmas, lasers, and more recently, in ultracold matter. In open-shell atoms with electronic nonzero angular momentum, a new type of electronic anisotropy is present which leads to the description of intermolecular forces in terms of manifolds of potential energy surfaces [1]. Such open-shell atoms are nonspherical in the sense that they possess nonzero permanent quadrupole moments and anisotropic dipole polarizability tensors describing a state-dependent response to the external electric field [2]. These properties give rise to the long-range induction terms and to the dispersion anisotropy in the interactions of these atoms with other spherically-symmetric species.

The *d*-electron transition metals may be viewed as the ultimate open-shell systems. The complexes of transition metal atoms (TM) with rare gases such as He are interesting for a variety of reasons. In such interactions the He atom serves as a unique probe for the energy levels of the $(n-1)d^N\ ns^2$ ($N = 1, 2, \ldots 10$) electron system. This level structure is quite different from that of the main-group elements due to a much higher density of states. For example, while carbon has four electronic states within 7.5 eV of the ground state, Ti has an infinite number (its ionization energy is 6.83 eV) [3]. Due to its small size and the absence of *p*-electrons, the He atom may be viewed as an ideal probe of the metal's electron distribution including such features as nodal planes [4,5].

The primary motivation for the study of the TM–He interactions is their relevance to recent experiments on trapping open-shell atoms and molecules at ultra cold temperatures. One of the most promising and general methods is based on buffer-gas loading [6]. The *d*-electron transition metal atoms with non-zero angular momentum are very appealing candidates for such experiments because they can be magnetically trapped. The efficiency of such a process depends critically on rate constants for elastic and inelastic collisions of TM atoms with He. Since paramagnetic atoms are trapped in the Zeeman level with the highest energy, collisions with helium atoms may induce transitions to lower Zeeman levels leading to energy release, heating and trap loss. Therefore, it is imperative for the development of the buffer-gas loading experiments to understand whether collisionally-induced Zeeman transitions are important on the time scale of the experiment [7]. A particular appeal of these experiments stems from the fact that the underlying physical principles can be reduced to the partners' collision properties and, ultimately, to the interactions between them.

This paper will examine the van der Waals interactions of Sc and Ti with He by an ab initio approach. There is a substantial body of ab initio work describing similar interactions involving open-shell, main-group elements with rare-gases [8,9]. Partridge and Bauschlicher [10] studied

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several low-lying states of cations of the first-row transition metals with rare gases. Wilson et al. [11] studied dications of the same group of metals interacting with He. However, no ab initio investigations have been reported to date on the neutral, most challenging equivalents.

The van der Waals interaction between a neutral TM atom and He poses a number of challenges to a computational treatment. The interaction is relatively weak and dominated by the dispersion effect. A removal of the degeneracy of the lowest atomic terms of TM leads to manifolds of closely-spaced states. The proximity of excited atomic states makes the single-reference approaches inapplicable. The computational treatment should efficiently account for electron correlation effects, precisely reproduce minute energy differences, and allow for the treatment of multiple, coupled electronic states. In this work the interaction potentials are calculated using a multireference configuration interaction approach, and where possible, compared with the single-reference coupled cluster results. The examination of the electronic anisotropy of these interactions, its magnitude, as well as its underlying origin is the primary goal of the present paper. It is hoped that by understanding the nature of these interactions it will be possible to identify the atoms amenable to cooling and trapping experiments. A quantitative measure of the interaction anisotropy in these complexes is provided by the ratio of the rate constants for elastic collisions and Zeeman relaxation. The calculations of such elastic-to-inelastic ratios on the potentials obtained here are reported in reference [12] and the experimental measurements of these quantities are presented in reference [13]. In the simultaneous development, the ab initio calculations of quadrupole moments and dipole polarizabilities of selected first-row transition metal atoms were carried out by Klos [14]. These results are of particular interest to the present work.

2 Methods

The interaction of ground-state Sc(^{2}D) atom with He gives rise to three adiabatic potentials V_Σ, V_Π, and V_Δ. The interaction of the ground state Ti(^{3}F) with He is described by four adiabatic potentials V_Σ, V_Π, V_Δ, and V_Φ.

Two types of electronic structure calculations were used. In the case where the single determinant wavefunction was suitable as a reference function, the unrestricted and restricted open-shell coupled cluster method with single, double and non-iterative triple excitations (U/RCCSD[T]) was used. Otherwise, the complete active space self-consistent field (CASSCF) method [15] was used to obtain the reference states; then the internally-contracted multi-reference configuration interaction (IC-MRCI) was applied [16]. All calculations were performed with the *MOLPRO* suite of computer programs [17].

The interaction potentials V_i ($i = \Sigma, \Pi, \Delta, \dots$) were obtained from the following energy differences which encompass both the size-consistency correction and the counterpoise procedure (CP) [18] individually applied to each state to correct for the basis set superposition error

$$V_i = E^i_{\mathrm{TM-He}}(R; DBS) - E^i_{\mathrm{TM}}(R; DBS) - E_{\mathrm{He}}(R; DBS) - \Delta E^i_{SC}. \quad (1)$$

DBS stands for the dimer basis set; ΔE_{SC} is a residual size-consistency correction, which is omitted in the coupled cluster calculations. DBS removes the degeneracy of the atomic states giving rise to 3(4) monomer states. In the MRCI calculations of TM-He and TM energies the effects of higher excitations were included using the IC-MRCI version of the Pople's size-consistency correction [19]. The ΔE_{SC} term was obtained by subtracting the dimer and monomer energies in equation (1) evaluated at $R = 24$ Å.

