Calculations of static dipole polarizabilities of alkali dimers.

Prospects for alignment of ultracold molecules.

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Abstract

The rapid development of experimental techniques to produce ultracold alkali molecules opens the ways to manipulate them and to control their dynamics using external electric fields. A prerequisite quantity for such studies is the knowledge of their static dipole polarizabilities. In this paper, we computed the variations with internuclear distance and with vibrational index of the static dipole polarizability components of all homonuclear alkali dimers including Fr\(_2\), and of all heteronuclear alkali dimers involving Li to Cs, in their electronic ground state and in their lowest triplet state. We use the same quantum chemistry approach than in our work on dipole moments (M. Aymar and O. Dulieu, J. Chem. Phys. 122, 204302 (2005)), based on pseudopotentials for atomic core representation, Gaussian basis sets, and effective potentials for core polarization. Polarizabilities are extracted from electronic energies using the finite-field method. For the heaviest species Rb\(_2\), Cs\(_2\) and Fr\(_2\) and for all heteronuclear alkali dimers, such results are presented for the first time. The accuracy of our results on atomic and molecular static dipole polarizabilities is discussed by comparing our values with the few available experimental data and elaborate calculations. We found that for all alkali pairs, the parallel and perpendicular components of the ground state polarizabilities at the equilibrium distance \(R_e\) scale as \((R_e)^3\), which can be related to a simple electrostatic model of an ellipsoidal charge distribution. Prospects for possible alignment and orientation effects with these molecules in forthcoming experiments are discussed.

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I. INTRODUCTION

The response of an atomic or molecular system to an external electric field is driven in many situations by its static electric polarizabilities which expresses the propensity of the electronic structure to be affected by the field [1]. In this respect, the static polarizability is sensitive to the details of the electronic wave function of the system, and yields a constraint for models aiming at evaluating it. The growing availability of samples of cold and ultracold molecules [2, 3] open new routes to manipulate their motion in the laboratory frame and control their dynamics using external electric fields. Spectacular achievements concern polar molecules, i.e. molecules with a permanent electric dipole moment: several species (CO, NO, NH, NH₃, OH, H₂CO...) have been slowed down to kinetic energy equivalent to a few millikelvins inside Stark decelerators [4, 5, 6], and subsequently trapped inside a storage ring (a ”molecular synchrotron” [7]). Slow ND₃ [8] and D₂O [9] molecules have been filtered out of a Maxwell-Boltzmann distribution and guided through an electrostatic quadrupole. In these arrangements, the response of the molecule to the external field is dominated by its permanent dipole moment, even if very high electric field values would be considered [10]. This effect is magnified when using a Rydberg atom or molecule, which possess a permanent dipole moment thousands times larger than the one for typical ground state molecules [11].

However, even non-polar species can be manipulated by strong electric fields produced by far-off resonant laser fields through the anisotropy of their static polarizability. Trapping in a quasi electrostatic laserfield has been experimentally demonstrated with cold Cs₂ molecules [12, 13, 14, 15], and cold collisions between Cs atoms and trapped Cs₂ molecules have been studied in such optical dipole traps [16, 17]. The deceleration and velocity bunching of a supersonic molecular beam using traveling optical lattices has been proposed for the iodine dimer [18], and first observed for CO molecules [19]. The interaction of molecules with strong polarized laser fields is also well-known for yielding the possibility to align the molecular axis along the electric field axis [20, 21, 22, 23], i.e. creating pendular states. In such situations, the fast-oscillating electric field averages its interaction with the permanent dipole moment of polar molecules to zero, so that only the quadratic interaction through the static polarizability persists. Recently, the combination of a strong electrostatic field and a non-resonant laser field has been proposed to enhance the orientation of polar molecules [24], and a first experimental evidence of this effect has been reported on the HXeI complex...
It is also worthwhile to mention the recent proposal for controlling ultracold polar molecules in an optical lattice combined with a suitable microwave field, relying on the dynamic polarizability of the molecule.

Such developments could clearly benefit from the accurate knowledge of the structure and properties of the concerned molecules. We started recently a new series accurate and systematic calculations of electronic properties of all alkali pairs, both homonuclear and heteronuclear, which are up to now systems of choice for ultracold molecules experiments. Our goal is to make available a complete treatment of these systems with the same accuracy for all combinations. For instance, we computed the permanent electric dipole moments of all heteronuclear species for which experimental data are still lacking for their ground state. We displayed their variation with the interatomic distance $R$, as well as with the vibrational level. Most of these results were not previously available. We also investigated the transition dipole moments for numerous transitions of NaK, NaRb, NaCs as only scattered results exist for the two latter species. We extended our calculations to the potential curves, and permanent and transition dipole moments of the francium diatomic compounds Fr$_2$, RbFr and CsFr which were determined for the first time, and we investigated the possibility of creating such diatomic compounds in an ultracold environment.

The present study deals with systematic calculations of static dipole polarizabilities of alkali atoms and dimers. Static dipole polarizabilities of ground state alkali atoms have been the subject of numerous calculations as it can be seen in the review by Teachout and Pack. Recently several systematic surveys of alkali atomic polarizabilities have been published. On the experimental side, Molof et al. have measured static dipole polarizabilities of all alkali atoms using a $E - H$ gradient balance technique, while other authors performed a similar study using an electric-field deflection method. Several measurements have been obtained with other methods like Stark-shift spectroscopy with lithium, atom interferometry with sodium and lithium.

Experimental results for alkali pairs are much scarcer than for the atoms. Most measurements have been achieved by deflecting a molecular beam inside an inhomogeneous electric field, for Li$_2$, Na$_2$, K$_2$, Rb$_2$, Cs$_2$, and NaLi, NaK, KCs, most often at different temperatures of the gaseous sample. Knight et al. reported a measurement for Na$_2$ and K$_2$ using a supersonic beam. As detailed later, various authors have computed the static dipole polarizabilities of homonuclear alkali dimers while results
on heteronuclear dimers are scarcer.

In this paper, we systematically calculate the static dipole polarizabilities of all alkali atoms including francium, of all homonuclear alkali dimers including Fr$_2$, and of heteronuclear alkali dimers, involving Li to Cs, in their ground and lowest triplet states. We use the same quantum chemistry approach as in our previous works \cite{28, 30}. The parallel and perpendicular components of the static dipole polarizabilities as functions of the internuclear distance $R$ are obtained with the finite-field method \cite{48}. We demonstrate that the polarizabilities at the equilibrium distance $R_e$ scale as $R_e^3$, so that all alkali dimers similarly behave as an ellipsoid charge distribution in an electric field. We analyze the accuracy of our calculations by comparing the average polarizabilities and their anisotropy with available experimental data and elaborate calculations. Finally, we discuss the possibility for the permanent alignment and the orientation of such ultracold molecules in strong optical and electrical fields. In the following we will use atomic units except otherwise stated.

