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Calculation of accurate permanent dipole moments of the lowest $1,3\Sigma^+$ states of heteronuclear alkali dimers using extended basis sets

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Abstract

Obtaining ultracold samples of dipolar molecules is a current challenge which requires an accurate knowledge of their electronic properties to guide the ongoing experiments. In this paper, we systematically investigate the ground state and the lowest triplet state of mixed alkali dimers (involving Li, Na, K, Rb, Cs) using a standard quantum chemistry approach based on pseudopotentials for atomic core representation, gaussian basis sets, and effective terms for core polarization effects. We emphasize on the convergence of the results for permanent dipole moments regarding the size of the gaussian basis set, and we discuss their predicted accuracy by comparing to other theoretical calculations or available experimental values. We also revisit the difficulty to compare computed potential curves among published papers, due to the differences in the modelization of core-core interaction.

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I. INTRODUCTION

Researches on ultracold molecules are progressing very fast since a couple of years, as a growing number of research groups are now involved in this field. Indeed, ultracold molecules offer many new opportunities compared to ultracold atoms, due to their more complex structure: they can carry an amount of internal energy larger by orders of magnitude than their kinetic energy, opening new areas like ultracold photochemistry [1] or also superchemistry [2, 3]. The ultimate control of elementary chemical reactions using short-pulse lasers is now foreseen [4], as both the internal and external degrees of freedom of the molecules can be well mastered. They allow the reinvestigation of phase transitions which up to now were explored only from the point of view of condensed matter physics, like the transition from bosonic to fermionic statistics [5, 6, 7], the superconductivity transition through the observation of the pairing gap in strongly interacting Fermi gases [8] or the superfluid transition via the study of the BEC-BCS crossover [9]. Spectacular achievements have been recently demonstrated as for instance the observation of molecular condensates with various alkali dimers [10, 11, 12], or of Feshbach resonance in molecule-molecule ultracold collisions [14].

Other interesting prospects concern dipolar molecules (ie with a permanent dipole moment), as it can be read through the special issue on this topic published in 2004 [13]. Among those are the possibility to design a quantum information device [15], or the test of fundamental theories like the measurement of the electron dipole moment [16, 17].

The formation process is obviously the key issue of these developments. An efficient approach which dramatically improved these last years is the so-called Stark deceleration technique, relying on the slowing and trapping of molecules with a permanent electric dipole moment (usually labelled as dipolar molecules) using inhomogeneous external electric fields [18]. Besides, the "historical" approach based on photoassociation of ultracold atoms which has first demonstrated the formation of ultracold molecules with cesium dimers [19], has recently progressed with the creation of ultracold samples of dipolar molecules composed of different alkali atoms like RbCs [20, 21], KRb [22, 23], and NaCs [24, 25].

In a previous paper [26] we computed the rates for the photoassociation of mixed alkali pairs, and for the subsequent formation of cold molecules, which showed that all alkali pairs involving either Rb and Cs are well suited for that purpose, as the cold molecule formation rate was only about ten times smaller than for Cs₂ formation. This result was found in good

agreement with the RbCs experiment of Kerman *et al* [20]. Potential curves available in the literature, and constant (atomic) transition dipole moment were proved to be sufficient to establish these estimates. However, the practical implementation of cold molecule formation via photoassociation will require a much better knowledge of their electronic properties like radial variation of permanent and transition dipole moments, in order to better guide the experimentalists towards specific systems and transitions with maximal efficiency. New spectroscopic studies on heteronuclear alkali pairs are also currently reinvestigated for NaRb [27] and NaCs [28], as well as the investigation of the effect of strong electric fields [29], which may also benefit of such a study.

To respond to these requirements, we started a new accurate analysis of electronic properties of all alkali pairs from Li to Cs, including potential curves for ground and excited states, permanent and transition dipole moments. We set up an automatic procedure based on the CIPSI package (Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively) [30] developed by the "Laboratoire de Physique Quantique de Toulouse (France)". Here we first investigate the permanent dipole moment of the ground state and the lowest triplet state of all mixed alkali pairs, for which only scattered experimental or theoretical results are available. We display their variation with the interatomic distance, as well as with the vibrational level. Most of these results were not previously available elsewhere. We emphasize on their convergence with respect to the size of the basis set. In the next section, we briefly recall the calculation procedure, which is well documented in many publications. We also review extensively the available calculations on these systems. In section III, we present our results obtained with basis sets published in the literature, and with new extended basis sets designed for all alkali atoms, in order to address convergence issues with respect to the size of the basis. We also discuss the comparison with other published papers, which is not often proposed, especially in the perspective of the addition of effective terms to the computed energies.

II. THEORETICAL CALCULATIONS

Many studies on heteronuclear alkali dimers have been performed using various quantum chemistry methods, restricted to the calculation of electronic potential curves for the ground and excited molecular states. The CIPSI package has been used to compute ground and

excited potential curves of RbCs [31, 32, 33], NaK [34, 35], KLi [36], LiRb, NaRb [37], LiCs, NaCs, KCs [38], KRb [39]. The method is based on the *ab initio* pseudopotentials of Durand and Barthelat [40, 41] for core representation, phenomenologic ℓ -dependent effective core polarization potential [42] and self-consistent calculation (SCF) combined with full valence configuration interaction interaction (CI) calculations. Additional effective terms may also be used to take in account short range core polarization terms (see for instance ref. [31]). Potential energy curves of ground and excited states of LiNa have been investigated by Davies *et al* [43] through many-body perturbation theory calculations, and by Schmidt-Mink *et al* [44] who have combined all-electron (SCF) calculations, valence CI calculations and have included an effective core polarization potential [45]. The electronic structure of KRb has been studied by Leininger *et al* [46] and by Park *et al* [47] using a method based on restricted Hartree-Fock (RHF) calculations, using the small-core (with nine electrons for each atom) relativistic pseudopotential of Christansen *et al* [49] and CI calculations. Park *et al* also introduced the effective core polarization potential of ref.[50]. Note that an extensive bibliographic overview on theoretical as well as experimental papers can be found in the "DiRef" database [51] devoted to diatomic molecules.

Only few papers include theoretical values for permanent dipole moments in addition to potential curve calculations. Igel-Mann *et al* [52] have performed a systematic study of the permanent dipole moments around the equilibrium distance of the ground state of all alkali dimers using the semi-empirical pseudopotential of Fuentealba [53] including a core polarization potential. All-electron SCF and valence CI calculations with or without core polarization correction have been performed by Müller and Meyer [45] for LiNa, LiK and NaK at the equilibrium distance. Janoschek *et al* [54] and Stevens *et al* [55] have reported permanent dipoles of NaK. The *ab initio* and pseudopotential calculations of Janoschek [54] concern only the ground state, while the more complete SCF and CI calculations including core-polarization effects done by Stevens *et al* [55] include the R -dependence of the ground and triplet state permanent dipole moment. SCF and CI calculations of permanent dipole moments for NaLi have been performed by Bertoncini *et al* and by Rosmus and Meyer [56, 57]. Bertoncini *et al* reported the R -dependence of the dipole in the ground and the lowest triplet states.

