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Theoretical Study of the Potential Energy Curves for the Ca–Ar and Sr–Ar Systems

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The $X^1\Sigma$ ground state and the low-lying $^{1,3}\Sigma$, $^{1,3}\Pi$ excited states of the Ca–Ar and Sr–Ar systems have been studied using pseudopotentials at MCSCF(CASSCF)-SDCI level. The results indicate that the $^{1,3}\Sigma$ excited states are essentially repulsive, but the $X^1\Sigma$ ground state and the $^{1,3}\Pi$ excited states have shallow potential minima at large equilibrium distance (R_e) values. Spectroscopic constants of the $X^1\Sigma$ ground state and the $^{1,3}\Pi$ excited states have been calculated and compared to those obtained by experiment.

A variety of metal-atom/rare-gas (M•RG) van der Waals complexes in both ground and electronically excited states have been characterized experimentally.[1—10] One class of such complexes includes groups 1, 2 and 12 metal atoms in which a ground state ns electron has been excited to a valence np orbital (experimentally, usually by laser excitation). These studies have contributed to a better understanding of the electronic nature of weak bonding interactions in the simplest of van der Waals clusters, diatomic molecules. Moreover, the studies of atomic and molecular collision processes are also critically important for one to completely understand the collision physics as well as chemical reaction dynamics. Many studies have been experimentally carried out on the orbital alignment of alkaline earth atoms in collisions with rare gases.[11—15]. In the theoretical aspects, Stwalley[16] and Hyman[17] first calculated the potential curves for alkaline earth-rare gas systems (they mainly estimated the van der Waals constants). Böttcher et al.[18] and Malvern[19] used a model potential method to calculate the excited states potential curves between Ca, Mg, and He, Ne. Schwerdtfeger et al.[20] reported potential curve crossing in M–Ar complexes (M = Mg, Ca, Sr, Ba); they treated the systems within the work frame of the single determinant Hartree–Fock self-consistent-field (HF-SCF) method. They also took interelectronic correlations into account using the spin-density functional approximation method, but they didn't report spectroscopic constants. Hliwa et al.[21] have theoretically studied the potential curves of the Mg–Ar system in which the rare gas atom was treated as a polarizable cloud. Nevertheless, for the heavier systems, there are no theoretical calculations at higher MCSCF (CASSCF)-SDCI level.

In this work, we use an effective core potential and treat the rare gas atom Ar as a polarizable cloud to describe the interacting potential curves of Ca–Ar and Sr–Ar systems at MCSCF(CASSCF)-SDCI level. The calculated results are compared with the experimental ones.

Methods

For the systems containing a heavier element, the all-electron SCF calculations are rather difficult. One should have a more economic method to solve this problem. The useful method is to treat core electrons as a simple effective core potential and to treat explicitly only the valence electrons. In the present calculations we use the relativistic effective core potential (ECP) which was developed by Hay and Wadt (HW).[22] For the HW ECP method, only the outer 4s shell of Ca, 5s shell of Sr and 3s3p shells of Ar atom were explicitly considered. The relativistic velocity-mass and Darwin effects in the valence shells were incorporated into the ECP. The basis sets used in the calculations are shown in Table 1. Initially, multiconfiguration self-consistent field (MCSCF) calculations are carried out using complete active space (CASSCF), and then configuration interaction (CI) calculations are carried out after MCSCF-CASSCF. The CI calculations are performed at the SDCI level, using MCSCF-CASSCF nature orbitals. For the configuration interaction (CI) calculations, the active space consists of the Ar $3p_{x,y,z}$, Ca 4s and Sr 5s orbitals. All remaining orbitals are taken to form the virtual space. In this work, twenty points have been calculated for the potential energy curves. All calculations in this work are carried out with the GAMESS programs package.[23]

Results and Discussion

The interaction in a van der Waals molecule is very weak and the description of the interactions in the excited states requires relatively more diffuse basis sets, which are less important for the description of the ground state. The use of a good basis set is the first step for obtaining reliable results. In this work, in order to confirm whether the HW ECP is reliable or not, we used the basis sets shown in Table 1 first to calculate the excited energies of the isolated atoms (see Table 2). It can be seen from Table 2 that the excited energy of $Ca(4s^2) \rightarrow Ca(4s4p)^1P$ is 0.109 au for HW-ECP method, which is close to the experimental value of 0.108 au. The values reported by Schwerdtfeger et al.[20] are 0.110 and 0.118 au

Table 1. Exponents and Contraction Coefficients of the Basis Sets Used for Ca, Sr, and Ar

