

Spectroscopic constants of the $X\ 2\Sigma^+$ and $A\ 2\Pi$ states of Sr^+Ar from first principles: Comparison with experiment

Sotiris S. Xantheas^{a)}

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, MS K1-96, Richland, Washington 99352

George S. Fanourgakis,^{b)} Stavros C. Farantos,^{b)} and Michalis Velegrakis

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 711 10 Heraklion, Greece

(Received 9 September 1997; accepted 25 September 1997)

We present the first nonempirically calculated spectroscopic constants for the recently observed [J. Chem. Phys. **105**, 2167 (1996)] ground ($X\ 2\Sigma^+$) and excited ($A\ 2\Pi$) states of Sr^+Ar . Our best results yield $D_e=694\text{ cm}^{-1}$, $R_e=3.662\text{ \AA}$, and $\omega_e=38.7\text{ cm}^{-1}$ for the ground and $D_e=1967\text{ cm}^{-1}$, $R_e=3.169\text{ \AA}$, and $\omega_e=99.1\text{ cm}^{-1}$ for the excited state. The calculated D_e 's are within the error bars of the experimentally determined one for the ground state favoring the low end and underestimate the corresponding one for the excited state by about 7%. The equilibrium separations (R_e 's) for the two states have not been experimentally determined, however our results accurately reproduce the estimated shift, ΔR_e , between the two states. The interaction is mainly electrostatic for the ground state for which the contribution of dynamic electron correlation was found to be more important than for the excited state. © 1998 American Institute of Physics. [S0021-9606(98)01301-4]

I. INTRODUCTION

Clusters of noble gas atoms serve as prototype systems in modeling solvation phenomena. Metal atoms embedded in these clusters function as "chromophores" used to probe their optical properties. The potential energy surfaces (PESs) of the metal atom-noble gas diatomic molecules are of particular importance since they represent the cornerstones in the parametrization of interaction potentials used to study the energetic and dynamical properties of the larger clusters.¹

Recently, Lüder and Velegrakis² have studied the photofragmentation spectrum of the Sr^+Ar complex in the 418–448 nm wavelength region. They observed vibrational progressions which they attributed to transitions from the $X\ 2\Sigma_{1/2}$ electronic ground state to the excited $A\ 2\Pi_{1/2}$ and $A\ 2\Pi_{3/2}$ states. From the experimental studies it was possible to deduce the harmonic frequencies (ω_e) and anharmonicities ($\omega_e\chi_e$) of the $X\ 2\Sigma_{1/2}$ and $A\ 2\Pi_i$ states but not the corresponding equilibrium separations (R_e). Furthermore, the experimental data allowed determination of the dissociation energies with respect to the corresponding asymptotes arising from the $\text{Sr}^+(5^2S_{1/2})$ and $\text{Sr}^+(5^2P_{1/2,3/2})$ limits with error bars of the order of 250 cm^{-1} which amount to 30% for the $X\ 2\Sigma_{1/2}$ and 10% for the $2\Pi_1$ states, respectively. It should be noted that, to the best of our knowledge, the only available theoretical results for this system prior to this study were obtained using pseudopotential models³ which, however, differ significantly with respect to the experimental data as noted by Lüder and Velegrakis.² In particular, the empirical calculations underestimate the dissociation energy

for the excited $A\ 2\Pi_i$ states by about 1000 cm^{-1} (or 40%) as well as the *shift* in the equilibrium separation between the ground $X\ 2\Sigma_{1/2}$ and $A\ 2\Pi_i$ excited states by 0.15 \AA (the empirical calculations predict $\Delta R_e=0.35\text{ \AA}$ vs $0.50\pm 0.05\text{ \AA}$ determined experimentally). To this end our study aims in complementing the experimental data by producing accurate potential energy curves for the ground and the excited states of Sr^+Ar towards our long term research effort to parametrize interaction potentials in order to study the energetic and dynamical properties of the $\text{Sr}^+(\text{Ar})_n$ clusters.⁴ In Sec. II we will describe the theoretical approach outlining the details of our calculations. The results for the ground and the observed excited state will be presented in Sec. III together with a discussion of the qualitative differences in the bonding for the two states. Final conclusions will be summarized in Sec. IV.

