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High-correlation methods for the calculations of the ground ($X^1\Sigma^+$) and first low-lying excited ($A^3\Sigma^+$ and $A^1\Sigma^+$) states dipole polarizabilities of NaLi

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Abstract

The dipole polarizability of the ground $X^1\Sigma^+$ and excited $A^3\Sigma^+$, $A^1\Sigma^+$ states of NaLi has been investigated at the ab initio level with effective core polarization potentials, by using the time-dependent gauge invariant method (TDGI). In the case of $X^1\Sigma^+$ and $A^3\Sigma^+$ states, alternative high-correlation methods have been applied for comparison. The accuracy of calculated polarizability components is supported by a careful check of the convergence with respect to the number of the spectroscopic states. The dependence of the polarizability on internuclear separation has also been computed. All the calculated electric properties of $A^3\Sigma^+$ and $A^1\Sigma^+$ excited states are new.

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1. Introduction

The dipole polarizability, which describes the redistribution of the electronic charge cloud in the presence of an electric field, is one of the most interesting and useful properties of an atom, ion or molecule. This property is generally used as first ingredient to explain or predict many phenomena such as for example, molecular interactions, absorption, refraction and light scattering. The polarizability is the proportionality constant linking the induced dipole moment to the field strength

and is directly related to the second-order perturbation correction to the energy, when the dipolar distortion is treated as a perturbation. The theoretical determination of the polarizability of ground state has now reached a very high level of accuracy. As regards the diatomic molecule considered in this study, the difference between the high-correlation ab initio and experimental results generally lies within experimental error [1]. On the other hand, very little is known about the polarizability of the molecules in electronically excited states. This is mostly due to the lack of accurate experimental data. In fact, most of the data arise from the study of molecular spectra in solutions, where the dipole moments (μ), polarizabilities (α) and their respective changes on electronic excitation ($\Delta\mu, \Delta\alpha$) are measured as properties of the

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total system consisting of the solute molecule and surrounding solvent [2,3]. The ground and excited states polarizabilities are thus evaluated from models with a large number of parameters [2,3]. Obviously, in this situation, the very short life time of molecules in their excited states strengthens the difficulty to perform accurate measurement. However, recent progress in laser Stark spectroscopy [4] has made possible the direct determination of the excited state polarizability in some cases, but such measurements still seem difficult to perform routinely. Therefore, quantitatively accurate calculations of both electronic ground and excited state polarizabilities are needed to correctly model the solvent-effects, particularly in highly polarizable systems. This stimulates the present study, by using sophisticated *ab initio* methods, to provide reliable values of the excited state dipole moments and polarizabilities.

In previous papers [5–7], we have shown that the time-dependent gauge invariant (TDGI) approach is an efficient and reliable method for calculating the ground and excited states polarizabilities of atoms and molecules. In this work, we present some fairly extensive calculations of the static dipole polarizabilities of the ground ($X^1\Sigma^+$) and excited ($A^3\Sigma^+$, $A^1\Sigma^+$) states of NaLi. Alkali metal systems are very important species, since they are used in a variety of physical processes, ranging from atomic beam experiments to laser trapping technologies. Effective core polarization potentials, where NaLi is treated as a two-electron system, have been used.

As regards polarizability calculations, it is well known that polarizability most often displays an almost variational behavior becoming increasingly saturated with increasing basis set size. A large basis set has been used for this two-valence electron system, and special care has been taken to investigate the convergence of the polarizability with respect to the number of spectroscopic states included in the description of the first-order wavefunction. The final converged values for the ground ($X^1\Sigma^+$) and excited ($A^3\Sigma^+$) are compared to those obtained from high-correlation methods, namely Moller–Plesset (MP) perturbation theory and coupled cluster (CC) method, both implemented in the GAUSSIAN 98 package [8].

Finally, the dependence of the dipole moment and polarizability on internuclear separation, which is an important element of the theory of low-energy scattering of electrons from diatomic molecules, as well as the frequency-dependent dipole polarizabilities at imaginary frequencies, have been computed.

In Section 2, we briefly present our computational formalism. The numerical results including values for the transition energies, oscillator strengths, dipole moments and electric dipole polarizabilities are presented, discussed and compared with earlier theoretical and experimental results in Section 3. Unless otherwise stated, atomic units are used throughout this paper.

