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van der Waals coefficients for systems with ultracold polar alkali-metal molecules

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A systematic study of the leading isotropic van der Waals coefficients for the alkali-metal atom + molecule and molecule + molecule systems is presented. Dipole moments and static and dynamic dipole polarizabilities are calculated employing high-level quantum chemistry calculations. The dispersion, induction, and rotational parts of the isotropic van der Waals coefficient are evaluated. The known van der Waals coefficients are then used to derive characteristics essential for simple models of the collisions involving the corresponding ultracold polar molecules.

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I. INTRODUCTION

Ultracold chemistry in submicrokelvin regime has emerged as one of the most exciting fields in atomic and molecular physics [1–3]. By tuning magnetic field across Feshbach resonances one can combine two free atoms into a bound state, with binding energy of order of MHz and then, with elaborated laser techniques, coherently transfer them into the deeply bound states—including the absolute rotational-vibrational-electronic ground state. At present two alkali-metal dimers have been produced in this manner KRb and Cs_2 [4,5]. It is also worth mentioning that LiCs molecules in the vibrational ground state have been produced by photoassociation followed by spontaneous emission [6]. At present, many experimental groups have focused on production of other heteronuclear alkali-metal dimers hoping to obtain ultracold quantum gases of polar molecules, stable with respect to the atom exchange and trimer formation [7]. Such quantum gases of polar molecules will be used to explore new ideas in quantum information theory [8,9], quantum simulations of condensed-phase physics [10], or fundamental studies of chemical reactions [11].

Description of chemical processes in the submicrokelvin regime is extremely difficult, because the full quantum calculation for such systems is nearly impossible. Thus only few quantum dynamics studies of ultracold atom + diatom collisions employing global potential energy surfaces have been performed so far concentrating on the homonuclear spin-polarized systems [12–18], where single-electronic-state approach provides good approximation [19]. Even then, the quantum dynamics calculations for heavier system are very challenging and have not been yet performed despite the fact that the corresponding quartet potential energy surfaces are rather simple [20,21].

Theoretical treatment of non-spin-polarized systems would be even more challenging. The calculations of triatomic and tetraatomic interaction potentials in such a case would have to include many active electrons and coupled potential energy surfaces, which at present is very far from routine. The following quantum dynamics calculations, especially in the presence of external fields, would be extremely demanding. The interaction potentials involving alkali-metal atoms and dimers are likely to be strongly anisotropic, and therefore the basis sets for such calculations would have to be very large. On the other hand, there is a very small number of observables as outcome of ultracold collisions. After all, in a laboratory we do not record state-resolved cross sections but only loss rates from the state prepared before the experiment. Thus, the recent theories of ultracold collisions [22–25], formulated to explain current experiments in this field, use only few simple parameters that catch the essential physics. Importantly enough, the feature of the intermolecular interaction that matters the most is the long-range shape of the interaction potential, usually represented analytically by the well-known van der Waals expansion with the most important term $-C_6 R^{-6}$ (R is the distance between the monomer centers of mass).

Properties of the alkali-metal dimers have been intensively studied using electronic structure methods. A systematic study of the dipole moments of all possible alkali-metal dimers was published by Aymar and Dulieu [26], and Deiglmeyr *et al.* [27] reported a systematic study of the static dipole polarizabilities for these systems. Their approach, based on large effective core potentials combined with appropriately set core-polarization potentials, was particularly successful in predicting binding energies and spectroscopic properties of the alkali-metal dimers in the ground and low-lying excited states.

In this paper we report a systematic *ab initio* study of the isotropic van der Waals C_6 coefficients for the alkali-metal atom + molecule ($A + AB$) and molecule + molecule ($AB + AB$) systems. We also derive characteristics essential for simple models of the corresponding ultra-low-energy collisions. In the following calculations masses of the bosonic ^{7}Li, ^{23}Na, ^{41}K, ^{87}Rb, and ^{133}Cs isotopes were used.

