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Calculations of transition and permanent dipole moments of heteronuclear alkali dimers NaK, NaRb and NaCs

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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 calculate permanent dipole moments and transition dipole moments for excited states for alkali dimers NaK, NaRb and NaCs using a standard quantum chemistry approach based on pseudopotentials for atomic core representation, Gaussian basis sets, and effective terms for core polarization effects. We provide an extensive set of data concerning transitions among the first seven molecular states of each symmetry $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, $^3\Pi$. The accuracy of our results is generally improved compared to previous similar calculations on NaK, while they are found to be in good agreement with the few NaRb states calculated with other methods. Results for NaCs transition dipole moments are given here for the first time.

Keywords: Alkali dimers; Transition dipole moments; Ultracold molecules; Effective core polarization potential; NaK; NaRb; NaCs

1. Introduction

Heteronuclear alkali dimers attract interest of both experimental and theoretical researchers working on cold molecules due to the promising prospects offered by their polar character, as can be read in recently published special issues on this topic [1, 2]. Fascinating properties are predicted for cold samples of such dipolar molecules (i.e. exhibiting a permanent dipole moment) due to their long-range dipole–dipole interaction and their ability to be manipulated by external electric fields (see for instance [3]). Field-linked quasibound states of a new kind are predicted to influence collisions between polar molecules [4]. Polar molecules could provide the toolbox for lattice–spin models as a representation of states of matter with topological order [5]. The anisotropy of the dipole–dipole interaction could allow one to control it inside a degenerate gas by varying the geometry of the trap [6]. Among the possible applications are the design of a molecular optics set-up [7] or a quantum information device [8], or to test fundamental theories by the measurement of the electron electric dipole moment [9, 10] or of the time independence of the electron-to-proton mass ratio [11].

The formation process is obviously the key issue for these developments. An efficient approach which has dramatically improved these last years is the so-called Stark deceleration technique, relying on the slowing and trapping of dipolar molecules using inhomogeneous external electric fields [12]. In addition, the 'historical' approach based on photoassociation of ultracold atoms which first demonstrated the formation of ultracold molecules with cesium dimers [13], has recently progressed with the creation of ultracold samples of dipolar molecules composed of different alkali atoms like RbCs [14, 15], KRb [16, 17], NaCs [18, 19], and LiCs [20].

In a previous paper [21], we computed the rates for the photoassociation of mixed alkali pairs, and for the susbsequent 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 Cs_2 formation. This result was found in good agreement with the RbCs experiment of Kerman *et al*. [14].

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Potential curves available in the literature, and constant (atomic) transition dipole moments were proved to be sufficient to establish these estimates. However, the practical implementation of cold molecule formation via photoassociation requires a much better knowledge of their electronic properties such as improved potential curves and radial variation of permanent or transition dipole moments, in order to better guide the experimentalists towards specific systems and transitions with maximal efficiency. It is also well known that the computation of transition dipole moments is a sensitive test of the variation of the electronic wavefunctions with the interatomic distance, in contrast with the calculation of potential energy resulting from an expectation value of the hamiltonian operator for a given electronic wavefunction. Moreover, permanent dipole moments of excited states are worthwhile to study, as they could be checked against spectroscopic measurements performed in the presence of electric fields [22].

Within such perspectives, we started recently a new accurate investigation of electronic properties of all alkali pairs from Li to Fr, such as potential curves for ground and excited states, and permanent and transition dipole moments. We used a quantum chemistry approach involving one active electron's effective potentials for the representation of the atomic cores. We first investigated the variation with the interatomic distance and with the vibrational level of the permanent dipole moment of the ground state and the lowest triplet state of all mixed alkali pairs from Li to Cs [23] for which only scattered experimental or theoretical results were available at that time. We extended our calculations to the electronic properties of francium diatomic compounds Fr_2, RbFr and CsFr [24]. Potential curves, permanent and transition moments were determined for the first time for these systems and we investigated the possibility of creating cold Fr_2 and RbFr molecules.

In the present paper, we extend this study to the sodium heteronuclear compounds NaK, NaRb, and NaCs. These molecules are indeed systems of choice for the creation of ultracold dipolar gases, due to their large permanent dipole moment $D_{v=0}$ in the lowest vibrational level of their ground state ($\approx$2.7, 3.3 and 4.6 D, respectively [23], with $1\text{au} = 2.541\,580\,59$ Debye). Progress toward such a perspective has been achieved with the first observation of ultracold NaCs molecules [19, 25], followed by the more recent detection of ultracold LiCs molecules [20] (with $D_{v=0} \approx 5.5$ D [23]), and also the formation of heteronuclear molecules with a smaller dipole moment like KRb [16, 17] and RbCs [14, 15].

A large number of spectroscopic studies have been devoted to NaK and to a much smaller extent to NaRb and NaCs. An extensive list of references is available through the bibliographic database DiRef [26], and we quote here only a few papers among the most recent or the most significant. Spectroscopic constants and potential curves for low electronic states of NaK [27–29], NaRb [30, 31], and NaCs [32, 33] were obtained by Fourier transform (FT) spectroscopy or laser-induced fluorescence (LIF) recorded at high resolution by FT spectrometry, and by sub-Doppler high resolution spectroscopy or Doppler-free laser high resolution spectroscopy [34–37]. Optical–optical double resonance (OODR) spectroscopy gave access to higher electronic states of NaK [38–43] and NaRb [22, 44–48]. Permanent dipole moments of NaK were extracted from microwave optical double resonance (MODR) spectroscopy by Wormsbecher *et al.* [40] and from OODR spectroscopy by Laub *et al.* [38] and Burns *et al.* [43]. Tamanis *et al.* [49] used radiofrequency optical double resonance (rf-ODR) to measure radiative lifetimes of $D^1\Pi$ levels of NaK and extracted permanent and transition moments. Other methods like Stark level crossing and $e-f$ mixing spectroscopy [50], time-resolved Stark spectroscopy [51], or LIF spectroscopy [29], also allowed the measurement of permanent electric dipole moments in NaK. Of particular interest is the time-resolved LIF experiment of Klincare *et al.* in NaRb, focused on the determination of the radiative lifetime and of the quenching collision cross-section [47, 48].