II. THEORETICAL BACKGROUND

Previous theoretical studies⁵ by Bauschlicher, Partridge, and Langhoff on metal noble-gas positive ions M^+Ar ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{Sc}, \text{Ti}, \text{Mn}, \text{Fe}, \text{Co}, \text{Cu}, \text{V}$) have accounted for an excellent overview of the bonding in these systems. These authors have elaborated on the importance of the rare gas atom basis set in accurately describing its polarizability, a requirement arising from the predominantly electrostatic interaction in these systems with the leading term being the one corresponding to the charge-induced dipole. They have also noted the possibility of charge donation from the ligand (rare gas atom) to the metal depending on the difference between the metal and ligand ionization potentials (IPs). However, for the system at hand, the large difference between the Ar and Sr IPs (15.77 and 5.692 eV , respectively⁶) suggests that this is most probably unlikely.

^{a)}Electronic mail: ss_xantheas@pnl.gov

^{b)}Also at Department of Chemistry, University of Crete, 711 10 Heraklion, Crete, Greece.

TABLE I. Calculated spectroscopic constants for the $X\ ^2\Sigma^+$ and $A\ ^2\Pi$ states of Sr⁺Ar and comparison with available experimental data. MCSCF-1, MCSCF-2, and MCSCF-3 denote active spaces of ($9e^-/5$ orbs), ($17e^-/9$ orbs), and ($17e^-/12$ orbs), respectively (see text). Experimental D_e values were extracted according to $D_e = D_0 + \omega_e/2 - \omega_e X_e/4$.

Level of theory	D_e (cm ⁻¹)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e X_e$ (cm ⁻¹)
$X\ ^2\Sigma^+$ state				
<i>ic</i> MRCI/MCSCF-1	326	3.953	23.8	0.19
<i>ic</i> MRCI+ <i>Q</i> /MCSCF-1	363	3.894	25.9	0.31
RCCSD(T)/ $9e^-$	380	3.870	27.0	0.31
MCSCF-2	139	4.479	14.8	0.43
<i>ic</i> MRCI/MCSCF-2	554	3.732	32.9	0.44
<i>ic</i> MRCI+ <i>Q</i> /MCSCF-2	655	3.664	37.5	0.64
RCCSD(T)/ $17e^-$	705	3.628	39.9	0.67
MCSCF-3	264	4.228	18.8	0.25
<i>ic</i> MRCI/MCSCF-3	620	3.709	35.2	0.64
<i>ic</i> MRCI+ <i>Q</i> /MCSCF-3	694	3.662	38.7	0.72
Experiment	828 ± 244	n/a	49.5	0.75
$A\ ^2\Pi$ state				
MCSCF-3	1126	3.275	79.1	1.68
<i>ic</i> MRCI/MCSCF-3	1814	3.183	95.8	1.61
<i>ic</i> MRCI+ <i>Q</i> /MCSCF-3	1967	3.169	99.1	1.57
Experiment	2363 ± 232 ($^2\Pi_{1/2}$) 2636 ± 256 ($^2\Pi_{3/2}$)	n/a	120.8 ± 0.5 ($^2\Pi_{1/2}$) 122.0 ± 0.5 ($^2\Pi_{3/2}$)	1.67 ± 0.04 ($^2\Pi_{1/2}$) 1.60 ± 0.04 ($^2\Pi_{3/2}$)

The potential energy curves for the ground ($X\ ^2\Sigma^+$) and the excited ($A\ ^2\Pi$) states of Sr⁺Ar arise from the interaction of Ar($1S$) with electrons in the $5s$ and $5p$ orbitals of Sr⁺, respectively. The $A\ ^2\Pi$ state is the second one of that symmetry, the lower one arising from the interaction of Ar with the $4d$ electrons of Sr⁺ which lie energetically between the $5s$ and $5p$ and produce a manifold of states ($^2\Sigma, ^2\Pi, ^2\Delta$) which, however, have not been observed experimentally for Sr⁺Ar but they have been observed for Ca⁺Ar.⁷ For the ground ($X\ ^2\Sigma^+$) state, the calculations were performed at the coupled cluster level of theory including single and double excitations with a perturbative estimation⁸ of the triple excitations [RCCSD(T)] from a restricted Hartree-Fock (RHF) reference wave function. In addition, we considered the internally contracted multi reference single and double excitation configuration interaction (*ic*MRCI) method⁹ from a multi configuration self-consistent field (MCSCF) wave function. We have chosen two active spaces in the MCSCF calculations, one including the Ar($3s,3p$) with the Sr($5s$) electrons (MCSCF-1: $9e^-/5$ orbitals) the other the Ar($3s,3p$) with the Sr($4s,4p,5s$) electrons (MCSCF-2: $17e^-/9$ orbitals). The number of internally contracted/uncontracted configuration space functions (CSFs) are 7896/26020 and 25946/155658 in the *ic*MRCI for the two active spaces, respectively. The RCCSD(T) calculations corresponding to the two previous active spaces are denoted as RCCSD(T)/ $9e^-$ and RCCSD(T)/ $17e^-$. We finally considered a larger active space (MCSCF-3: $17e^-/12$ orbitals) in order to incorporate the states that arise from the ($4d$) and ($5p$) orbitals of Sr. For the calculations with the last active space we have performed a four-state averaged MCSCF calculation (15128 CSFs) with equal weights for the ground state, the $^2\Sigma$ and $^2\Delta$ states coming from the Sr⁺($4d$) orbitals and the $B\ ^2\Sigma^+$ state arising from the Sr⁺($4p$) orbitals and