Ab initio calculations of the R -dependent dipole moments of the $1,3\Sigma^+$ states of KRb have been performed by Kotochigova *et al* [58], using Hartree-Fock or Dirac-Fock orbital basis

set complemented by Sturmian functions to describe virtual orbitals and CI valence-bond calculations. Core-valence correlations are accounted by allowing single electron excitation from the closed $3p^6$ of K and $4p^6$ of Rb and by introducing several virtual orbitals. Core polarization effects are not explicitly mentioned by the authors in their papers. They found a large influence of relativistic effects on the dipole moments, with an increase of about 20% for the ground state and of about 50% for the $a^3\Sigma^+$ case, in the region of the potential minimum.

Besides, only a few experimental values for the permanent dipole moments of the ground state obtained by different techniques have been reported. Dagdigian and Wharton [59, 60, 61] used molecular beam electric deflection and resonance spectroscopy to determine the molecular electric dipole of several heteronuclear alkali dimers. The permanent dipole of NaLi or KLi molecules have been determined by Engelke *et al* using laser induced fluorescence [62, 63], and the one of NaK by Wormsbecher *et al* using microwave optical double resonance technique [64]. Finally, Tarnovsky *et al* [65] have measured the electric dipole polarizabilities of alkali homonuclear and NaK and KCs heteronuclear dimers using molecular beam deflection in an inhomogeneous electric field. This led the authors to set up two empirical rules for determining polarizabilities and dipole moments of all heteronuclear alkali dimers, yielding then the values of the dipole moments for all mixed pairs from the difference between the polarizabilities of their respective homonuclear dimers.

As mentioned above, we use here the CIPSI package to investigate the electronic structure of mixed alkali pairs MM' , and we recall now the main features of this code. In this method, the atomic cores are described by the pseudopotentials of Durand and Barthelat [40, 41] whose parameters have been adjusted to reproduce the energies and valence orbitals of all-electron Hartree-Fock SCF calculation for the atomic ground state. For Rb and Cs, the pseudopotential includes the mass-velocity, and the Darwin relativistic corrections. Each atom is described by a Gaussian basis set. As the alkali atoms are treated as one-electron species, correlations are not explicitly introduced. Core polarization is taken in account through an ℓ -dependent effective core polarization potential (ECP) [42] depending on the dipole polarizability $\alpha_d^{M^+}$ and $\alpha_d^{M'^+}$ of the M^+ and M'^+ ions and of ℓ -dependent cut-off parameters ρ_ℓ adjusted to reproduce the experimental energies [66, 67, 68] of the two lowest s , p and d atomic levels. Molecular orbitals are then determined by restricted Hartree-Fock calculations and full valence CI are performed.

Additionally, the potential energy should include the core-core interaction potential $V_{cc}(R)$ which is modelled as long as the cores are far enough from each other with the pure repulsive $1/R$ term, and an attractive charge-induced dipole term $V_{cc}^{ind}(R) = -(\alpha_d^{M^+} + \alpha_d^{M'^+})/2R^4$. When the cores come close to each other, such an approximation is not sufficient due to their strong electrostatic repulsion, and further short-range effective terms have to be included in V_{cc} . As discussed for instance in the case of alkali dimers [31, 69, 70], the core-core repulsion $V_{cc}^{rep}(R)$ has to be evaluated from ab-initio calculations according to various assumptions. The frozen core approach is then often used, in which the repulsion between the two ionic cores is obtained from a SCF calculation where the two ionic cores are represented by frozen atomic orbitals. It has been shown [31] that this term can be fitted by an exponential form. The contribution of the core-core dispersion energy has also to be taken in account, approximated by the London formula (see for instance ref.[31]):

$$V_{cc}^{disp}(R) = -\frac{3\alpha_d^{M^+}\alpha_d^{M'^+}}{2R^6}\frac{E_I^{M^+}E_I^{M'^+}}{E_I^{M^+} + E_I^{M'^+}} \quad (1)$$

where $E_I^{M^+}$ and $E_I^{M'^+}$ are the ionisation energies of the M^+ and M'^+ ions respectively.

We performed three different series of calculations, described below, characterized by different Gaussian basis sets summarized in Tables I, II, and III. The resulting atomic energies are displayed in Table IV, while the size of the generated molecular basis set is given in Table V for mixed alkali pairs.

- Prior to our new calculations, we checked the code and our procedure by first reproducing the computations performed by previous authors, employing the contracted Gaussian basis sets, the ionic core dipole polarizabilities and the ℓ -dependent cut-off radii ρ_ℓ published by Poteau *et al* [71] for Li, by Magnier *et al* [72] for Na, by Magnier *et al* [34] for K, and by Pavolini *et al* for Rb and Cs [31]. Note that in these calculations, the values of α_d may come from different sources [45, 73]. These calculations will be referred to as belonging to the "A" series.
- Then we removed the contracted orbitals from the basis sets quoted just above, and introduced the ℓ -dependent ECP's afterwards. For all atoms, we obtained a better description for atomic energy levels than with the contracted basis sets. Guided by this trend, our next series of calculations (labelled as series "B") involve uncontracted

Gaussian basis extended with respect those used in the "A" series, and dipole polarizabilities all coming from the same paper by Wilson *et al* [73]. Some basis coefficients, and the cut-off radii, have been reoptimized, in order to improve the quality of calculated atomic energy levels. Note that the Li basis set has been considerably increased compared to ref.[71]. In contrast, the K basis set is the same than in ref.[34], but without contraction coefficients. The K basis has been recently extended by Magnier *et al* [74] to study highly excited states of the K₂ dimer.

- Due to the current interest for cold molecule studies about heteronuclear alkali pairs involving Cs, [20, 25], we set up a third series of computations (C series) for LiCs, NaCs, KCs, and RbCs, using a basis set and cut-off parameters for Cs, which will be illustrative for the discussion of convergence issues.

As seen in Table IV we obtained in most cases slight improvements on the atomic energy levels when A and B calculations are compared to the experimental ones, which confirms that previously published basis sets were already quite well optimized. However, as it will be discussed in the next section, the improvement is more spectacular for potential curves, due to the cumulative effect of better defined static polarizabilities, and extended basis sets.