2. Method and computational details

A detailed description of the TDGI approach adopted here has been published elsewhere [9,10] and only a brief outline will be presented in this section. The method employs a variation-perturbation scheme in which the first-order Schrödinger equation which incorporates the dipole perturbation, is solved by an equivalent variational procedure. Both the zero-order and first-order perturbed wave-functions are expressed in terms of a configuration interaction (CI) expansion. We use an original expression of the first-order wavefunction $|1\rangle$ which is built from the combination of a first degree polynomial function [11] $g(r)$, true spectral states ψ_n and quasi-spectral series ϕ_m .

$$|1\rangle = g(r)|\psi_0\rangle + \sum_{n \neq 0}^N b_n |\psi_n\rangle + \sum_{m \neq 0}^M C_m |\phi_m\rangle$$

The expansion coefficients are obtained variationally. The polarizability α is then related to the second-order perturbation energy.

In short, we have shown [9,10] that the use of such a function (i) ensures gauge invariance, (ii) simulates part of the continuum contribution and (iii) partly corrects the restricted number of states in the construction of the first-order wavefunction, giving rise to a consistent method which is suitable for the calculation of the static or dynamic ground and excited states dipole polarizabilities of atoms and molecules [5–7].

Electron correlation effects on the electric properties have been taken into account by means of the multireference second-order many-body perturbation theory through the configuration interaction selected by an iterative process (CIPSI) algorithm [12,13]. Single and double excitations relative to the multireference were included to separately build the first excited states of each symmetry. For each symmetry, static dipole polarizabilities have been computed by including in the first-order wave-function the first 20 low-lying spectroscopic states and taking into account the quasi-spectral series and the first degree polynomial function. Thus, the convergence of the calculated properties with respect to the number of spectroscopic states can be investigated, as well as the evaluation of the contribution of each spectroscopic state to the dipole polarizability components. This will therefore support the accuracy of the converged values.

Pseudo-potential calculations with the core polarization potential (CPP) of Poteau and Spiegelmann [14] and that of Durand–Barthelat [15], for Li and Na, respectively, have been used. The core polarization potential operator is defined as in Meyer's initial formulation [16]. We followed the extension of Meyer's approach proposed by Foucrault et al. [17] with an l -dependent cutoff function.

The Gaussian-type orbital (GTO) basis sets for Li and Na built from Jeung's original basis sets [18,19] are taken from [14,20]. These basis sets including more diffuse functions consist of contracted [7s,5p,3d,1f] and [7s,5p,5d,2f], for Li and Na, respectively. The most diffuse exponents have been slightly modified.

As in our previous work [5,7], a correction of the oscillator strengths has been taken into account as proposed by Hameed et al. [21,22]. This correction slightly decreases the oscillator strengths, making them consistent with experiment and all-electron calculations.

As regards the $X^1\Sigma^+$ and $A^3\Sigma^+$ states, all-electron Møller–Plesset perturbation theory, where the correlation energy correction is truncated at second-order (MP2), third-order (MP3), fourth-order (MP4) and the Coupled-Cluster with single, double and a perturbative treatment of the connected tri-

ple excitation (CCSD(T)) method have been carried out by using the basis set of contracted Gaussian functions developed for the purpose of accurate high-level-correlated calculations of electric properties by Sadlej and Urban [23]. The s-, p- and d-type Gaussian-type-functions (GTFs) consist of (10s6p4d) contracted to [5s,3p,2d], and (13s10p4d) contracted to [7s,5p,2d], for Li and Na, respectively.

Finally, The dipole moment and dipole polarizability as a function of internuclear distances have been computed for small and large internuclear separations up to dissociation.

3. Results and discussion

Accurate calculation of the dipole polarizability, requires an adequate representation of the low-lying transition energies with a correct ordering of the spectrum. An explicit geometry optimization has been performed for each state considered in this work. We found the equilibrium distances of 2.908, 4.812, and 3.381 Å, for the $X^1\Sigma^+$, $A^3\Sigma^+$ and $A^1\Sigma^+$ states, respectively, in very good agreement with the experimental [24] value of 2.885 Å, for the $X^1\Sigma^+$ state, and previous pseudo-potential calculations [25] of 4.754, and 3.371 Å, for the excited $A^3\Sigma^+$ and $A^1\Sigma^+$ states, respectively. The vertical excitation energies and oscillator strengths calculated at optimized equilibrium geometries, from the pseudo-potential approach, are reported in Table 1, together with previous all-electron calculations [26] and experimental data [24,27,28]. Most of our calculated energy differences are within 2–10% of the measurements. On the other hand, we emphasize that the TDGI method is based on non-degenerate perturbation theory, and therefore is not suitable for degenerate or near-degenerate states. As can be seen from Table 1, all the calculated first few excited states are sufficiently separated in energy for the TDGI method to work well.