These molecules have also been investigated in several quantum chemistry works that we will quote in the next section to compare them with our own computations. In the past, systematic computations of permanent and transition dipole moment functions have been only reported for NaK [52–55], while scattered data are available for NaRb [49] and NaCs [56]. In the following, we determine accurate values of permanent dipole and transition dipole moments for excited states of alkali dimers NaK, NaRb and NaCs. We will consider the lightest species NaK as a benchmark for our computations. In the next section, we briefly recall our approach, emphasizing the possible empirical corrections which are sometimes added to the computed potential energy curves, while results for permanent and transition dipole moments are displayed in sections 3 and 4. The paper is completed with tables for potential energy curves and permanent and transition dipole moment functions as supplementary material (deposited with British Library Supply Centre: reference number SUP 16180).

2. Effective potential calculations and empirical contributions to the molecular energy

We used the same automated procedure that we developed in [23, 24], based on the CIPSI package (Configuration Interaction by Perturbation of a multiconfiguration wavefunction Selected Iteratively) [57] developed by the 'Laboratoire de Physique Quantique de Toulouse (France)'. The approach is based on the ℓ-dependent pseudopotentials of Durand and Barthelat [58, 59] for atomic core representation, Gaussian basis sets, and effective terms for core polarization (CPP) [60, 61]. The CPPs involve empirical cut-off radii which are varied in order to reproduce the lowest atomic level of *s*, *p* and *d* symmetries. We performed potential curve calculations via a full configuration interaction (CI), with extended Gaussian basis sets in order to check the convergence of the results with respect to the basis set size. Extensive details on the method can be found in [23, 24] and are not repeated here.

As a supplementary check of the consistency of our calculations, we calculated the electron affinities of the alkali atoms Li, Na, K, Rb, and Cs with both A and B basis sets defined in [23]. The inclusion of additional diffuse orbitals in basis set B indeed seems to improve the results (see table 1) at the level of the accuracy of a few tens of wavenumbers expected for such calculations.

Table 1. Electronic affinities (in cm^{-1}) of the alkali atoms as computed in the resent work, and compared to experiment.

Atom	Basis A	Basis B	Expt.[ref]
Li	4924	5054	4984 [62]
Na	4386	4420	4419 [62]
K	3995	4004	4043 [62]
Rb	3836	3866	3920 [62]
Cs	3684	3736	3920 [62]

Potential energy curves of ground and excited states of sodium alkali compounds have been determined previously, using the same CIPSI package as in the present study, by Jeung *et al.* [64] and by Magnier *et al.* [54, 55] for NaK, and by Korek *et al.* [65, 66] for NaRb and NaCs. Other *ab initio* and pseudopotential approaches have also been used by Janoschek and Lee for NaK [67] and Stevens *et al.* [52]. It is worthwhile mentionning that comparison with other works is not always easy, as basis sets or effective potential parameters are sometimes not fully reported (see for instance our discussion in [68]). Moreover in effective potential methods, empirical terms are sometimes added *a posteriori* to the potential energy like those proposed in [69] to account for the deviation of the core–core interaction from the $1/R$ asymptotic behaviour. This is the case for computations involving a large core potential, i.e. where only valence electrons are treated explicitly. A dispersive term $V_{\mathrm{cc}}^{\mathrm{disp}}(R)$ is usually expressed with the London formula:

$$V_{\mathrm{cc}}^{\mathrm{disp}}(R) = -\frac{3\alpha_{\mathrm{d}}^{\mathrm{Na}^+}\alpha_{\mathrm{d}}^{\mathrm{Y}^+}}{2R^6}\frac{E_{\mathrm{I}}^{\mathrm{Na}^+}E_{\mathrm{I}}^{\mathrm{Y}^+}}{E_{\mathrm{I}}^{\mathrm{Na}^+}+E_{\mathrm{I}}^{\mathrm{Y}^+}}, \quad (1)$$

where $E_{\mathrm{I}}^{\mathrm{Na}^+}$ and $E_{\mathrm{I}}^{\mathrm{Y}^+}$ are the ionization energies of the Na^+ and Y^+ (Y=K, Rb, Cs) ions, respectively. A short-range term accounting for the repulsion between the two ionic cores is represented in [69] with an exponential term like $V_{\mathrm{cc}}^{\mathrm{rep}}(R) = a_1 R^{a_2}\exp(-a_3 R)$, parameters of which are for instance adjusted on the value yielded by a Hartree–Fock calculation of the energy of the doubly-charged ion, assuming that both ionic cores are frozen. The arbitrariness of the implementation of such terms may lead to accidental agreement (or disagreement) when comparing to available experimental potential curves. Indeed, the $V_{\mathrm{cc}}^{\mathrm{disp}}(R)$ term has to be cut off at an arbitrary small distance R. The calculation of the $V_{\mathrm{cc}}^{\mathrm{rep}}(R)$ term is actually very sensitive to the way core polarization effects are treated in the quantum chemistry approach [70]. Then these two contributions are not independent from each other so that it is hopeless to try to establish the accuracy of the computed potential curves to an amount smaller than the magnitude of these terms, i.e. typically several tens of wavenumbers.

An even more empirical way to evaluate these terms relies on the difference between the computed ground state potential $U_X^{\mathrm{qc}}(\mathrm{R})$ of a given molecule with its supposedly well-known experimental determination $U_X^{\mathrm{exp}}(\mathrm{R})$, for instance through an analysis of molecular spectra. The so-called 'difference-based' potential curve $U_Y^{\mathrm{diff}}(\mathrm{R})$ for an excited state Y is then defined as $U_Y^{\mathrm{diff}}(R) = U_Y^{\mathrm{qc}}(R) + (U_X^{\mathrm{qc}}(R) - U_X^{\mathrm{exp}}(R))$. Such a model is valid if we assume that the difference on the X state potential can be transferred to excited states, i.e. that the missing part of the short-range interaction is independent of the excited state Y of the molecule. This trick has been recently used by molecular spectroscopy groups [32, 37] in order to define a good quality initial potential curve for electronically excited states to start the fitting procedure of their large set of spectroscopic lines. For instance, the main spectroscopic constants of the NaRb molecule such as transition energy, well depth, and harmonic and rotational constants are indeed improved using this empirical procedure [37]. We illustrate this procedure with the ground state of the