	Shell	Exponent	Coefficient
Ca	s	0.2342	−0.697597
		0.14470	0.689719
		0.03500	0.883358
		0.41190	−0.073543
	p	0.070500	0.57974
		0.0263	0.512346
		0.059	1.0
		0.029	1.0
		0.015	1.0
	d	0.10	1.0
		0.05	1.0
Sr	s	0.186500	−0.712319
		0.109900	0.732711
		0.029200	0.847010
	p	0.273500	−0.098949
		0.057000	0.595981
		0.022200	0.503935
		0.048	1.0
		0.02	1.0
		0.01	1.0
	d	0.11	1.0
		0.05	1.0
Ar	s	2.613000	−0.297740
		0.573600	0.739985
		0.201400	0.455346
	p	7.860000	−0.031974
		0.738700	0.582615
		0.208100	0.532129
	d	0.85	1.0

using all-electron ab initio and semiempirical pseudopotential methods. The excited energy of Ca(4s^2) → Ca(4s4p)^{3}P is 0.061 au in our calculation, whereas the experimental and all-electron calculated values as well as semiempirical pseudopotential data are 0.069, 0.059, and 0.067 au, respectively. From the above comparisons we see that our calculated data are in good agreement with experimental ones. The atomic singlet (^{1}S → ^{1}P) excitation energy of Sr is 0.097 au for HW-ECP method, which agrees with experimental value of 0.099 au very well. The triplet (^{1}S → ^{3}P) excitation energy of Sr is 0.056 au, the experimental value is 0.069 au (see Table 2). Based on these comparisons, we believe that the HW ECP is suitable for these systems.

We have calculated the Σ, Π potential curves correlating with the Ar(^{1}S) ground state and Ca(4s^2, ^{1}S), Sr(5s^2, ^{1}S) ground states as well as the corresponding excited states (4s4p, ^{1,3}P), (5s5p, ^{1,3}P). The potential energy curves are shown in Figs. 1 and 2, respectively. Tables 3 and 4 show the calculated spectroscopic parameters.

1 Ca-Ar System. For the ground state, there is a very shallow potential minima at large internuclear distance. Our theoretical value D_e is 42.7 cm^{-1} (for $R_e = 6.2$ Å), which is smaller than the experimental value ($D_e = 62 \pm 10$ cm^{-1}).[10] The dispersion and quadrupolar energies (i.e. $(C_6 + \beta_q)/R^6$) between the core of the Ca atom and the Ar atom were not included in the present calculation. The C_6 van der waals constant has been found (by the mean of London's formula) to be 205 au[10] and quadrupolar polarizability β_q has been taken as 54.40 au, a value recommended by Patil.[24] After adding the R^{-6} contributions, we obtain $D_e = 72.6$ cm^{-1} (for $R_e = 5.9$ Å). Clearly, the calculated values of D_e (72.6 cm^{-1}) and ω_e (12.7 cm^{-1}) by HW ECP method are close to the

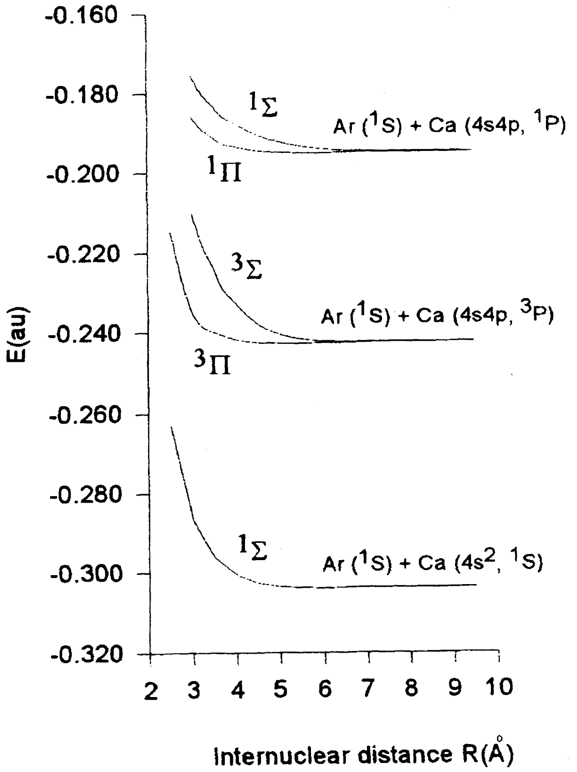

Fig. 1. Potential curves of Ca–Ar correlating with the Ar(^{1}S) ground state and Ca ground state ^{1}S(4s^2) or excited states ^{1,3}P(4s4p).