subsequently successive projected *ic*MRCI calculations for four states. It should be noted that the potential energy surface of the $B\ ^2\Sigma^+$ state is needed in order to parametrize¹⁰ classical interaction potentials for the triatomic Sr⁺(Ar)₂ system; results regarding the $B\ ^2\Sigma^+$ state obtained from these calculations will be reported in subsequent publications together with the potential development.⁴ The states of Π symmetry were obtained by a similar procedure, viz, a two-state average MCSCF (14204 CSFs) and subsequent projected *ic*MRCI calculations for two states. The corresponding number of internally contracted CSFs in the *ic*MRCI is 2140732 for the $l=0$ and 2122179 for the $l=1$ states out of about 135 million uncontracted. In the *ic*MRCI calculations the “+*Q*” designation denotes the multi reference analog¹¹ of the Davidson correction¹² that provides an estimate of higher-than-double excitations from the MCSCF active space.

For the Sr atom we used the quasi-relativistic effective core potential (ECP) from the Stuttgart group¹³ (28 core electrons) in conjunction with the ($6s6p5d$) valence set contracted to [$4s4p2d$] for the remaining electrons. This ECP/valence set combination yields a second IP of 10.80 eV for Sr at the CCSD(T) level of theory (compared to 11.03 eV experimentally⁶) and a 5^2S-5^2P excitation of 2.93 eV for Sr⁺ (compared to the averaged spin-orbit value⁶ of 2.99 eV). For Ar we used the doubly augmented correlation-consistent polarized valence double zeta (d-aug-cc-pVDZ) basis set.¹⁴ This consists of the regular aug-cc-pVDZ set¹⁵ augmented with one additional diffuse function of each symmetry (s,p,d) whose exponents are determined in an even-tempered fashion. The d-aug-cc-pVDZ set produces 11.05 a.u. for the polarizability of Ar at the CCSD(T) level of theory, a value very close to the basis set limit of 11.19 a.u.

We computed the potential energy curves using the en-

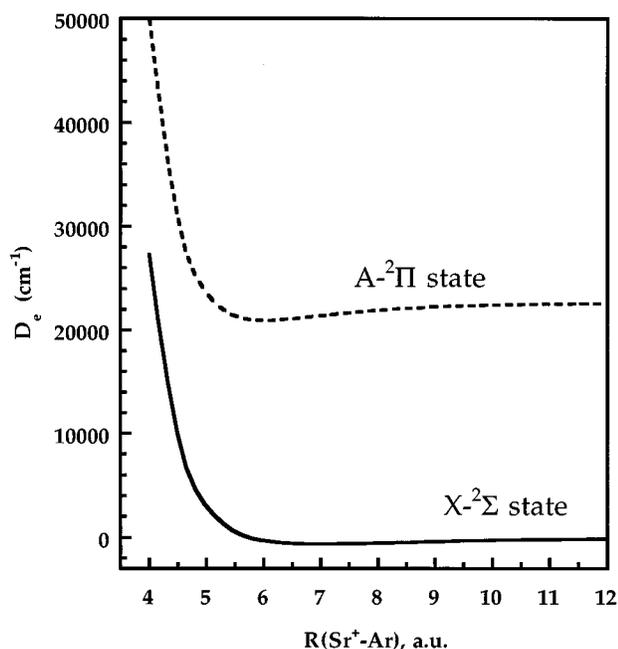


FIG. 1. Calculated potential energy curves for the $X^2\Sigma^+$ and $A^2\Pi$ states of Sr⁺Ar at the *icMRCI/MCSCF-3* level of theory.

ergies of 14–17 internuclear separations around the minimum. A Dunham analysis¹⁶ was used to extract the equilibrium bond length (R_e), the dissociation energy (D_e), the harmonic frequency (ω_e), and the anharmonicity ($\omega_e\chi_e$). The largest difference between the calculated energies and those predicted by the fit was 10^{-6} hartree (0.22 cm^{-1}). The dissociation limit for the separated atoms was calculated using the supermolecule approach at the *icMRCI* (the energy is computed at an internuclear separation of $100a_0$) and the sum of the separated atoms at the *RCCSD(T)* levels of theory, respectively. All calculations were performed using the *MOLPRO* program suite.¹⁷