NaRb and NaCs molecules (figure 1). As expected from our previous works, the convergence of the potential energy with the size of the basis is fulfilled. The depth of the X potential is deeper by $59\,\mathrm{cm}^{-1}$ and $34\,\mathrm{cm}^{-1}$ with basis B rather than with basis A, for NaRb and NaCs, respectively. Comparatively, the depth of the a potential well is converged at a few percent level as well, i.e. it is $2\,\mathrm{cm}^{-1}$ in NaRb and $9\,\mathrm{cm}^{-1}$ deeper in NaCs with basis B than with basis A. The difference between the experimentally determined ground state potential curves [30–32] and the computed ones almost vanishes around the equilibrium distance R_e, and keeps a magnitude within a few tens of wavenumbers for $R > R_e$ over the range of the exchange interaction (say for $R < 20\,a_0$), representative of the typical accuracy of quantum chemistry calculations for such systems. For distances smaller than R_e, our computed curve has a smaller potential energy, and is somewhat deeper than the experimental one. Therefore the theoretical equilibrium distance R_e and the vibrational constant ω_e are slightly smaller than the experimental ones (figure 1), which confirms that our calculations—without including any empirical contribution—underestimate the repulsive interaction between the ionic cores. In such circumstances, it is not meaningful to discuss in detail the standard spectroscopic constants, as the computed values will generally be in agreement with the experimental ones within the above limits, with occasional coincidences. Such a trend is also obtained in other published calculations, as for instance in Rb_2 [71] or RbCs [69, 72], but as already noticed, the comparison is not easy as the details of the included empirical terms are not always available. The difference $U_X^{\mathrm{qc}}(R)$–$U_X^{\mathrm{exp}}(R)$ actually shows an exponentially decreasing behaviour with increasing R (figures 1(c) and (d)), in accordance with the empirical terms discussed above.

We compared the difference-based potentials constructed from our calculations to the few experimentally-determined excited potential curves for NaRb ($(2)^1\Pi$ [32], $(3)^1\Sigma^+$ [73], $(6)^1\Sigma^+$ [45]), and NaCs ($(3)^1\Pi$) [33] reported in the literature. We display an illustration for the last case (figure 2). It is not easy to draw a general conclusion from such tests. As expected, the position of the repulsive wall of the excited potential is greatly improved (see the dashed curve in figure 2), as we already knew that our calculations without empirical terms underestimate the core–core repulsion. In the region of the equilibrium distance, the difference between the computed and experimental potential energy curves has a similar magnitude as the one for the X state, so that the improvement yielded by the difference-based potential is not clear. In particular, the variation of $(U_Y^{\mathrm{diff}}(R) - U_Y^{\mathrm{exp}}(R))$ is less smooth than the one of $(U_Y^{\mathrm{qc}}(R) - U_Y^{\mathrm{exp}}(R))$, which simply shows that this approximation is not valid, as the curve reflects the different nature of the electronic wavefunctions of the X and the $(3)^1\Pi$ states.

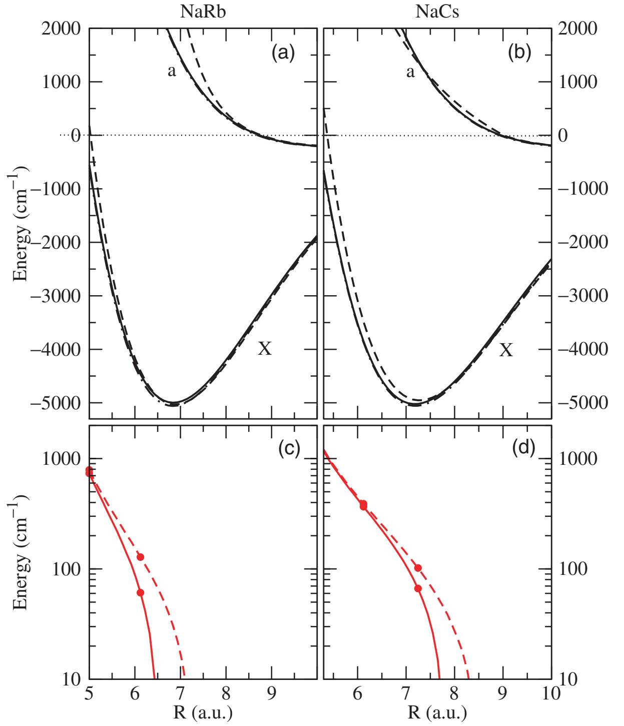

Figure 1. Potential curves for the ground state $X^1\Sigma^+$ and $a^3\Sigma^+$ of the NaRb (panel (a)) and NaCs (panel (b)) molecules. Full lines and dot-dashed lines: our calculations with basis A and B, respectively, for both atoms. Dashed lines: experimental curve from [30, 31] and [32]. In panels (c) and (d), we show the difference of the experimental ground state potential with the computed ones $U_X^{\mathrm{exp}}(R)) - U_X^{\mathrm{qc}}(R)$ on a logarithmic scale, for basis A (full line) and basis B (dashed line), respectively. The exponential variation of this quantity is clear almost up to the equilibrium distance.

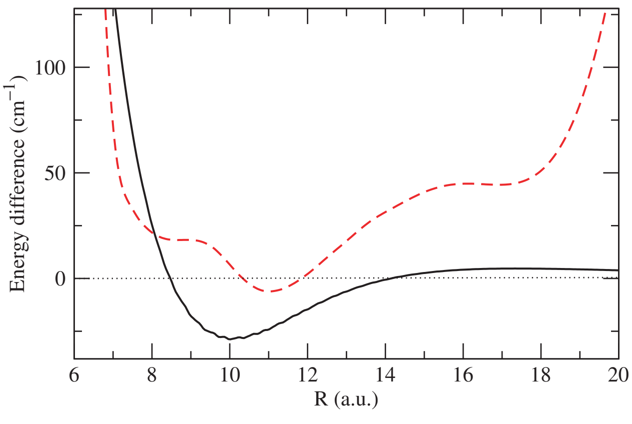

Figure 2. Radial variation of $(U_Y^{\mathrm{qc}}(R) - U_Y^{\mathrm{exp}}(R))$ (full line) and $(U_Y^{\mathrm{diff}}(R) - U_Y^{\mathrm{exp}}(R))$ (dashed line), for the $Y \equiv (3)^1\Pi$ state of NaCs, experimentally determined in [33].

An exhaustive comparison of our results with the wealth of other theoretical data is tedious to describe in detail within the body of the present paper. For the interested reader, the corresponding numerical data is attached to this paper as supplementary material, for further reference. In these tables, we have not included any of the empirical contributions above, in order to allow unambiguous comparison with other works.