II. METHODOLOGY

The purpose of this paper is to provide essential parameters for modeling of collisions between the polar molecules in their ground rovibrational state. If colliding molecules are in

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$j = 0$ states only the isotropic part of the interaction potential governs its scattering properties at very long range—larger than $R_{\mathrm{vdW}} = (2mC_6/\hbar^2)^{\frac{1}{4}}$, where m is the reduced mass of the colliding system. If the strength of the anisotropy of the potential becomes comparable with spacing of the appropriate rotational energy levels of the molecule, then the anisotropic term becomes important: For example, in case of $A + AB$ collisions, the coupling driven by C_{62} between $j = 0$ and $j = 2$ channels becomes important if the potential anisotropy is comparable with $6B$. The same argument holds also for the $AB + AB$ collisions.

It is well known [28,29] that within the Born-Oppenheimer approximation the isotropic van der Waals C_6 coefficient of a two-monomer system (X + Y) can be decomposed into two contributions each corresponding to a different effect. First, it contains a *dispersion* contribution C_6^{disp} that physically represents the interaction of fluctuating instantaneous dipole moments, which are due to the movements of electrons, which correlate between interacting species at long range. Secondly, in the case of the heteronuclear dimers, a permanent molecular dipole moment induces a dipole moment on the atom, which in turn interacts with the permanent molecular dipole moment. This *induction* contribution C_6^{ind} is usually smaller than the dispersion contribution.

The dispersion contribution to the isotropic van der Waals C_6 coefficient can be calculated from the following integral,

$$C_6^{\mathrm{disp}} = \frac{3}{\pi}\int_0^{\infty} \bar{\alpha}_{\mathrm{X}}(i\omega)\bar{\alpha}_{\mathrm{Y}}(i\omega)d\omega, \tag{1}$$

where i is the unit imaginary number, ω is frequency, and

$$\bar{\alpha}_{\mathrm{mol}}(i\omega) = \tfrac{1}{3}[\alpha_{\mathrm{xx}}(i\omega) + \alpha_{\mathrm{yy}}(i\omega) + \alpha_{\mathrm{zz}}(i\omega)] \tag{2}$$

is the orientation-averaged molecular dynamic dipole polarizability. The induction contribution to the isotropic van der Waals C_6 coefficient can be expressed as

$$C_6^{\mathrm{ind}} = \mu_X^2\bar{\alpha}_{\mathrm{Y}}(0) + \mu_Y^2\bar{\alpha}_{\mathrm{X}}(0), \tag{3}$$

where μ is the corresponding permanent molecular dipole moment. If the monomer X is an atom in the spherical-symmetry ground state and the overlap of the charge distribution of interacting species can be neglected, the first term in the above equation vanishes. The total isotropic C_6 coefficient of the atom + molecule system is a sum of the dispersion and induction contributions.

For molecule + molecule systems in their ground rotational state there also exists a (non-Born-Oppenheimer) *rotational* contribution to the effective isotropic C_6 resulting from a second-order coupling of the dipole-dipole term [30–32]. It has the form $C_6^{\mathrm{rot}} = \mu^4/6B$ where B is the molecule rotational constant. Then the total isotropic C_6 coefficient for the molecule + molecule system is a sum of the dispersion, induction, and rotational contributions.

Proper choice of the electron basis set is crucial for quantum chemistry calculations of the dipole moments and polarizabilities. For lithium and sodium atoms we have used available core-valence correlation-consistent basis sets cc-pCV5Z designed by Prascher *et al.* [33], which we augmented by one set of diffuse functions. Effective-core potentials (ECPs) with tailored valence basis sets for heavy (K-Fr) alkali-metal atoms have been optimized by Lim *et al.* [34]. These ECPs are small-core type potentials, i.e., the outermost nine electrons are described explicitly. To eliminate possible errors due to the basis incompleteness we have improved the original valence basis sets by adding g and h functions. and augmenting the basis sets by one set of diffuse functions. These basis sets have been tested on the atomic static dipolar polarizabilities, which have been calculated with the spin-restricted open-shell coupled cluster method [35] with single, double, and noniterative triple excitations [RCCSD(T)] employing a finite-field approach. In all cases the agreement with the reference values of Derevianko *et al.* [36] was very good (the difference for Na was 2.2 a.u.; less than one atomic unit for other alkali metals).