Table 2. Atomic Singlet (ns^2 → nsnp ^{1}P) and Triplet (ns^2 → nsnp ^{3}P) Excitation Energies (in au)

		All electron[20]	Semiempirical pseudopotentials[20]	HW-ECP (this work)	Experiment[20,25]
Ca	^{1}P	0.110	0.118	0.109	0.108
	^{3}P	0.059	0.067	0.061	0.069
Sr	^{1}P	—	0.109	0.097	0.099
	^{3}P	—	0.064	0.056	0.067

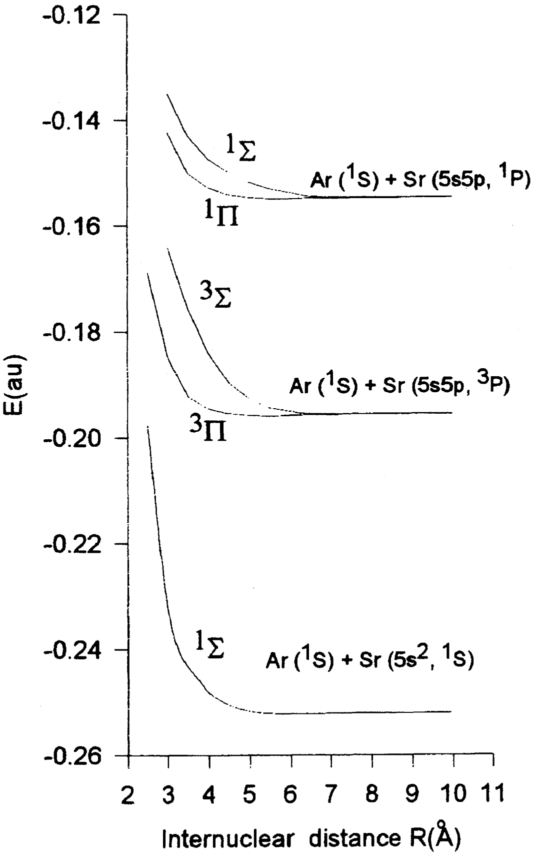

Fig. 2. Potential curves of Sr–Ar correlating with the Ar(^{1}S) ground state and Sr ground state ^{1}S(5s^2) or excited states ^{1,3}P(5s5p).

experimental data ($D_e = 62\pm10$ cm^{-1}) and $\omega_0 = 18$ cm^{-1}) when consider the R^{-6} corrections.

For the $^1\Pi$ excited state correlates with Ca(4s4p, ^{1}P)+Ar(^{1}S) are improved by this correction to $D_e = 134.7$ cm^{-1} ($R_e = 5.5$ Å), while the experimental D_e value is 134±10 cm^{-1}. The ω_e of $^1\Pi$ is 16.4 cm^{-1}; Its experimental value (ω_0) is 22 cm^{-1}. The $^3\Pi$ also has a shallow van der Waals minimum at $R = 5.6$ Å, with the vibrational constant ω_e of 14.5 cm^{-1}. The depth of the potential well is calculated to be 69.8 cm^{-1}. The spectroscopic parameters without R^{-6} contributions are also shown in Table 3.

Table 3. Spectroscopic Parameters of Ca–Ar System: R_e in Å, D_e, and ω_e in cm^{-1}
R_e^* and D_e^* are the spectroscopic parameters without considering the R^{-6} contribution. The values in parentheses are available experimental data from Ref. 10.

Ca–Ar system	R_e^*	R_e	D_e^*	D_e	ω_e	$R_e(^1\Sigma)/R_e(^1\Pi)$
$^1\Sigma$(4s^2)	6.2	5.9	42.7	72.6 (62±10)	12.7 ($\omega_0 = 18$)	
$^1\Pi$(4s4p)	5.9	5.5	98.7	134.7 (134±10)	16.4 ($\omega_0 = 22$)	1.07 (1.06)
$^3\Pi$(4s4p)	5.8	5.6	47.5	69.8	14.5	

2 Sr-Ar System. The calculated spectroscopic parameters R_e, D_e, and ω_e as well as the spectroscopic parameters without R^{-6} contributions of Sr–Ar system are shown in Table 4. After considering the R^{-6} contribution, the D_e and ω_e for the $^1\Sigma$ ground state are 63.5 cm^{-1} ($R_e = 6.2$ Å) and 8.7 cm^{-1}, respectively, which are close to the experimental data of $D_e = 68\pm15$ cm^{-1} and $\omega_0 = 12$ cm^{-1}. But for the $^1\Pi$ excited state, $D_e = 98.1$ cm^{-1} ($R_e = 5.8$ Å) with $\omega_e = 13.0$ cm^{-1}, while the experimental D_e is 136±15 cm^{-1} and ω_0 is 17 cm^{-1}. The discrepancy of D_e in our calculation is the same order of magnitude as that of the Mg–Ar system[21] (calculated $D_e = 181.3$ cm^{-1} versus the experimental value of 246.0 cm^{-1}). The discrepancy between the calculated and the experimental data may be attributed to our limited Gaussian basis set on the alkaline earth atoms. One thing we want to note is the BSSE (basis set superposition error). Generally, we can estimate the function counterpoise correction δ^{CP},[25] which is a measure of BSSE, is given by