3. Results for permanent dipole moments of excited states

In contrast with potential curves, systematic computations of permanent or transition dipole moments as functions of the internuclear distance are not often performed, and only a few data are actually available for alkali dimers. In this respect, the NaK molecule represents a favourable case, as several works using similar ECP approaches by Magnier *et al.* [54, 55], Stevens *et al.* [52] and Ratcliff *et al.* [53] yield extended tables of transition dipole moments. Using the multipartitioning perturbation theory (MPPT) Tamanis *et al.* [49, 74] have calculated transition and permanent dipole moments of the lowest electronic states of NaK. The MPPT theory has also been used by Nikolayeva *et al.* [22] to calculate permanent dipole moments of several NaRb states and by Zaitsevskii *et al.* and by Klincare *et al.* [46, 48] to calculate transition moments of NaRb. To our knowledge, only one computation of these quantities for NaCs has been published up to now [56].

It is worthwhile to mention that the empirical energy corrections discussed above have no influence on the electronic wavefunctions, so that only the vibrational wavefunctions and then the spectroscopic constants may be affected by them. We carried out our calculations of permanent and transition dipole moments using the extended basis ‘B’ of uncontracted Gaussian functions introduced in [23]. For the three molecules, we computed all possible dipole moment functions between $4\,a_0$ and $30\,a_0$ ($a_0 = 0.052\,9177$ nm) involving the first seven states of ${}^1\Sigma^+$, ${}^3\Sigma^+$, ${}^1\Pi$, ${}^3\Pi$ symmetries (see the supplementary material deposited with the British Library Supply Centre). The grid step ($0.2\,a_0$) is significantly smaller than in other papers, which ensures that the abrupt variations of the dipole moment functions due to sudden changes of the electronic wavefunctions are properly described.

In the following we illustrate this huge amount of data with a selection of figures concerning molecular states relevant for experimental studies. Figure 3 reveals the similarities and differences between the three molecules

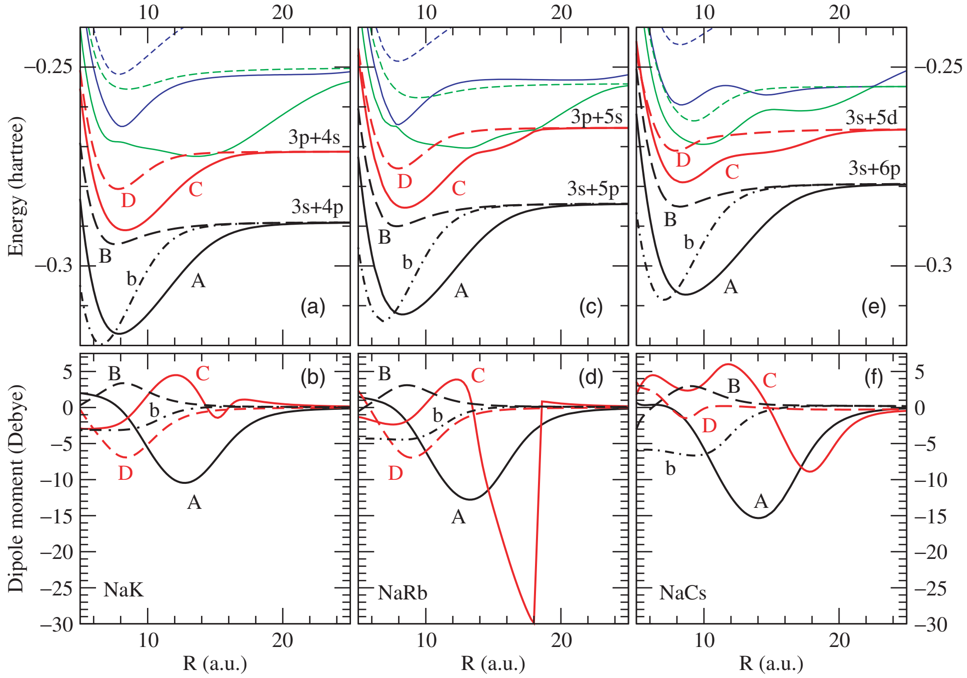

Figure 3. Computed potential curves and permanent dipole moments (in basis B) for the lowest singlet excited states of NaK ((a), (b)), NaRb ((c), (d)), NaCs ((e), (f)). $A^1\Sigma^+$ and $C^1\Sigma^+$ curves are drawn with full lines, and $B^1\Pi$ and $D^1\Pi$ curves with dashed lines. The lowest $b^3\Pi$ curves are also displayed (dot-dashed line), due to the well-known spin–orbit interaction with the A state. The upper ${}^1\Sigma^+$ and ${}^1\Pi$ potential curves (thin full and dashed lines, respectively, in panels (a), (c), (e)) are drawn in order to visualize possible avoided crossings with the lower curves.