All alkali-metal dimers in their ground electronic state $X^1\Sigma^+$ (near their equilibrium lengths) have their excited states significantly separated in energy, thus we can properly describe them by a single-reference Slater determinant, which is ideal for using the coupled cluster approach [35]. For the molecular calculations we took the equilibrium distances, which were optimized by the Paris group [26,27].

For the molecular dynamic polarizability calculations we employed the time-independent coupled cluster polarization propagator method in singles and doubles approximation (TI-CCSD). This was introduced by Moszynski *et al.* [37] and implemented in MOLPRO 2010.2 program [38]. Several approximations to the full time-independent polarization propagator were discussed by Korona *et al.* [39]. In our study, we used the so-called CCSD(3) approximation of the TI-CCSD method, which is exact to the third order of the electronic correlation operator. In benchmark calculations against the dynamic dipole polarizabilities based on the full-configuration-interaction response functions, the CCSD(3) approximation demonstrated systematically a smaller error than the other approximations introduced there [37,39]. Finally, in this paper we have used a finite-field CCSD(T) approach in order to evaluate dipole moments and static dipole polarizabilities of the alkali-metal dimers. Such calculations were also needed to verify the accuracy of the TI-CCSD dynamic polarizabilities.

III. RESULTS AND DISCUSSION

The dipole moments of the heteronuclear alkali-metal dimers calculated with the finite-filed CCSD(T) method as the first derivatives of energy with respect to the electric field applied are collected in Table I). The FF-CCSD(T) data are in good agreement with those obtained by Aymar and Dulieu [26], with an error of at most 10% for LiNa and KRb molecules; note that for these species the dipole moment and charge separation between atoms is significantly smaller than in other cases and the corresponding dipole moments are small. The dipole moment we have obtained for KRb (0.62 D) is somewhat larger than the experimental value (0.566 ± 0.017 D [4]) and the value in Ref. [32]. For the sake of consistency we used our calculated values in further calculations. In addition to the finite-field CCSD(T) values we also calculated the finite-field CCSD values in order to check how important is the inclusion of triply excited configurations in calculations of the alkali-metal dimer dipole moments. The FF-CCSD values

TABLE I. Dipole moments (in Debye), rotational constant (in cm^{-1}), the orientation-averaged molecular static dipole polarizability (in atomic units), and the anisotropy of the molecular static dipole polarizability (in atomic units) of the ground $X^1\Sigma^+$ states of heteronuclear alkali-metal dimers calculated at the equilibrium interatomic distances from Ref. [26].

Dimer	r_e/a_0 [26]	B/hc	μ	$\bar{\alpha}^{\mathrm{FF}}_{\mathrm{mol}}(0)$	$\bar{\alpha}^{\mathrm{TI}}_{\mathrm{mol}}(0)$	$\Delta\alpha^{\mathrm{FF}}_{\mathrm{mol}}(0)$	$\Delta\alpha^{\mathrm{TI}}_{\mathrm{mol}}(0)$
LiNa	5.4518	0.425	0.48	237.7	237.6	156.3	155.7
LiK	6.268	0.293	3.41	324.2	326.9	234.5	240.7
LiRb	6.5	0.254	3.99	347.2	352.1	262.0	272.7
LiCs	6.93	0.218	5.39	391.9	399.1	317.8	333.1
NaK	6.61	0.094	2.72	358.1	362.7	247.2	260.9
NaRb	6.88	0.070	3.31	387.1	393.9	279.2	299.7
NaCs	7.27	0.058	4.63	439.3	448.0	339.4	364.1
KRb	7.688	0.037	0.62	523.5	532.3	367.6	409.5
KCs	8.095	0.030	1.98	596.0	606.8	436.1	488.9
RbCs	8.366	0.017	1.32	638.6	653.0	462.1	531.1

are also in good agreement with our reference FF-CCSD(T) data (the FF-CCSD values are systematically higher by 10%). The fact that the triples contribution to the dipole moments is not too substantial indicates that the FF-CCSD(T) result might be very close to real values as the expansion of the molecular wave function in terms of number of excitations should converge rather quickly.