As introduced earlier, we have performed a state by state contribution of the close-lying spectroscopic state to total polarizability. Then, the convergence of the polarizability components with respect to the number of spectroscopic states

Table 1

First oscillator strengths (f_{ik}) and vertical transition energies (ΔE_{ik}) needed in the calculations of the TDGI (pseudo-potential) dipole polarizabilities of the ground ($X^1\Sigma^+$) and excited ($A^3\Sigma^+$, $A^1\Sigma^+$) states of NaLi, at their respective calculated equilibrium geometry of 2.908, 4.812 and 3.381 Å

| Transitions | ΔE_{ik} | f_{ik} | Transitions | ΔE_{ik} | f_{ik} |
|---|---|--------------------------|------------------------------------|---|--------------------------|
| $X^1\Sigma^+ \rightarrow A^1\Sigma^+$ | 0.067806 0.0694 ^a 0.064685 ^b | 1.580 1.650 ^a | $X^1\Sigma^+ \rightarrow B^1\Pi$ | 0.093858 0.0947 ^a 0.091414 ^c | 1.461 1.550 ^a |
| $X^1\Sigma^+ \rightarrow C^1\Sigma^+$ | 0.099793 0.1004 ^a 0.084753 ^b | 0.044 0.042 ^a | $X^1\Sigma^+ \rightarrow D^1\Pi$ | 0.109489 0.1126 ^a 0.101439 ^b | 0.094 0.042 ^a |
| $X^1\Sigma^+ \rightarrow E^1\Sigma^+$ | 0.123476 0.1241 ^a 0.120631 ^b | 0.002 0.002 ^a | $X^1\Sigma^+ \rightarrow G^1\Pi$ | 0.139618 0.1401 ^a | 0.090 0.122 ^a |
| $X^1\Sigma^+ \rightarrow F^1\Sigma^+$ | 0.136330 0.1357 ^a 0.133112 ^b | 0.021 0.024 ^a | $X^1\Sigma^+ \rightarrow I^1\Pi$ | 0.146519 0.1465 ^a | 0.094 0.010 ^a |
| $X^1\Sigma^+ \rightarrow H^1\Sigma^+$ | 0.140623 0.1429 ^a | 0.010 0.010 ^a | $X^1\Sigma^+ \rightarrow J^1\Pi$ | 0.154728 0.1669 ^a | 0.003 0.110 ^a |
| $A^3\Sigma^+ \rightarrow (2)^3\Sigma^+$ | 0.066309 | 1.368 | $A^3\Sigma^+ \rightarrow (1)^3\Pi$ | 0.067592 | 0.396 |
| $A^3\Sigma^+ \rightarrow (3)^3\Sigma^+$ | 0.078245 | 0.354 | $A^3\Sigma^+ \rightarrow (2)^3\Pi$ | 0.077583 | 1.324 |
| $A^3\Sigma^+ \rightarrow (4)^3\Sigma^+$ | 0.115254 | 0.001 | $A^3\Sigma^+ \rightarrow (3)^3\Pi$ | 0.122086 | 0.002 |
| $A^3\Sigma^+ \rightarrow (5)^3\Sigma^+$ | 0.122038 | 0.001 | $A^3\Sigma^+ \rightarrow (4)^3\Pi$ | 0.131529 | 0.006 |
| $A^3\Sigma^+ \rightarrow (6)^3\Sigma^+$ | 0.126376 | 0.004 | $A^3\Sigma^+ \rightarrow (5)^3\Pi$ | 0.135426 | 0.007 |
| $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ | -0.060088 | -1.658 | $A^1\Sigma^+ \rightarrow B^1\Pi$ | 0.028214 | 0.003 |
| $A^1\Sigma^+ \rightarrow C^1\Sigma^+$ | 0.028281 | 0.221 | $A^1\Sigma^+ \rightarrow D^1\Pi$ | 0.038446 | 0.104 |
| $A^1\Sigma^+ \rightarrow E^1\Sigma^+$ | 0.056245 | 0.553 | $A^1\Sigma^+ \rightarrow G^1\Pi$ | 0.072370 | 0.074 |
| $A^1\Sigma^+ \rightarrow F^1\Sigma^+$ | 0.068385 | 0.087 | $A^1\Sigma^+ \rightarrow I^1\Pi$ | 0.077702 | 0.382 |
| $A^1\Sigma^+ \rightarrow H^1\Sigma^+$ | 0.069641 | 1.542 | $A^1\Sigma^+ \rightarrow J^1\Pi$ | 0.086314 | 0.006 |