III. RESULTS AND DISCUSSION

The results of our calculations are listed in Table I; the potential energy curves for the two states are shown in Fig. 1. For the ground $X^2\Sigma^+$ state, dynamic electron correlation results in a contraction of R_e by almost 0.8 \AA with a fivefold increase in the corresponding D_e . The effect of correlation of the Sr($4s,4p$) electrons is also large as is evident from the difference between both the *icMRCI* ($+Q$) with the *MCSCF-1* and *MCSCF-2* active spaces and the *RCCSD(T)* $9e^-/17e^-$ results. It amounts to a contraction of 0.24 \AA for R_e and an increase of 326 cm^{-1} for D_e at the *RCCSD(T)* level of theory. The effect on R_e is similar at the *icMRCI* level of theory (0.22 \AA), although the differential effect on D_e is only 70% of that at the *RCCSD(T)* level. The $+Q$ correction seems, however, to compensate for the yielding differential correlation effects of 0.23 \AA and 298 cm^{-1} for R_e and D_e , respectively, values that are closer to the ones obtained at the *RCCSD(T)* level of theory. The largest [*RCCSD(T)/17e^-* and *icMRCI+Q/MCSCF-3*] calculations

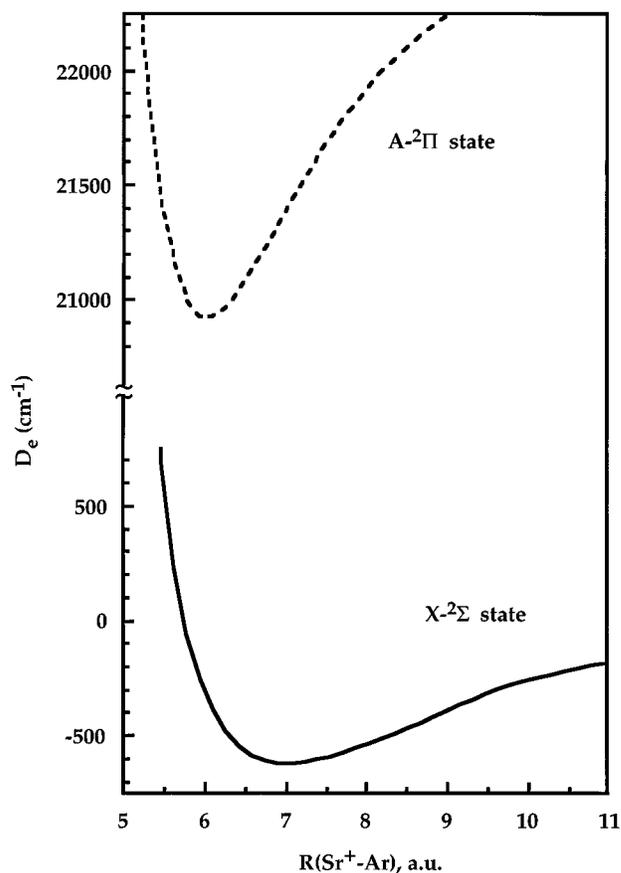


FIG. 2. Area around the two minima to indicate the contraction of R_e for the $A^2\Pi$ state with respect to the ground state.

for the ground state yield dissociation energies within 11 cm^{-1} of each other, both lying within the experimental error favoring the lower end. The corresponding harmonic frequencies are within 1 cm^{-1} of each other, both $\sim 10\text{ cm}^{-1}$ smaller than the experiment. In addition, the predicted R_e values between the two methods are within 0.034 \AA of each other. For the ground state the interaction is mainly electrostatic as indicated by the magnitude of the charge-induced dipole term $V=q^2\alpha/2R^4$ which yields 78% of D_e (α is the dipole polarizability of Ar).