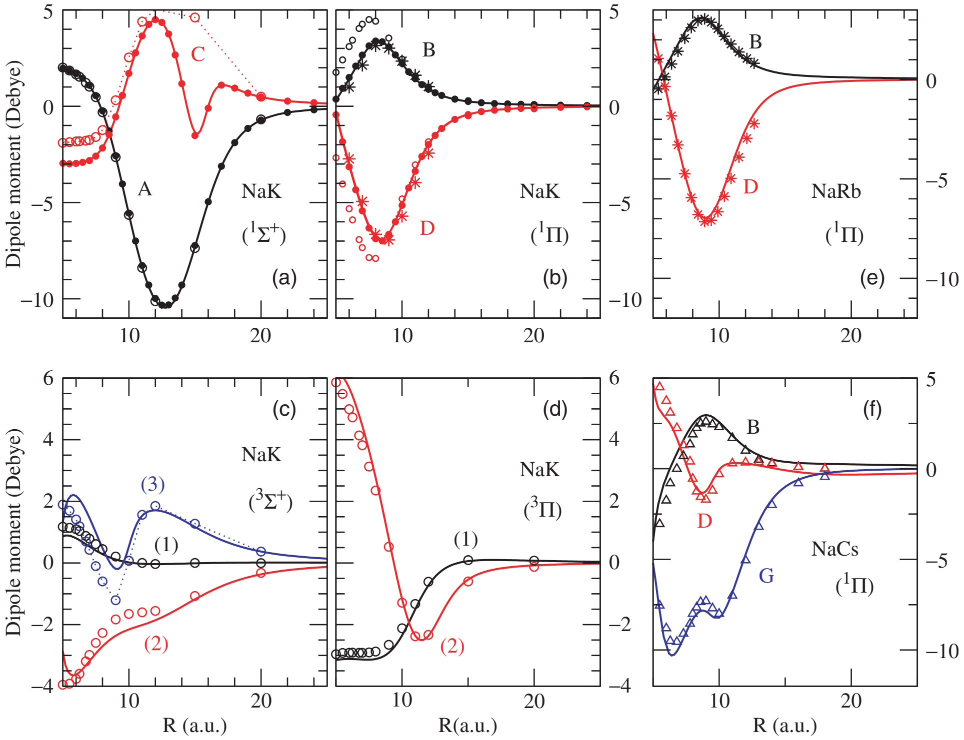

Figure 4. Present computed (with basis B) permanent dipole moments (full lines) compared to other theoretical values, for the NaK (panels (a)–(d)), NaRb (panel (e)), and NaCs (panel (f)). Full circles: [55]; Open circles: [52]; Stars: [74] for NaK and [22] for NaRb; Triangles: [56].

through the permanent dipole moment of their four lowest singlet excited states and the lowest $^3\Pi$ state, as an extension of the discussion on the ground state permanent dipole moments of [23]. Let us recall that the $(2)^1\Sigma^+$, $(3)^1\Sigma^+$, $(1)^1\Pi$, $(2)^1\Pi$ and $(1)^3\Pi$, are usually referred to as A, C, B, D and b states in molecular spectroscopy, as reported in figure 3. We chose the following sign convention as in [24]: a negative value indicates the charge asymmetry Na^+K^-, Na^+Rb^- and Na^+Cs^-. It is clear that the positions of the irregularities in the R-dependence of permanent dipole are correlated to the avoided crossings between potential curves, which are both manifestations of abrupt changes of the character of the electronic wavefunctions.

Let us note Magnier *et al.* [54, 55] employed the contracted Gaussian basis sets labelled as 'A' in [23] for their study on NaK. They provided permanent and transition dipole moment functions concerning the lowest 8 $^{1,3}\Sigma^+$, 8 $^{1,3}\Pi$ states and 6 $^{1,3}\Delta$ symmetries. Previously Ratcliff *et al.* [53] reported data for transitions between the lowest 5 $^{1,3}\Sigma^+$, 3 $^{1,3}\Pi$ states and 3 $^{1,3}\Delta$ states, using a rather small basis set. As a general statement, we checked that the results are converged with respect to the size of the basis, as transition dipole moments obtained with basis 'A' or 'B' always differ by less than 1%. This confirms the trend we previously observed for permanent dipole moment functions [23], and then confirms the good quality of the computed electronic wavefunctions. This is illustrated with figure 4 which displays our results compared to permanent dipole moments which are available in the literature for the excited states. It concerns electronic states correlated to the two lowest excited asymptotes where one atom is in the ground state and the other in the lowest p level: the $A(2)^1\Sigma^+$, $C(3)^1\Sigma^+$, $B(1)^1\Pi$, $D(2)^1\Pi$, $(2)^3\Sigma^+$, $(3)^3\Sigma^+$, $b(1)^3\Pi$, $d(3)^3\Pi$. We used here the numbering with increasing energy, together with the standard spectroscopic notations with letters. It is clear that our results and those of [55] (with the opposite sign convention) for NaK are identical. The agreement is also very good with the MPPT studies of [22, 49, 56], as already observed by the same group on a couple of transition dipole moments [48]. This actually represents an important statement, as the methods are really different. It probes directly the electronic wavefunctions for which effective core polarization potentials accurately describe core excitations. The agreement for NaK with the results of [52] is also satisfactory, however with several differences for the B, C, D and $(3)^3\Sigma^+$ states. First the size of the grid step is crucial to properly

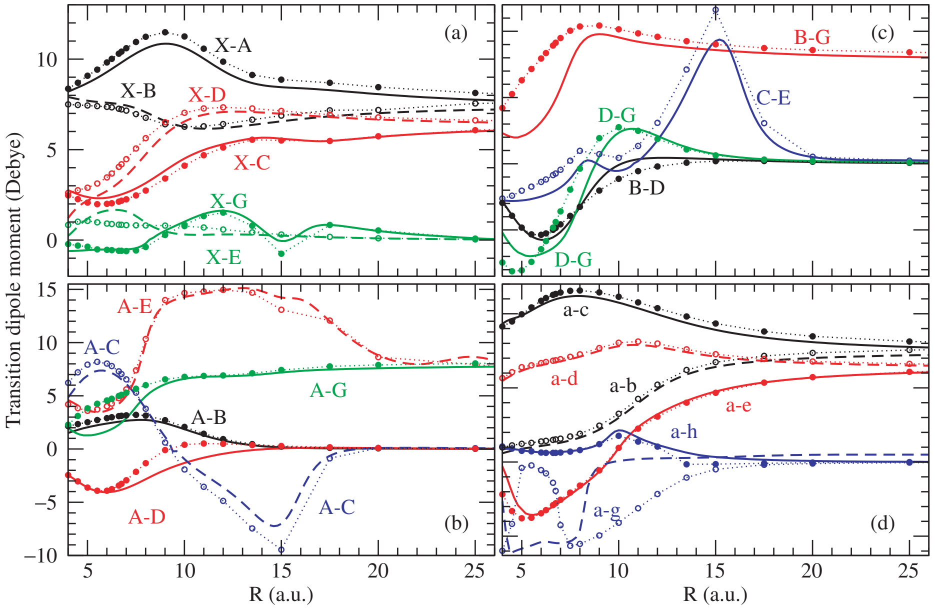

Figure 5. Comparison of the present computed (with basis B) NaK transition dipole moments (in full lines and dashed lines) with the values of [53] (closed and open circles), for a selected set of singlet and triplet transitions labelled with letters according to standard spectroscopic notation: $X\equiv(1)^1\Sigma^+$; $A\equiv(2)^1\Sigma^+$; $C\equiv(3)^1\Sigma^+$; $E\equiv(4)^1\Sigma^+$; $B\equiv(1)^1\Pi$; $D\equiv(2)^1\Pi$; $G\equiv(3)^1\Pi$; $a\equiv(1)^3\Sigma^+$; $c\equiv(2)^3\Sigma^+$; $e\equiv(3)^3\Sigma^+$; $b\equiv(1)^3\Pi$; $d\equiv(2)^3\Pi$; $g\equiv(3)^3\Pi$. The $\Sigma^+-\Pi$ transition dipole moments of [53] have been divided by $2^{1/2}$. By convention we chose transition dipole moments positive at large distances so that we changed the sign of a few moments of [53].

describe the abrupt variations of the C and $(3)^3\Sigma^+$ dipole moments. The other differences are probably due to the different nature of the basis functions in [52] (Slater-type orbitals) and the smaller size of the basis set.

