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RESEARCH ARTICLE

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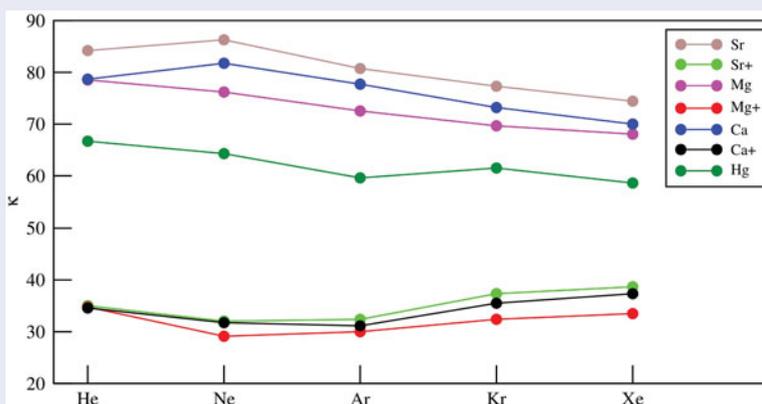
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ABSTRACT

The potential energy curves and spectroscopic constants of the ground-state of the Mg–Rg (Rg = He, Ne, Ar, Kr, and Xe) van der Waals complexes are generated by the Tang–Toennies potential model and a set of derived combining rules. The parameters of the model are calculated from the potentials of the homonuclear magnesium and rare-gas dimers. The predicted spectroscopic constants are comparable to other available theoretical and experimental results, except in the case of Mg–He, we note that there are large differences between various determinations. Moreover, in order to reveal *relative* differences between species more obviously we calculated the reduced potential of these five systems. The curves are clumped closely together, but at intermediate range the Mg–He reduced potential is clearly very different from the others.



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1. Introduction

The potential energies describing the interaction of the atomic and molecular systems are of fundamental importance for the understanding of the physical properties of matter [1]. Due to the recent progress in magneto-optical traps [2,3], a number of fields in ultracold atomic physics such as photoassociation [2,4], optical frequency standards [5,6], as well as possible Bose–Einstein condensates [7,8] have been initiated recently. Therefore, accurate interaction energies of alkali and alkali earth rare-gas dimers are required for these investigations and also for further simulations.

During the past decade, special intense interest was focused on the study of atomic collision process of diatomic van der Waals complexes. In particular and

because of cold atoms physics, considerable attention has been focused recently on diatomic alkaline earth and alkaline earth-noble gas diatomic systems. The Mg₂ homonuclear molecule has constituted the first van der Waals system for which the ground-state potential energy has been constructed from spectroscopic measurements and it became a benchmark system. Indeed, there are many experimental and theoretical determinations of the ground-state potentials of Mg–RG dimers. The efficient cooling by supersonic expansion developed in the early 1980s made the formation of weakly bound van der Waals molecules possible. Since then, magnesium rare-gas complexes in both ground and electronically excited states have been characterised [9–19] by laser spectroscopy in supersonic jet expansions. Indeed, the parameters of the potential functions for the ground and appropriate

excited states are obtained by vibrational analysis of laser excitation spectra. In theory, the ground-state and several excited states of the MgRg systems have been calculated by various methods, such as surface integral [20], pseudopotential SCF/CI [21,22] non-empirical pseudopotentials [23], Møller–Plesset perturbation [24], and coupled cluster [25].

Although, with modern computers, various *ab initio* calculations are possible and the progress in experimental process, calculations for such weakly bound van der Waals molecules are still challenging. Usually, *ab initio* methods are used to calculate van der Waals potential of dimers, but they are complicated, time consuming and difficult to apply to complex systems. Therefore, calculations using relatively simple and reliable model potentials offer a very interesting alternative. For this, Tang and Toennies proposed a potential model based on universal damping functions for the dispersion coefficients for van der Waals interaction known as Tang–Toennies (TT) potential. It has been found that this relatively simple analytical expression provides an accurate description of the van der Waals potentials. Since its introduction in 1984, predictions of the shapes of van der Waals potentials based on this model have been confirmed for many systems by detailed comparisons with the best available experimental and theoretical data [26–28]. Recently, it has been used to calculate successfully the van der Waals potentials of the alkaline earth dimers except Be₂ (Ca₂, Sr₂, Mg₂, and Ba₂). Moreover, some alkaline earth rare-gases interaction potentials, such as those of Sr–RG and Ca–RG systems, are successfully predicted with this model together with a new set of combining rules.

The request of this combining rules for predicting the parameters of the interaction potential of the mixed system *ij* from the parameters of the like systems *ii* and *jj* has a long history [29]. Some of these rules are very useful. For example, very accurate combining rules were developed for calculating the well depth D_e and equilibrium distance R_e of the van der Waals potentials of the mixed rare-gas systems from the corresponding values of the homogeneous dimers [30]. They have been also used recently to predict the interaction potential of the Hg–Rg systems [31] from the homogenous dimers Hg₂ and Rg₂. This has motivated the investigation of the possible determination of the interaction between a magnesium atom and rare-gas atoms from the homonuclear magnesium and rare-gas dimers potentials using combining rules. The accuracy of the parameters and the potential energy curves was demonstrated by comparisons with the previous theoretical and experimental studies.

For the interactions between two rare-gas atoms, the dispersion coefficients are known to a high degree of accuracy [32–34]. A variety of experimental data made

it possible for the well depth (D_e) and equilibrium distance (R_e) of the rare gas potentials [35]. Consequently, we dispose now with a remarkably accurate knowledge of the potential curves of these systems, which can be easily described by the Tang–Toennies analytical expression.