All quantities are given in a.u.

^a Ref. [26]: All electron calculation, at experimental equilibrium bond distance of 2.885 Å.

^b Ref. [27,28]: Experiment.

^c Ref. [24]: Experiment.

can be explored (see Table 2 and Fig. 1). As regards the ground state which involves only positive contributions of the close-lying excited states, we found that the main contributors to the polarizability components are the first excited state of each symmetry, 97.5% and 91% of the total value of α_{zz} and α_{xx} , respectively. In the case of this state, the convergence is practically complete with the first five low-lying spectroscopic states. However, for the sake of comparison in the same scale (see Fig. 1), we have performed the polarizability component calculation including in the first-order-perturbed wave-function a number of spectroscopic states up to twenty. The final converged polarizability components are listed in Table 3 and compared with the values computed by using the CCSD(T) method and with experiment [1,29]. The agreement between the TDGI and CCSD(T) methods is excellent, all the TDGI polarizability

components (α_{zz} , α_{xx}) compare very well within a deviation less than 2%, with the CCSD(T) all-electron values, but also with the CCSD(T) values [30] with 12 correlated electrons when the electron correlation contribution from the next-to-valence shell electrons and relativistic correction are taken into account. Since the core-valence intershell correlation, which has been shown to be responsible for changes in the dipole moment [31], has been correctly treated, the calculated TDGI value of $\mu = 0.470$ D for the $X^1\Sigma^+$ ground state is found to be in perfect agreement with the observed experimentally value of 0.49 ± 0.02 D [1] and 0.46 ± 0.01 D [32].

Considering now the $A^3\Sigma^+$ excited state, the situation is quite similar to that of the ground state. This state is the lowest triplet state, therefore, to calculate the polarizability components ($\alpha_{zz}(A^3\Sigma^+)$, $\alpha_{xx}(A^3\Sigma^+)$) only positive contributions

Table 2

Contributions of the low-lying spectroscopic states to the parallel (α_{zz}) and perpendicular (α_{xx}) dipole polarizability components, of the ground $X^1\Sigma^+$ and excited $A^3\Sigma^+$, $A^1\Sigma^+$ states, at their calculated equilibrium geometries

| | State | Cont ^a | α_{zz} ^b | State | Cont ^a | α_{xx} ^b |
|---------------|-------------------|-------------------|----------------------------|-------------|-------------------|----------------------------|
| $X^1\Sigma^+$ | $A^1\Sigma^+$ | 343.7 | (97.5%) | $B^1\Pi$ | 165.9 | (91%) |
| | $C^1\Sigma^+$ | 4.42 | (1.3%) | $D^1\Pi$ | 7.84 | (4.3%) |
| | $E^1\Sigma^+$ | 0.13 | (0.04%) | $G^1\Pi$ | 4.62 | (2.5%) |
| | $F^1\Sigma^+$ | 1.13 | (0.32%) | $I^1\Pi$ | 4.38 | (2.4%) |
| | $H^1\Sigma^+$ | 0.51 | (0.14%) | $J^1\Pi$ | 0.13 | (0.07%) |
| $A^1\Sigma^+$ | $X^1\Sigma^+$ | −459.2 | (−102.8%) | $B^1\Pi$ | 3.77 | (1.44%) |
| | $C^1\Sigma^+$ | 276.3 | (61.8%) | $D^1\Pi$ | 70.36 | (26.8%) |
| | $E^1\Sigma^+$ | 174.8 | (39.1%) | $G^1\Pi$ | 14.13 | (5.38%) |
| | $F^1\Sigma^+$ | 18.6 | (4.2%) | $I^1\Pi$ | 63.27 | (24.11%) |
| | $H^1\Sigma^+$ | 318.0 | (71.5%) | $J^1\Pi$ | 0.81 | (0.31%) |
| $A^3\Sigma^+$ | (2) $A^3\Sigma^+$ | 311.1 | (83.7%) | (1) $^3\Pi$ | 86.68 | (28.1%) |
| | $3^3\Sigma^+$ | 57.82 | (15.6%) | (2) $^3\Pi$ | 220.0 | (71.2%) |
| | $4^3\Sigma^+$ | 0.08 | (0.02%) | (3) $^3\Pi$ | 0.13 | (0.04%) |
| | $5^3\Sigma^+$ | 0.07 | (0.02%) | (4) $^3\Pi$ | 0.35 | (0.11%) |
| | $6^3\Sigma^+$ | 0.25 | (0.07%) | (5) $^3\Pi$ | 0.38 | (0.12%) |