For the interpretation of our calculations it is convenient to define the isotropic (V_0) and anisotropic (V_2, V_4, ...) parts of the interaction potentials [20]. For a D-state atom one has

$$\begin{aligned} V_0 &= (V_\Sigma + 2V_\Pi + 2V_\Delta)/5 \\ V_2 &= (V_\Sigma - V_\Delta) + (V_\Pi - V_\Delta) \\ V_4 &= 9/5(V_\Sigma - V_\Delta) + 3/5(V_\Delta - V_\Pi), \end{aligned} \quad (2)$$

and for the F-state atom one has [21]

$$\begin{aligned} V_0 &= (V_\Sigma + 2V_\Pi + 2V_\Delta + 2V_\Phi)/7 \\ V_2 &= 5/7(V_\Sigma - V_\Phi) + 15/14(V_\Pi - V_\Phi) \\ V_4 &= 9/7(V_\Sigma - V_\Delta) + 3/7(V_\Pi - V_\Delta) + 9/7(V_\Phi - V_\Delta) \\ V_6 &= 13/7(V_\Sigma - V_\Pi) + 13/14(V_\Delta - V_\Pi) \\ &\quad + 13/70(V_\Delta - V_\Phi). \end{aligned} \quad (3)$$

The one-electron basis set consisted of the Bauschlicher ANO contracted basis set [22] (denoted ANO) for Sc and Ti, and for the He atom, of the contracted aug-cc-pVQZ basis set [23] with g-type atomic orbitals omitted (denoted avqz). Some calculations also included a set of bond functions with $3s3p2d2f1g1h$ uncontracted Gaussian functions with the exponents *sp* 0.9, 0.3, 0.1; *df* 0.6, 0.2; *gh* 0.3. Bond functions, which help saturate dispersion energy [24], were placed in the middle of van der Waals bond.

In the correlation calculations we varied the number of orbitals excluded (i.e. frozen) from the single and double excitations. Calculation with the 1*s* orbital of TM frozen is denoted “core 1”, whereas keeping the two innermost shells (i.e. 5 lowest orbitals) frozen, is denoted “core 5”.

The CASSCF calculations for Sc–He and Ti–He included five *d* orbitals of the metal and one orbital of He in active space. In Sc–He calculations the 4-state CASSCF calculations with state averaging was carried out to generate the reference functions for the MRCI calculations. For Ti–He the 10 state-averaged CASSCF was used to construct the reference functions for the MRCI calculations of the four lowest states correlating with the ^{3}F term and 3 states corresponding to the next triplet ^{3}P located ca. 8400 cm^{-1} above the ground state.

Table 1. Calculated equilibrium positions (R_e) and well-depths (D_e) of minima of three states of Sc–He and Sc^{2+}–He. Energies are in cm^{-1} and distances in Å; the parameters were obtained from spline fits. All values (except for the indicated "no CP") are BSSE corrected.

Computational approach	Σ		Π		Δ	
	R_e	D_e	R_e	D_e	R_e	D_e
Sc–He						
CCSD[T]/ANO+avqz+bf core 1	5.60	4.09	5.60	4.01	5.75	3.84
CCSD[T]/ANO+avqz core 1	5.71	3.39	5.71	3.33	5.81	3.16
CCSD[T]/ANO+avqz core 5	5.71	3.39	5.71	3.32	5.81	3.16
MRCI/ANO+avqz core 5	5.62	4.00	5.65	3.82	5.79	3.33
MRCI/ANO+avqz core 5/no CP	4.75	38.00	4.75	31.80	5.00	26.68
Sc^{2+}–He						
RCCSD[T]/ANO+avqz core 5	2.545	769.5	2.175	1724.8	2.21	1737.5

3 Results and discussion

3.1 Coupled cluster calculations: Sc–He, Sc^{+2}–He

The three states, $^2\Sigma$, $^2\Pi$, and $^2\Delta$ of both the neutral and the ionic systems differ by the single d electron occupying three types of d-orbitals: $d_\sigma(\Sigma)$, $d_\pi(\Pi)$, and $d_\delta(\Delta)$. For this reason the single-reference coupled cluster approach can be used for these calculations. Below Sc–He will also be studied using the MRCI method for the purpose of comparison.

The calculated potential energy curves for Sc–He interaction obtained at the UCCSD[T]/ANO+avqz+bf (core 1) level of theory are shown in Figure 1. The potential curves are strikingly close to each other. The order of well-depths of the minima is $^2\Sigma$: ($D_e = 4.09$ cm^{-1} at the minimum distance $R_e = 5.60$ Å) > $^2\Pi$: ($D_e = 4.01$ cm^{-1} at $R_e = 5.60$ Å) > $^2\Delta$: ($D_e = 3.84$ cm^{-1} at $R_e = 5.75$ Å). At short distances ($R < 3.0$ Å) the order of curves is the following: Π is the least repulsive and Σ is the most repulsive.

The presence of bond functions, which improves the description of dispersion, but increases the BSSE, may pose problems in the context of the CP correction of the MRCI calculations. The calculations without bond functions reveal that the potential wells become considerably shallower (see Tab. 1). The Σ state has $D_e = 3.39$ cm^{-1}, Π of 3.33 cm^{-1}, and Δ of 3.16 cm^{-1}. The difference of about 0.6–0.7 cm^{-1} represents a significant fraction of the well depth of these complexes.