Recently, it has been shown in reference [36] that with set of dispersion coefficients calculated by Porsev and Derevianko [37] using relativistic many-body perturbation theory, and the experimentally determined equilibrium distance R_e and the well depth D_e taken from IPA potential of Tiesinga et al [38] which is estimated from the absorption spectrum of magnesium vapor successfully photographed with a high resolution spectrograph by Balfour and Douglas [39] in 1970s the van der Waals potential of the magnesium dimer was successfully described by the Tang–Toennies potential [36]. The two missing parameters in the TT potential (A and b) are determined with a simple program in the appendix in Ref. [30] from which with a given set of dispersion coefficients, the program converts R_e and D_e into A and b . The predicted potential energy curve is in excellent agreement, in the van der Waals region, with the RKR potentials constructed from spectroscopic measurements. Even in the short range, the predicted potential is in good agreement with the experimental repulsive potentials obtained from the Frank–Condon factors of the bound-free transitions.

This paper is organised as follows. In Section 2, we present the main lines of the potential model and the combining rules. Then the five parameters (A , b , C_6 , C_8 , and C_{10}) for the Mg–RG complexes calculated from the homonuclear magnesium and rare-gas dimer potentials are presented. The spectroscopic constants D_e , R_e , w_e , and $w_e x_e$ obtained from the predicted potentials compared with the previous available experimental and theoretical determinations are reported in Section 3. Finally, we present our conclusions in Section 4.

2. Method

2.1. Potential model

The interaction potential energy curve for the diatomic complexes Mg–Rg is generated by the TT model proposed by Tang and Toennies in 1984 [26]. The basic idea of this model is to modify the formula proposed in 1973 by one of these authors [40] in which the Born–Mayer repulsive potential [$A \exp(-bR)$] with parameters from SCF calculations was added to the first three terms of the asymptotically ($R \rightarrow \infty$) correct *ab initio* dispersion:

$$V(R) = V_{SCF}(R) - \sum_{n=3}^{n_{\max}} \frac{C_{2n}}{R^{2n}} \quad (1)$$

Unexpectedly, this simple model was able to predict accurately the experimental available rare gas dimer potential well parameters. This observation has stimulated Tang and Toennies to modify the formula of Equation (1) in order to take into account the effect of charge overlap on the dispersion interaction in the region of the potential well. This is done by the insertion of the damping function $f_{2n}(bR)$ to the long range attractive dispersions series. Thus, the latter formula of Equation (1) becomes:

$$V(R) = Ae^{(-bR)} - \sum_{n=3}^{n_{\max}} f_{2n}(bR) \frac{C_{2n}}{R^{2n}} \quad (2)$$

It is known that the TT potential which consists of the sum of the short range repulsive Born–Mayer potential $Ae^{(-bR)}$ and the long-range attractive potential of the damped asymptotic dispersion series. R is the internuclear distance, A and b are the parameters of the Born–Mayer repulsive potential, C_{2n} are the dispersion coefficients, and $f_{2n}(bR)$ is the radial dependent damping function for the individual dispersion coefficient C_{2n} .

Tang and Toennies finished to the conclusion that the damping function is an incomplete gamma function founded on the form of the exchange correction to the dispersion series. In addition, they were derived from simple arguments to satisfy physical boundary conditions:

$$f_{2n}(bR) = 1 - e^{(-bR)} \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \quad (3)$$

It is interesting to note that b is the same as the range parameter of the Born–Mayer repulsion. This can be explained by the fact that both the repulsion and dispersion damping are consequences of the wave function overlap. The most discriminating test of Equation (3) is provided by the accurate *ab initio* calculations of Koide, Meath, and Allnatt for H(1S)–H(1S). [41]. It was in best agreement with them. In addition, accurate damping functions for many other systems became available [42–47] and they are found to be all in close agreement with Equation (3). The use of this damping function is observed in the work of Jeziorski and co-workers [48].

The model potential of Equation (2) has been tested successfully for several chemically different types of van der Waals interactions [26–28]. They could fit nearly perfectly the van der Waals potentials for different types of systems such as the triplet state of H_2 and the van der Waals dimers He_2 and Ar_2 , as well as the van der Waals molecules with open shell atoms NaAr and LiHg.

Recently, this later model has been successfully used to predict the entire ground-state potential energy curves

for the systems of group IIA [49,50,36,51] and group IIB [31,52]. While the shapes of these potentials are different, they are all accurately predicted by Equation (2). Moreover, this model has shown to have a firm foundation within the generalised Heitler–London theory [53]. For many systems, the first three dispersion coefficients C_6 , C_8 and C_{10} are available. For the higher-order terms it is not necessary to have accurate information since these may be generated using the semi-empirical recursion relationship:

$$C_{2n+4} = \left(\frac{C_{2n+2}}{C_{2n}} \right)^3 C_{2n-2} \quad (4)$$

This relationship has been tested for the case of H(1S)–H(1S) and He–He interaction [54] and it has been found that it can predict the theoretical values of C_{12} , C_{14} , and C_{16} to better than 4%. Usually, terms beyond C_{16} do not make any noticeable contribution to the potential. Thus, the model potential is determined by five parameters A , b , C_6 , C_8 , and C_{10} . If the first three dispersion coefficients are available, only two parameters (A , b) require to be known in order to employ the TT model.

In the next part, we present the combining rules for predicting the potential parameters of the mixed systems ij from the known parameters of the like systems ii and jj . These values when used together with Tang Tonnie's model for van der Waals potentials make possible the accurate prediction of mixed magnesium-rare gas potential energy curves.