^a Contributions to dipole polarizability components

^b Percentage with respect to total polarizability component (Table 3), calculated with twenty spectroscopic states and taking into account the polynomial and quasi-spectral series contributions

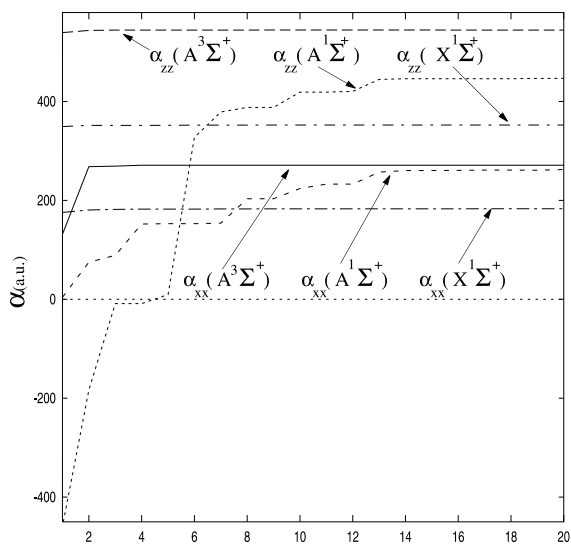


Fig. 1. Convergence of dipole polarizability components of NaLi with respect to the number of spectroscopic states, calculated at TDGI level.

of the triplet ($n^3\Sigma^+$ and $n^3\Pi$) excited states above are needed. A glance at the different contributions of the low-lying triplet states given in Table 2, shows that the main contributors to the total di-

pole polarizability components of the $A^3\Sigma^+$ state are the (2) $^3\Sigma^+$ and (2) $^3\Pi$ states for the parallel and perpendicular components, respectively. Also, in this case we found that convergence is rapidly reached with the first five low-lying spectroscopic states of each symmetry. The final converged dipole polarizability components given in Table 3, are between 32% and 37% larger than that of the ground electronic state. The dipole moment and dipole polarizability components of the $A^3\Sigma^+$ state calculated by using the CCSD(T) and the Moller–Plesset perturbations theories are listed in Table 3. The CCSD(T) all-electron gives generally slightly larger values of the dipole polarizability components compared to the values computed from the TDGI pseudo-potential with core-valence correlation approach. We think that these small discrepancies 2.5% and 2%, for the parallel and perpendicular components, respectively are due to the treatment of excited states with two different kinds of basis sets. In fact, for the ground electronic state of NaLi, TDGI and CCSD(T) all-electron methods have reproduced almost the same values [26,30], when the same basis set is used. Finally, we note that there is good agreement between all the methods. Considering now the

Table 3

Dipole polarizabilities (a.u.) of the $X^1\Sigma^+$, $A^3\Sigma^+$ and $A^1\Sigma^+$ states of NaLi at optimized equilibrium internuclear distances of 2.908, 4.812 and 3.381 Å, respectively, calculated by using the TDGI (pseudo-potential) and different (all electron) methods, comparison with literature