The effect of correlation of the innermost electrons on the van der Waals interaction was also explored by keeping the first 2 inner shells (core 5) frozen. These results (Tab. 1) show that the core correlation has no effect on the interaction energies (differences are of the order of less then 0.01 cm^{-1}). However, it should be added that the ANO basis set may be viewed as insufficient for the purposes of accounting for the core correlation energy. From this point forward the calculations employed the 5-orbital frozen core.

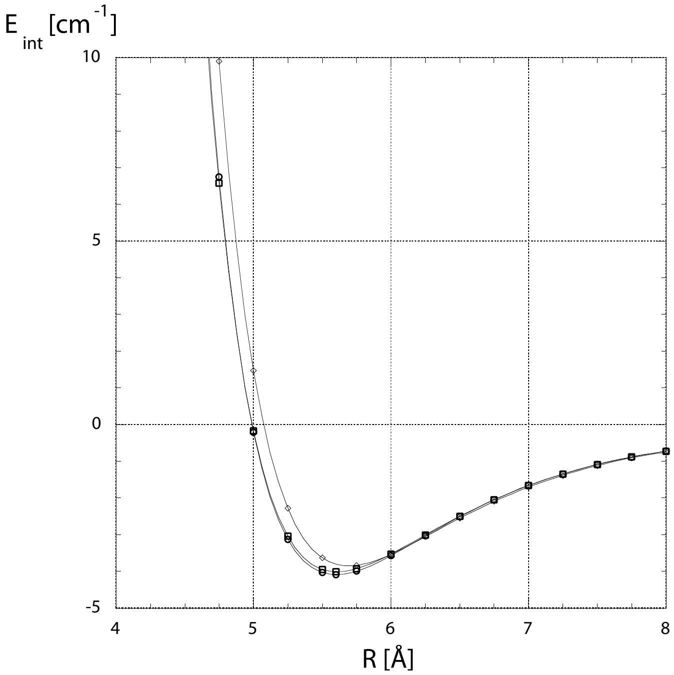


Fig. 1. RCCSD[T] interaction potentials for Sc–He. Σ state – circles; Π state – squares; Δ state – diamonds.

In order to understand the source of near degeneracy of the interaction potentials in Sc–He, the calculations for the Sc di-cation interacting with He were performed. In the Sc^{+2} ion the 4s electrons are removed. The results of the RCCSD[T]/ANO+avqz/core 5 calculations are shown in Figure 2. The three interaction potentials for Sc^{+2}–He are much deeper than in the neutral system. The order of the well-depths of the potentials is Δ: 1737 cm^{-1} at $R_e = 2.21$ Å, very close to Π: 1725 cm^{-1} at $R_e = 2.17$ Å > Σ: 769 cm^{-1} at $R_e = 2.54$ Å. The positions

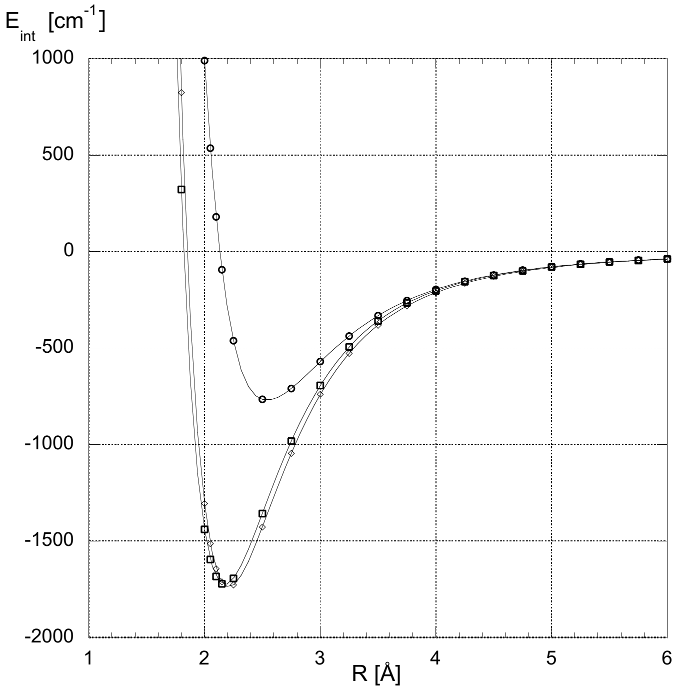


Fig. 2. RCCSD[T] interaction potentials for Sc^{2+}–He. Σ state – circles; Π state – squares; Δ state – diamonds.