2.2. Combining rules

The interatomic potentials of both magnesium and rare-gas dimers can be expressed in terms of the TT potential model. This makes it possible to describe the interaction between a magnesium atom and a rare-gas atom by the TT analytical expression. We will first separately discuss the combining rules for short range Born–Mayer parameters and the long range dispersion coefficients. Then we will use the results to construct the interaction potentials for magnesium rare-gas complexes.

2.2.1. Combining rules for A and b

Considerable effort has gone into the empirical search for combining rules allowing the short range Born–Mayer repulsive potential parameters A and b for a mixed system such as ij to be deduced from the potentials for two known systems ii and jj . Then, a number of reasonably accurate combining rules are available [55–58]. Böhm–Ahlrichs [58] tested four different sets of combining rules for A and b , (Equations (30)–(33) of Ref. [58]). They established that all sets are useful; however, the results are not same.

In fact, these rules are based on heuristic arguments, their validity can only be discussed by the accuracy of the predict results.

In our study, based on the recent work of Yang and co-workers [49] and Yin and co-workers [50], we will assume that the following set of combining rules of Equation (31) of Ref. [58] are generally the most appropriate to all the alkaline earth rare-gas systems. They have been applied, recently, with great success in the case of calcium rare-gas and strontium rare-gas interactions:

$$A_{ij} = [A_i A_j]^{1/2}, \quad b_{ij} = 2 \frac{b_i b_j}{b_i + b_j} \quad (5)$$

The indices i and j label the potential parameter for the like system.

Thus, using these combining rules, the requested values A and b for the interaction of a magnesium atom and a rare-gas atom can be obtained from the Born–Mayer parameters A and b of the magnesium dimer and those of rare-gas dimers given in Refs [36] and [59], respectively.

2.2.2. Combining rules for C_6 , C_8 , and C_{10}

These combining rules are obtained using the different terms rising from the multipole expansion of the perturbation operator as it was demonstrated in the Casimir–Polder theory of dispersion coefficients [60,61]:

$$C_6 = C^{ij}(1, 1) \quad (6)$$

$$C_8 = C^{ij}(1, 2) + C^{ij}(2, 1) \quad (7)$$

$$C_{10} = C^{ij}(1, 3) + C^{ij}(2, 2) + C^{ij}(3, 1) \quad (8)$$

where $C^{ij}(1, 1)$, $C^{ij}(1, 2)$, $C^{ij}(2, 2)$, and $C^{ij}(1, 3)$ are, respectively, the dipole–dipole, the dipole–quadrupole, the quadrupole–quadrupole, and the dipole–octupole interactions. Each of the terms $C^{ij}(l_1, l_2)$ are given by the exact formula [60,62]:

$$C^{ij}(l_1, l_2) = \frac{(2l_1 + 2l_2)!}{4(2l_1)!(2l_2)!} \left(\frac{2}{\pi} \right) \int_0^\infty \alpha_1^i(i\omega) \alpha_2^j(i\omega) d\omega \quad (9)$$

$\alpha_1^i(i\omega)$ and $\alpha_2^j(i\omega)$ are the dynamic multipole polarisabilities of atom i and j at the frequency ω . Note that this expression is an integral over imaginary frequency of the product of the dynamic polarisabilities of the interacting atoms. This expression reduces the original two centred problem to a one centred problem of evaluating the frequency dependent polarisabilities. In order to approximate the dynamic dipole polarisability $\alpha_1(i\omega)$, a one term

approximant of Tang [$\alpha_l(i\omega)$] should be introduced [63]:

$$[\alpha_l(i\omega)] = \frac{\alpha_l}{1 + (\omega/\Omega_l)^2}, \quad l = 1, 2, 3 \quad (10)$$

where α_l is the static polarisability $\alpha_l(0)$ and Ω_l is an effective energy. Using this approximation and the mathematical identity [64]:

$$\frac{2}{\pi} \int_0^\infty \frac{ab}{(a^2 + \omega^2)(b^2 + \omega^2)} d\omega = \frac{1}{a + b} \quad (11)$$

We can easily show that

$$C^{ij}(1, 1) = \frac{3}{\pi} \int_0^\infty [\alpha_1^i(i\omega)] [\alpha_1^j(i\omega)] = \frac{3}{2} \left[\frac{\alpha_1^i \alpha_1^j \Omega_1^i \Omega_1^j}{\Omega_1^i + \Omega_1^j} \right] \quad (12)$$

Similarly,

$$C^{ij}(1, 2) = \frac{15}{4} \left[\frac{\alpha_1^i \alpha_2^j \Omega_1^i \Omega_2^j}{\Omega_1^i + \Omega_2^j} \right] \quad (13)$$

$$C^{ij}(1, 3) = 7 \left[\frac{\alpha_1^i \alpha_3^j \Omega_1^i \Omega_3^j}{\Omega_1^i + \Omega_3^j} \right] \quad (14)$$

$$C^{ij}(2, 2) = \frac{35}{2} \left[\frac{\alpha_2^i \alpha_2^j \Omega_2^i \Omega_2^j}{\Omega_2^i + \Omega_2^j} \right] \quad (15)$$