For the $A^2\Pi$ excited state we compute a dissociation energy (D_e) of 1126 cm^{-1} at the *MCSCF* and 1814 cm^{-1} at the *icMRCI* levels of theory; the $+Q$ correction increases our estimate to 1967 cm^{-1} . The effect of dynamic electron correlation for the $A^2\Pi$ state is important, although not to the degree observed for the ground state. For instance, the ratio of the *CASSCF* to *icMRCI+Q* D_e 's is 0.38 for the ground and 0.57 for the excited state. Furthermore, the calculated R_e is 3.183 \AA at the *icMRCI* level of theory, decreasing to 3.169 \AA when the $+Q$ correction is taken into account. Our estimated *shift* in the corresponding R_e 's between the ground and the $A^2\Pi$ excited state (cf. Fig. 2) is therefore 0.526 \AA (*icMRCI*) and 0.493 \AA (*icMRCI+Q*), in excellent agreement with the experimentally² estimated value of $\Delta R_e = 0.50 \pm 0.05\text{ \AA}$. Our best estimate for the har-

monic frequency of the excited state is 20 cm⁻¹ lower than the one determined experimentally. Furthermore, the calculated T_e is 22 532 cm⁻¹ in good agreement with the value of 22 287 cm⁻¹ deduced from the measured ν_{00} and the experimental zero-point energies for the two states. The fact that the excited ²Π state is more strongly bound and has a shorter R_e than the ground ²Σ state is expected as the orientation of the p orbital of Sr perpendicular to the intermolecular axis allows a closer approach of the Ar atom.

IV. CONCLUSIONS

In this study we present, to the best of our knowledge, the first nonempirical calculations for the ground and the first observed excited state of Sr⁺Ar. Our calculations produce a dissociation energy for the ground state that is within the experimental error bar favoring the lower end while underestimating the one for the excited state by about 7%; they also accurately reproduce the observed contraction of the equilibrium separation in the excited state with respect to the ground state. Our results are in much better agreement with the available experimental data for this system than the results of previous empirical calculations.³ To this end our calculations complement the available experimental data for this system by providing accurate equilibrium distances (R_e 's) and potential energy curves for the two states, information which will be used to parametrize interaction potentials in subsequent studies.⁴

ACKNOWLEDGMENTS

This work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory. Computer resources were provided by the Division of Chemical Sciences and by the Scientific Computing Staff, Office of

Energy Research, at the National Energy Research Super-computer Center (Berkeley, CA). S.S.X. and S.C.F. gratefully acknowledge support from the Hellenic General Secretariat for Research and Technology under the program for support of scientific staff ΠΕΝΕΔ-1994 (15774/296).

- ¹G. S. Fanourgakis and S. C. Farantos, *J. Phys. Chem.* **100**, 3900 (1996).
- ²C. Lüder and M. Velegarakis, *J. Chem. Phys.* **105**, 2167 (1996).
- ³H. Harima, T. Ihara, Y. Urano, and K. Tachibana, *Phys. Rev. A* **34**, 2911 (1986).
- ⁴G. S. Fanourgakis, S. C. Farantos, S. S. Xantheas, C. Lüder, and M. Velegarakis (work in progress).
- ⁵C. W. Bauschlicher, Jr., H. Partridge, and S. R. Langhoff, *J. Chem. Phys.* **91**, 4733 (1989); H. Partridge, C. W. Bauschlicher, Jr., and S. R. Langhoff, *J. Phys. Chem.* **96**, 5350 (1992); C. W. Bauschlicher, Jr., and H. Partridge, *Chem. Phys. Lett.* **239**, 241 (1995).
- ⁶C. E. Moore, *Atomic Energy Levels* (Nat. Bur. Stand., 1949), Circular 467, Vols. I–III.
- ⁷T. Buthelezi, D. Bellert, V. Lewis, and P. J. Brucat, *Chem. Phys. Lett.* **246**, 145 (1995).
- ⁸C. Hampel, K. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992); J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- ⁹H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988); H.-J. Werner and E. A. Reinsch, *J. Chem. Phys.* **76**, 3144 (1982); H.-J. Werner, *Adv. Chem. Phys.* **LXIX**, 1 (1987).
- ¹⁰L. C. Balling and J. J. Wright, *J. Chem. Phys.* **79**, 2941 (1983).
- ¹¹M. R. A. Blomberg and P. E. M. Siegbahn, *J. Chem. Phys.* **78**, 5682 (1983).
- ¹²S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).
- ¹³M. Kaupp, P. V. R. Schleyer, H. Stoll, and H. Preuss, *J. Chem. Phys.* **94**, 1360 (1991).
- ¹⁴D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- ¹⁵D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); T. H. Dunning, Jr., *ibid.* **90**, 1007 (1989).
- ¹⁶J. L. Dunham, *Phys. Rev.* **41**, 713 (1932).
- ¹⁷MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, M. E. Mura, A. Nicklass, K. Peterson, R. Pitzer, P. Pulay, M. Shultz, H. Stoll, A. J. Stone, P. R. Taylor, and T. Thorsteinsson. For the RCCSD(T) implementation in MOLPRO see P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).