| State | Method | $\mu(D)$ | α_{zz} | α_{xx} | $\bar{\alpha}$ | $\Delta\alpha$ |
|---------------|----------------------|-------------------------------------|---------------|---------------|-------------------------------|----------------|
| $X^1\Sigma^+$ | SCF | 0.705 | 301.6 | 202.7 | 235.6 | 98.9 |
| | TDGI ^a | 0.470 | 352.3 | 183.1 | 239.5 | 169.2 |
| | CCSD(T) ^b | 0.529 | 350.6 | 187.7 | 242.0 | 162.9 |
| | CCSD(T) ^c | 0.452 | 352.4 | 189.2 | 243.6 | 163.2 |
| | CCSD(T) ^d | 0.432 | 362.1 | 195.2 | 246.8 | 172.9 |
| | MP2 ^e | 0.279 | 314.1 | 188.3 | 230.2 | 125.8 |
| | MP3 ^e | 0.391 | 325.4 | 187.6 | 233.5 | 137.8 |
| | MP4 ^e | 0.425 | 331.9 | 187.1 | 235.4 | 144.8 |
| | Exp. | 0.49 ± 0.02^f 0.47 ± 0.01^g | | | 263 ± 20^f 250 ± 20^h | |
| $A^3\Sigma^+$ | SCF | 0.082 | 620.6 | 294.8 | 403.4 | 325.7 |
| | TDGI ^a | 0.130 | 544.6 | 271.4 | 362.5 | 273.5 |
| | CCSD(T) ^b | 0.188 | 557.9 | 276.5 | 370.3 | 281.5 |
| | MP2 ^e | 0.171 | 557.9 | 276.9 | 370.6 | 281.0 |
| | MP3 ^e | 0.198 | 555.9 | 276.1 | 369.4 | 279.5 |
| | MP4 ^e | 0.209 | 551.8 | 274.9 | 367.2 | 276.9 |
| $A^1\Sigma^+$ | TDGI ^a | 1.235 | 449.3 | 265.9 | 327.0 | 183.4 |

^a This work: TDGI, pseudo-potential calculations.

^b This work: CCSD(T), all-electron calculations.

^c Ref. [30]: Next-to-valence shell electrons and relativistic correction (12 correlated electrons).

^d Ref. [30]: 2 correlated electrons.

^e This work: Moller–Plesset perturbation theory, all-electron calculations.

^f Experimental result of Ref. [1].

^g Experimental result of Ref. [32].

^h Ref. [29]: Empirical estimates by Tarnovsky et al.

electronic correlation effects, for the ground state as well as for the $A^3\Sigma^+$ excited state, the SCF method predicts values of dipole polarizabilities which are within 8–15% of the TDGI values.

We have computed the dipole moment, the polarizability components (α_{zz} , α_{xx}), the polarizability anisotropy ($\Delta\alpha$) and the mean polarizability ($\bar{\alpha}$) of the $A^3\Sigma^+$ state, as a function of internuclear separation. Their changes with respect to the internuclear distances are presented in Figs. 2–4. At small interatomic separation, the α_{zz} curves have a maximum corresponding to $R \simeq 3$ Å. Such behavior has also been found for the ground state of Li_2 , Na_2 and K_2 dimers from the calculations of Müller and Meyer [33] and for H_2 from the calculations of Kolos and Wolniewicz [34]. At large inter-atomic distances, the polarizability components α_{zz} and α_{xx} of the $X^1\Sigma^+$ state tend to the sum of the isotropic dipole polarizabilities of the corresponding atoms in their ground (^2S) state, namely, $\alpha(1^2\text{S}, \text{Li}) + \alpha(2^2\text{S}, \text{Na}) = 327.23$ a.u. The

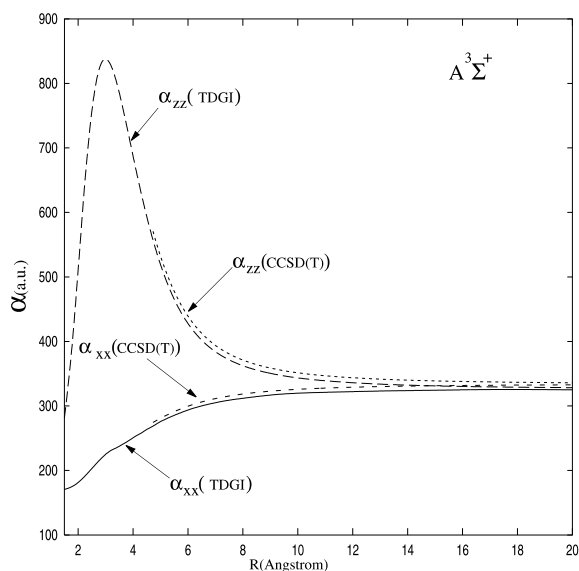


Fig. 2. Dipole polarizability components of the $A^3\Sigma^+$ excited state of NaLi as a function of inter-atomic distance, calculated with the TDGI and CCSD(T) methods.