II. COMPUTATIONAL METHOD

A detailed presentation of our approach for calculating electronic molecular structure of alkali dimers can be found in our previous papers \cite{28, 30}, and we only recall the main lines here. We set up an automated procedure based on the CIPSI package (Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively) \cite{49}. The approach is based on the $\ell$-dependent pseudopotentials of Durand and Barthelat \cite{50, 51} for atomic core representation, Gaussian basis sets, and effective potentials to account for core polarization (CPP) \cite{52, 53}. Molecular orbitals are determined by restricted Hartree-Fock single-electron calculations, yielding the potential curves for the relevant molecular cations. A full valence configuration interaction (CI) is then performed for each involved molecular symmetry, providing potential curves and permanent and transition dipole moments.

If the $z$ axis is chosen along the internuclear axis in a molecule-fixed reference frame $(x,y,z)$, they are two independent components of the molecular polarizability tensor, i.e., the parallel component $\alpha_{\parallel} \equiv \alpha_{zz}$ and the perpendicular one $\alpha_{\perp} \equiv \alpha_{xx} = \alpha_{yy}$. Two related quantities are usually defined: the average polarizability $\overline{\alpha} = (\alpha_{zz} + 2\alpha_{\perp})/3$ and the polarizability anisotropy $\gamma = \alpha_{\parallel} - \alpha_{\perp}$. Atomic and molecular static dipole polarizabilities have been calculated using finite-field method \cite{48} implemented in the quantum chemistry
approach above. For each molecular system we calculated the energies at fixed $R$ for several values of the external electric field ($1 \times 10^{-4}$ to $5 \times 10^{-4}$ a.u. depending on the molecule, with 1 a.u. = $5.142206281 \times 10^{11}$ V.m$^{-1}$) in the perturbative regime. We extracted the polarizability from their quadratic dependence against the electric field magnitude.

As for dipole moments, we checked the dependence of our results with the size of the basis set, using both basis sets labeled A and B in Ref. [28]. Figure I illustrates this influence on the $R$-dependence of $\alpha_{\parallel}$ for Cs$_2$ and LiCs ground state and lowest triplet state: the difference between the two calculations never exceeds 1%, which we will consider as non-significant for our present purpose (see also the discussion on atomic polarizabilities in the next section).

III. ATOMIC STATIC POLARIZABILITIES

As usual in molecular calculations, we checked the quality of the atomic representation yielded by our molecular basis with the computation of the static dipole polarizabilities for all alkali atoms (Li to Fr) with the finite-field method [48], and compared them in table II to various experimental determinations and various recent high-precision calculations. We first checked our values against the size of the basis set, using both basis sets labeled A and B in Ref. [28]. The differences in the obtained values never exceeded 1% when using basis A or B. For Li, K, Rb, and Cs atoms, our results for $\overline{\alpha}$ agree at the 1% level or better with the experimental central values of Molof et al. [36] obtained with a 10% error bar. Our value for Na is also in agreement at the same 1% level with the improved experimental value of Ekstrom et al. [41].

As shown in Table II, all available elaborate calculations agree with each other for the light species Li, Na, and K. This is mainly due to the weakness of the relativistic effects in these systems, whose magnitude can be evaluated through the work by Kellö et al. [54], who computed atomic polarizabilities in the framework of a complete active space self-consistent field (CASSCF) approach, where electron correlation and relativistic effects are included as perturbations up to the second-order. As expected, the relativistic contribution is hardly noticeable for K, while it cannot be omitted for the heavier species Rb, Cs, and Fr. This is probably the explanation of the discrepancy found for these atoms with the ECP approach used in Ref. [35], so-called model potential approach, which does not include explicitly such relativistic terms. In contrast, the present ECP’s include the effect of the mass-velocity and
Darwin terms, so that we obtain the same result than Ref. [54] for K, while this paper slightly overestimates the polarizabilities for Rb, Cs, and Fr. Let us note that as already predicted in the latter paper, the francium polarizability does not follow a monotonic increase along the series of alkali atoms due to relativistic effects: it is about 22% smaller than the cesium one. Let us note that we also found previously a manifestation of relativistic effects in the permanent dipole moment of FrCs compared to the RbCs one [30].

In contrast, our results are in very good agreement with those of Safronova et al. [33] and Derevianko et al. [32]. These authors used the relativistic single-double all-order (SD-AO) method combined with relativistic random-phase approximation (RRPA). In the latter paper, the authors claim that their theoretical values are in agreement but more accurate than the experimental ones of Ref. [36], as they introduced experimental values of energy levels and high-precision experimental values for dipole matrix elements of the principal transition in the computation of the polarizability. The uncertainty on their values is then directly related to the uncertainty of these experimental data. The difference with our values remains within a 1% to 2% range. One of the largest discrepancy is found for Cs, which could be due to the fact that we do not use relativistic atomic orbitals in our calculations, in contrast with francium for which we designed an averaged relativistic core pseudopotential [30]. Nevertheless, our results confirm that in alkali species, relativistic effects beyond mass-velocity and Darwin terms can be accounted for through an averaged effective core potential, which would be certainly relevant for Cs in further calculations. Using a relativistic coupled-cluster approach, Lim et al. [34] also claim that their values should be more accurate than the available experimental ones. However, their values are systematically larger (just like the relativistic values of Ref. [54] than ours and those of Ref. [32] (except for Li and Na), by 2% to 3% for K, by 2% for Rb, and by 5% for Cs and Fr.

To summarize, our atomic calculations seem to correctly account for relativistic effects when they are noticeable, and represent a satisfactory starting point for the computation of molecular polarizabilities.
|              | Li  | Na  | K   | Rb  | Cs  | Fr  |
|--------------|-----|-----|-----|-----|-----|-----|
| This work    | 164.4 | 164.1 | 294.3 | 318.1 | 406.1 | 316.6 |
| Miffre et al. [42] | (E) 164.2(1) |     |     |     |     |     |
| Ekstrom et al. [41] | (E) 162.7(8) |     |     |     |     |     |
| Molof et al. [36] | (E) 164(3) | 159(3) | 293(6) | 319(6) | 402(8) |     |
| Hall and Zorn [38] | (E) 165(11) | 305(22) | 329(23) | 427(31) |     |     |
| Derevianko et al. [32] | (T) 162.6(3) | 290.2(8) | 318.6(6) | 399.9(1.9) | 317.8(2.4) |     |
| Kellö et al. [54]a | (T) |     |     | 301.0 | 410.3 | 491.3 | 552.0 |
| Kellö et al. [54]b | (T) |     |     | 295.6 | 330.0 | 413.7 | 325.9 |
| Safronova et al. [33] | (T) 163.07 | 290.10 | 317.39 | 399.8 | 314.8 |     |
| Lim et al. [34] | (T) 163.74 | 164.89 | 301.28 | 324.24 | 432.71 | 330.70 |
| Magnier and Aubert-Frécon [35] | (T) 164 | 165 | 302 | 335 | 434 |     |

TABLE I: Static dipolar polarizabilities (in atomic units) of alkali atoms compared to available experimental (E) and recent theoretical (T) works. Both non-relativistic (a) and relativistic (b) values calculated by Kellö et al. [54] are displayed.

IV. STATIC POLARIZABILITY FUNCTIONS FOR HOMONUCLEAR ALKALI DIMERS

As we will see in section VI, most calculations of molecular static polarizabilities are restricted to their value at the equilibrium distance. In Figures 2 and 3 we display the variation of $\alpha_\parallel$ and $\alpha_\perp$ with the internuclear distance, respectively for the $X^1\Sigma_u^+$ ground state and for the lowest $a^3\Sigma_u^+$ triplet state of the homonuclear alkali dimers. The results for the heavy species Rb$_2$, Cs$_2$, and Fr$_2$ are presented for the first time, while to our knowledge, only one other theoretical determination was available for the ground state of the light species Li$_2$, Na$_2$, and K$_2$ [55], and for the lowest triplet state of Li$_2$, Na$_2$ [56], and K$_2$ [57].

The $R$-variation of $\alpha_\parallel$ and $\alpha_\perp$ are similar for all systems, and their magnitude increases with increasing mass, as expected when the electronic clouds become larger and larger. As seen above for the francium atom, the francium dimer polarizability is predicted with the same magnitude than the Rb$_2$ one, which is again a manifestation of the contraction of electronic orbitals due to relativistic effects. The parallel polarizabilities for the ground state
exhibits a maximum at a distance around 1.3 to 1.5 times the equilibrium distance $R_e$ of the dimers. In contrast the perpendicular components always have a smaller magnitude than $\alpha_{||}$, and monotonically increase towards the asymptotic limit. At large distances, the polarizability components converge toward twice the atomic values $\alpha_{at}$, and as already noted by Mérawa and Rérat [57], the parallel component varies two times faster than the perpendicular one and with an opposite variation. This is a well-known result of the asymptotic atom-atom picture, which yields $\alpha_{||} = 2\alpha_{at} + 4\alpha^2/R^3$ and $\alpha_{\perp} = 2\alpha_{at} - 2\alpha^2/R^3$.

The magnitude and variations of the polarizabilities for the triplet state are very similar to those of the ground state. However, the maximum in the parallel component occurs in the region of the repulsive wall of the triplet state, so that it monotonically decreases with increasing $R$ over the range of the triplet potential well.

In Figure 4a, we compare the present $R$-dependent polarizabilities to those computed with the finite-field method [48] by Müller and Meyer [55] for the Li$_2$, Na$_2$, and K$_2$ ground state, obtained by all-electron ab initio calculations which include complete valence self-consistent approach, configuration interaction, and core-polarization potentials to account for core-valence correlation [52]. Our functions for the Li$_2$, Na$_2$, and K$_2$ lowest triplet states are compared in Figure 4b to the determination of Refs. [56, 57], based on an asymptotic expression for static polarizabilities [58]. In both cases, the agreement among all these quite different approaches is very good, which is a convincing argument to assess the accuracy of our results for the heavier species.

V. STATIC POLARIZABILITIES FUNCTIONS FOR HETERONUCLEAR ALKALI DIMERS

The $R$-dependent static polarizabilities for all heteronuclear alkali pairs but NaLi (see Ref. [45, 59]) are computed here for the first time. Indeed, the main response of such systems to external electric fields is expected from their permanent dipole moments, on which most theoretical studies concentrated in the past (see for instance Ref. [28]). However, dipolar traps for ultracold atomic or molecular systems rely on the magnitude of static polarizabilities, while we already mentioned above the proposal by Friedrich and Herschbach [24] to manipulate polar or non-polar molecules with a combination of strong laser field and a weak static field, to enhance their orientation along the electric-field axis.
As it can be seen in Figures 5 and 6, the $R$-variation of the static polarizability components are similar to those for the homonuclear species: the same shift by a factor of 1.3 to 1.5 of the maxima of the parallel component compared to the equilibrium distance is visible for the ground state, while the maxima in the triplet state lies in the range of the repulsive wall of the triplet state. As expected, the pairs containing heavy species are more polarizable than those including light species. The RbCs ground state is then found with the highest parallel polarizability around the equilibrium distance, with the same magnitude than the one of KCs and LiCs. In contrast, for all other cases the hierarchy among the polarizabilities is governed by the ordering of the sum of atomic polarizabilities. As the atomic polarizability of lithium and sodium are almost equal and the smallest ones of the alkali atoms, pairs involving Li or Na, and another atom among K, Rb, or Cs, exhibit a polarizability magnitude quite close to each other, i.e., dominated by the polarizability of the heavy species inside the concerned pairs. We note that for each heteronuclear AB molecule the maximum value of $\alpha_{\parallel}$ is given with a good approximation by the averaged values of the corresponding homonuclear $A_2$ and $B_2$ species.

VI. STATIC POLARIZABILITIES AT THE MOLECULAR EQUILIBRIUM DISTANCE

In contrast with previous sections, much more work has been devoted to the computation of the static polarizabilities at the equilibrium distance of the alkali pairs, as it is the value which could be accessible for instance from deflection experiments of molecules in the lowest vibrational level of their ground state. In this respect, there is an interesting output of the present systematic study performed with comparable accuracy for all alkali pairs. It is well-known from classical electrostatics that the polarizability of a charge distribution is proportional to its volume. If we plot the ground state polarizabilities at the equilibrium distance $R_e$ of homonuclear alkali and heteronuclear alkali dimers as a function of $(R_e)^3$ (Figure 7), it is striking that all species are well aligned. A linear fit shows that the parallel component varies two times faster than the orthogonal component. As expected, the francium dimer deviates from this phenomenological law, due to its strong relativistic character.

Many authors already worked at designing models to relate the polarizability of atomic
and molecular systems to an effective volume. Politzer et al. \[60\] have shown that atomic polarizabilities are proportional to an atomic volume derived from the mean radii of Hartree-Fock outer-shell orbitals. For different types of molecules, Laidig and Bader \[61\] and Brinck et al. \[62\] have also found a proportionality between polarizabilities and molecular volume calculated within a self-consistent field approach. Specific studies performed on hydrocarbons molecules \[63\] or on sodium clusters \[64\] have found a linear correlation between the molecular polarizability and a characteristic volume. Other models have been elaborated in different contexts, based on the electrostatics of an ellipsoidal charge distribution like the jellium model \[65\]. For instance, Ambjörnsson and Apell \[66\] investigated the drift of ellipsoidal polarizable particles through a viscous fluid induced by an electric field gradient. Kornyushin \[67\] proposed a general model for dipole plasma oscillations in an ellipsoidal sample. Following the latter author, one can derive an expression for the polarizability components $\alpha_b$ and $\alpha_a$ along the principal axis of a symmetrical ellipsoid with a longitudinal radius $b$ and a transverse radius $a$:

$$
\alpha_\perp \equiv \alpha_a = (2a^2 + 1) \frac{V}{4\pi} \quad \alpha_\parallel \equiv \alpha_b = (b^2 + 2) \frac{V}{4\pi}
$$

where $V = \frac{4\pi}{3}ab^2$ is the volume of the ellipsoid. One immediately sees on this expression than the ratio of 2 between both components is obtained if $b = \sqrt{2}a$. It is not straightforward however to deduce an effective radius for each alkali pair from the fitting formula reported in Figure 7, as the lines do not go through the origin.

Various theoretical methods have been used to compute the two components of the static dipole polarizabilities of alkali dimers, and we recollected several of them in the following tables to compare with our present values. Generally, the extraction of static polarizabilities relies on two steps: the calculation of electronic structure, for which almost all available modern methods have been considered, and the extraction of the polarizability values themselves through a perturbative approach in most cases.

Bishop and Pouchan \[68\] have employed a pseudopotential treatment for core electrons and included core-valence correlation through a configuration interaction (CI) treatment. In a next paper, Bishop et al. \[69\] have performed all-electron self-consistent field (SCF) and CI calculations for electronic structure (just like in the work of Müller and Meyer \[55\]), and extracted the polarizability values via a charge perturbation approach, deduced from the energies of the system perturbed by a charge -1 located at $25a_0$ ($a_0 = 0.0529177$ nm) from
the center of the molecule. Spelsberg et al. extended the work of Ref. [55] by computing static polarizabilities for Li$_2$, Na$_2$, and K$_2$ at different levels of approximation in their full CI treatment [70]. Polarizabilities of Na$_2$ and Na$_3$ have been determined by Moullet et al. [71] using pseudopotential local-spin density (LSD) calculations. The CIPSI approach for molecular electronic structure has been combined with the time-dependent gauge invariant method (TDGI) by M´ erawa and Dargelos [72] to calculate static polarizabilities, dynamic polarizabilities and Van der Waals coefficients Li, Na, Li$_2$ Na$_2$ and NaLi, while Antoine et al. [45] used Density Functional Theory (DFT) and CI for the same purpose. An SCF and many-body perturbation theory (MBPT) treatment, combined with finite-field method has been used by Maroulis [73, 74] for Li$_2$ and Na$_2$ molecules. Urban and Sadlej [75] combined the MBPT and coupled-cluster (CC) theories at different levels of approximation and finite-field perturbation to determine static polarizabilities of homonuclear and heteronuclear dimers not involving the Cs atom. More recently, newly adjusted energy-consistent nine-valence-electron scalar pseudopotentials including effective CPP [52] have been developed by Lim et al. [76] to investigate the properties of alkali dimers from K$_2$ to Fr$_2$. Calculation of spectroscopic properties including static dipole polarizabilities have been done using various models based on CC and DFT theories, combined with finite-field method.

Table II compares our values for the two components $\alpha_{\parallel}$ and $\alpha_{\perp}$, and for the average polarizability $\bar{\alpha}$ and its anisotropy $\gamma$ taken either at the experimental equilibrium distance (when available) or at the computed one [28] of each pair, with the previous theoretical determinations quoted above, in the case of the ground state homonuclear alkali dimers. Due to the amount of papers already published on Li$_2$, we quote only the most recent data, and the interested reader could find a more complete compilation of older works in Ref. [55]. The above-quoted authors often reported several polarizability values obtained within various approximations, and we only display in Table II the value corresponding to their most elaborate model.

|        | $R_e$ ($a_0$) | $\alpha_{\parallel}$ | $\alpha_{\perp}$ | $\bar{\alpha}$ | $\gamma$ |
|-------|-------------|------------------|-----------------|----------------|---------|
| Li$_2$(X$^1\Sigma^+_g$) | This work | 5.051 [77] | 305.2 | 162.4 | 210.0 | 142.8 |
|       | Bishop and Pouchan [68] | 5.051 [77] | 357 | 140 | 213.3 | 217 |
|       | Bishop et al. [69] | 5.051 [77] | 324 | 173 | 223.0 | 151 |
|       | M¨ uller and Meyer [55] | 5.051 [77] | 301.8 | 169.9 | 213.8 | 131.9 |
| Molecule     | Authors          | Polarizability (a.u.) | Distance (Å) | Angle (°) | Value (°) |
|--------------|------------------|-----------------------|--------------|-----------|-----------|
| Na$_2$(X$^1\Sigma_g^+$) | This work        | 5.818 [79]            | 378.5        | 199.6     | 259.2     |
|              | Müller and Meyer | 5.818 [79]            | 375.5        | 197.2     | 256.6     |
|              | Moullet et al.   | 5.818 [79]            | 318.5        | 199.73    | 259.1     |
|              | Maroulis         | 5.818 [79]            | 377.7        | 206.6     | 263.3     |
|              | Urban and Sadlej | 5.818 [79]            | 386.9        | 209.7     | 268.7     |
|              | Mérawa and Dargelos | 5.818 [79]     | 375.3        | 208.2     | 263.9     |
|              | Antoine et al.   | 5.84 [79]             | 360.4        | 207.8     | 258.7     |
| K$_2$(X$^1\Sigma_g^+$) | This work        | 7.416 [80]            | 708.2        | 359.6     | 475.8     |
|              | Müller and Meyer | 7.379 [52]            | 691.8        | 348.0     | 462.6     |
|              | Urban and Sadlej | 7.379 [52]            | 753.6        | 376.2     | 502.0     |
|              | Lim et al.       | 7.408 [81]            | 712.2        | 374.0     | 486.7     |
|              | Spelsberg et al. | 7.379 [52]            | 677.8        | 363.3     | 468.1     |
| Rb$_2$(X$^1\Sigma_g^+$) | This work        | 7.956 [82]            | 789.7        | 405.5     | 533.5     |
|              | Urban and Sadlej | 8.1225 [75]           | 916.1        | 445.4     | 602.3     |
|              | Lim et al.       | 7.90 [83]             | 815.2        | 419.9     | 551.6     |
| Cs$_2$(X$^1\Sigma_g^+$) | This work        | 8.78 [84]             | 1012.2       | 509.0     | 676.7     |
|              | Lim et al.       | 8.77                  | 1073.7       | 536.9     | 715.8     |
| Fr$_2$(X$^1\Sigma_g^+$) | This work        | 8.45 [30]             | 844.8        | 405.9     | 552.2     |
|              | This work        | 8.6795 [76]           | 881          | 408.4     | 603.7     |
|              | Lim et al.       | 8.6795 [76]           | 848.2        | 408.4     | 603.7     |

TABLE II: Present polarizability values (in a.u.) for the ground state of homonuclear alkali dimers, taken at the experimental equilibrium distance (except for Fr$_2$), and compared to available theoretical works. For the latter, the distance at which the polarizabilities are calculated is also displayed, when available.
One immediately sees in Table II the broad dispersion of the reported values, which can be understood by looking again at Figure 2. The equilibrium distance is located in the steep part of the polarizability functions, so that any small difference between the electronic wave functions yielded by the various methods will result in a large variation of the polarizability components, which will be even enhanced for the average polarizability and the anisotropy.

