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Ground state of the polar alkali-metal-atom–strontium molecules: Potential energy curve and permanent dipole moment

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In this study, we investigate the structure of the polar alkali-metal-atom–strontium diatomic molecules as possible candidates for the realization of samples of ultracold polar molecular species not yet investigated experimentally. Using a quantum chemistry approach based on effective core potentials and core polarization potentials, we model these systems as effective three-valence-electron systems, allowing for calculation of electronic properties with full configuration interaction. The potential curve and the permanent dipole moment of the $^2\Sigma^+$ ground state are determined as functions of the internuclear distance for LiSr, NaSr, KSr, RbSr, and CsSr molecules. These molecules are found to exhibit a significant permanent dipole moment, though smaller than those of the alkali-metal-atom–Rb molecules.

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I. INTRODUCTION

The prospects of the realization of quantum degenerate gases composed of polar systems, that is, exhibiting a permanent dipole moment, either magnetic or electric, are among the most fascinating ones in the context of researches on ultracold matter [1], related to many-body physics, quantum information, or quantum simulators of solid-state physics. Indeed, neutral particles usually weakly interact via van der Waals short-range potentials varying with their mutual distance R as R^{-6}, which has been a key condition for the observation of Bose-Einstein condensation in weakly interacting gases of ultracold alkali-metal atoms [2–4]. In contrast, particles with a permanent dipole moment interact through a long-range dipole-dipole potential varying as R^{-3} which dominates the van der Waals interaction. Ultracold gases of such particles are predicted to evolve in an entirely new regime of strong interactions with pronounced anisotropy. For instance, the chromium atom has a large magnetic dipole moment of about $6\mu_B$, and once condensed [5,6], the manifestation of anisotropic interactions has been observed experimentally [7,8]. Ground-state polar molecules, having permanent dipole moment (in the body-fixed frame) ranging between a few tenths of a debye, such as LiNa or KRb, up to several debye, such as LiCs [9], are actually strongly interacting with larger forces than in the chromium case and are expected to be better candidates for studying strongly interacting degenerate gases. Up to now, several attempts to observe ultracold ground-state polar molecules have been successful with bialkali-metal molecules, namely, KRb [10,11], LiCs [12], NaCs [13], and RbCs [14]. However, the achievement of quantum degeneracy of ultracold molecules is conditioned by the phase-space density of molecules in a unique quantum state, preferably the absolute ground state, defined not only by their vibrational and rotational quantum numbers, but also by their hyperfine structure [15–17].

As the number of atomic species other than alkali-metal atoms, which are laser-cooled and subsequently brought to quantum degeneracy is continuously increasing, the formation of novel species of polar molecules will soon be investigated in the ultracold regime [18]. For instance, photoassociation (PA) of Yb_2 [19,20] and YbRb [21] molecules has already been reported, while quantum degeneracy in ytterbium [22,23], calcium [24], and strontium [25,26] atomic gases have recently been obtained. In the present article, we investigate theoretically the unknown structure of diatomic molecules composed of one strontium atom and one alkali-metal atom (Li, Na, K, Rb, Cs). In the following, we refer to them as *A*Sr molecules. In particular, we determined the permanent dipole moment of their ground state in order to provide guidance to the experimentalists to choose the appropriate combination of atomic species. In contrast with alkali-metal dimers, such species also have a magnetic moment in the ground state due to their three valence electrons, which therefore makes them suitable for their manipulation with both electric and magnetic external fields. In Sec. II, we first recall our methodology based on quantum chemistry computations involving effective core potentials (ECPs), reducing the problem to an effective three-valence-electron system, for which full configuration interaction can be achieved. Molecular potential curves and permanent dipole moments for the LiSr, NaSr, KSr, RbSr, and CsSr molecules in their electronic ground state are presented in Secs. III and IV, emphasizing the dipolar character of these molecules compared to bialkali-metal molecules.

II. METHOD OF CALCULATION

We use the configuration interaction by perturbation of a multiconfiguration wave function selected iteratively (CIPSI) set of programs developed at the Université Paul Sabatier in Toulouse (France). The CIPSI package incorporates the use of both ECPs [27,28] and ℓ-dependent core polarization potentials (CPPs) [29,30]. ECPs model the effect of inner-shell electrons into a semiempirical potential, thus reducing the number of active electrons on each atom, namely, one for the alkali-metal atom and two for the strontium atom. CPPs embody the polarization effects of these effective cores with the valence ones. Thanks to the reduced number of active electrons, it becomes possible to perform a full configuration interaction (FCI) in the valence space. This gives us a number

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of excited molecular states in addition to the lowest state in each symmetry. This method has proven to be efficient and accurate for alkali-metal diatomics which are treated as two-electron systems [9,31], and we modified the CIPSI package accordingly for effective three-electron systems.