In order to verify the quality of the molecular dynamic dipole polarizabilities calculated with TI-CCSD we performed further tests by checking their values in the static limit against the polarizabilities calculated with the FF-CCSD(T) approach and literature data. As the reference values we have used those published by Deiglmayr *et al.* [27] who used a two-electron full configuration interaction method with carefully tailored large-core effective core potentials including core polarization potentials. This approach has proven to be accurate, for example, in predicting experimental values of the dipole moments of KRb [4], LiCs [40], and transition dipole moments RbCs [41]. We have also used for comparison the values of Urban and Sadlej [42], which were obtained with an entirely different approach—using all-electron basis sets with scalar relativistic effects included. Our finite-field results agree very well with the results from Refs. [27,42]; our FF-CCSD(T) values of the orientation-averaged molecular static dipole polarizability are systematically right in between their values with differences not exceeding 6%. The agreement between our TI-CCSD and FF-CCSD(T) values of the orientation-averaged molecular static dipole polarizability is even better (see Table I). With the exception of LiNa, where the difference is indeed negligible, the TI-CCSD values are systematically higher than the FF-CCSD(T) values with the differences never exceeding 2.5%. The anisotropy of the molecular static dipole polarizability $\Delta\alpha_{\mathrm{mol}}(0)$ exhibits the same tendency. With the exception of LiNa the TI-CCSD values are systematically higher than the FF-CCSD(T) values with the differences ranging from 2.5% to 13%.

In the evaluation of formulas (1) and (3) we used the TI-CCSD values of the molecular dynamic dipole polarizabilities, the FF-CCSD(T) values of the molecular dipole moments and molecular static dipole polarizabilities, and the values of the atomic static and dynamic polarizabilities from Ref. [36]. The integral in Eq. (1) was evaluated using Gauss quadrature for 50 frequencies also provided by Derevianko *et al.* [36].

Tables II and III contain the predicted isotropic van der Waals C_6 coefficients for the $A+AB$ and $AB+AB$ systems, respectively. In the case of the $A+AB$ systems there is a very clear progression in increase of the C_6 coefficient for both A and B from Li toward Cs. The induction contribution to C_6 is usually small; only in the case of significantly polar LiCs, LiRb, NaCs, and NaRb molecules it is within the range 10–23%. Our C_6 values for the K + KRb, Rb + KRb, Rb + RbCs, and Cs + RbCs systems are systematically larger than those reported by Kotochigova [24] by 8%, 6%, 35%, and 41%, respectively. The result for KRb + atom is clearly in good agreement with the result of Kotochigova, however,

TABLE II. The isotropic C_6 van der Waals coefficients (in atomic units) for the alkali-metal $A+AB$ systems. The last column shows the value based on the pairwise atom-atom additive model.

Atom	Dimer	C_6^{disp}	C_6^{ind}	C_6	C_6^{add}
Li	LiNa	2217	6	2223	2856
	LiK	2885	294	3179	3711
	LiRb	3098	407	3505	3934
	LiCs	3452	740	4192	4454
Na	LiNa	2358	6	2364	3023
	NaK	3405	187	3592	4003
	NaRb	3673	275	3948	4239
	NaCs	4092	539	4631	4783
K	LiK	4821	520	5341	6219
	NaK	5364	334	5698	6344
	KRb	7428	17	7445	8171
	KCs	8298	175	8473	9056
Rb	LiRb	5688	790	6478	7235
	NaRb	6357	539	6896	7373
	KRb	8154	19	8173	8964
	RbCs	9751	87	9838	10 353
Cs	LiCs	7652	1803	9455	9911
	NaCs	8555	1324	9879	10 073
	KCs	10 995	242	11 237	12 005
	RbCs	11 772	110	11 882	12 509

TABLE III. The isotropic C_6 van der Waals coefficients (in atomic units) for the alkali-metal $AB+AB$ systems.

Dimer	C_6^{disp}	C_6^{ind}	C_6^{rot}	C_6
LiNa	3582	17	110	3709
LiK	6024	1167	404 491	411 682
LiRb	6963	1711	876 031	884 705
LiCs	8670	3520	3 397 216	3 409 406
NaK	7461	820	508 325	516 606
NaRb	8696	1313	1 497 080	1 507 089
NaCs	10 822	2916	6 932 958	6 946 696
KRb	14 202	62	3456	17 720
KCs	17 716	723	450 681	469 120
RbCs	20 301	345	160 336	180 982

the difference for RbCs + atoms is significantly larger. The dynamic polarizability in Ref. [24] has been obtained as a sum-over state with appropriate transition dipole moments of the RbCs molecule. It is likely that this way the RbCs dynamic polarizability might have been underestimated using such a procedure by neglecting some contributions or underestimating the continuum contribution. Note also that the induction contribution for atom + diatom has not been included in Ref. [24].