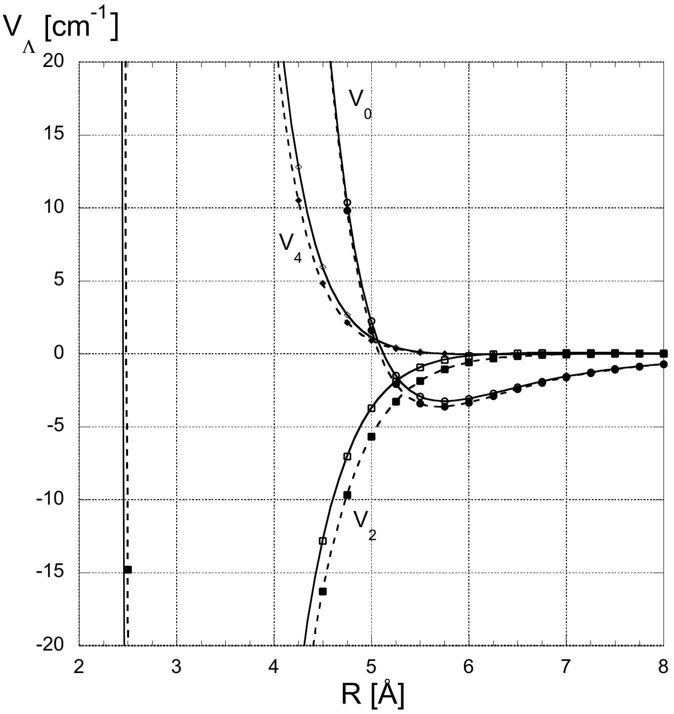


Fig. 3. Comparison of V_0, V_2, V_4 potentials (see Eq. (2)) for Sc–He obtained by RCCSD[T] (solid lines) and MRCI (dashed lines): V_0 – circles, V_2 – squares, V_4 – diamonds.

of minima shift toward the distances more than twice as short as in the neutral system, indicating a strong backward shift in the repulsive walls of the potentials. These features suggest that the removal of 4*s* electrons drastically reduces the exchange repulsion. There is also some increase in the attractive interaction due to the charge-induce dipole effect (see below for more discussion).

Our results can be compared with the work of Wilson et al. [11]. Their calculations predict that the Δ state is substantially deeper (1704 cm^{-1}) than Π (1562 cm^{-1}) with the Σ state being much shallower (451 cm^{-1}). This discrepancy with reference [11] cannot be explained because our calculations with their basis set lead to the following values: Σ: 722.9 cm^{-1}, Φ: 1705.5 cm^{-1}, and Δ: 1712.1 cm^{-1}.

3.2 MRCI calculations: Sc–He

MRCI/core 5 calculations employed ANO+avqz basis set without bond functions. The MRCI approach predicts the same order of minima. The Σ state well-depth is 4.00 cm^{-1} followed by that of the Π state, 3.82 cm^{-1}, and that of the Δ state, 3.33 cm^{-1}. The MRCI calculations carried out in the identical basis set as RCCSD[T] provide slightly deeper potentials and the values are spread slightly wider indicating that the MRCI anisotropy of potentials is slightly larger. To quantify this observation, we have compared in Figure 3 the isotropic V_0 terms and the anisotropic V_2 and V_4 terms generated by the two methods. It is seen that the isotropic potentials V_0 are almost identical in both approaches; V_2 is more attractive in the coupled cluster approach, and V_4 is less repulsive at the MRCI level of theory. If we focus at the minimum region (5 Å $< R <$ 6 Å) V_0 is slightly more attractive in the MRCI, V_2 is considerably more attractive in MRCI and V_4 is nearly the same in both calculations.

The MRCI potentials were obtained by applying individual counterpoise corrections to each of the states as described in the previous section. In order to underscore the necessity of the CP correction, the CP uncorrected values are also included in Table 1. The well-depths from the uncorrected calculations are nearly ten times larger and vary from 38.0 cm^{-1} for the Σ state to 26.7 cm^{-1} for the Δ state. It is clear that in such weak interactions a CP correction of the MRCI interaction energies is of crucial importance.

3.3 MRCI calculations for Ti–He and Ti^{+2}–He

The CASSCF+MRCI/ANO+avqz/core 5 calculations of the Σ, Π, Δ, and Φ states correlating with the lowest atomic term ^{3}F show that the potential curves are very close to each other (Fig. 4). The minimum parameters shown in Table 2 indicate that the order of the well-depths of the minima is $\Sigma < \Delta < \Pi < \Phi$, while the differences are of the order of a fraction of cm^{-1}. It appears that the Ti–He interaction is more isotropic than Sc–He. The isotropic potential V_0 and the anisotropic terms V_2, V$_4$, and V_6 are shown in Figure 5. The average potentials V_0 are very similar in both cases, whereas the leading anisotropic term V_2 in Ti–He is indeed closer to zero in the region of the minimum than in Sc–He.

Table 2. Calculated equilibrium positions (R_e) and well-depths (D_e) of minima of three states of Ti–He and Ti^{2+}–He. Energies are in cm^{-1} and distances in Å; the parameters were obtained from spline fits. All values are BSSE corrected.

Computational approach	Σ		Π		Δ		Φ	
	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e
Ti–He MRCI/ANO+avqz core 5	5.45	4.22	5.48	4.09	5.48	4.11	5.50	4.04
Ti^{2+}–He MRCI/ANO+avqz core 5	2.06	2166.5	2.17	1649.0	2.37	1135.8	2.08	2192.6