Since the static polarisability $\alpha_l(0)$ for most of systems are available, the determination of these coefficients requires essentially the knowledge of the effective energy Ω_l . To determine it, we apply the formula for homonuclear dipole–dipole interaction; Equation (12) reduces to

$$C_6^i = C^{ii}(1, 1) = \frac{3}{4} (\alpha_1^i)^2 \Omega_1^i \quad (16)$$

where a single index means that, the coefficient stands for the homonuclear dimer. This leads to

$$\Omega_1^i = \frac{4}{3(\alpha_1^i)^2} C_6^i \quad (17)$$

According to Tang's theorem [63], the approximant [$\alpha_1^i(i\omega)$] with this Ω_1^i must intersect $\alpha_1^i(i\omega)$ once and only once beside $\omega = 0$. Therefore, the combining rule obtained by substituting Equation (17) into Equation (12) gives very accurate coefficients:

$$C_6^{ij} = C^{ij}(1, 1) = \frac{2\alpha_1^i \alpha_1^j C_6^i C_6^j}{(\alpha_1^i)^2 C_6^j + (\alpha_1^j)^2 C_6^i} \quad (18)$$

A few representative interactions were used by Tang to show that is indeed the case [63]. This was confirmed with further testing by Kramer and Herschbach [65], by Zeiss and Meath [66], and by Kutzelnigg and Maeder [67]. Thakkar [68] carried out the most comprehensive testing with 210 interactions and found a rms error of only 0.52%.

In the same way, precise combining rules for C_8 and C_{10} can be arised [30]. For homonuclear interactions, $C^i(l_1, l_2) = C^i(l_2, l_1)$ and $C_8^i = 2C^{ij}(1, 2)$, the effective energy Ω_2^i can be derived from Equation (13):

$$\Omega_2^i = \frac{2C_8^i \Omega_1^i}{15\alpha_1^i \alpha_2^i \Omega_1^i - 2C_8^i} \quad (19)$$

Solving for Ω_3^i from Equation (14), we have

$$\Omega_3^i = \frac{C^i(1, 3)\Omega_1^i}{7\alpha_1^i \alpha_3^i \Omega_1^i - C^i(1, 3)} \quad (20)$$

where $C^i(1, 3)$ can be expressed as

$$C^i(1, 3) = \frac{1}{2} [C_{10}^i - C^i(2, 2)] = \frac{1}{2} \left[C_{10}^i - \frac{35}{4} (\alpha_2^i)^2 \Omega_2^i \right] \quad (21)$$

Consequently, the three effective energies Ω_1^i , Ω_2^i , and Ω_3^i can be evaluated using the homonuclear dispersion coefficients C_6^i , C_8^i , and C_{10}^i and the polarisabilities α_1^i , α_2^i , and α_3^i . The heteronuclear coefficients C_6^{ij} , C_8^{ij} , and C_{10}^{ij} can then be determined from Equations (6), (7), and (8).

In this work, the above expressions will be used to calculate the dispersion coefficient of the heteronuclear systems Mg–RG. For the homogeneous rare-gas dimers, C_6^i , C_8^i , and C_{10}^i are taken from Ref. [59] and α_1^i , α_2^i , and α_3^i are taken directly from Ref. [30] and they are listed in Table 1. For magnesium dimer, all polarisabilities and dispersion coefficients are taken directly from Ref. [37] and they are also listed in Table 1. The dispersion coefficients of the interactions between a magnesium atom and a rare-gas atom calculated from these combining rules are also shown in Table 2.

Table 2. Potential parameters for the magnesium rare-gas systems derived from the combining rules, all values are in atomic units.

System	C_6	C_8	C_{10}	A	b
Mg–Ar	157.864	7719.39	388,658.33	74.1549552	1.3821
Mg–He	20.936	879.91	38,135.76	17.5598194	1.4804
Mg–Kr	232.053	11,904.29	621,118.60	78.2110903	1.3415
Mg–Ne	41.143	1811.19	81,869.52	38.2889762	1.4689
Mg–Xe	363.250	19,759.15	962,936.26	83.6325145	1.2907

2.3. Spectroscopic constant

The TT model potential is presented by five parameters: A , b , C_6 , C_8 , and C_{10} , which are sufficient to reproduce the potential energy following the expression of Equation (2). Therefore, the minimum of the potential, the equilibrium distance R_e , and the well depth D_e can be determined easily.

The energy of vibrotational levels in a diatomic molecule is given by the following expression:

$$E(v, J) = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2} \right)^i \left(J + \frac{1}{2} \right)^j, \quad (21)$$

where Y_{ij} are known as Dunham coefficients. Spectroscopic parameters ω_e , B_e , and $\omega_e \chi_e$ are related to the Dunham coefficients [69] as

$$Y_{10} \approx \omega_e \quad (22)$$

$$Y_{20} \approx \omega_e \chi_e \quad (23)$$

$$Y_{01} \approx B_e \quad (24)$$

where ω_e is the classical frequency, $\omega_e \chi_e$ is the anharmonicity, and B_e is the vibrotational coupling constant. The exact expressions for Y_{10} , Y_{20} , and Y_{11} are given by Dunham in Ref. [70].

In order to evaluate the unknown spectroscopic constant, it is convenient to write the potential in its reduced form. Let

$$x = \frac{R}{R_e} \text{ and } U(x) = V(R_e x) / D_e \quad (25)$$

Table 1. Theoretical parameters for the rare gas the magnesium dimers used in the present work. All values are in atomic units.