III. RESULTS

Before discussing in detail our results on permanent dipole moments, we first check the reliability of our extended basis sets by looking at the potential curves obtained for the ground state and lowest triplet state of the mixed pairs, concentrating on two specific examples, RbCs and KRb. We first look at the potential energies $V'(R)$ including only the $1/R$ term of $V_{cc}(R)$. As it is shown in Figure 1, the minimum energy for $V'(R)$ curves is found in general at distance R_m larger than the equilibrium distance R_e of the full $V(R) = V'(R) + V_{cc}^{ind}$ curves. The combined influence of the addition of diffuse orbitals and the improved adjustment of the cut-off radii in series B compared to series A is clear, as the X and a states are found 48 cm⁻¹ and 6 cm⁻¹ deeper than in series A, respectively. In the latter case, the basis C for Cs still increases the a well depth by 6 cm⁻¹, while no effect is visible for the X state. The same trend is observed for all pairs: as a further example, the KRb ground state is found in the B case about 70 cm⁻¹ deeper than in the A case, while

the depth of the a state is increased by 2 cm^{-1} . Excited potential curves are also modified from A to B calculations, and will be investigated in further work.

We then computed the permanent dipole moment of X and a states for all heteronuclear pairs. The sign of the permanent dipole moment of a molecule depends on the interatomic axis orientation, which is assumed here to be oriented along the MM' direction, where M is the lightest atom of the mixed pair. A negative dipole moment then implies an excess electron charge on the M atom. In the following, values are given in Debye, with 1 atomic unit = 2.54158059 Debye.

Here again we first check the influence of the optimization of the basis set and of the cut-off parameters on the RbCs permanent dipole moment (figure 2). Note that $V_{cc}(R)$ does not influence the electronic wave functions, neither the dipole moments functions. The R dependence is found very similar for all A, B, C calculations, with a minimum around $9.3a_0$ for the X state (slightly larger than the minimum distance $R_m^X = 8.5a_0$), and around $13.4a_0$ for the a state (slightly larger than the minimum distance $R_m^a = 12.6a_0$). Increasing the size of the basis changes the dipole moment of the X state in the region of the minimum by only 2 to 5%, while the moment for the a state, which is much smaller in magnitude, changes (around the location of its minimum) by about 50% from A to B calculations, and only by 7% from B to C calculations. A similar trend is observed for the other mixed pairs (see table VI), as the change from A to B or C approaches in the ground state dipole moment never exceeds a few percents, being most often smaller than 1%. So we can safely estimate that the B calculations are converged with respect to the size of the basis set.

The R -variation of the permanent dipole moment for the $X^1\Sigma^+$ and $a^3\Sigma^+$ states deduced from calculations B (figure 3a) is found similar for the ground state of all pairs. Apart for the LiNa dipole moment which remains close to 0 Debye, the curves present a minimum at a distance R_d^X systematically larger by about $1a_0$ to $1.5a_0$ than the equilibrium distance R_e^X of the ground state, and vanishes at large R as expected. The magnitude of the dipole strongly depends of the chosen pair, the largest being for LiCs around -6 Debye. In contrast, the R -dependence of the dipole moment in the a state is more irregular over the mixed pair series, with a minimum for some species (LiCs, RbCs, KRb) and a maximum for the other dimers.

Figure 4 shows the variation of the permanent dipole moment with the vibrational level of the X and a states, obtained after averaging the dipole moment function over the vibrational

wave functions of the potential functions $V(R) = V'(R) + V_{cc}^{ind}$. This figure partly reflects the R -dependence drawn in Figure 3: the ground state dipole moment is almost constant for the lowest forty levels for the less polar species, while it varies more rapidly for LiRb, LiCs, NaRb. As expected, all these curves vanish at large distances (not shown on the figure).

For the purpose of comparison with other works, we summarize our results for the ground state in a tabular form (Table VI), displaying the value of the permanent dipole moment at the equilibrium distance R_e^X , at its extremum value R_m^X , and averaged for the $v = 0$ vibrational level. To the best of our knowledge, the other available theoretical values for the permanent dipole moment of the mixed alkali pairs concern the ground state at its equilibrium distance R_e^X . In contrast, only the value of the permanent dipole moment for a given vibrational level of molecules is obtainable in an experiment, limited to $v = 0$ up to now. Note that for simplicity we reported absolute values in table VI: indeed, the experimentalists cannot determine the sign of the dipole moment, while it is not always clear in the theoretical papers what is the choice of the authors for the orientation of the molecular axis.

As expected, the dipole moment of $v = 0$ is close to the value of the dipole function at the equilibrium distance. Our results are in good agreement with the available experimental values, within a 2% for LiK, NaK, and NaCs, and slightly more (6%) for NaRb. The difference is found much larger (around 20%) for the less polar molecule LiNa. We confirm that the approximate scaling law proposed in ref.[65] overestimates the dipole moment, except for the less polar molecules KRb and RbCs, which in contrast are underestimated. Our results are in excellent agreement with those of ref.[52], which a similar approach without the ℓ -dependence of the core polarization terms.

We have already mentioned that very few other theoretical variations of the permanent dipole moment with the interatomic distance are available in the literature. The R -dependence of the dipole moment in the ground state of NaLi molecule obtained by Bertocini *et al* [56] and by Rosmus and Meyer [57] disagree with each other both in sign and in magnitude. Our negative value for LiNa supports the prediction of Rosmus and Meyer but not their R -variation. Note that the authors of ref.[57], and later on in another paper [50], underlined the great sensitivity of the dipole moment of NaLi to valence correlations and core polarization effects. Similarly, results by Stevens *et al* on NaK [55] also differ strongly from ours, which can be attributed to the absence of an ℓ -dependence in the effective core

potentials, included afterwards in the NaK study of Magnier and Millié [34].

The KRb molecule is an attractive case in the cold molecule field, as two recent calculations of the X and a states of KRb including the R -dependence of the permanent dipole moments have been performed by Park *et al* [47, 48] and by Kotochigova *et al* [58] using quite different theoretical approaches. Their predictions are compared with our calculations A and B in figure 5. It is striking to see that quite large differences are observed, up to 20% with the non-relativistic result of ref.[58], and 40% with ref.[47] or with the relativistic calculations of ref.[58]. It is not easy to understand such large differences. One reason could be the different ways to treat the core polarization effects. Kotochigova *et al* [58] indicate that the implementation of core polarization effects may reduce their dipole moment by about 50%. They also mention that their convergence with respect to the number of basis functions is of the same order than the difference between their relativistic and non-relativistic calculations. It would be interesting to perform these kind of comparisons for molecules with a larger dipole moment, as we may expect larger core polarization effects. Given the good agreement we obtain with available experimental values on other systems, we believe that our values are quite accurate.