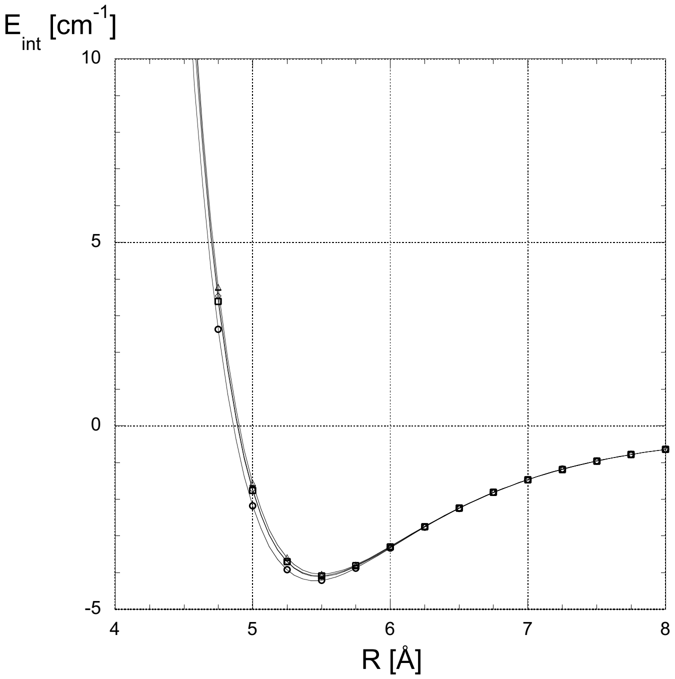


Fig. 4. MRCI interaction potentials for Ti–He. Σ state – circles; Π state – squares; Δ state – diamonds; Φ state – triangles.

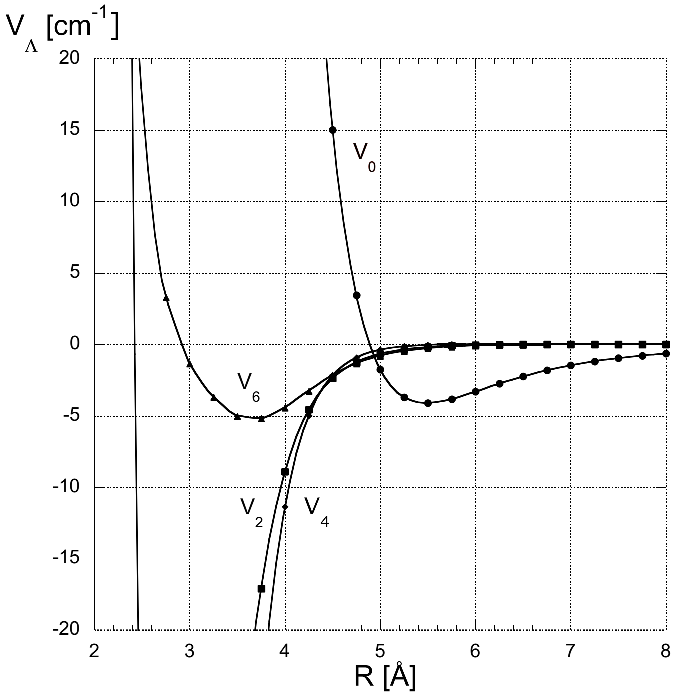


Fig. 5. Isotropic V_0 and anisotropic terms for Ti–He from MRCI calculations. V_0 – circles, V_2 – squares, V_4 – diamonds, V_6 – triangles.

The Δ state of the Ti–He interaction is the only state in this system that has an essentially single-determinant reference function. Therefore, this state can be examined by both the RCCSD[T] and MRCI treatments. A detailed comparison indicates that both approaches lead to nearly identical potentials. This provides further verification of our calculations.

The Ti^{+2}–He interaction reveals the effects of removing the 4*s* electrons from Ti on the anisotropy of the interaction. The MRCI calculations similar to those applied to Ti–He were carried out for the four lowest states of this complex. As for Sc–He, the removal of the 4*s* electrons leads to a drastic reduction of repulsion and shifts the minima toward much shorter distances. The strongest interaction of the Φ state (D_e = 2193 cm^{-1}) is closely followed by the Σ state (D_e = 2166 cm^{-1}). The Π state is considerably weaker (D_e = 1649 cm^{-1}) and the weakest is Δ (D_e = 1136 cm^{-1}). These values can be compared with the results of Wilson et al. [11] who used UCCSD(T) to calculate three out of four states (Π, Δ, Φ) of this complex. Their results are in the same order as our values, namely, Φ (D_e = 2132 cm^{-1}) > Π (D_e = 1789 cm^{-1}) > Δ (D_e = 1187 cm^{-1}). However, their Π state is significantly deeper.

3.4 Accuracy of the MRCI calculations of interaction potentials

The Sc–He results allow for a detailed comparison of RCCSD[T] and MRCI approaches. Such insights are essential because very little is known about the performance of MRCI in very weak van der Waals interactions involving open-shell species. Furthermore, MRCI is the only approach that can be applied to Ti–He.

One of the main differences between the approaches consists of MRCI lacking the triple excitations present in RCCSD[T]. The triples are essential for the description of the dispersion energy, so one can expect the RCCSD[T] potentials to be deeper than those obtained with RCCSD (see e.g. [25]). In the present context the direct comparison between MRCI and RCCSD[T] may be complicated by the fact that the inclusion of triples may compensate for the deficiencies of the reference function. Nevertheless, the following can be safely noted: the MRCI potentials are slightly deeper but otherwise in good qualitative (the order of well-depths) and quantitative (the magnitude of anisotropy) agreement with RCCSD[T].

Second, our one-electron basis set is far from saturated as revealed by the strong effect of bond functions (see Tab. 1). Our estimate is that the potentials obtained with ANO+avqz basis set may be underestimated by ca. 25% due to the incompleteness of the one-electron basis set. The MRCI calculations did not use bond functions because, in our experience, bond functions may lead to erratic results when the CP correction is applied to the MRCI energies.