System	α_1	α_2	α_3	C_6	C_8	C_{10}	A	b
He–He	1.383	2.443	10.603	1.461	14.11	183.6	41.96	2.523
Ne–Ne	2.66	6.42	30.4	6.383	90.34	1536	199.5	2.458
Ar–Ar	11.1	52.4	490	64.30	1623	49,060	748.3	2.031
Kr–Kr	16.7	92.7	793	129.6	4187	155,500	832.4	1.865
Xe–Xe	27.3	170	2016	285.9	12,810	619,800	951.8	1.681
Mg–Mg	71.33	812	13,510	627	41,500	2,757,000	7.3486	1.047

Therefore,

$$V(R) = A^* e^{-b^* x} - \sum_{n=3}^{n_{\max}} f_{2n}^*(x) \frac{C_{2n}^*}{x^{2n}} \quad (26)$$

where

$$f_{2n}^*(x) = 1 - e^{-b^* x} \sum_{k=0}^{2n} \frac{(b^* x)^k}{k!}, \quad (27)$$

$$A^* = \frac{A}{D_e}, \quad b^* = bR_e, \quad C_{2n}^* = \frac{C_{2n}}{D_e R_e^{2n}} \quad (28)$$

By expanding the reduced potential function near the equilibrium into a power series with respect to the relative distance x , the spectroscopic parameters can be expressed in terms of the expansion coefficients:

$$U(x) = -1 + a_0(x-1)^2 + (1 + a_1(x-1) + a_2(x-1)^2 + \dots) \quad (29)$$

The coefficients a_n of the power series expansion is given by

$$a_0 = \frac{1}{2} U^{(2)}(1), \quad a_1 = \frac{1}{3} \frac{U^{(3)}(1)}{U^{(2)}(1)}, \quad a_2 = \frac{1}{12} \frac{U^{(4)}(1)}{U^{(2)}(1)}, \dots \quad (30)$$

It can be proved that the following three dimensionless quantities can be expressed in terms of the expansion coefficients a_n [70,71]:

$$\frac{B_e D_e}{\omega_e^2} = \frac{1}{4a_0} \quad (31)$$

$$\frac{\alpha_e \omega_e}{B_e^2} = -6(1 + a_1) \quad (32)$$

$$\frac{\omega_e \chi_e}{B_e} = -\frac{3}{2} \left(a_2 - \frac{5}{2} a_1^2 \right) \quad (33)$$

with $B_e = \frac{h}{8\pi^2 \mu c R_e^2}$ become in terms of atomic units

$$B_e = \frac{1}{2\mu R_e^2} \quad (34)$$

The equilibrium distance R_e and the reduced mass μ is in atomic units (1 amu = 1822.8 m_e , where m_e is the mass of the electron which is equal to one in atomic unit).

To evaluate $U^{(2)}(1)$, $U^{(3)}(1)$, and $U^{(4)}(1)$, it is convenient to define

$$U^n(x) = \frac{d^n U(x)}{dx^n} \quad (35)$$

At the potential minimum $x = 1$, the reduced potential provides us with two conditions

$$U(1) = -1 \quad (36)$$

$$U^{(1)}(1) = 0 \quad (37)$$

Therefore,

$$U^{(2)}(1) = b^{*2} A^* e^{-b^*} + \sum_{n=3}^{n_{\max}} e^{-b^*} (b^{*2} + 2nb^*) \frac{(b^*)^{2n}}{(2n)!} C_{2n}^* - \sum_{n=3}^{n_{\max}} \left[1 - e^{-b^*} \sum_{k=0}^{2n} \frac{(b^*)^k}{k!} \right] 2n(2n+1) C_{2n}^* \quad (38)$$

$$U^{(3)}(1) = -b^{*3} A^* e^{-b^*} - \sum_{n=3}^{n_{\max}} e^{-b^*} (b^{*3} + 2nb^{*2} + 4n(n+1)b^*) \frac{(b^*)^{2n}}{(2n)!} C_{2n}^* + \sum_{n=3}^{n_{\max}} \left[1 - e^{-b^*} \sum_{k=0}^{2n} \frac{(b^*)^k}{k!} \right] 2n(2n+1)(2n+2) C_{2n}^* \quad (39)$$

$$U^{(4)}(1) = -b^{*4} A^* e^{-b^*} + \sum_{n=3}^{n_{\max}} e^{-b^*} (b^{*4} + 2nb^{*3} + 2n(2n+3)b^{*2} + 4n(n+1)(2n+3)b^*) \frac{(b^*)^{2n}}{(2n)!} C_{2n}^* - \sum_{n=3}^{n_{\max}} \left[1 - e^{-b^*} \sum_{k=0}^{2n} \frac{(b^*)^k}{k!} \right] \times 2n(2n+1)(2n+2)(2n+3) C_{2n}^* \quad (40)$$

Therefore, with these derivatives, we can find the expansion coefficients a_n . With D_e , R_e , a_0 , a_1 , and a_2 , the spectroscopic parameters ω_e , $\omega_e \chi_e$, and B_e can be easily determined from Equations (31)–(34).

3. Results

3.1. Spectroscopic constants

In Figure 1, we report the ground-state potential energy curves for all five systems of the dimers Mg–Rg. These potential energy curves are calculated from the TT model using Equation (2) with the parameters listed in Table 2. The full potential energy curves obtained by summing the dispersion series up to $n_{\max} = 5$ and using the corresponding A and b parameters calculated above. It is known that most ground-state neutral atom/rare-gas complexes are very weakly bound [72]. One point of