4. Results for transition dipole moments

4.1. *NaK*

As already quoted, the NaK molecule has been the only one of the present group to be extensively studied in previous works using the ECP approach [53–55]. As expected, the present numerical values are in good agreement with those of Magnier *et al.* [55]. However, we note that the results in the supplementary tables of [55] are reported in absolute values, so that all changes of sign are converted into angular points in the corresponding curves. This may have important consequences for the strength of some electronic transitions. In this respect, we recommend to use the tables attached to the present paper, which can be considered as an update of those of [55].

Figure 5 displays results for transitions involving singlet and triplet states which are—or could be—relevant for molecular spectroscopy or for detection schemes of ultracold NaK molecules. The agreement with the extensive data set of Ratcliff *et al.* [53] is generally satisfactory, as the global variation of the functions are similarly reproduced by both approaches. First we see the interest of computing such functions on a thin grid in R, as their abrupt variations and changes of sign are well described and properly identified. A few discrepancies occur when highly-excited states are concerned, visible at short distances for the $X-E$, $A-D$, $D-G$ singlet transitions, and for the $a-g$ triplet transitions. Note that we use here the letter symbols to label the molecular states, which are explained in the caption of figure 5. Also, the extrema of the $A-C$ and $C-E$ transition functions are more smoothly described in our results than in those of [53]. Changes of sign like those in the $X-G$ and $A-C$ transitions correspond to sudden changes of the electronic wavefunctions, most often linked to avoided crossings in potential curves. This is also the case when the transition function drops down to zero at quite large distance, like for the $A-E$ transition beyond $15\,a_0$.

4.2. *NaRb and NaCs*

As already mentioned, the comparison of our data is limited to a couple of theoretical papers from the groups in Riga and Moscow [46, 48], who used an entirely different method (MPPT). They reported results for singlet transitions on a rather restricted R-range relevant for their related spectroscopy investigations. The agreement is excellent with our data (figure 6). This suggests that both the Riga–Moscow approach and our approach have converged to accurate results.

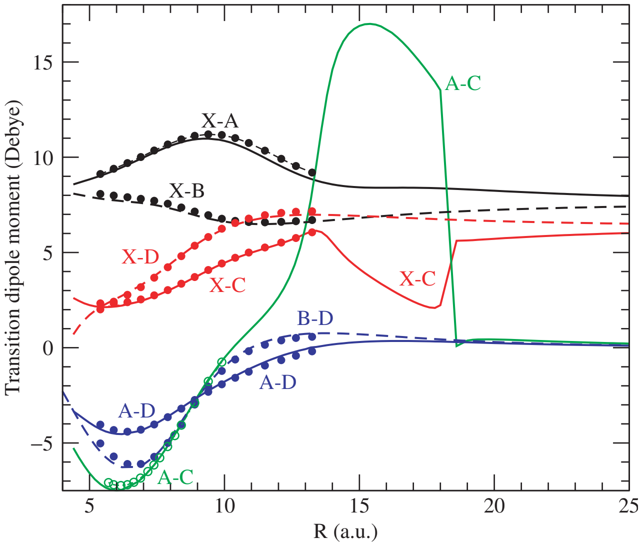

Figure 6. Comparison of the present computed (with basis B) NaRb transition dipole moments (in full lines and dashed lines) with those calculated for several singlet transitions in [46, 48] (closed and open circles, respectively). Molecular states are labelled with letters according to standard spectroscopic notations: $X\equiv(1)^1\Sigma^+$; $A\equiv(2)^1\Sigma^+$; $C\equiv(3)^1\Sigma^+$; $E\equiv(4)^1\Sigma^+$; $B\equiv(1)^1\Pi$; $D\equiv(2)^1\Pi$; $G\equiv(3)^1\Pi$. By convention we chose transition dipole moments positive at large distances.

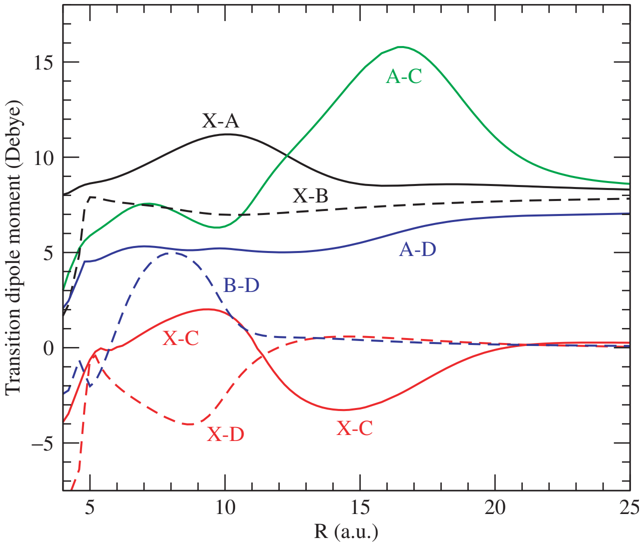

Figure 7. NaCs transition dipole moments (in full lines and dashed lines) computed (with basis B) in the present work. Molecular states are labelled with letters according to standard spectroscopic notations: $X\equiv(1)^1\Sigma^+$; $A\equiv(2)^1\Sigma^+$; $C\equiv(3)^1\Sigma^+$; $E\equiv(4)^1\Sigma^+$; $B\equiv(1)^1\Pi$; $D\equiv(2)^1\Pi$; $G\equiv(3)^1\Pi$. By convention we chose transition dipole moments positive at large distances.

The dipole functions for the triplet transitions in NaRb are provided here for the first time (see the supplementary tables accompanying the present paper). Again, the abrupt variation of the $X-C$ and $A-C$ functions arise from the avoided crossing in the C state, related to strong interaction of the covalent state with the ion-pair state around 20 a_0. The associated energy range was not explored in the spectroscopic investigations of [46, 48].