IV. DISCUSSION

We performed potential curves and transition dipole moments calculations for all heteronuclear alkali pairs, in order to investigate the influence of the basis set size on higher excited electronic states, which is expected to be significant. The comparison of these potential curves with other existing calculations will be presented in further publications, as well as results for dipole transition moments which are not available elsewhere for most species. These data are of particular importance for the optimization of multiple-step schemes for ultracold molecule formation, like the one performed by Sage *et al* [21], or for the interpretation of recent observation of Autler-Townes effect in highly excited molecular states [79]. An important issue is also the evaluation of the accuracy of potential curves (by looking for instance at well depths and equilibrium distances) compared to experimental determinations, in relation with the choice of the effective terms included in the core-core potential: Table VII displays the contributions of the V_{cc}^{disp} term, as evaluated with equation 1, and of the V_{cc}^{rep} term from refs.[31, 69] close to the equilibrium distance of the ground state of the

KRb and RbCs systems. The largest effect is obtained for the heaviest pair RbCs. Furthermore, the V_{cc}^{disp} term should be cut off at a somewhat arbitrary distance, when ionic cores become close to each other. Jeung [69] discussed various approximations for the repulsive term, leading to very different estimates, depending on the chosen model (see the table). Therefore it is tedious to predict well depths with an accuracy better than a few tens of wave numbers. An empirical solution to this problem is offered when an experimental determination of the ground state potential is available, as illustrated for example in the spectroscopic analysis of NaRb states by Docenko *et al* [28]: the difference between the experimentally determined ground state potential curve and the computed curves of ref.[38] is attributed to the cumulative effect of the different terms of the core-core interaction. This difference is then assumed to be independent of the molecular electronic excitation: it can be added in turn to the computed excited potential curves, yielding then a good representation of the excited molecular states.

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Atom	basis (A)	basis(B)	basis(C)
Li	$8s7p4d1f/[7s5p3d1f]$	$10s7p5d3f$	
Na	$7s5p5d2f/[5s5p3d2f]$	$8s6p5d2f$	
K	$7s5p7d2f/[6s4p4d2f]$	$7s5p7d2f$	
Rb	$7s4p5d1f/[6s4p4d1f]$	$9s6p6d4f$	
Cs	$7s4p5d1f/[6s4p4d1f]$	$7s4p5d4f$	$9s6p6d4f$

TABLE I: Gaussian basis sets for each studied alkali atom. The contractions are specified in brackets for the "A" basis. The "C" basis is set up only for Cs.

TABLE II: Exponents of the Gaussian functions introduced in the various basis A, B, C. When appropriate, contracted orbitals are displayed in brackets, with contraction coefficients in parenthesis.

Atom	Basis	ℓ	Exponents
Li	A	s	[2.464(-0.013829),1.991(-0.032077)],0.582,0.2,0.07,0.031,0.015,0.007
		p	[0.630(0.052433),0.240(0.078566)],0.098,0.043,0.02,[0.01(0.01445),0.005(0.00657)]
		d	0.2,0.07,[0.022796(0.491521),0.008574(0.549272)]
	B	f	0.01
		s	2.464,1.991,1.,0.582,0.2,0.136,0.07,0.011,0.008,0.004
		p	0.630,0.24,0.098,0.03,0.02,0.01,0.004
Na	A	s	[2.8357(0.007043),0.49318(-0.1871),0.072085(0.3679)],0.036061,0.016674,0.00693,0.00287
		p	[0.431(-0.01778),0.09276(0.2003)],0.03562,0.01447,0.0058,0.00023
		d	[0.292(0.01454),0.06361(0.123)],0.02273,0.008852,0.00352
	B	f	0.015,0.0055
		s	2.8357,1.,0.49318,0.072085,0.036061,0.017674,0.00693,0.00287
		p	0.431,0.09276,0.03562,0.1447,0.0058,0.00023
K	A	s	[0.9312(0.02463),0.2676(-0.2628)],0.0417,0.02815,0.01448,0.0055,0.0026
		p	0.133,0.05128,0.01642,0.0052,0.0022
		d	[1.255(0.02754),0.4432(0.05391),0.109(0.1083)],0.02994,0.01013,0.0037,0.0018
	B	f	0.015,0.005
		s	0.9312,0.2676,0.051,0.02715,0.01448,0.0055,0.0026
		p	0.134,0.05328,0.01642,0.0053,0.002
Rb	A	s	[1.292561(-0.065450),0.824992(0.037862)],0.234682,0.032072,0.013962,0.005750,0.0025
		p	0.128,0.040097,0.014261,0.004850
		d	[0.408807(0.0943),0.096036(0.1846)],0.026807,0.009551,0.0004
	B	f	0.2
		s	2.5,1.292561,0.824992,0.5,0.234682,0.032072,0.013962,0.00575,0.025
		p	0.25,0.128,0.040097,0.03,0.014261,0.00485
Cs	A	s	[0.328926(0.411589),0.241529(-0.682422)],0.050502,0.029302,0.013282,0.00528,0.003
		p	0.12,0.0655,0.0162,0.00443
		d	[0.196894(0.18965),0.067471(0.22724)],0.027948,0.010712,0.003
	B	f	0.1
		s	0.328926,0.221529,0.050502,0.029302,0.013282,0.00528,0.003
		p	0.155,0.0655,0.0162,0.00443
C	d	0.18894,0.067471,0.027948,0.010712,0.003	
	f	0.05,0.025,0.0125,0.005	
	s	2.5,0.328941,0.241529,0.1,0.050502,0.029302,0.012,0.005,0.002	
C	p	0.25,0.12,0.0655,0.03,0.012,0.005	
	d	0.3,0.196894,0.09,0.03	
	f	0.05,0.025,0.0125,0.005	

Atom	Basis	$\alpha_d^{M^+}$	ρ_s	ρ_p	ρ_d	ρ_f
Li	A	0.1915[45]	1.434	0.979	0.6	0.4
	B	0.1997[73]	1.315	0.999	0.6	0.9
Na	A	0.9947[45]	1.42	1.625	1.5	1.5
	B	0.9987[73]	1.456	1.467	1.5	1.5
K	A	5.354[45]	2.067	1.905	1.96	1.96
	B	5.472[73]	2.11439	1.97355	1.9884	1.9884
Rb	A	9.245	2.513	2.279	2.511	2.511
	B	9.245[73]	2.5538	2.349	2.5098	2.5098
Cs	A	15.117[31]	2.6915	1.8505	2.807	2.807
	B	16.33[73, 75]	2.8478	1.981	2.904	2.904
	C	16.33[73, 75]	2.8864	2.7129	2.8963	2.8963

TABLE III: Dipole polarizabilities $\alpha_d^{M^+}$ and semiempirical cutoff parameters ρ_ℓ introduced in the basis A, B, C. For previously published basis (A), the authors used the theoretical values quoted in the quoted references for $\alpha_d^{M^+}$, while for basis (B) we used instead the experimental values of Wilson *et al* [73]. Note that for Cs, Allouche and coworkers [38, 76] referred to Wilson *et al*, but do not actually use his value.