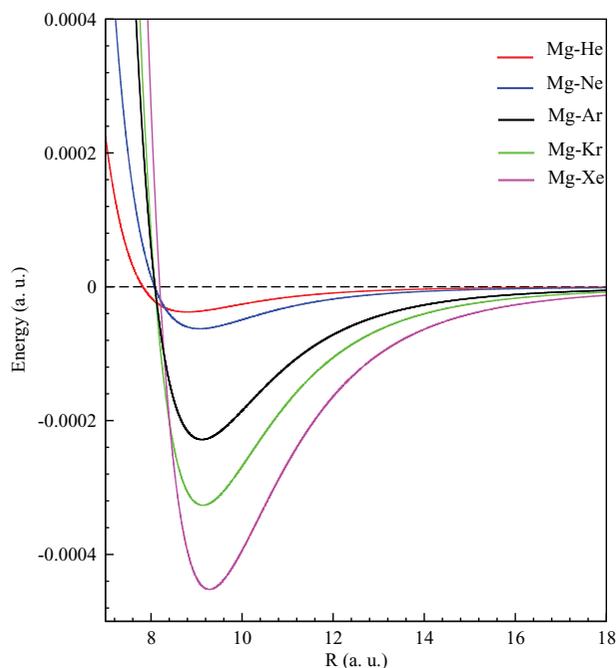


Figure 1. The ground-state van der Waals potentials of Mg–RG (RG = He, Ne, Ar, Kr, and Xe). These potentials are generated by the TT potential model with A , b , C_6 , C_8 , and C_{10} calculated from the corresponding parameters of the homonuclear magnesium and rare-gas dimers with combining rules.

interest concerning these results is that the depth of the potential well D_e for the Mg–Rg molecules increases regularly with increasing mass of the rare gas atom, this is a consequence of the increasing polarisability, going from He to Xe, while the corresponding equilibrium position R_e increases only slightly with the size of the rare-gas atom.

The derived spectroscopic constants: the well depth D_e , the equilibrium distance R_e , the vibrational frequency

ω_e , the rotation constant B_e , and the anharmonicity $\omega_e\chi_e$ of Mg–RG dimers with $n_{\max} = 5$ are given in Table 3. In this table, we compare the present D_e , ω_e , β_e , and $\omega_e\chi_e$ reported all in the units of cm^{-1} and R_e reported in the units of a.u. with the available experimental and theoretical results.

Focusing in turn on each species for which there are previous results, we see that for Mg–He there are only theoretical values available, and these are presented in Table 3 together with those from the present work. We note that there are large differences between various determinations. In fact, the surface integral calculations of Kleinekathöfer [20] yielded values in better agreement with our present prediction for R_e and D_e . In contrast, the Møller–Plesset four order perturbation (MPPT) of Funk and co-workers [24], the coupled cluster (CC3) of Chilies and co-workers [25] and the pseudopotential SCF/CI of Czuchaj and co-workers [21] yielded values of $D_e = 4.6$, 2, and 2.3 cm^{-1} , respectively, much smaller well depths than the present prediction. This difference can be explained by the possibility that the combining rules we used for the repulsive potential are not accurate or adequate enough for the Mg–He system because of the small number of electrons in the helium atom.

For the Mg–Ne ground state, there are two previous studies from the experimental and theoretical investigation. Experimentally, Wallace et al. [14] employed the laser induced fluorescence (LIF) in a supersonic jet in order to characterise the ground state and excited state of the Mg–Ne molecule. The well depth D_e of this potential was calculated from the observed ω_e and $\omega_e\chi_e$ with an assumed Morse potential. It is important to keep in mind that ω_e and $\omega_e\chi_e$ are the quantities more directly measured in the experiment. The experimental values of R_e , D_e , ω_e , and $\omega_e\chi_e$ of the ground state are listed in Table 3.

Table 3. Comparison of the spectroscopic constant of the van der Waals ground-state potentials of the magnesium rare-gas systems with other available results.

System	R_e (a.u.)	D_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	References
Mg–He	8.79	8	16.88	8.9042	0.226727	This work
	9.75	4.6			[24] MPPT	
	10.63	2.1			[25] CC3	
	10.7	2.3			[21] SCF/CI	
	8.89	7.70			[20] surface integral	
Mg–Ne	9.07	14	11.90	2.52	0.066382	This work
	8.31 ± 0.28	23 ± 5	14.0 ± 0.5	3.0 ± 0.5	[14] Exp (LIF)	
	10.5	7.70			[21] SCF/CI	
Mg–Ar	9.12	50	18.64	1.73	0.047866	This work
	9.06	40.8	15.2		[23] pseudopotentials	
	9.00	55.7			[24] MPPT	
	44			[11] expt		
	8.5 ± 0.10	65 ± 3	24.1 ± 1.0	1.75 ± 0.3	0.0558 ± 0.0026	[18] expt (LIF)
	7.99	116	31.84	1.55		[22] pseudopotentials
Mg–Kr	9.14	72	29.59	1.33	0.038411	This work
Mg–Xe	9.28	99	13.65	0.47	0.013846	This work
	8.69	100	25 ± 2	1.04 ± 0.2	0.0398 ± 0.002	[73] expt (LIF)

All these parameters are reported with an error bar. Theoretically, Czuchaj et al. [21] reported pseudopotential SCF/CI calculations to obtain ground-state potentials of the M–He and M–Ne systems (M = Mg, Cd, and Hg) in which the rare gas atoms were treated as a polarisable cloud. From these two studies, it can be seen that our values for $\omega_e = 11.90 \text{ cm}^{-1}$ and $\omega_e x_e = 2.52 \text{ cm}^{-1}$ are in reasonable agreement with the experimental values $\omega_e = 14.0 \pm 0.5 \text{ cm}^{-1}$ and $\omega_e x_e = 3.0 \pm 0.5 \text{ cm}^{-1}$ of Wallace and co-workers [14]. For the well depth D_e , our value of 14 cm^{-1} is within the experimental $23 \pm 5 \text{ cm}^{-1}$ and theoretical 7.70 cm^{-1} values. Thus, our estimations are overall consistently with the experimental limits.