Finally, no published data are available on permanent or transition moments in NaCs to our knowledge, although the Riga–Moscow–Hannover groups are pursuing the spectroscopic investigations on this molecule [75]. We display in figure 7 a selection of results corresponding to the same transitions as those reported in figure 6. As in the case above, the avoided crossings of the potential curves also correspond to abrupt variations of the dipole moment functions. However the variations for NaCs are smoother than for NaRb, as the avoided crossings are larger, or in other words, 'more avoided' than in NaRb.

5. Conclusion

With this paper, we provided careful calculations of the electronic structure of heteronuclear alkali diatomics involving sodium atoms, accompanied with extensive supplementary material for potential energy curves, as well as permanent and transition dipole moment functions. Our goal was to deliver a set of data as complete as possible concerning molecular systems which are among the preferred prototypes for pioneering experiments and theoretical investigations with dipolar molecules. This work represents an update for data previously published by various groups on the NaK species, emphasizing the evaluation of their accuracy with respect to the size of the basis sets, and the comparison with other methods. Only a few calculations using a different method have been previously reported for NaRb dipole moment functions related to singlet transitions, with which our results are in good agreement. The present work therefore extends the knowledge of the NaRb structure to higher excited states. Our results concerning NaCs are entirely new, and will certainly be helpful for the preparation of ultracold samples of this strongly dipolar species [25]. The inclusion of the molecular spin–orbit interaction for these systems are in progress in our group.

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References

[1] Special issue on ultracold polar molecules Eur. Phys. J. D **31,** 149 (2004).

[2] Special issue on ultracold polar molecules J. Phys. B **39,** S213 (2006).
[3] B. Friedrich and D. Herschbach, J. Chem. Phys. **111,** 6157 (1999).
[4] J. L. Bohn and A. V. Avdeenkov, Phys. Scr. **T110,** 292 (2004).
[5] A. Micheli, G. K. Brennen, and P. Zoller, Nat. Phys. **2,** 341 (2006).
[6] M. A. Baranov, L. Dobrek, and M. Lewenstein, New J. Phys. **6,** 198 (2004).
[7] S. Kallush, B. Segev, and R. Côté, Phys. Rev. Lett. **95,** 163005 (2005).
[8] D. DeMille, Phys. Rev. Lett. **88,** 067901 (2002).
[9] M. G. Kozlov and D. DeMille, Phys. Rev. Lett. **89,** 133001 (2002).
[10] J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. **89,** 023003 (2002).
[11] S. Schiller and V. Korobov, Phys. Rev. A **71,** 032505 (2005).
[12] H. L. Bethlem, G. Berden, and G. Meijer, Phys. Rev. Lett. **83,** 1558 (1999).
[13] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, and P. Pillet, Phys. Rev. Lett. **80,** 4402 (1998).
[14] A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, Phys. Rev. Lett. **92,** 153001 (2004).
[15] J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, Phys. Rev. Lett. **94,** 203001 (2005).
[16] M. W. Mancini, G. D. Telles, A. R. L. Caires, V. S. Bagnato, and L. G. Marcassa, Phys. Rev. Lett. **92,** 133203 (2004).
[17] D. Wang, J. Qi, M. F. Stone, O. Nikolayeva, B. Hattaway, S. D. Gensemer, H. Wang, W. T. Zemke, P. L. Gould, E. E. Eyler, and W. C. Stwalley, Eur. Phys. J. D **31,** 165 (2004).
[18] J. P. Shaffer, W. Chalupczak, and N. P. Bigelow, Phys. Rev. Lett. **82,** 1124 (1999).
[19] C. Haimberger, J. Kleinert, M. Bhattacharya, and N. P. Bigelow, Phys. Rev. A **70,** 21402 (2004).
[20] S. D. Kraft, P. Staanum, J. Lange, L. Vogel, R. Wester, and M. Weidemüller, J. Phys. B **39,** S993 (2006).
[21] S. Azizi, M. Aymar, and O. Dulieu, Eur. Phys. J. D **31,** 195 (2004).
[22] O. Nikolayeva, I. Klincare, M. Auzinsh, M. Tamanis, R. Ferber, E. A. Pazyuk, A. V. Stolyarov, A. Zaitsevskii, and R. Cimiraglia, J. Chem. Phys. **113,** 4896 (2000).
[23] M. Aymar and O. Dulieu, J. Chem. Phys. **122,** 204302 (2005).
[24] M. Aymar, O. Dulieu, and F. Spiegelmann, Eur. Phys. J. D **39,** S905 (2006).
[25] C. Haimberger, J. Kleinert, O. Dulieu, and N. P. Bigelow, J. Phys. B **39,** S957 (2006).
[26] P. F. Bernath and S. McLeod, J. Molec. Spectrosc. **207,** 287 (2001).
[27] A. J. Ross, C. Effantin, J. d'Incan, and R. F. Barrow, Molec. Phys. **56,** 903 (1985).
[28] A. J. Ross and G. H. Jeung, Chem. Phys. Lett. **132,** 44 (1986).
[29] R. Ferber, E. A. Pazyuk, A. V. Stolyarov, A. Zaitsevskii, P. Kowalczyk, H. Chen, H. Wang, and W. C. Stwalley, J. Chem. Phys. **112,** 5740 (2000).
[30] O. Docenko, M. Tamanis, R. Ferber, A. Pashov, H. Knöckel, and E. Tiemann, Phys. Rev. A **69,** 042503 (2004).
[31] A. Pashov, O. Docenko, M. Tamanis, R. Ferber, H. Knöckel, and E. Tiemann, Phys. Rev. A **72,** 062505 (2005).
[32] O. Docenko, M. Tamanis, R. Ferber, A. Pashov, H. Knöckel, and E. Tiemann, Eur. Phys. J. D **31,** 205 (2004).
[33] O. Docenko, M. Tamanis, J. Zaharova, R. Ferber, A. Pashov, H. Knöckel, and E. Tiemann, J. Chem. Phys. **124,** 174310 (2006).
[34] U. Diemer, H. Weickenmeier, M. Wahl, and W. Demtröder, Chem. Phys. Lett. **104,** 489 (1984).
[35] M. Baba, S. Tanaka, and H. Kato, J. Chem. Phys. **89,** 7049 (1988).
[36] Y.-C. Wang, M. Kajitani, S. Kasahara, M. Baba, K. Ishikawa, and H. Kato, J. Chem. Phys. **95,** 6229 (1991).
[37] M. Tamanis, R. Ferber, A. Zaitsevskii, E. A. Pazyuk, A. V. Stolyarov, H. Chen, J. Qi, H. Wang, and W. C. Stwalley, J. Chem. Phys. **117,** 7980 (2002).
[38] E. Laub, I. Mazsa, S. C. Webb, J. La Civita, I. Prodan, Z. J. Jabbour, R. K. Namiotka, and J. Huennekens, J. Molec. Spectrosc. **193,** 376 (1999).
[39] S. Kasahara, H. Ikoma, and H. Kato, J. Chem. Phys. **100,** 63 (1994).
[40] R. F. Wormsbecher, M. M. Hessel, and F. J. Lovas, J. Chem. Phys. **74,** 6983 (1981).
[41] Z. J. Jabbour and J. Huennekens, J. Chem. Phys. **107,** 1094 (1997).
[42] A. Pashov, I. Jackowska, W. Jastrzebski, and P. Kowalczyk, Phys. Rev. A **58,** 1048 (1998).
[43] P. Burns, L. Sibbach-Morgus, A. D. Wilkins, F. Halpern, L. Clarke, R. D. Miles, L. Li, A. P. Hickman, and J. Huennekens, J. Chem. Phys. **119,** 4743 (2003).
[44] S. Kasahara, T. Ebi, M. Tanimura, H. Ikoma, K. Matsubara, M. Baba, and H. Kato, J. Chem. Phys. **105,** 1341 (1996).
[45] P. Kortyka, W. Jastrzebski, and P. Kowalczyk, Chem. Phys. Lett. **404,** 323 (2005).
[46] A. Zaitsevskii, S. O. Adamson, E. A. Pazyuk, A. V. Stolyarov, O. Nikolayeva, O. Docenko, I. Klincare, M. Auzinsh, M. Tamanis, R. Ferber, and R. Cimiraglia, Phys. Rev. A **63,** 052504 (2001).
[47] I. Klincare, M. Tamanis, and R. Ferber, Chem. Phys. Lett. **382,** 593 (2003).
[48] I. Klincare, M. Tamanis, R. Ferber, A. Zaitsevskii, E. A. Pazyuk, and A. V. Stolyarov, Eur. Phys. J. D **39,** 373 (2006).
[49] M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, R. Ferber, A. Zaitsevskii, E. A. Pazyuk, and A. V. Stolyarov, J. Chem. Phys. **109,** 6725 (1998).
[50] M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, A. V. Stolyarov, and R. Ferber, J. Chem. Phys. **106,** 2195 (1997).
[51] J. Derouard, H. Debontride, T. D. Nguyen, and N. Sadeghi, J. Chem. Phys. **90,** 5936 (1989).
[52] W. J. Stevens, D. Konowalow, and L. R. Ratcliff, J. Chem. Phys. **80,** 1205 (1984).
[53] L. R. Ratcliff, D. Konowalow, and W. J. Stevens, J. Molec. Spectrosc. **110,** 242 (1985).
[54] S. Magnier and P. Millié, Phys. Rev. A **54,** 204 (1996).
[55] S. Magnier, M. Aubert-Frécon, and P. Millié, J. Molec. Spectrosc. **200,** 96 (2000).