It was proposed recently to approximate the C_6 coefficients by simply adding the pairwise atom-atom C_6 coefficients [24,43]. Our calculations have verified this model as seemingly reasonably good for heavy atoms (Cs and Rb) interacting with weakly polar molecules. This nice agreement is, however, fortuitous, since this additive approximation includes only dispersion and no induction. In this case, the approximation of the trimer dispersion forces by simply adding them among dimers overcompensates the lack of the induction interaction.

As expected, the effective isotropic C_6 coefficients for the $AB+AB$ systems very strongly depend on the AB dipole moment. Only the LiNa and KRb dimers with the smallest dipole moments are dominated by electronic contribution to the C_6 coefficient, in other cases rotational contribution completely dominates the total C_6 coefficient. For the $AB+AB$ systems, there is also a very distinct pattern in increase of the electronic contribution similar to the $A+AB$ systems. The KRb isotropic C_6 coefficient is higher by 10% compared to the value of Kotochigova [24] and by 6% with respect to the value given by Buchachenko and coworkers [32]. Our results are in agreement with those reported by Quéméner *et al.* [25] for the LiNa (difference of 4%), LiK (20%), LiRb (17%), and LiCs (11%) systems. These values are very sensitive to the dipole moment and rotational constant of the molecule, thus even small differences in these characteristics can easily translate into a 20% difference in the dominating rotational part of the C_6 coefficient.

Known C_6 coefficients allow us to determine the energy limits for single partial-wave scattering. The p-wave or d-wave scattering starts to dominate if the collision energy is comparable to the appropriate centrifugal barrier heights: For the $A+AB$ collisions it is the p wave, while for the bosonic $AB+AB$ collisions it is the d-wave scattering. In Table IV we have included the centrifugal barrier heights for the $A+AB$ scattering and bosonic $AB+AB$ scattering. Their values approximately determine the single partial-wave regime. The same table contains also the mean scattering lengths [44], which illustrate, in a sense, a characteristic length scale of the corresponding interaction potential.

TABLE IV. Heights (in μK) of p-wave centrifugal barriers V_{p} for the $A+AB$ systems and d-wave centrifugal barriers V_{d} for the $AB+AB$ systems, respectively, with mean scattering lengths $\bar{a}$ (in a_0) for the corresponding collisions.

Atom	Dimer	V_{p}	$\bar{a}$	Dimer	V_{d}	$\bar{a}$
Li	LiNa	2442	39	LiNa	2293	30
	LiK	1844	44	LiK	111	110
	LiRb	1581	46	LiRb	28	157
	LiCs	1397	48	LiCs	8	244
Na	LiNa	684	49			
	NaK	380	58	NaK	64	125
	NaRb	300	61	NaRb	16	187
	NaCs	256	65	NaCs	6	251
K	LiK	221	68			
	NaK	177	71			
	KRb	112	81	KRb	119	64
	KCs	95	85	KCs	15	155
Rb	LiRb	64	86			
	NaRb	56	89			
	KRb	47	95			
	RbCs	32	104	RbCs	17	131
Cs	LiCs	29	105			
	NaCs	26	108			
	KCs	23	112			
	RbCs	19	117			

IV. CONCLUSIONS

In conclusion, we have reported a complete *ab initio* study of the isotropic C_6 van der Waals coefficients in all possible $A+AB$ and $AB+AB$ systems, where A and B are two distinct alkali-metal atoms and AB are molecules in their ground state. Given the rapid development of the field and many ongoing experiments with polar alkali-metal molecules, we expect that these results will be beneficial for modeling their collisional properties, which are crucial for stability studies of the ultracold molecular dipolar gases in traps. In future studies we would like to pay increased attention to the role of anisotropy in ultracold collisions, and we would also like to exploit our results when constructing potential energy surfaces for various collisional systems.

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