ECPs are from Ref. [32]. For the strontium atom, we use the so-called "large-core" ECP for the 36 electrons of the Sr^{2+} core and basis sets composed of uncontracted Gaussian functions. The basis sets for alkali-metal atoms are taken from Ref. [9], where f Gaussians have been removed to reduce the size of the configuration space. We checked on the alkali-metal atoms that this has no influence on the lowest energy levels in which we are interested here. The basis set for the strontium atom is taken from [33]. We actually used two slightly different basis sets: We first designed sets for $A\mathrm{Sr}^+$ ions, that is, $8s7p4d$ for lithium, $7s6p5d$ for sodium, $7s5p7d$ for potassium, $7s4p5d$ for rubidium, $7s4p5d$ for cesium, and $7s6p7d$ for strontium ions whose exponents are reported in Table I. These results will be discussed in a separate publication. For the neutral-system $A\mathrm{Sr}$, we reduced the Sr^+ set by a few orbitals down to $5s5p6d$ due to size constraints. The influence on the atomic energy levels remains small, as can be seen in what follows.

In total, the number of configurations for the diatomic calculations is larger than 10^5 and depends on the molecular symmetries. We use a recently modified version of the ℓ-dependent CPP initially proposed by Foucrault *et al.* [30], which yields the correct asymptotic behavior of the potential energy at large internuclear distance [34], in contrast with most of the previous calculations performed on alkali-metal dimers with this method. A set of cutoff radii, reported in Table II, are optimized to reproduce experimental values for the lowest s, p, and d atomic levels of the alkali-metal atoms and of the strontium cation (Table III). Polarizabilities for the relevant cores Li^+, Na^+, K^+, Rb^+, Cs^+, and Sr^{2+} cores are taken from experimental and semiempirical values of Refs. [35,36].

Table III shows that such an optimization yields a satisfactory representation of the strontium cation spectrum. The corresponding fitted levels of the alkali-metal atoms are not reported here, as we are mainly interested in the lowest level

TABLE II. Optimized cutoff radii ρ_ℓ (in atomic units a_0) and core polarizabilities α of the relevant ionic cores Li^+, Na^+, K^+, Rb^+, Cs^+ [35], and Sr^{2+} [36] entering into the CPPs.

	Li	Na	K	Rb	Cs	Sr^+
ρ_s	1.451 956 5	1.450 275	2.108 16	2.5365	2.855 85	2.13
ρ_p	1.013	1.645 259 1	1.9722	2.279	2.544	2.183
ρ_d	0.6	1.5	1.9405	2.5217	2.898 15	1.706
	Li^+	Na^+	K^+	Rb^+	Cs^+	Sr^{2+}
α	0.1997	0.9987	5.472	9.245	16.33	5.67

TABLE I. Gaussian basis-set exponents used to represent the effective one-electron systems of the present work and resulting number of configurations representing the effective three-electron diatomic systems $A\mathrm{Sr}$ (with $A \equiv$ Li, Na, K, Rb, Cs) for the relevant molecular symmetries. The actual basis sets used for $A\mathrm{Sr}$ neutral molecules include all exponents except the ones in italic, while the whole set has been used for $A\mathrm{Sr}^+$ systems. The three lowest lines provide the size of the Hamiltonian for the FCI.

Angular momentum	Li	Na	K	Rb	Cs	Sr^+
s	2.464	2.8357	0.9312	1.292 561	0.328 926	0.791 74
	1.991	0.493 18	0.2676	0.824 992	0.241529	0.316 178
	0.582	0.072 085	0.0427	0.234 682	0.050 502	0.066 565
	0.200	0.036 061	0.039 15	0.032 072	0.029 302	0.026 99
	0.070	0.016 674	0.014 48	0.013 962	0.013 282	0.0134 95
	0.031	0.006 93	0.0055	0.005 75	0.005 28	*0.009*
	0.015	0.002 87	0.0026	0.0025	0.003	*0.003*
	0.007					
p	0.630	0.431	0.133	0.128	0.1	0.225 825
	0.240	0.092 76	0.051 28	0.040 097	0.0405	0.095 691
	0.098	0.035 62	0.016 42	0.014 261	0.0162	0.042 077
	0.043	0.014 47	0.0052	0.004 85	0.004 43	0.018 077
	0.020	0.0058	0.0022			0.009 038 5
	0.010	0.000 23				*0.005*
	0.005					
d	0.180	0.292	1.255	0.408 807	0.196 894	3.618 081
	0.080	0.063 61	0.343	0.096 036	0.067 471	0.999 656
	0.227 96	0.022 73	0.109	0.026 807	0.027 948	0.390 735
	0.008 574	0.008 852	0.0294	0.009 551	0.010 712	0.122 77
		0.003 52	0.010 13	0.004	0.003	0.036 655
			0.0039			0.018 327
			0.0018			*0.009*
Symmetry	LiSr	NaSr	KSr	RbSr	CsSr	
$\{\Sigma^+, \Delta_{x^2-y^2}\}$	129 945	132 792	161 703	110 337	110 337	
Π	120 032	123 684	151 478	102 540	102 540	
$\{\Sigma^-, \Delta_{xy}\}$	110 240	114 840	142 138	95 457	95 457	

TABLE III. Binding energies (in a.u.) of Sr^+ levels obtained with (a) the small basis set and (b) the large basis set for Sr^+ (Table I) and their deviations Δ_E (in cm^{-1}) from experiment [39]. The ionization limit of Sr^+ is taken at 88 965.18 cm^{-1} [42] to calculate the experimental binding energies in a.u.. We use the mass-corrected Rydberg constant 109 736.63 cm $^{-1}$. The theoretical values of [41] have been spin averaged.

State	Expt. [39]	(a)	Δ_E	(b)	Δ_E	[40]	Δ_E	[41]	Δ_E
$5s$	−0.405 356 9	−0.405 354	0	−0.405 358	0	−0.405 522	36	−0.408 39	666
$4d$	−0.338 268 5	−0.338 269	0	−0.338 269	0	−0.338 247	−4	−0.341 908	799
$5p$	−0.294 867 4	−0.294 868	0	−0.294 869	0	−0.294 854	−2	−0.295 88	222
$6s$	−0.187 851 9	−0.187 521	−73	−0.187 544	−68	−0.187 469	−84		
$5d$	−0.162 328 2	−0.160 856	−323	−0.160 947	−303	−0.161 237	−239		
$6p$	−0.150 374 4	−0.150 234	−31	−0.150 237	−30	−0.150 150	−49		
$7s$	−0.109 356 8			−0.109 138	−48				
$6d$	−0.975 880 6			−0.096 543	−230				
$7p$	−0.921 336			−0.091 920	−46				
$8s$	−0.716 620 3			−0.075 047	−34				

of s, p, and d symmetry whose energies are represented exactly after the tuning of the cutoff radii of Table II. Therefore, the energies of a pair composed of one alkali-metal atom and a strontium cation in their lowest levels at infinite separations are well modeled here.

III. THE GROUND-STATE POTENTIAL CURVE OF ALKALI-METAL-ATOM–STRONTIUM MOLECULES

As dissociation limits of ASr molecules involve a neutral alkali-metal atom and a neutral strontium atom, we first performed a first FCI calculation with the small and large basis sets and involving two electrons in order to calculate the lowest strontium energy levels. Results are given in Table IV and are compared to experimental values. The differences range between less than 200 cm^{-1} for the ground state up to about 450 cm^{-1} for the lowest excited levels, as was the case also for the magnesium atom [37]. We note that such an accuracy is typical for this kind of calculation, as illustrated also by ECP + CPP FCI calculations on calcium [38]. The use of the small basis set does not significantly affect the quality of the results.

We display in Fig. 1(a) the potential energy curves (PECs) for the $X\,^2\Sigma^+$ ground state of the ASr systems, relative to the same origin of energies fixed at the dissociation limit Ans + Sr($5s^2\,^1S$) for comparison purposes. The corresponding main spectroscopic constants are reported in Table V. The strontium atom in its ground state is a closed-shell atom, so the alkali-metal-atom–strontium molecules are expected to have a van der Waals character with a somewhat large equilibrium distance and weak binding energy, compared, for instance, to alkali-metal diatomics with comparable masses like alkali-metal-atom–rubidium molecules. This feature is clearly visible in the figure, as the typical binding energies are three to five times smaller than for the related ARb molecules. The equilibrium distances are also systematically larger for ASr than for ARb molecules, except for LiSr. The LiSr molecule is a bit peculiar, as its ground state is quite deep, with an equilibrium distance comparable to the LiRb one.

The potential depths of the ASr molecules immediately show that in ultracold conditions these molecules will not be stable against collisions between them, just like KRb molecules [43]. The reaction channel yielding a Sr_2 molecule and an alkali-metal dimer is energetically open for all alkali-metal species. Indeed, the Sr_2 well depth is about 1061 cm^{-1} [44], while those of the alkali-metal dimers are 8517 cm^{-1} [45], 6022 cm^{-1} [46], 4451 cm^{-1} [47], 3993 cm^{-1} [48], and 3649 cm^{-1} [49], for Li_2, Na_2, K_2, Rb_2, and Cs_2, respectively.

From the long-range part of these curves we can estimate the coefficient C_6 of the leading term of the van der Waals interaction.

IV. THE PERMANENT DIPOLE MOMENT OF ALKALI-METAL-ATOM–STRONTIUM MOLECULES

As stated in the Introduction, an important property of these molecules, in the perspective of cooling and trapping them

TABLE IV. Computed strontium binding energies E_b (in a.u. relative to the double ionization threshold of strontium) and excitation energies E_e (in cm^{-1}), compared to the experimental values of Ref. [39] ($E_b^{\rm exp}$ and $E_e^{\rm exp}$), and their differences ($\delta_b = E_b - E_b^{\rm exp}$ and $\delta_e = E_e - E_e^{\rm exp}$) in cm^{-1}, resulting from a two-electron FCI calculation with (a) the large basis set, and (b) the small basis set for Sr^+ (Table I). The experimental values are averaged over fine structure energies when appropriate. We use the mass-corrected Rydberg constant 109 736.63 cm $^{-1}$.

		(a)		(b)			(a)		(b)	
	Expt. $E_b^{\rm exp}$	E_b	δ_b	E_b	δ_b	Expt. $E_e^{\rm exp}$	E_e	δ_e	E_e	δ_e
$5s^2\,^1S$	−0.614 641 48	−0.615 471	−182	−0.615 484	−184	0	0	0	0	0
$5s5p\,^3P^o$	−0.547 651 55	−0.548 880	−269	−0.548 899	−273	14 702.6	14 613	−87	14 613	−88
$5s4d\,^3D^e$	−0.531 470 99	−0.529 868	351	−0.529 907	343	18 253.7	18 779	533	18 781	528
$5s4d\,^1D^e$	−0.522 832 08	−0.520 684	471	−0.520 733	460	20 149.7	20 793	653	20 795	645
$5s5p\,^1P^o$	−0.515 775 30	−0.517 756	−434	−0.517 792	−442	21 698.5	21 447	−252	21 440	−257

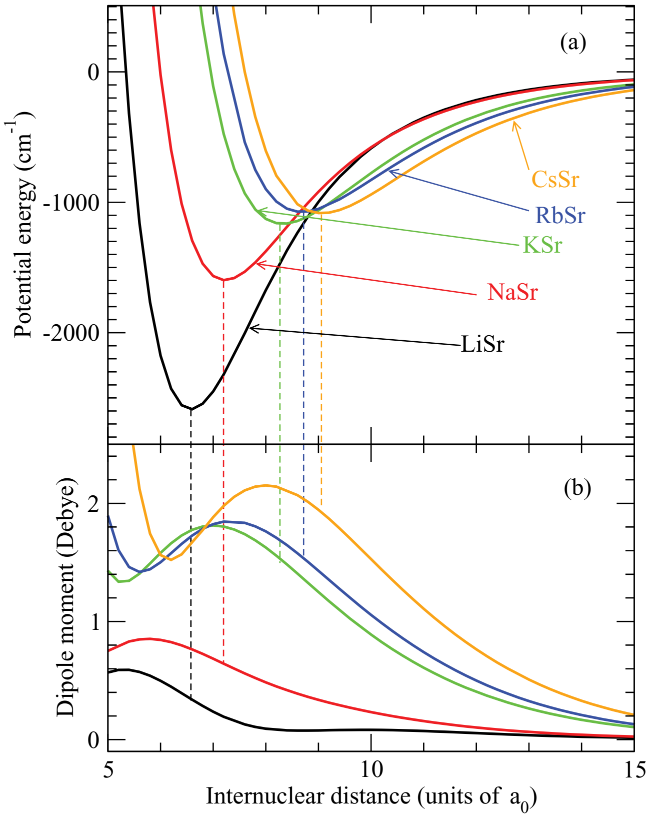

FIG. 1. (Color online) (a) Potential energy curves and (b) permanent dipole moments (PDMs) for the $X\,^2\Sigma^+$ ground state of the *A*Sr molecules (*A* = Li, Na, K, Rb, Sr). Vertical lines guide the eye to locate the value of the PDM at the equilibrium distance.

at ultracold temperatures, is the permanent dipole moment (PDM), which is illustrated in Fig. 1(b) and reported as well in Table V. We used the convention of a molecular axis oriented from the Sr atom toward the alkali-metal atom. The displayed positive values imply an excess of negative charge on the latter atom, which is expected as its electron affinity is larger than the Sr one. The accuracy of these results can be appreciated from our previous calculations on alkali dimers [9], together with the recent experimental determinations of the PDM of KRb [15] and LiCs [51]. A typical agreement at the level of 0.1 D or less is found for the lowest vibrational level. The PDMs for ground-state *A*Sr molecules are predicted to be noticeable, even if they do not reach such high values as those of the alkali-metal dimers [9]. It is worthwhile to mention that the relation between the magnitude of the PDM and the difference in the mass (and then in the size) of the constituting atoms is inverted compared to alkali-metal dimers: The PDM of LiCs and LiRb are the largest ones among all alkali-metal atom pairs, while the PDM of LiSr is by far the smallest one compared to the other *A*Sr species. This feature is amplified by the mismatch of the minimum of the PEC of LiSr and NaSr, and the maximum of the PDM curve, in contrast with those of the other species.

TABLE V. Main spectroscopic constants for the lowest electronic states of the *A*Sr molecules (*A* = Li, Na, K, Rb, Sr): well depth D_e, equilibrium distance R_e, harmonic constant ω_e, and rotational constant B_e. The value of the dipole moment d_e at the equilibrium distance and averaged for the $v = 0$ level (d_0) are also reported. Data for the related ARb molecules are displayed for comparison, following our computations reported in Refs. [9,31,50].

	D_e (cm^{-1})	R_e (a.u.)	ω_e (cm^{-1})	B_e (cm^{-1})	d_e (D)	d_0 (D)
LiSr	2587	6.57	184.9	0.21	0.34	0.34
NaSr	1597	7.22	85.4	0.063	0.62	0.63
KSr	1166	8.33	52.4	0.032	1.52	1.50
RbSr	1073	8.69	32.3	0.018	1.54	1.53
CsSr	1084	9.06	33.8	0.013	1.91	1.91
LiRb	6044	6.49	210		4.168	4.165
NaRb	5076	6.82	107		3.304	3.306
KRb	4199	7.63	76		0.615	0.615
CsRb	3907	8.29	50.0		1.238	1.237

V. CONCLUSION

In this article we investigate the electronic structure of the alkali-metal-atom–strontium molecules with a quantum chemistry approach which accurately treats correlation between valence electrons through a FCI, while the correlation between valence and core electrons is accounted for through effective potentials. This approach has proven to be powerful for similar calculations on alkali-metal dimers. The potential curve and the main spectroscopic constants, as well as the PDM of the $^2\Sigma^+$ ground state, have been determined for LiSr, NaSr, KSr, RbSr, and CsSr molecules. Though their PDM is generally smaller than the alkali-metal-atom–Rb molecules, these systems are possible candidates for achieving a different kind of ultracold molecular sample with anisotropic interactions. Just like heteronuclear alkali-metal dimers, ultracold molecules in their ground state can probably be created by PA, and this will be the topic of a further study.

Note added. While completing this article, Żuchowski, Aldegunde, and Hutson informed us about their study on the structure of the RbSr ground state [52] using an all-electron quantum chemistry approach. Their results are in good agreement with ours. For instance, they obtained an equilibrium distance $R_e = 8.86$ a.u., a well depth of about 1000 cm^{-1}, and a PDM of 1.36 D at R_e (compared to our values $R_e = 8.69$ a.u., $D_e = 1073$ cm^{-1}, and $d_e = 1.54$ D). The slight differences are probably due to the sensitivity of the results on the treatment of electron correlation, and further experiment should help to clarify the situation. In their article, Żuchowski *et al.* demonstrated the existence of Feshbach resonances in RbSr. Therefore, our next study on excited states of these molecules should guide experimentalists in designing ways to achieve adiabatic population transfer from molecules created by Feshbach association down to the lowest energy level of the molecule, just like it has been recently done for Cs$_2$ [17,53] and KRb [15] molecules.

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