Third, our adiabatic potentials do not include any relativistic effects. It has recently been shown by Klos [14] that the inclusion of the Douglas-Kroll term (D-K) [26] reduces the mean dipole polarizabilities of the first-row transition metal atoms by ca. 1–7%. One should expect a similar effect on the leading dispersion coefficient. Sadlej and collaborators [27] found that the D-K correction affects considerably the interaction potentials of Cu with H_2O and NH_3.

To conclude, we believe that the MRCI approach leads to reliable results for weak van der Waals interactions between first-row transition metals (with non-zero angular momentum) and rare gases. Our calculated states are underestimated by 25–30% in the minimum region; however, it is expected that all the states should be rather uniformly affected [4,5].

4 Sources of anisotropy

An open-shell atom with non-zero angular momentum L is anisotropic in the sense that it possesses a permanent quadrupole moment, as well as anisotropic dipole polarizability [2]. In the interactions of such atoms with spherically-symmetric rare gases these properties give rise to state-dependent long-range interaction energy components: induction and dispersion. The quadrupole moment is related to the anisotropic induction energy with the leading term vanishing as R^{-8}. The dipole polarizability anisotropy is related to the anisotropic dispersion term with the leading component vanishing as R^{-6}. The exchange effect in such interactions is also anisotropic and offers important clues concerning the electronic structure of the anisotropic atom. It is well-known that in the interactions between an atom in a ^{2}P state (e.g. a boron atom; see [9]) with He, the exchange term provides a strong distinction between the He approaching toward the singly occupied $2p$ orbital (Σ) or toward the nodal plane of this orbital (Π) due to the vastly different overlap. Both the Heitler-London-exchange and induction energies contribute to the Hartree-Fock (HF) interaction energy, whereas the dispersion term appears in the post-HF interaction energy term.

4.1 The short-range anisotropy

A partitioning into the HF and post-HF interaction energy terms (E_{int}(HF) and E_{int}(corr)) was possible only for Sc–He and Sc^{+2}–He. The HF interaction energies are shown in Figure 6a for the former and Figure 6b for the latter. The neutral interaction is purely repulsive at the HF level and nearly isotropic. The repulsive walls of Σ and Π states are almost identical and that of Δ is slightly more protruding. The induction interaction appears to be too small to make the interaction energy negative in the asymptotic region. We conclude that the exchange repulsion reflects the isotropic behavior of the overlap of the $1s$ orbital of He with the filled $4s$ orbital of Sc. Removing these outer $4s$ electrons, as in the case of Sc^{+2}–He, exposes the $3d$ orbitals to the overlap with the $1s_{\mathrm{He}}$ orbital. As shown in Figure 6b the HF interaction energy displays deep minima and the interaction becomes strongly anisotropic. The Δ curve lies below the Π curve by ca. 100 cm^{-1} whereas the Σ curve is much less attractive. The minima at the E_{int}(HF) curves occur at short distances 2.25 Å for Δ and Π and 2.75 Å for Σ. The anisotropy of this interaction can be explained as follows: in the Σ state, He atom faces the singly occupied d_σ orbital which results in a larger overlap and stronger repulsion, whereas in both Π and Δ states it lies in the nodal planes of d_π or d_δ orbitals which leads to a reduced exchange repulsion. When the repulsion is reduced the atoms are allowed to approach closer and the attractive induction effect (isotropic in C_4, but anisotropic in C_6 term [2]) could take over.

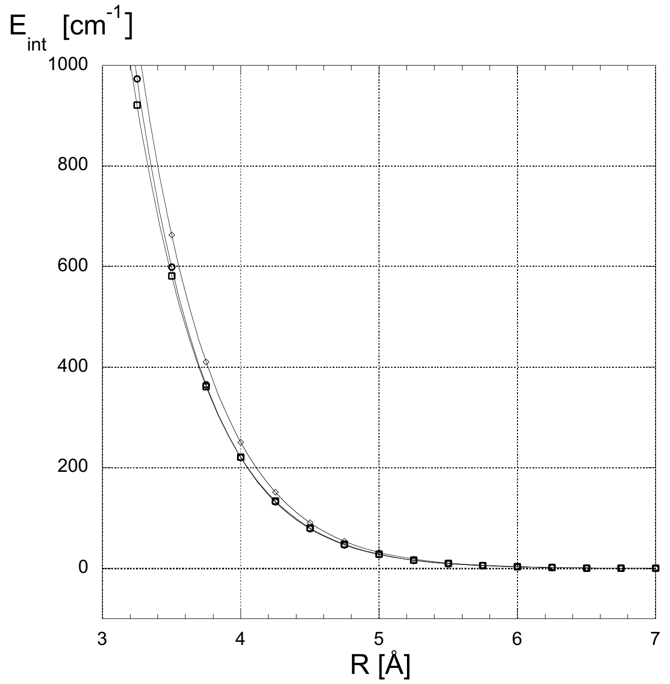
4.2 Dispersion anisotropy

The information concerning the dispersion interaction can be extracted from the post-HF, E_{int}(corr), contribution to the interaction energy. This contribution is expected to also include other effects that are of different physical origin [4,5]. Nevertheless, the asymptotic behavior in the neutral Sc–He is to a good approximation determined by the dispersion energy. Following Aquilanti and Grossi [20] we can define the leading dispersion coefficients of Σ, Π, and Δ states as:

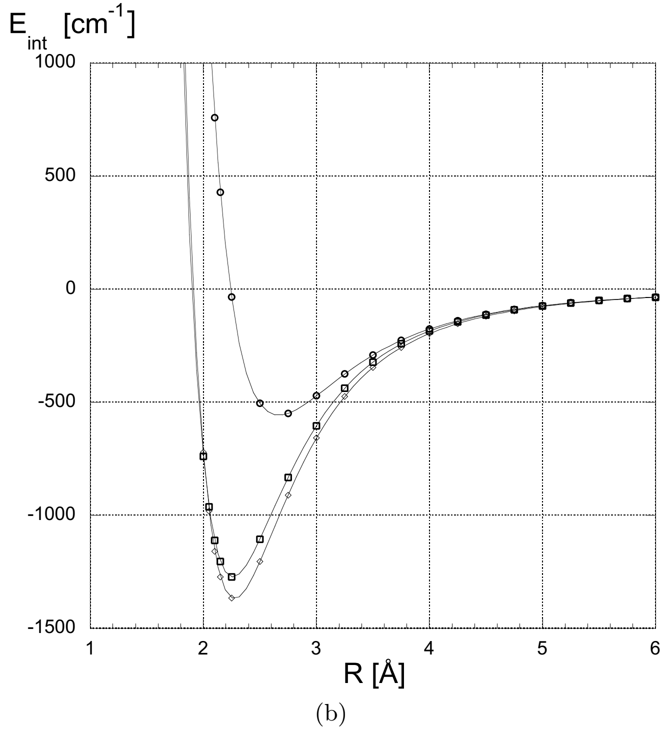
$$\begin{aligned} C_6^{\Sigma} &= C_{6,0} + 2/7 C_{6,2} \\ C_6^{\Pi} &= C_{6,0} + 1/7 C_{6,2} \\ C_6^{\Delta} &= C_{6,0} - 2/7 C_{6,2} \end{aligned} \tag{4}$$

where the $C_{6,0}$ and $C_{6,2}$ denote the average and anisotropic dispersion coefficients, respectively, and $V_{4,disp}$ is assumed to be equal to zero.

In order to determine the values of $C_{6,0}$ and $C_{6,2}$ the values of E_{int}(corr) for the three states were used to construct $V_{0,corr}$, $V_{2,corr}$, and $V_{4,corr}$ according to equation (2). These terms multiplied by R^6 are shown in Figure 7a as a function of $1/R$. The $C_{6,0}$ obtained from the

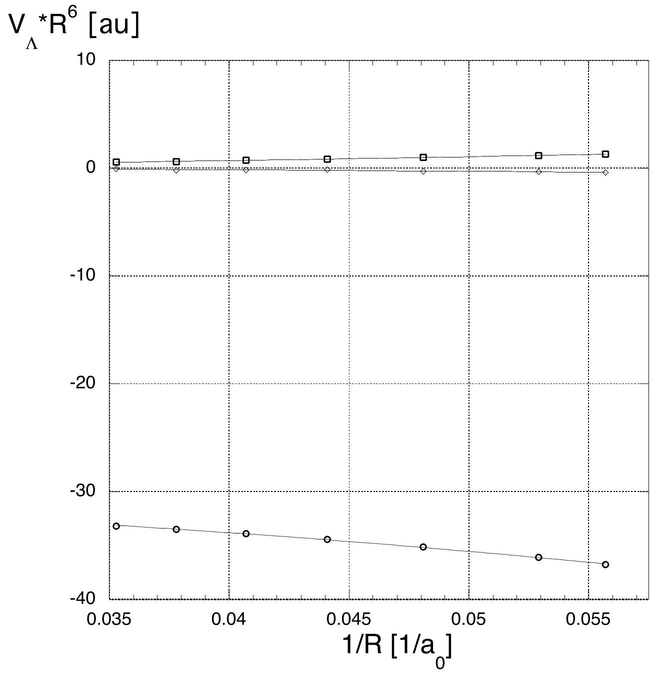


(a)

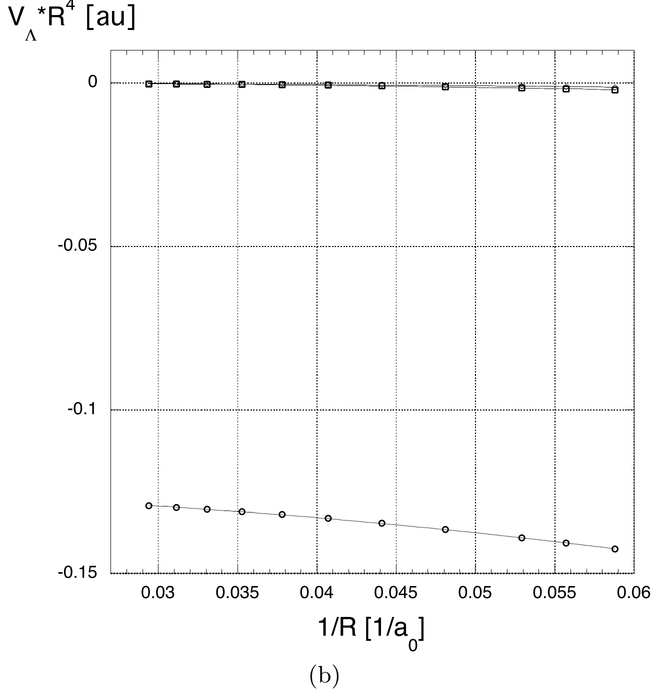


(b)

Fig. 6. Hartree-Fock interaction potentials E_{int}(HF) for (a) Sc–He; (b) Sc^{+2}–He. Σ state – circles; Π state – squares; Δ state – diamonds.