$$\delta^{CP} = E(A) - E(AG)$$

where E(A) and E(AG) are both the total energies of the A atom but E(AG) is different in that it is calculated by using a ghost nucleus G (a set of the same A basis set with a nuclear charge of zero) at R_{A-A}. The δ^{CP} for Ne–Ne system[26] is in the range of 0.15—0.6 μhartree. The δ^{CP} in this work is probably the same order of magnitude as that of Ref. 26 because of the use of the ECP. Therefore, the calculated interaction energy should be the real one reflecting the quality of the basis set.

3 Comparison between the Two Systems. It is easily seen from Tables 3 and 4 that the vibrational constant

Table 4. Spectroscopic Parameters of Sr–Ar System: R_e in Å, D_e, and ω_e in cm^{-1}
R_e^* and D_e^* are the spectroscopic parameters without considering the R^{-6} contribution. The values in parentheses are available experimental data from Ref. 10.

Sr–Ar system	R_e^*	R_e	D_e^*	D_e	ω_e	$R_e(^1\Sigma)/R_e(^1\Pi)$
$^1\Sigma$(5s^2)	6.5	6.2	31.5	63.5 (68±15)	8.7 ($\omega_0 = 12$)	
$^1\Pi$(5s5p)	6.0	5.8	63.7	98.1 (136±15)	13.0 ($\omega_0 = 17$)	1.07 (1.07)
$^3\Pi$(5s5p)	5.8	5.5	44.6	60.15	14.4	

ω_e decreases with increasing atomic number from Ca to Sr for the three $^1\Sigma$, $^1\Pi$, and $^3\Pi$ states. In general, the excited state has higher ω_e that he corresponding ground state in the both systems. This trend is agrees well with the experimental one.[10] We also see that the $R_e(^1\Sigma)/R_e(^1\Pi)$ estimated by experiment[10] is 1.06 and 1.07 for Ca–Ar and Sr–Ar systems, respectively. Our calculated value is 1.07 for the both systems. The equilibrium distance of $^1\Pi$ excited state is about 7% shorter than that of $^1\Sigma$ ground state, but it is close to the $^3\Pi$ excited state in the both systems. From calculated values (Figs. 1 and 2) we see the $^{1,3}\Sigma$ excited states arising from Ca(4s4p, ^{1,3}P), Sr(5s5p, ^{1,3}P)+Ar(^{1}S) asymptotes are apparently repulsive, which are in agreement with experimental results.[10] Our potential curves are similar to that of Mg–Ar system determined by Hliwa et al.[21] From Figs. 1 and 2 we seen the main feature of the potential energy curves. For the asymptotes Ca(4s4p, ^{1,3}P)+Ar(^{1}S), Sr(5s5p, ^{1,3}P)+Ar(^{1}S), $^{1,3}\Pi$ states are moderately attractive, whereas the $^{1,3}\Sigma$ states are essentially repulsive in the range of R explored. The reason is that the binding character of the M(nsnp)·RG excited states depends dramatically on the alignment of the np orbital with respect to the internuclear axis. Sigma alignment of the np orbital has stronger M(npσ)·RG(σ) electron–electron repulsion at large distance. Therefore, the M(nsnpσ)·RG states are essentially repulsive. In contrast, for Pi alignment of the M(np) orbital, because the RG atom is approaching along the npπ orbital nodal axis, electron–electron repulsion does not become appreciable until relatively smaller values of R. Therefore, the M(nsnpπ)·RG states are more bound than M(nsnpσ)·RG states.

Conclusion

The ground electronic states X$^1\Sigma$ of the van der Waals molecules Ca–Ar and Sr–Ar have shallow potential minima at large R, the $^{1,3}\Sigma$ excited states are essentially repulsive, but $^{1,3}\Pi$ excited states are moderately attractive because of the different alignment of the 4p and 5p orbitals of Ca and Sr atoms. For the both systems, the ω_e of the excited states is higher than that of the ground state. R^{-6} contribution is important to obtain suitable well parameters at a given internuclear distance for ground and excited states.

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