		Δ_A	Δ_B			Δ_A	Δ_B			Δ_A	Δ_B
Li	2s	5.67	0.55	Na	3s	-2.26	0.00	K	4s	0.10	-0.18
	2p	0.21	-0.76		3p	-1.46	0.47		4p	0.03	0.14
	3s	7.79	26.67		4s	19.81	2.50		5s	-5.49	-9.99
	3p	1.80	8.47		3d	0.64	0.01		3d	0.58	-0.61
	3d	7.94	0.20		4p	3.94	2.67		5p	47.01	39.38
	4s	1684.04	54.70		5s	11.75	7.54		4d	23.07	21.30
	4p	4069.42	236.05		4d	13.70	13.39		6s	3.01	0.01
	4d		40.36		4f		57.45		4f	46.32	46.30
	4f	721.84	51.28		6p	50.12	59.90				
		Δ_A	Δ_B			Δ_A	Δ_B	Δ_C			
Rb	5s	0.08	-0.03	Cs	6s	0.32	0.15	0.31			
	5p	0.00	0.00		6p	0.05	-0.85	0.10			
	4d	0.13	0.03		5d	-18.85	-0.51	0.46			
	6s	-32.17	-32.56		7s	1.50	10.40	7.09			
	6p	32.67	22.92		7p	68.43	91.63	17.40			
	5d	7.29	4.15		6d	186.58	203.32	85.30			
	7s	-10.39	-10.79		8s	37.55	41.02	20.20			
					4f		23.64	23.47			

TABLE IV: Differences (in cm^{-1}) between computed and experimental atomic binding energies for A, B, and C basis sets. Experimental values are taken from refs.[66, 67, 68].

Molecule	LiNa	LiK	LiRb	LiCs	NaK	NaRb	NaCs	KRb	KCs	RbCs
basis (A)	98	104	89	89	114	99	99	105	105	90
basis (B)	142	148	162	149	136	143	137	156	143	157
basis (C)	-	-	-	162	-	-	156	-	156	170

TABLE V: Size of the molecular basis set generated from method A, B and C.

TABLE VI: Computed permanent dipole moments $|D|$ of the $X^1\Sigma^+$ state (in Debye) at equilibrium distances R_e^X , at the minimum distance R_d^X (in a.u.), and for the $v = 0$ level of the X state. Our results are compared to available experimental and theoretical values.

	This work						Exp.			Th		
		$D(R_e^X)$	R_e^X	$D(R_d^X)$	R_d^X	$D(v=0)$	D	R_e	ref.	$D(R_e)$	R_e	ref.
LiNa	(A)	0.561	5.43	0.630	6.85	0.566	0.45()		[62]	1.24	5.64	[56]
	(B)	0.554	5.42	0.633	6.89	0.556	0.47(3)	5.33	[59]	0.485	5.429	[57]
							0.463(10)	5.31	[61]	0.485	5.42	[77]
							0.45		[65]	0.487	5.47	[45]
										0.53	5.42	[52]
LiK	(A)	3.558	6.21	3.807	7.50	3.565	3.510(5)		[63]	3.437	6.292	[45]
	(B)	3.533	6.21	3.792	7.49	3.555	3.45(2)	6.18	[61]	3.50	6.25	[52]
							3.87		[65]			
LiRb	(A)	4.168	6.52	4.442	7.78	4.165	4.05		[65]	4.13	6.52	[52]
	(B)	4.142	6.48	4.414	7.78	4.131						
LiCs	(A)	5.520	6.81	6.023	8.33	5.529	6.30		[65]	5.48	6.89	[52]
	(B)	5.512	6.82	5.998	8.31	5.524						
	(C)	5.462	6.81	5.970	8.33	5.478						
NaK	(A)	2.760	6.50	2.854	7.42	2.759	2.73(9)		[64]	3.6	6.9	[54]
	(B)	2.763	6.49	2.862	7.47	2.762	2.690(14)	6.55	[61]	2.735	6.36	[45]
							3.42		[65]	2.95	6.614	[55]
										2.54	6.59	[52]
										2.78	6.6	[35]
NaRb	(A)	3.304	6.84	3.413	7.75	3.306	3.10(3)	6.73	[61]	3.33	6.85	[52]
	(B)	3.301	6.84	3.413	7.76	3.301	3.51		[65]			
NaCs	(A)	4.613	7.20	4.821	8.26	4.607	4.75(20)	6.91	[61]	4.60	7.23	[52]
	(B)	4.661	7.20	4.864	8.26	4.660	4.75		[78]			
	(C)	4.580	7.20	4.793	8.29	4.579	5.86		[65]			
KRb	(A)	0.615	7.64	0.620	8.20	0.615	0.20		[65]	0.64	7.65	[52]
	(B)	0.589	7.64	0.605	8.49	0.589				0.71	7.7	[58]
										1.06	7.7	[48]
KCs	(A)	1.906	8.01	1.957	8.87	1.906	2.58		[65]	1.92	8.05	[52]
	(B)	1.921	8.02	1.967	8.85	1.921						
	(C)	1.835	8.02	1.891	8.93	1.837						
RbCs	(A)	1.238	8.28	1.278	9.19	1.237	2.39		[65]	1.26	8.71	[52]
	(B)	1.278	8.30	1.309	9.12	1.280						
	(C)	1.205	8.30	1.240	9.19	1.204						

	$R_e^X(a_0)$	V_{cc}^{disp}	V_{cc}^{rep}		
			[31]	[69]-A	[69]-E
KRb	7.64	-6.41	-	≈ 17	≈ -507
RbCs	8.30	-10.22	18.42	≈ 25	≈ -500

TABLE VII: Contribution (in cm^{-1}) of the V_{cc}^{disp} and V_{cc}^{rep} terms around the equilibrium distance R_e^X of the KRb and RbCs ground state. The V_{cc}^{disp} term is estimated following equation 1 and parameters from method A. Both two results (labelled as A and E) from ref. [69] are displayed.