For the lighter species Li$_2$ and Na$_2$, our values for $\alpha_{\parallel}$ and $\alpha_{\perp}$ agree well with those of Müller and Meyer [55] and of Urban and Sadlej [75], as well as with the other recent determinations. However, for K$_2$, the value of Ref. [75] seems to be overestimated by about 7%, and by about 16% for Rb$_2$. The values of Lim et al. [76] are also slightly larger than ours by about 3% and 6% for Rb$_2$ and Cs$_2$ respectively, while the situation in Fr$_2$ is less clear as equilibrium distances differ significantly between Ref. [76] and the present ones. However the differences observed among the average polarizabilities stay within a 10% range representative of the typical uncertainty of the experimental values. As we will see in the next section, only the polarizability values integrated over the wave function of the lowest vibrational level of the ground state can be directly compared to the experiment, which may help to discriminate among theoretical determinations. Only few results have been published for the lowest triplet state (Table III), and our values agree well with them, within a few percent range.

| Species | $R_e$ ($a_0$) | $\alpha_{\parallel}$ | $\alpha_{\perp}$ | $\alpha_{\gamma}$ |
|---------|---------------|----------------------|------------------|------------------|
| Li$_2$(a$^3\Sigma_u^+$) | 7.88 [85] | 700.3 | 252.2 | 401.6 | 448.2 |
| | This work | | | | |
| | Mérawa and Rérat [78] | 7.88 [85] | 698 | 252 | 401 | 446 |
| | Rérat and Bussery-Honvault [56] | 7.88 [85] | 695.8 | 253.1 | 400.7 | 442.7 |
| Na$_2$(a$^3\Sigma_u^+$) | 9.62 [86] | 495.0 | 278.2 | 350.4 | 216.9 |
| | This work | | | | |
| | Rérat and Bussery-Honvault [56] | 9.62 [86] | 487.7 | 276.9 | 347.2 | 210.7 |
| K$_2$(a$^3\Sigma_u^+$) | 10.9 [87] | 956.4 | 477.3 | 637.0 | 479.1 |
| | This work | | | | |
| | Mérawa et al. [57] | 10.9 [87] | 953.8 | 476.8 | 635.8 | 477.0 |
| Rb$_2$(a$^3\Sigma_u^+$) | 11.4 [30] | 1016.4 | 508.0 | 677.5 | 508.4 |
| | This work | | | | |
| Cs$_2$(a$^3\Sigma_u^+$) | 11.9 [88] | 1322.8 | 641.2 | 868.4 | 681.5 |

TABLE III: Same as Table II for the lowest triplet state of Li$_2$, Na$_2$, K$_2$, Rb$_2$ and Cs$_2$.

Similarly, we set up a table for polarizabilities of the ground state of heteronuclear alkali pairs (Table IV), for which very few other theoretical values are available (except for LiNa):
Urban and Sadlej [75] considered the six molecules LiNa, LiK, LiRb, NaK, NaRb, and KRb, in their coupled-cluster approach, while Tarnovsky et al [44] proposed an estimate of the average polarizability $\overline{\alpha}$ based on their measurements of polarizabilities for homonuclear species (see next section). All determinations are consistent for the lightest species LiNa, while the values of Urban and Sadlej [75] are significantly larger than ours for the heavy species LiRb, NaRb, and KRb.

|      | $R_e$ ($a_0$) | $\alpha_\parallel$ | $\alpha_\perp$ | $\overline{\alpha}$ | $\gamma$ |
|------|--------------|-------------------|----------------|---------------------|---------|
| LiNa | This work    | 5.4518 [89]       | 347.6          | 181.8               | 237.0   | 165.8   |
|      | Urban and Sadlej [75] | 5.4518 [89]       | 352.1          | 188.8               | 243.2   | 163.2   |
|      | Mérawa and Dargelos [72] | 5.4518 [89]       | 351.7          | 191.5               | 249.9   | 160.2   |
|      | Mérawa et al. [59] | 5.4518 [89]       | 350.6          | 187.7               | 242.0   | 162.9   |
|      | Antoine et al. [45] | 5.4518 [89]       | 352.2          | 188.9               | 234.4   | 163.3   |
| LiK  | This work    | 6.268 [90]        | 489.7          | 236.2               | 320.7   | 253.5   |
|      | Urban and Sadlej [75] | 6.268 [90]        | 484.8          | 246.6               | 326.0   | 238.2   |
| LiRb | This work    | 6.5 [28]          | 524.3          | 246.5               | 339.1   | 277.8   |
|      | Urban and Sadlej [75] | 6.609            | 558.2          | 268.7               | 365.2   | 289.5   |
| LiCs | This work    | 6.93 [91]         | 597.0          | 262.5               | 374.0   | 334.5   |
| NaK  | This work    | 6.61 [92]         | 529.2          | 262.3               | 351.3   | 266.9   |
|      | Urban and Sadlej [75] | 6.61 [92]         | 537.5          | 279.6               | 365.5   | 257.9   |
| NaRb | This work    | 6.88 [93]         | 572.0          | 280.3               | 377.5   | 291.7   |
|      | Urban and Sadlej [75] | 6.967            | 606.3          | 303.2               | 404.2   | 303.1   |
| NaCs | This work    | 7.27 [94]         | 670.7          | 304.2               | 426.4   | 366.5   |
| KRb  | This work    | 7.688 [95]        | 748.70         | 382.9               | 504.8   | 365.8   |
|      | Urban and Sadlej [75] | 7.786            | 842.4          | 411.5               | 555.1   | 430.9   |
| KCs  | This work    | 8.095 [96]        | 822.3          | 425.62              | 571.1   | 436.7   |
| RbCs | This work    | 8.366 [97]        | 904.0          | 492.3               | 602.8   | 491.7   |

TABLE IV: Present polarizability values (in a.u.) for the ground state of heteronuclear alkali dimers, taken at the experimental (when available) or the theoretical (from Ref. [28]) equilibrium distances, and compared to other published theoretical results.
VII. AVERAGE POLARIZABILITIES AND THEIR ANISOTROPY FOR MOLECULAR VIBRATIONAL LEVELS

In most experiments the only accessible physical quantity is the average polarizability of the molecule measured for a given vibrational level, while the alignment properties is controlled by the anisotropy of the polarizability. We determine these quantities by averaging their $R$-dependence over the vibrational wave functions $|v\rangle$ of the electronic ground state and of the lowest triplet state of the molecules, i.e.: $\beta_v \equiv \langle v | \beta(R) | v \rangle$, where $\beta$ is one of the quantities $\alpha_{\parallel}, \alpha_{\perp}, \alpha, \gamma$. Thus we assumed that the the vibrational motion is not distorted by the polarization of the molecule, following the discussion of ref. [98]. In any case, the potential curves computed with a non-zero electric field are always found very close to the field-free ones.

Figure 8 summarizes the dependence of these quantities for the two lowest electronic states of all pairs with the vibrational level, while we extracted in Table V the main relevant features of these variations. As expected from their monotonic $R$-dependence, the average polarizability of the lowest triplet states is slowly decreasing down to the sum of atomic values with increasing vibrational index, while the anisotropy monotonically drops to zero. In contrast both quantities exhibit a maximum for a quite high vibrational level of the electronic ground state, due to the combined influence of the previously mentioned difference between the equilibrium distance and the position of the maximum value of the parallel component, and of the increase of the perpendicular component with the distance.

From the previous section, it is not obvious to discriminate among the various theoretical determinations, and we examine here if the reported experimental works can help for this purpose. Only few experimental works reported values for the average polarizability of alkali dimers. Molof et al. [43] and Tarnovsky et al. [44] measured the deflection of a thermal molecular beam of alkali dimers in an inhomogeneous electric field, and both investigated the series of homonuclear species from Li$_2$ to Cs$_2$. In addition, Tarnovsky et al. [44] also studied the NaK and KCs systems, and extracted an average static polarizability from their measurement by subtracting the effect of the permanent dipole moment as calculated in Ref. [99]. Using the same technique in their cluster experiment, Antoine et al. reported average polarizabilities for Na$_2$, Li$_2$ and NaLi form a thermal molecular beam. The drawback of using a thermal beam is that the deduced values depends on the temperature of the
TABLE V: Average polarizabilities and anisotropies computed in the present work for the singlet ground state and lowest triplet states of all alkali pairs. Values are listed for the lowest vibrational level (ν = 0), and for the level where the maximum value is reached for the ground state.

| molecule | Singlet ground state | Lowest triplet state |
|----------|----------------------|----------------------|
|          | α|v|=0 | γ|v|=0 | α|v|=max | γ|v|=max | α|v|=0 | γ|v|=0 |
| Li₂      | 226.8 | 169.6 | 359.0 | 23 | 339.2 | 16 | 399.4 | 438.6 |
| Na₂      | 259.7 | 179.5 | 357.5 | 40 | 299.3 | 28 | 347.9 | 200.7 |
| K₂       | 473.0 | 343.7 | 601.2 | 61 | 496.4 | 43 | 636.6 | 476.4 |
| Rb₂      | 530.6 | 378.8 | 656.1 | 88 | 526.2 | 63 | 685.5 | 493.5 |
| Cs₂      | 670.3 | 490.8 | 819.2 | 110 | 677.1 | 79 | 865.4 | 667.6 |
| LiNa     | 236.5 | 166.6 | 339.2 | 37 | 286.3 | 27 | 365.0 | 288.6 |
| LiK      | 318.7 | 250.3 | 474.2 | 38 | 451.5 | 29 | 514.6 | 442.5 |
| LiRb     | 340.4 | 280.4 | 504.5 | 39 | 499.3 | 30 | 535.5 | 429.0 |
| LiCs     | 368.8 | 326.7 | 594.2 | 42 | 654.9 | 33 | 631.0 | 533.7 |
| NaK      | 352.3 | 261.4 | 472.1 | 54 | 407.1 | 38 | 485.8 | 303.5 |
| NaRb     | 375.6 | 288.2 | 501.5 | 61 | 443.1 | 44 | 510.1 | 310.1 |
| NaCs     | 421.9 | 359.4 | 584.1 | 64 | 567.0 | 46 | 589.7 | 351.3 |
| KRb      | 502.0 | 360.3 | 629.1 | 71 | 511.2 | 51 | 661.5 | 484.6 |
| KCs      | 566.0 | 426.7 | 712.0 | 76 | 609.3 | 54 | 749.2 | 564.3 |
| RbCs     | 597.6 | 440.9 | 737.3 | 74 | 609.4 | 53 | 773.2 | 567.5 |

beam, i.e. of the population of vibrational levels above the lowest one. In contrast in their experiment on sodium and potassium clusters, Knight et al. [47] reported on the deflection of a supersonic molecular beam, in which dimers can safely be considered as being in the ν = 0 level (i.e. at T = 0 K). All these values are measured with a typical 10% error bar, and they are compiled in Tables VII and VIII, together with the present computed average polarizabilities for the ν = 0 level of the ground state of all alkali pairs. First we note that the values of Knight et al. [47] agree well with those of Tarnovsky et al. [44] extrapolated to T = 0 K for Li₂, Na₂ and K₂, which then validates the procedure proposed in Ref. [99]. Tarnovsky et al. suggested that the low values of Molof et al. may be due to deviation from the thermodynamic equilibrium between monomers and dimers in the latter work.
Even if no values extrapolated to $T = 0$ K were available for Rb$_2$ and Cs$_2$, our results still lie within the somewhat large error bars obtained in the thermal beam of Ref. [44]. This can be understood from the previous figures as the polarizability smoothly increases for the lowest vibrational levels. The same conclusion holds for the NaK and KCs values measured by the same authors, while the two measured values for LiNa are significantly larger than our prediction. All the other values for Rb$_2$ and Cs$_2$ and for the heteronuclear species displayed in Ref. [44] are obtained from an empirical rules involving polarizabilities of homonuclear species and permanent dipole moments of heteronuclear pairs known at the time of that work. Their validity is difficult to estimate. However, as we performed a systematic investigation of all alkali pairs with similar numerical conditions, we think that such an empirical rules generally overestimates the average polarizabilities, even if our values stay within the estimated uncertainty, apart from LiK, LiRb, and LiCs. In conclusion, the present study show that more experimental work would be needed, for instance using supersonic beams of alkali pairs, if they were available.

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & Li$_2$ & Na$_2$ & K$_2$ & Rb$_2$ & Cs$_2$ \\ \hline
$\bar{\alpha}|_{v=0}$ & 226.8 & 259.7 & 473 & 530.6 & 670.3 \\ \hline
[44](a) & 229±20 (948 K) & 270±20 (676 K) & 519±41 (542 K) & 533±41 (527 K) & 701±54 (480 K) \\ \hline
[44](b) & 216±20 (0 K) & 256±20 (0 K) & 499±41 (0 K) & 553±41 (est.) & 675±54 (est.) \\ \hline
[43] & 229±20 (990 K) & 202±20 (736 K) & 411±34 (569 K) & 459±34 (534 K) & 614±54 \\ \hline
[47] & 221±10 (1100 K) & 269±10 (1100 K) \\ \hline
\end{tabular}
\end{center}
\caption{Present average polarizability $\bar{\alpha}|_{v=0}$ (in a.u.) for the ground state of homonuclear alkali dimers, computed for their $v = 0$ level. The values for $\bar{\alpha}$ are compared to the experimental measurements of Ref. [43, 47] and Ref. [44] (row (a)) at various temperatures of their thermal beam, and extrapolated to $T = 0$ K following Ref. [55] and Ref. [44] (row (b)), i.e. for the $v = 0$ level. In this respect, the supersonic beam used by Knight et al. [47] is considered to be at $T = 0$ K.}
\end{table}
TABLE VII: Present average polarizability $\alpha|_{v=0}$ (in a.u.) ground state of heteronuclear alkali dimers, computed for their $v = 0$ level. As for the homonuclears we report the experimental values for NaK and KCs, as well as the estimates for all the heteronuclear species from Ref. [44] (see text and Table VI) and the experimental value of Ref. [45] for NaLi.

VIII. CONCLUSION: PROSPECTS FOR ALIGNMENT OF ALKALI DIMERS BY EXTERNAL ELECTRIC FIELDS

The accurate knowledge of the electric properties of alkali pairs is particularly relevant in the context of recent developments of researches in cold molecules. Several authors have recently addressed the possibility to observe peculiar properties of ultracold gases of dipolar molecules if they could be partially aligned or oriented in the presence of external fields [100, 101] to enhance their mutual interaction. Studies of pendular states using intense laser pulses usually involve light molecules with static polarizabilities and anisotropies quite small compared to those of the mixed alkali pairs. In this context, it is worthwhile to revisit the idea proposed by Friedrich and Herschbach [24, 102, 103] for aligning polar molecules by combining an intense laser field and an external electric field. The interactions between the molecule and the external fields can be characterized by two dimensionless parameters $\omega_{or}$ for orientation and $\Delta \omega_{al}$ for alignment:

$$\omega_{or} = \frac{\mu \varepsilon S}{B_v}, \quad \Delta \omega_{al} = \frac{\gamma I_e}{2B_v}$$

They are related respectively to the interaction potential of the molecule with perma-
nent dipole moment $\mu$, anisotropy $\gamma$, and rotational constant $B_v$ in a vibrational level $v$ with an external static electric field of amplitude $\varepsilon_S$, and with a laser field of intensity $I_L$. The values of these orientation and alignment parameters can be conveniently evaluated with practical units according to:

$$\omega_{or} = 0.0168\mu(\text{Debye})\varepsilon_S(\text{kV/cm})/B(\text{cm}^{-1}),$$

and

$$\Delta\omega_{al} = 10^{-11}\gamma(\text{Å})I_L(\text{W/cm}^{-2})/B(\text{cm}^{-1}).$$

The pendular hybridization of (polar) molecules by only a static electric field or only a laser field would require values of these parameters considerably larger than 1 in order to couple several rotational states (see also [10]). Especially for the orientation of ultracold heteronuclear molecules produced in a current laser cooling experiment, the application of large static electric fields is often incompatible with other experimental requirements such as good optical access to the sample and the fast switching of high magnetic fields.

Friedrich and Herschbach suggested that the combination of static and laser fields would result in a double hybridization of the polar molecules. By plotting electronic wave functions in polar coordinates, the authors showed that an almost perfect orientation of a $^1\Sigma$ molecule in the rotational ground state can already be achieved with typical values of $\omega_{or} = 1$ and $\Delta\omega_{al} = 20$.

We display in tables VIII and IX the required amplitudes of the fields yielding $\omega_{or} = 1$ $\Delta\omega_{al} = 1$ for all alkali pairs, which can easily be scaled to any field strength depending on the considered experimental arrangement. Friedrich and Herschbach [102] displayed such a table for typical values of static fields and laser pulses intensities, for a series of linear polar molecules like alkali halides or molecules of atmospheric relevance.

The alignment of molecules in pulsed laser fields with typical intensities of $10^{12}\text{W/cm}^2$ on timescales of nanoseconds is an established technique [104]. Alkali dimer ground states combine large anisotropies, which reduce the required intensities for alignment, with large permanent dipole moments, which make permanent orientation of molecules in combined continuous fields possible. In the following we will describe the experimental parameters for the permanent orientation of these molecules, using RbCs as an example. RbCs has a favorable ratio of anisotropy to rotational constant and has already been produced at ultracold temperatures in the absolute ground state $X^1\Sigma^+ v=0$, using photoassociation followed by a laser-stimulated state transfer process [105]. As mentioned above, in order to reach nearly perfect orientation of the molecule the interactions with the external fields have to reach at least $\omega_{or} = 1$ and $\Delta\omega_{al} = 20$. According to table VIII, $\omega_{or} = 1$ is already reached for a static
|   | $v_0$ | $γ$ (a.u.) | $B_v \times 10^{-2}$cm$^{-1}$ | $I_{al} \times 10^8$W/cm$^2$ | $d_v$ (Debye) | $E_{or}$ (kV/cm) |
|---|---|---|---|---|---|---|
| RbCs | 0 | 441 | 2.90 | 0.44 | -1.237 | 1.4 |
| KCs | 0 | 427 | 3.10 | 0.49 | -1.906 | 1.0 |
| KRb | 0 | 360 | 3.86 | 0.72 | -0.615 | 3.7 |
| NaCs | 0 | 359 | 5.93 | 1.1 | -4.607 | 0.8 |
| NaRb | 0 | 288 | 7.11 | 1.7 | -3.306 | 1.3 |
| NaK | 0 | 261 | 9.62 | 2.5 | -2.579 | 2.2 |
| LiCs | 0 | 327 | 19.4 | 4.0 | -5.523 | 2.1 |
| LiRb | 0 | 280 | 22.0 | 5.3 | -4.165 | 3.1 |
| LiK | 0 | 250 | 26.1 | 7.1 | -3.565 | 4.4 |
| LiNa | 0 | 167 | 38.0 | 15 | -0.566 | 39.9 |
| RbCs | 77 | 488 | 1.65 | 0.23 | -0.906 | 1.1 |
| KCs | 78 | 483 | 1.71 | 0.24 | -0.843 | 1.2 |
| KRb | 73 | 400 | 2.07 | 0.35 | -0.257 | 4.8 |
| NaCs | 63 | 483 | 3.46 | 0.48 | -2.375 | 0.9 |
| NaRb | 61 | 355 | 3.82 | 0.73 | -1.558 | 1.5 |
| NaK | 55 | 321 | 4.98 | 1.0 | -1.254 | 2.4 |
| LiCs | 41 | 565 | 10.8 | 1.3 | -3.051 | 2.1 |
| LiRb | 39 | 415 | 11.8 | 1.9 | -1.947 | 3.6 |
| LiK | 39 | 352 | 12.7 | 2.4 | -1.205 | 6.3 |
| LiNa | 38 | 211 | 16.4 | 5.3 | -0.026 | 374.9 |