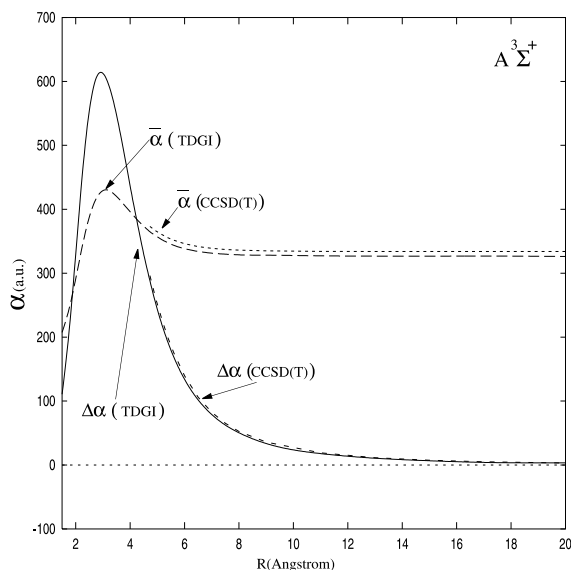


Fig. 3. Isotropic ($\bar{\alpha}$) and anisotropic ($\Delta\alpha$) dipole polarizabilities of the $A^3\Sigma^+$ excited state of NaLi as a function of inter-atomic distance, calculated with the TDGI and CCSD(T) methods.

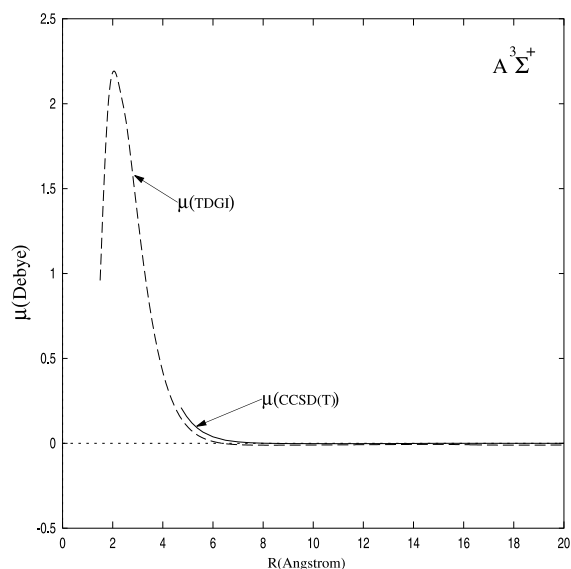


Fig. 4. Dipole moment of the $A^3\Sigma^+$ excited state of NaLi as a function of inter-atomic distance, calculated with the TDGI and CCSD(T) methods.

anisotropy, $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ falls to zero (see Fig. 3), the isolated alkali-metal atom being isotropically polarizable (S states), in their ground state.

For the $A^1\Sigma^+$ excited state, the exact positioning and ordering of the excited states turn out to be crucial. In the case of the α_{zz} component of the excited $A^1\Sigma^+$ state, a large negative contribution (-459.2 a.u.) comes from the lower $X^1\Sigma^+$ state. In contrast to the $X^1\Sigma^+$ and $A^3\Sigma^+$ cases, where the electric field perturbation relates to positive transitions (absorbed photon), the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ transition (emitted photon) which is responsible of the negative contribution to the polarizability of the $A^1\Sigma^+$ reference state, calculated from the usual sum-over-states expressions, can be interpreted in the spectroscopic point of view as a destabilization of this reference state with respect to the electric field perturbation. This negative contribution, is compensated by the positive contributions of the $(n)^1\Sigma^+$ states above the $A^1\Sigma^+$ state. The final converged polarizability values are $\alpha_{zz} = 449.3$ a.u. and $\alpha_{xx} = 265.9$ a.u., 21% and 30%, respectively larger than the ground state TDGI polarizability components. The α_{xx} component has only positive contributions. We have plotted in Fig. 1, the convergence pattern with respect to the number of spectroscopic states. More than fourteen spectroscopic states are needed to achieve good converged values of the polarizability components of this state. Owing to the excellent agreement obtained for the polarizability components of the $X^1\Sigma^+$ and $A^3\Sigma^+$ states calculated through TDGI, and CCSD(T) methods, since similar approach has been applied for the $A^1\Sigma^+$ state, we think that the calculated TDGI polarizability components of excited $A^1\Sigma^+$ state are of the same level of accuracy. The change upon excitation of the dipole moment of this state, found to be 1.235 D, is surprising, an increase by a factor more than two compared to that of 0.47 D, computed for the ground state.