Among all Mg–Rg systems, one of the experimentally best characterised systems is Mg–Ar, where Breckenridge and co-workers in a series of papers [74–78,16] have studied the bonded complexes corresponding to a Mg atom in the ground and electronically excited states. For Mg–Ar ground state overall our results are in agreement with all previous investigations except the pseudopotential calculation reported by Gaied and co-workers [79] who found a dissociation energy $D_e = 116 \text{ cm}^{-1}$ at $R_e = 7.19 \text{ a.u.}$ From the experimental point of view, the present D_e from the TT model falls in the experimental range from 40 to 65 cm^{-1} . There are two available data. The first, is from the laser-induced excitation spectra in a supersonic jet of Kowalski and co-workers [11], from where a reported value of the well depth $D_e = 44 \text{ cm}^{-1}$ corroborating a former experimental value of Jovet and co-workers [80]. The second is from the LIF of Bennet and co-workers [18] who found $D_e = 65 \pm 3 \text{ cm}^{-1}$ at $R_e = 8.5 \pm 0.10 \text{ a.u.}$ The spectroscopic constants of $\omega_e = 24.1 \pm 1.0 \text{ cm}^{-1}$, $\omega_e x_e = 1.75 \pm 0.30 \text{ cm}^{-1}$, and $B_e = 0.0558 \pm 0.0026 \text{ cm}^{-1}$ reported by Bennet and co-workers are in, a reasonable, agreement with the values reported here. Theoretically, the present D_e of 50 cm^{-1} is within the theoretical range that varies from 40.8 cm^{-1} carried out by Hliwa and co-workers [23] and 55.7 cm^{-1} of Funk and co-workers [24]. Hliwa and co-workers [23] used non-empirical pseudopotentials for Mg^{2+} and Ar^{8+} cores and an SCF+CI treatment for the Mg valence electrons in the field of frozen Ar. However, Funk and co-workers used the Møller–Plesset fourth order perturbation, including single (S), double (D), triple (T), and quadruple (Q) excitation of the valence electron out of the restricted Hartree–Fock reference determinants. The equilibrium distance R_e from these two theoretical studies is even closer to each other ranging from 9 to 9.06 a.u. They are in good agreement with the present R_e of 9.12 a.u.

For the Mg–Xe, an LIF measurements of the $\text{Mg}(3s3p^1P_1).Xe(^1\Pi_1) \leftarrow \text{Mg}(3s3s^1S_0).Xe(X^1\Sigma^+)$ transition of the jet-cooled MgXe complex reported by McCaffery and co-workers [73] yielded a value of D_e

$= 100 \text{ cm}^{-1}$. This well depth is in excellent agreement with the present calculation ($D_e = 99$); however, their equilibrium distance $R_e = 8.69 \text{ a.u.}$ is slightly below our $R_e = 9.28 \text{ a.u.}$ Likewise the present calculated spectroscopic quantities ω_e , $\omega_e x_e$, and B_e are almost half of these reported experimental determination.

To our best knowledge, the neutral ground-state of $\text{Mg}(3s3s^1S_0) - \text{Kr}(X^1\Sigma^+)$ has not yet been characterised, but from Ref. [72] is expected to be very weakly bound, with $D_e < 100 \text{ cm}^{-1}$ and $R_e > 7.93 \text{ a.u.}$ Our present prediction is summarised in Table 3 and it represents the first spectroscopic parameters reported for this specie and they are consistent with the experimental observation.

3.2. Reduced potential plots and the k parameter

To emphasise the well region and to facilitate comparison of the relative differences among many potential function it is interesting to plot these functions in a reduced coordinates system, scaling lengths by the equilibrium bound length, R_e , and energy by the dissociation energy, D_e , for each system. The use of reduced parameter plots has been employed [81,82] and examined by many workers [83,84] in order to examining the existence of a universal diatomic function [85,86]. In this context we replotted Figure 1 in these coordinates, in which the function $U(x) = \frac{V(xR_e)}{D_e}$ is plotted as function of $x = \frac{R}{R_e}$. The shapes of this plot are reported in Figure 2. As it can be seen from this figure, the reduced potentials of these five systems have the same shape and the curves are clumped closely together.

Another method to understand the interaction differences consists in using the κ parameter [82], which is the Sutherland parameter introduced in 1938, [87] and has been symbolised by Δ in a recent work of Xie and Hsu [86]. It was called the ‘reduced curvature of the potential at R_e ’ [82], and is defined as

$$\kappa = \frac{R_e^2}{D_e} \left(\frac{d^2 V(R)}{dR^2} \right)_{R_e} = \frac{R_e^2}{D_e} k_e \quad (41)$$

In terms of spectroscopic constants

$$\kappa = \frac{\omega_e^2}{2B_e D_e} \quad (42)$$

where ω_e is the equilibrium harmonic vibration constant, D_e is the well depth, and B_e is the equilibrium rotation constant. All these values are defined in the caption of Table 1.