**TABLE VIII:** Summary of the properties (anisotropy $γ$, rotational constant $B_v$, permanent dipole moment $d_v$) of mixed alkali pairs relevant for their orientation and alignment induced by external fields, for the lowest vibrational level of their $X^1Σ^+$ ground state. The values for the laser intensity $I_{al}$ of a cw laser field, and for an external static electric field $E_{or}$ correspond to $Δ\omega_{al} = 1$ and $\omega_{or} = 1$ respectively (see text). We also report such properties for the vibrational level with maximal computed anisotropy.
electric field of 1.4 kV/cm which can be easily realized by a set of largely spaced electrodes, therefore not reducing the optical access to the sample. In order to reach $\Delta \omega_{al} = 20$, a laser intensity of roughly $10^9$ W/cm$^2$ is necessary. Such intensities can be reached continuously in a resonator-enhanced dipole trap [106]. Here, Mosk and co-workers have coupled a 1.2 W Nd:YAG laser beam into an actively stabilized confocal resonator. The intensity in the anti-nodes of the standing wave inside the resonator is then given by

$$I_0 = 4 \times A \times \frac{2P_L}{\pi\omega_0^2}$$

(3)

where the factor 4 is due to the coherent addition of fields in a standing wave, $A$ is the power enhancement factor of the resonator, $P_L$ the laser power coupled into the cavity and $\omega_0$ the waist in the focus of the cavity. In Ref. [106] a power-enhancement of nearly $A=150$ was reported. Using such a setup with currently available laser powers of the order of 100 W, the required intensity of $10^9$ W/cm$^2$ is reached at a realistic focus size of $\sim 60\mu$m. Additionally to the alignment of the molecules, the anti-nodes of the standing wave would also trap the molecules via the interaction with the average polarizability $\bar{\alpha}$ [107]. This leads to the formation of a stack of pancake-shaped, individually aligned ensembles at distances of $\lambda/2$ where $\lambda$ is the wavelength of the alignment laser.

Even the lowest triplet states of alkali dimers appear to be good candidates for such a combined arrangement, despite their very low dipole moment. In ultracold LiCs [108] for example, values like $\omega_{al} = 10$ and $\omega_{or} = 0.1$ seem within reach.

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|               | $\gamma$ (a.u.) | $B_v$ ($\times 10^{-2}$ cm$^{-1}$) | $I_{ul}$ ($\times 10^8$ W/cm$^2$) | $d_v$ (Debye) | $E_{op}$ (kV/cm) |
|---------------|----------------|-----------------------------------|-------------------------------|--------------|-----------------|
| RbCs          | 568            | 1.46                              | 0.17                          | 0.0003       | -2887.9         |
| KCs           | 564            | 1.53                              | 0.18                          | -0.013       | 69.9            |
| KRb           | 485            | 1.81                              | 0.25                          | -0.011       | 98.1            |
| NaCs          | 351            | 2.60                              | 0.50                          | 0.005        | -309.3          |
| NaK           | 303            | 3.87                              | 0.86                          | 0.008        | -287.6          |
| NaRb          | 310            | 2.97                              | 0.65                          | -0.002       | 883.2           |
| LiCs          | 534            | 9.27                              | 1.2                           | -0.145       | 38.1            |
| LiRb          | 429            | 9.72                              | 1.5                           | -0.123       | 47.1            |
| LiK           | 443            | 11.5                              | 1.8                           | -0.113       | 60.6            |
| LiNa          | 289            | 14.1                              | 3.3                           | -0.068       | 123.6           |

TABLE IX: Same as Table VIII for the lowest $a^3\Sigma^+$ triplet state, all $v=0$.

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FIG. 1: (Color on line) Parallel static dipole polarizability (1 a.u. = 0.1481847093 Å$^3$) of the $X^1\Sigma^+_g^+$ ground state and of the lowest $a^3\Sigma_u^+$ triplet state of Cs$_2$ (resp. crosses and plus symbols) and LiCs (resp. closed circles and open circles) as computed with our quantum chemistry approach using basis set A (full lines) or basis set B (dashed lines) of Ref. 28 (of Ref. 30 for Cs).
FIG. 2: (Color on line) Parallel (full lines) and perpendicular (dashed lines) static dipole polarizability functions for the $X^1\Sigma^+_g$ ground state of homonuclear alkali dimers, as computed in the present work. Experimental equilibrium distances are also indicated for further discussion in the text.
FIG. 3: (Color on line) Parallel (full lines) and perpendicular (dashed lines) static dipole polarizability functions for the lowest $a^3\Sigma_u^+$ triplet state of homonuclear alkali dimers, as computed in the present work.
FIG. 4: (Color on line) Comparison of the present $\alpha_{\parallel}(R)$ (full lines) and $\alpha_{\perp}(R)$(dashed lines) functions of Li$_2$, Na$_2$ and K$_2$ (a) with those of Müller and Meyer [55] for the ground state (symbols), and (b) with those of Rérat and Bussery-Honvault [56, 57] for the lowest triplet state (symbols). Crosses, closed circles, and plus signs hold for Li$_2$, Na$_2$, and K$_2$ respectively.
FIG. 5: (Color on line) Parallel (upper panel) and perpendicular (lower panel) static dipole polarizability functions for the $X^1\Sigma^+$ ground state of heteronuclear alkali dimers, as computed in the present work.
FIG. 6: (Color on line) Parallel (upper panel) and perpendicular (lower panel) static dipole polarizability functions for the lowest $a^3\Sigma^+$ triplet state of heteronuclear alkali dimers, as computed in the present work.
FIG. 7: (Color on line) Parallel (full circles) and perpendicular (open circles) static dipole polarizabilities as functions of $V_e = 4\pi R^3_e/3$, where $R_e$ is the equilibrium distance of the ground state of every alkali pair. The straight lines show a linear fit of this variation excluding Fr$_2$ values, corresponding to the formula (in atomic units): $\alpha_\parallel = 0.31V_e + 153.5$ (dashed line) and $\alpha_\perp = 0.16V_e + 71.2$ (full line).
FIG. 8: (Color on line) Dependence of average polarizabilities and anisotropies as functions of vibrational levels: (a)-(d) for the singlet ground state, (e),(f) for the lowest triplet state.