(a)



(b)

Fig. 7. Asymptotic region of the correlation contribution to the interaction potentials, E_{int}(corr), (for definitions see the text) of (a) Sc–He; (b) Sc^{+2}–He; V_0 – circles, V_2 – squares, V_4 – diamonds.

fit is 31.4 au and $C_{6,2}$ is –0.14 au. As seen in Figure 7a the term $V_{4,disp}$ is very close to zero as predicted. The anisotropy of the dispersion energy is very small.

Another source of information on the ratio of the anisotropic to isotropic dispersion coefficients of Sc can be obtained from $C_{6,2}/C_{6,0} = 7\Delta\alpha/6\overline{\alpha}$ [14]. The components of the dipole polarizability tensor evaluated via the MRCI method in reference [14] lead to the ratio $7\Delta\alpha(2,0)/6\overline{\alpha} = -0.077$. The ratio of the coefficients obtained above is equal to –0.0045. This discrepancy can be, at least partially, explained by comparing results of different methods RCCSD[T] (C_6), and MRCI (a), (see Ref. [14] for more details).

Finally, let us examine the long range behavior of E_{int}(corr) in the Sc^{+2}–He cation. The interaction correlation in this case behaves asymptotically as R^{-4} indicating that E_{int}(corr) is dominated by the induction effects. Such a charge-induced dipole, C_4/R^4, induction effect is isotropic. By constructing $V_{0,corr}$, $V_{2,corr}$, and $V_{4,corr}$ correlation-interaction potentials (see Fig. 7b) the following long range coefficients were extracted: the isotropic $C_4 = -0.124$ au, $C_{6,0} = 5.11$ au, and $C_{6,2} = 0.7$ au. The ratio of $C_{6,2}/C_{6,0} = 0.14$ is very similar to that resulting from the ratio of polarizabilities from reference [14] which amounts to 0.54. It should be mentioned, however, that both $C_{6,0}$ and $C_{6,2}$ may not be entirely due to the dispersion effect, but may also include an induction component (see Ref. [2]).

The accuracy of long-range MRCI potentials was not sufficient to perform a similar fit to both the isotropic and anisotropic C_6 coefficients in Ti–He potentials. It was only sufficient to provide an estimate of the $C_{6,0}$ coefficient as 25 au. Interestingly, this value is smaller than $C_{6,0}$ for Sc–He and their ratio, $25/31.4 = 0.80$, is very close to that of the mean dipole polarizabilities of these two atoms, $100.16/118.71 = 0.84$ [14].

5 Conclusions

He atom interacting with the first-row transition metals Sc and Ti forms very weak van der Waals complexes with well-depths in the range of 4–5 cm^{-1}. These interactions are characterized by nearly-degenerate manifolds of adiabatic states with splittings of the order of 0.1 cm^{-1}. The anisotropy of the Ti–He interaction is smaller than that in the Sc–He interaction.

The methodology of computing such weak, nearly degenerate interaction potentials has been examined. The three states of Sc–He, Σ, Π, and Δ, as well as one of the four states of Ti–He, Δ, can be computed using both RCCSD[T] and MRCI. The calculations for these states served as a basis for the evaluation of the efficiency of the MRCI method in the study of very weak van der Waals interactions with multiple potentials. Our conclusion is that the MRCI method can reliably reproduce such interactions. We found that both the well-depths of these potentials and the anisotropy are adequately described. A state-specific counterpoise correction is mandatory in such calculations. We estimate that the adiabatic potentials presented in this work are ca. 25–30% underestimated (in the minimum region) due, primarily, to the unsaturated one-electron basis sets, and also due to the limited treatment of the electron correlation. However, all the states are expected to be uniformly affected.

The analysis of the nature of the Sc–He interaction sheds light on the suppression of anisotropy. Our calculations demonstrate that in this complex the HF interaction, which is dominated by the exchange repulsion is nearly the same in the Σ, Π, and Δ states as a result of the d-electrons being submerged under the filled $4s$ electron sub-shell. Consequently, the overlap between the interacting atoms (chiefly due to the $4s_{\mathrm{Sc}}$ and the $1s_{\mathrm{He}}$ orbitals) is the same in all the states, and so is the exchange repulsion. The results for the Sc^{+2}–He and Ti^{+2}–He, where the outer $4s$ electrons are removed, indicate that the exposure of d-electrons to the interaction leads to drastic differences in the short-range repulsion among the states. The anisotropy of the interaction in the neutral systems is therefore controlled by the dispersion attraction.

The anisotropic properties of dispersion interaction were examined by analyzing the correlation contribution to the interaction energy in the asymptotic region. The isotropic $C_{6,0}$ and the anisotropic $C_{6,2}$ dispersion coefficients were obtained for the Sc–He interaction. For the Ti–He dispersion energy an estimate of the $C_{6,0}$ coefficient was obtained. The small anisotropy of dispersion energy is in good agreement with the predictions based on the dipole polarizability calculations. These polarizability-based predictions suggest that, in the first-row transition metals interacting with He, the dispersion effect should become more isotropic as the number of electrons, n, in the $3d^n$ sub-shell increases.

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Note added in proof

Calculated ground states D_0 ($J_a = 2$, $J = 2$, and parity $+$) are: for Ti–He 0.726 cm^{-1} and Ti^{2+}–He 1671.38 cm^{-1}.

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