In summary, we have shown that the TDGI method with a pseudo-potential approach including core-valence correlation is an efficient and suitable method for the calculation of the ground and low-lying excited states dipole polarizabilities of NaLi. The final converged value for the ground $X^1\Sigma^+$ and excited $A^3\Sigma^+$ states support comparison with the high-correlation methods available in the literature. Then we use the TDGI method to provide reliable values of the polarizability com-

Table 4

Frequency-dependent dipole polarizability components at imaginary frequencies (a.u.), for the $X^1\Sigma^+$, $A^3\Sigma^+$ and $A^1\Sigma^+$ states of NaLi at optimized equilibrium internuclear distances, calculated by using the TDGI (pseudo-potential) method

| ω (a.u.) | $X^1\Sigma^+$ | | $A^3\Sigma^+$ | | $A^1\Sigma^+$ | |
|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | α_{zz} | α_{xx} | α_{zz} | α_{xx} | α_{zz} | α_{xx} |
| 0.000 | 352.3 | 183.1 | 544.6 | 271.4 | 449.3 | 265.9 |
| 0.005 | 350.4 | 182.6 | 540.4 | 270.3 | 440.5 | 264.0 |
| 0.010 | 344.9 | 181.1 | 527.9 | 267.1 | 417.0 | 258.6 |
| 0.020 | 324.6 | 175.5 | 483.4 | 255.1 | 351.1 | 240.3 |
| 0.030 | 295.5 | 166.8 | 424.0 | 237.5 | 289.8 | 217.6 |
| 0.040 | 262.8 | 156.1 | 361.9 | 216.6 | 242.5 | 194.7 |
| 0.050 | 230.0 | 144.2 | 304.7 | 194.6 | 206.4 | 173.4 |
| 0.060 | 199.8 | 131.9 | 255.6 | 173.3 | 177.9 | 154.1 |
| 0.070 | 173.0 | 119.9 | 214.8 | 153.5 | 154.6 | 136.9 |
| 0.080 | 149.9 | 108.6 | 181.5 | 135.6 | 135.2 | 121.8 |
| 0.090 | 130.3 | 98.1 | 154.4 | 119.9 | 119.0 | 108.6 |
| 0.100 | 113.7 | 88.6 | 132.4 | 106.2 | 105.1 | 97.0 |
| 0.200 | 38.5 | 35.5 | 41.3 | 38.3 | 39.0 | 37.5 |
| 0.300 | 18.7 | 17.9 | 19.5 | 18.7 | 19.8 | 19.0 |
| 0.400 | 11.0 | 10.7 | 11.3 | 11.0 | 11.9 | 11.3 |
| 0.500 | 7.3 | 7.0 | 7.4 | 7.2 | 8.0 | 7.5 |
| 1.000 | 1.9 | 1.9 | 1.9 | 1.9 | 2.2 | 2.0 |
| 2.000 | 0.5 | 0.5 | 0.5 | 0.5 | 0.6 | 0.5 |

ponents of the excited $A^1\Sigma^+$. For a given excited state, the vicinity of other electronic states of appropriate symmetry is one of the main factors leading to a considerable increase of the polarizability components, and even to a negative contribution.

In the case of the $A^3\Sigma^+$ state, the dependence of the dipole moment and polarizability on internuclear distance has been calculated. TDGI and CCSD(T) results display similar behavior. The change is more pronounced for the parallel component (α_{zz}), which exhibits a maximum around $R = 3 \text{ \AA}$.

Finally, correlation effects are found to be important and of the same order of magnitude for the ground and excited state. We have found neither theoretical nor experimental results in the literature for the excited $A^3\Sigma^+$ and $A^1\Sigma^+$ states. The dependence with imaginary frequencies (Table 4), can be used as first ingredients to evaluate the long-range dispersion coefficients between two interacting NaLi dimers, in their ground and excited states.

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