[56] J. Zaharova, O. Nikolayeva, M. Tamanis, M. Auzinsh, R. Ferber, A. Zaitsevskii, E. A. Pazyuk, and A. V. Stolyarov, J. Chem. Phys. **124,** 184318 (2006).
[57] B. Huron, J.-P. Malrieu, and P. Rancurel, J. Chem. Phys. **58,** 5745 (1973).
[58] P. Durand and J. C. Barthelat, Chem. Phys. Lett. **27,** 191 (1974).
[59] P. Durand and J. C. Barthelat, Theor. Chim. Acta **38,** 283 (1975).
[60] W. Müller and W. Meyer, J. Mod. Opt. **80,** 3311 (1984).
[61] M. Foucrault, Ph. Millié, and J. P. Daudey, J. Chem. Phys. **96,** 1257 (1992).
[62] T. Andersen, H. K. Haugen, and H. Hotop, J. Phys. Chem. Ref. Data **28,** 1511 (1999).
[63] K. T. Andersson, J. Sandstrom, I. Yu. Kiyan, D. Hanstorp, and D. J. Pegg, Phys. Rev. A (At. Molec. Opt. Phys.) **62,** 022503 (2000).
[64] G.-H. Jeung, J.-P. Daudey, and J.-P. Malrieu, Chem. Phys. Lett. **94,** 300 (1983).
[65] M. Korek, A. R. Allouche, K. Fakhreddine, and A. Chaalan, Can. J. Phys., **78,** 977 (2000).
[66] M. Korek, A. R. Allouche, M. Kobeissi, A. Chaalan, M. Dagher, K. Fakherddin, and M. Aubert-Frécon, Chem. Phys. **256,** 1 (2000).
[67] R. Janoschek and H. U. Lee, Chem. Phys. Lett. **58,** 47 (1978).
[68] M. Aymar and O. Dulieu, J. Chem. Phys. **125,** 047101 (2006).
[69] D. Pavolini, T. Gustavsson, F. Spiegelmann, and J.-P. Daudey, J. Phys. B **22,** 1721 (1989).
[70] G.-H. Jeung, J. Molec. Spectrosc. **182,** 113 (1997).
[71] F. Spiegelmann, D. Pavolini, and J.-P. Daudey, J. Phys. B **22,** 2465 (1989).
[72] A. R. Allouche, M. Korek, K. Fakherddine, A. Chaalan, M. Dagher, F. Taher, and M. Aubert-Frécon, J. Phys. B **33,** 2307 (2000).
[73] W. Jastrzebski, P. Kortyka, P. Kowalczyk, O. Docenko, M. Tamanis, R. Ferber, A. Pashov, H. Knöckel, and E. Tiemann, Eur. Phys. J. D **36,** 57 (2005).
[74] M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, R. Ferber, E. A. Pazyuk, A. V. Stolyarov, and A. Zaitsevskii, Phys. Rev. A **58,** 1932 (1998).
[75] A. V. Stolyarov, private communication.