Before the discussion of these results, it is interesting to recall that Winn [82] presented κ values for a range

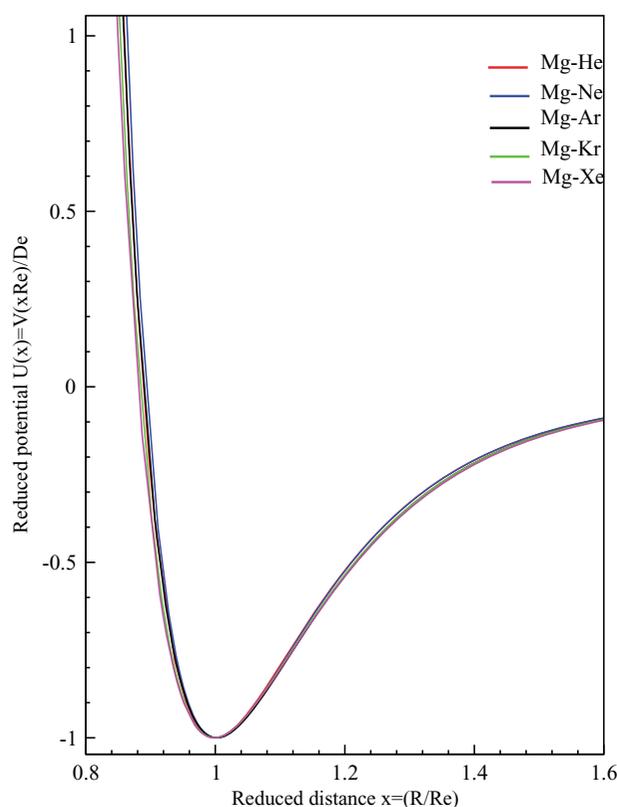


Figure 2. The reduced potentials of Mg-He, Mg-Ne, Mg-Ar, Mg-Kr, and Mg-Xe.

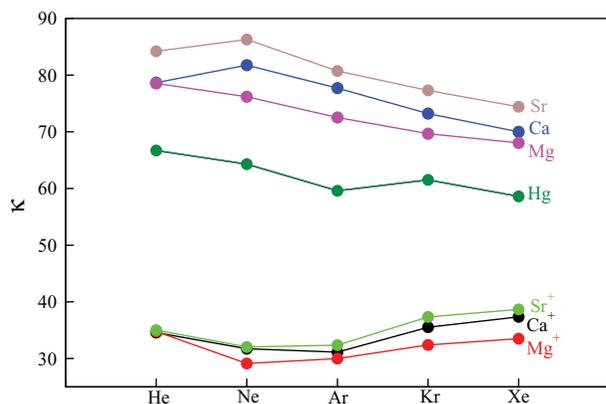


Figure 3. Plot of κ for the M-RG (M = Mg, Sr, and Ca, and RG = He, Ne, Ar, Kr, and Xe).

of species, he found that, for chemically bound species, κ is confined to a tight range of values, whereas for weakly bound molecules it is generally large to enormous in comparison.

The variations of the k value of Mg-RG versus the atomic mass of rare-gas are shown in Figure 3. It can be seen from this figure that the values of κ are similar to each other and they are decreasing with the atomic number of the RG atom.

In Figure 3, we presented the constant k of Mg-RG together with other analogous systems, such as Sr-Rg,

Ca-Rg, and Hg-Rg, as they are isoelectronic with the closed shell species. For more information and best comprehension, we reported equally the reduced curvature k of one-valence electron alkaline earth rare-gas systems, such as Sr^+Rg , Ca^+Rg , and Mg^+Rg . Relevant spectroscopic values taken from the data presented in Refs [31,49,50,88,89] have been used to calculate the k constants for the M-RG systems. As the rotational constant B_e is not available for Sr-RG, Ca-RG, and Hg-RG, we used the data reported in Refs [31,49,50] to derive this constant.

$$B_e = \frac{1}{2\mu R_e^2} \quad (43)$$

It can be seen from Figure 3 that κ is not constant, but the values are close to each other for the same series of M-RG and $\text{M}^+\text{-RG}$. The M-RG complexes have very similar trends, with a decreasing κ value from He to Xe, with the exception of the small increase of the k value from M-He to M-Ne for M = Sr and Ca. The different behaviors observed in k values may be the consequence of the distribution of the charge density of atoms. In the case of $\text{M}^+\text{-RG}$, we observe again that the values of κ are similar to each other, but this time they are increasing with the atomic number of the RG atom with the exception of the small decrease from $\text{M}^+\text{-He}$ to $\text{M}^+\text{-Ne}$, in contrast to the values for the M-RG complexes. The different behaviors observed in k values may be the consequence of the distribution of the charge density of atoms as was shown in Ref. [89].

4. Conclusion

In this work, we have evaluated and detailed the full potential energy surface of the Mg-RG ground-state complexes. We have used The Tang Toennies Model. The short range and long range parameters of the Tang-Toennies potentials for the magnesium rare-gas complexes are calculated from the combining rules with input data from the corresponding parameters of the homonuclear magnesium and rare-gas dimer potentials.

Although no unequivocal conclusion can be drawn for Mg-RG potentials because of the differences in the results of various calculations, as seen in Table 3, the present results are within the range of other theoretical and experimental determinations. Considering the simplicity of the TT potential, this is a remarkably good performance. The present method should be useful, at least, as a starting point for the interplay between theory and experiment. Mathematically the present potential is an entire function where derivatives exist everywhere and to all orders. It can be easily used in theories requiring an analytic extension

into the complex plane, such as theories of predissociation of van der Waals complexes [90].

To emphasise the well region and to facilitate comparison of the relative differences between the five van der Waals systems we plotted the reduced potentials. We note that the predicted reduced potentials of these five systems have the same shape and they are essentially identical within a few percent except the slight remarkable difference of Mg–He at the middle part of the potential well region.

In addition, we determined and plotted the reduced curvature of the potential at R_e for M–Rg (M = Mg, Sr, and Ca, and Rg = He–Xe) and their corresponding mono-cation systems M^+ –Rg. We observe that both the M–Rg and M^+ –Rg complexes have very similar trends, with an increasing κ value from He to Xe for M^+ –Rg and a decreasing κ value from He to Xe for M–Rg with the exception of the small increase of the k value from M–He to M–Ne.

Disclosure statement

No potential conflict of interest was reported by the authors.

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