V. FIGURE CAPTIONS

Figure 1: (*Color on line.*) The potential curves $V'(R)$ (including only the $1/R$ term of $V_{cc}(R)$) around their minimum for (a) the $X^1\Sigma^+$ and (b) the $a^3\Sigma^+$ states of RbCs, as obtained through the three approaches A (black full lines), B (red dashed lines), C (blue dashed line with dots), described in the text. In (a), results for B and C approaches are superimposed. In addition, the black dot-dashed lines represent $V'(R) + V_{cc}^{ind}(R)$ for both states, in the A case.

Figure 2: (*Color on line.*) The permanent electric dipole moments (in Debye) of (a) the $X^1\Sigma^+$ (b) the $a^3\Sigma^+$ states, in RbCs, as obtained through the three approaches A, B, C, described in the text.

Figure 3: (*Color on line.*) The permanent electric dipole moments (in Debye) of (a) the $X^1\Sigma^+$ state (b) the $a^3\Sigma^+$ state, as functions of the internuclear distance, obtained from calculation B. Results are displayed in black for Li compounds (dashed line for LiNa, dot-dashed line for LiK, double-dot-dashed line for LiRb, full line for LiCs), in red for Na compounds (open circles for NaK, upper triangles for NaRb, closed circles for NaCs), and in blue for K compounds (lower open triangles for KRb, crosses for KCs) and for RbCs (lower closed triangles).

Figure 4: (*Color on line.*) The permanent electric dipole moments (in Debye) of the $X^1\Sigma^+$ state of the mixed alkali pairs as functions of the vibrational level, obtained from calculations B. The color and line code is the same than in figure 3.

Figure 5: (*Color on line.*) The permanent electric dipole moments (in Debye) of (a) the $X^1\Sigma^+$ state (b) the $a^3\Sigma^+$ state of KRb as functions of the internuclear distance, obtained from calculations A (full line) and B (dashed line). Our results are compared to other available theoretical determinations: non-relativistic (open circles) and relativistic (closed circles) results from ref.[58], and non-relativistic results from ref.[47, 48] (dot-dashed blue line). The vertical dashed line in (b) panel indicates the location of the repulsive wall of the potential at the energy of its dissociation limit.

Figure 1, Aymar and Dulieu, Journal of Chemical Physics

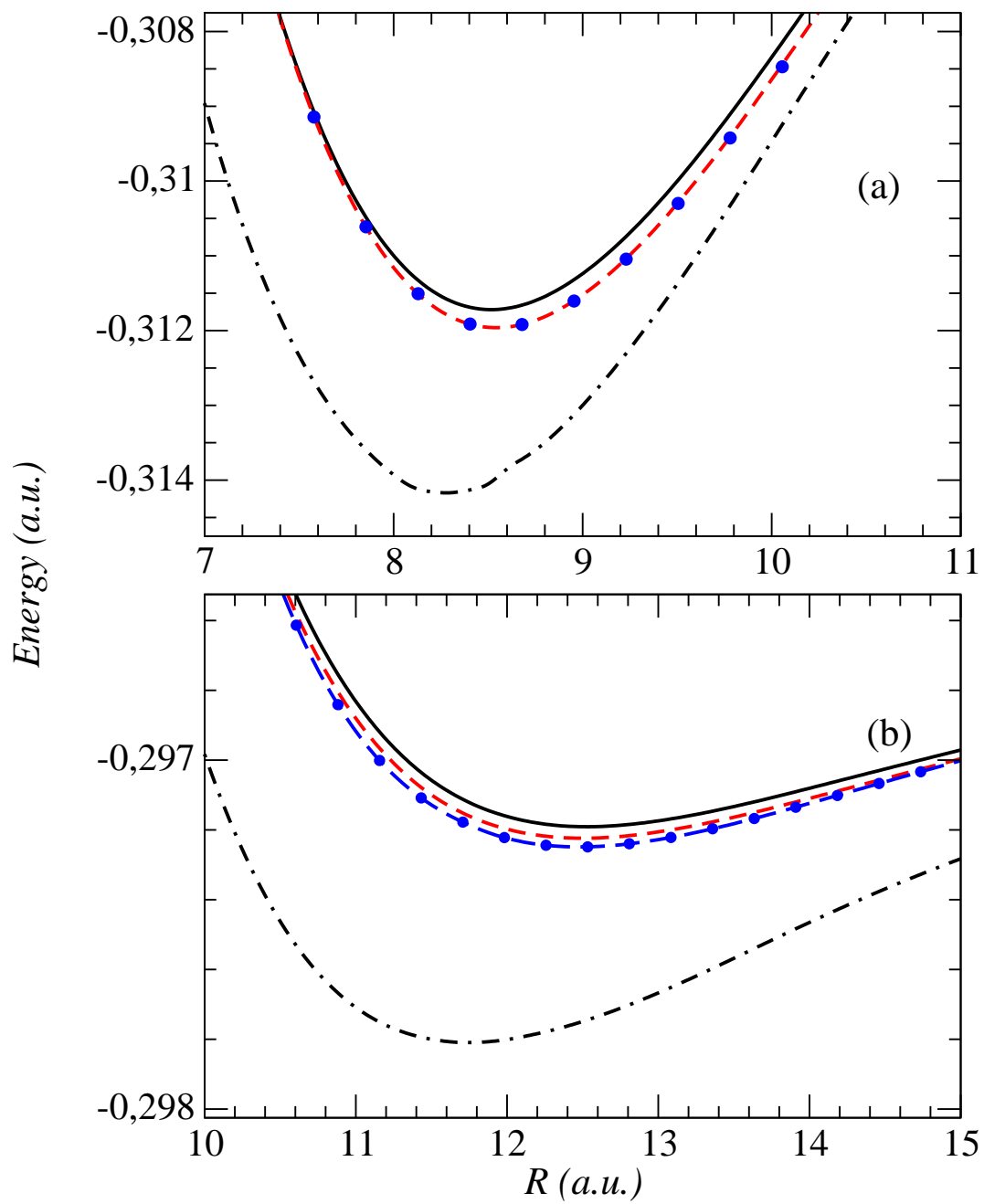


FIG. 1:

Figure 2, Aymar and Dulieu, Journal of Chemical Physics

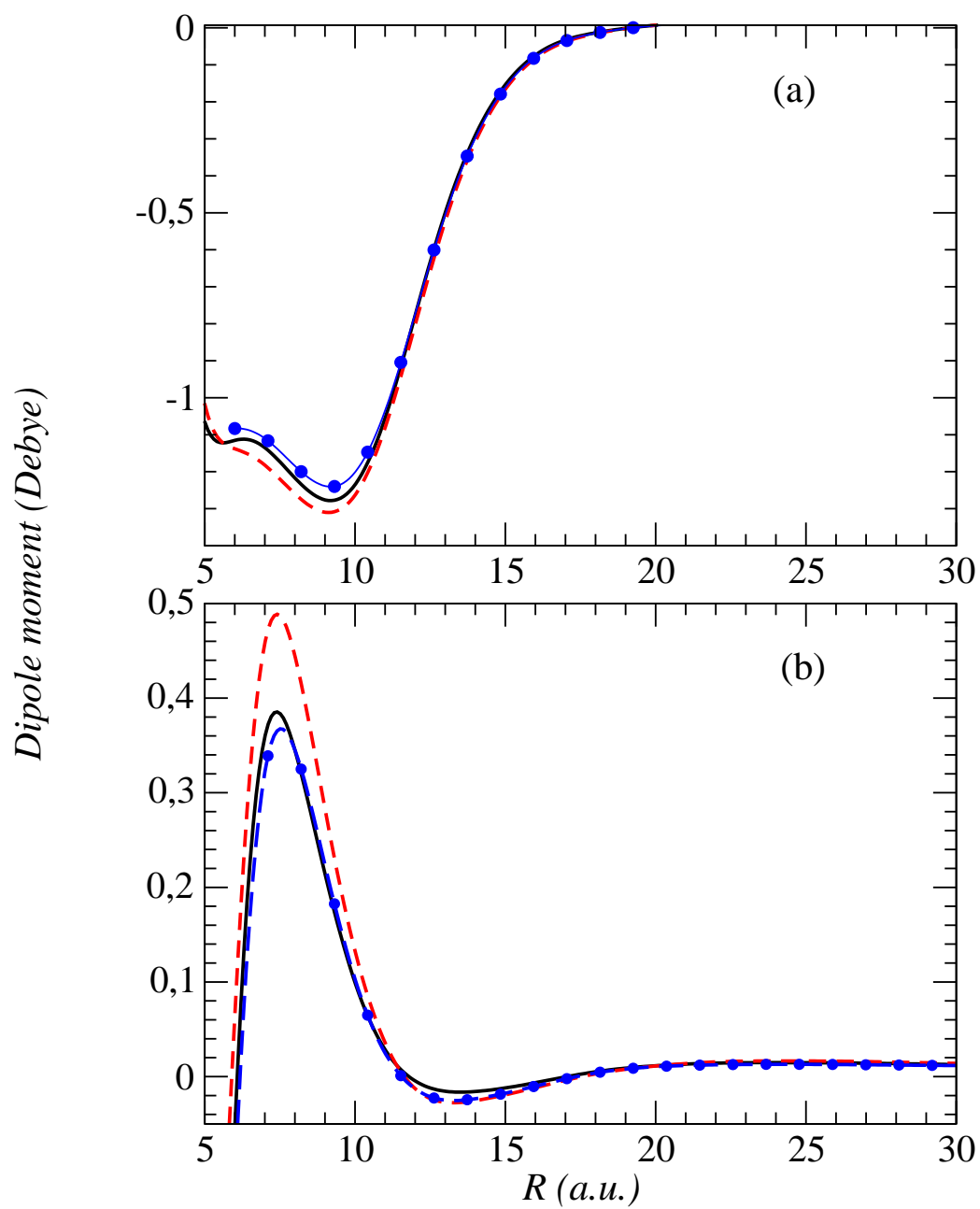


FIG. 2:

Figure 3, Aymar and Dulieu, Journal of Chemical Physics

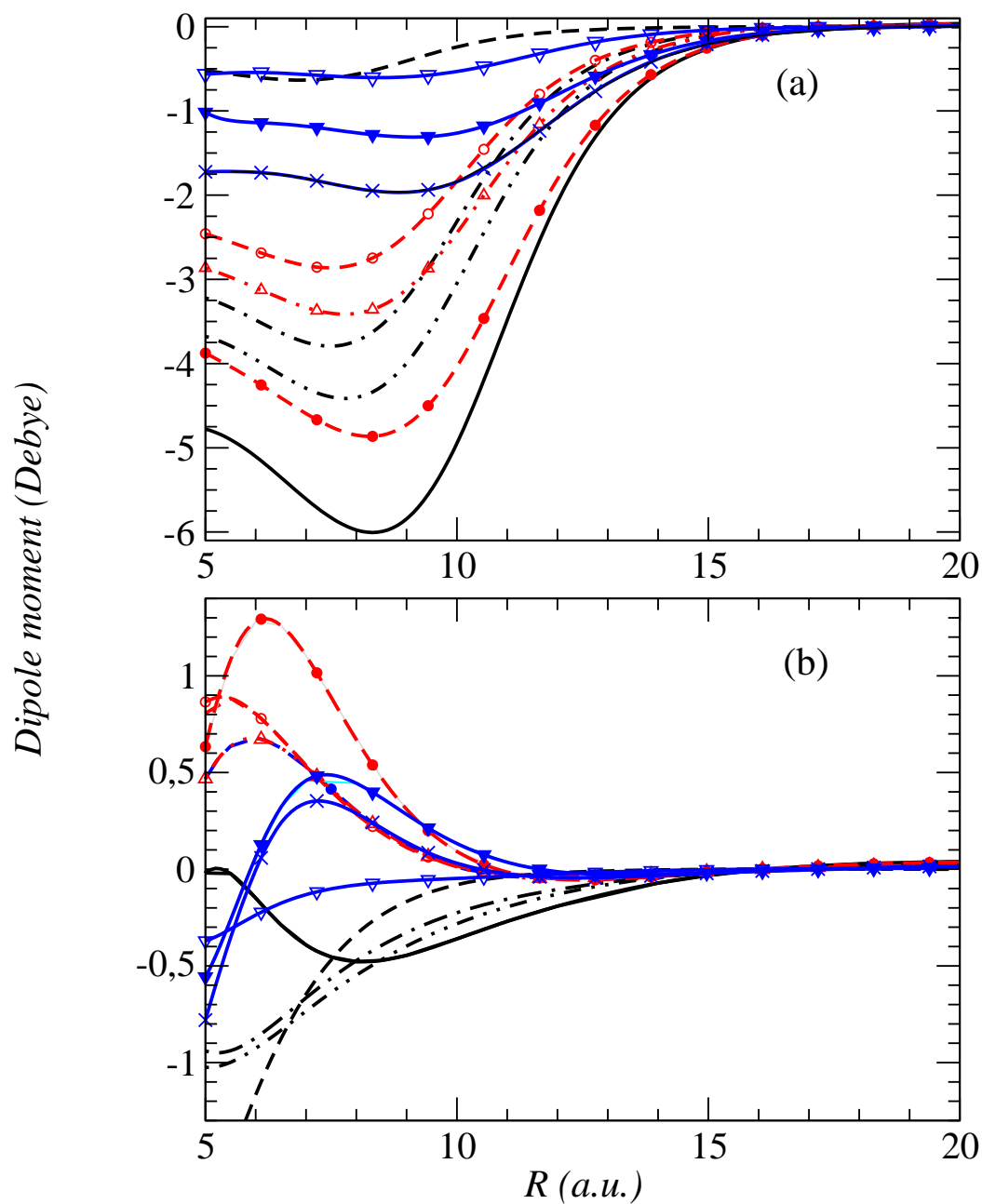


FIG. 3:

Figure 4, Aymar and Dulieu, Journal of Chemical Physics

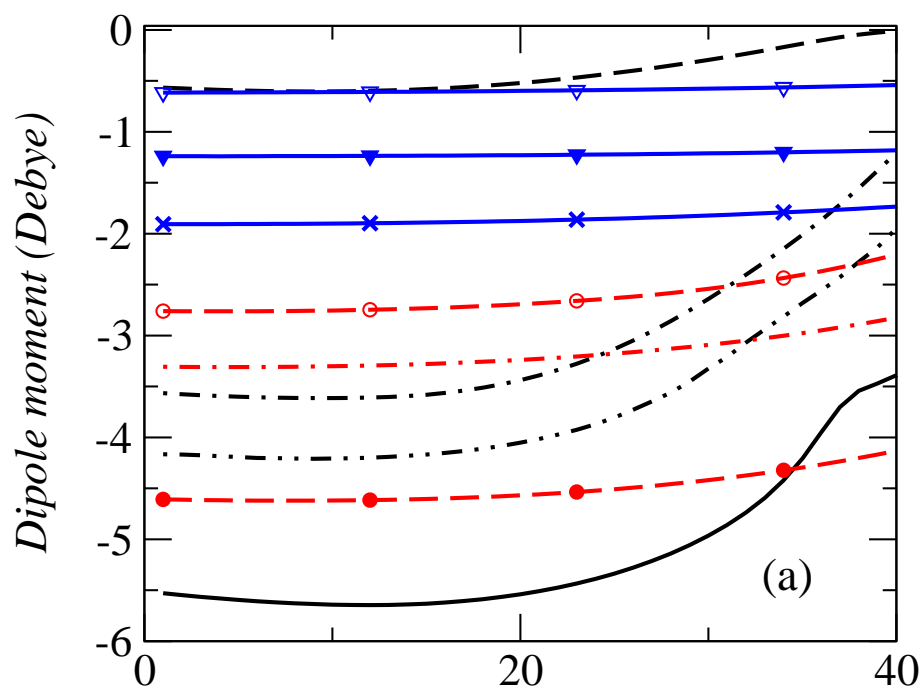


FIG. 4:

Figure 5, Aymar and Dulieu, Journal of Chemical Physics

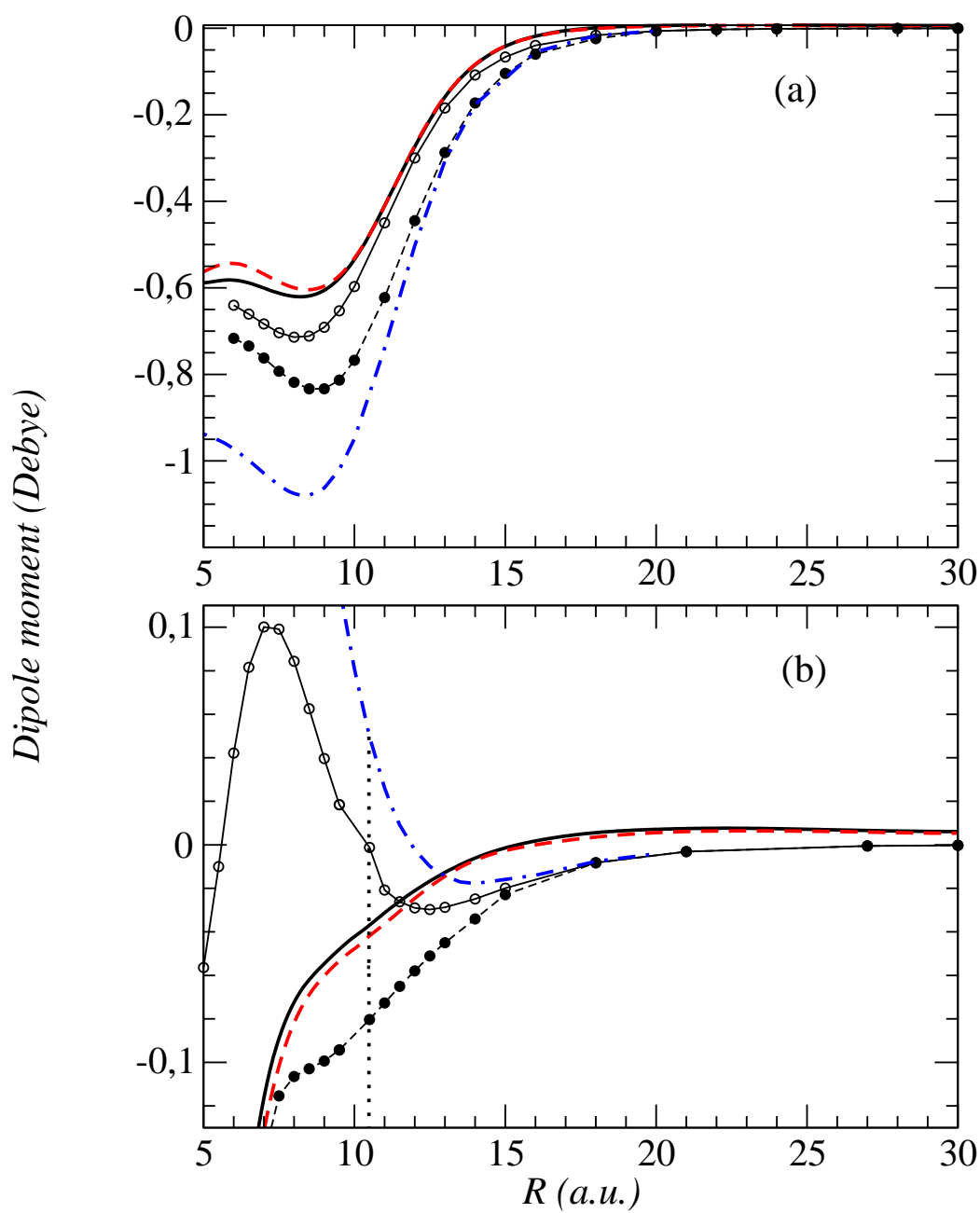


FIG. 5: