Article

Basis Set Convergence on Static Electric Dipole Polarizability Calculations of Alkali-Metal Clusters

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Uma sequência hierárquica de conjuntos de bases de contração segmentada para todos os elétrons de qualidades dupla, tripla e quádrupla zeta de valência mais funções de polarização aumentadas com funções difusas para os átomos de H a Ar foi desenvolvida. Um estudo sistemático dos conjuntos de bases necessários para obter valores confiáveis e precisos de polarizabilidades de dipolo estáticas de aglomerados de lítio e sódio (n = 2, 4, 6 e 8) em suas geometrias de equilíbrio é reportado. Três métodos foram examinados: Hartree-Fock (HF), teoria de perturbação de Møller-Plesset de segunda ordem (MP2) e teoria do funcional da densidade (DFT). Por cálculos diretos ou por ajuste de valores calculados diretamente através de um esquema de extrapolação, os limites dos conjuntos de bases completos HF, MP2 e DFT foram estimados. Dados teóricos e experimentais relatados previamente na literatura são comparados.

A hierarchical sequence of all-electron segmented contracted basis sets of double, triple and quadruple zeta valence qualities plus polarization functions augmented with diffuse functions for the atoms from H to Ar was constructed. A systematic study of basis sets required to obtain reliable and accurate values of static dipole polarizabilities of lithium and sodium clusters (n = 2, 4, 6 and 8) at their optimized equilibrium geometries is reported. Three methods are examined: Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2), and density functional theory (DFT). By direct calculations or by fitting the directly calculated values through one extrapolation scheme, estimates of the HF, MP2 and DFT complete basis set limits were obtained. Comparison with experimental and theoretical data reported previously in the literature is done.

Keywords: AXZP basis sets, DFT, MP2 calculations, geometry and electric dipole polarizability, lithium and sodium clusters, CBS limit estimates

Introduction

In the last years, the static polarizabilities of atoms and free clusters have been extensively studied both theoretically and experimentally.[1,2] The static polarizability (α) represents one of the most important observables for the understanding of the electric properties of clusters since it is very sensitive to the delocalization of valence electrons, as well as the structure and shape. Despite numerous investigations on metal clusters, static polarizability measurements are only available for alkali-metal clusters such as sodium, lithium and potassium.[3-5] Because of their particular configuration, homonuclear alkali-metal clusters are often considered to be the simplest metal clusters, so that they have become the prototype systems for understanding size effects in metal clusters. The

experimental work of Knight et al.[3] by electric deflection techniques showed the existence of a pronounced size dependency in the polarizability of small sodium and potassium clusters. More recently, Benichou et al.[4] measured static electric polarizabilities of lithium clusters up to 22 atoms by deflecting a well collimated beam through a static inhomogeneous transverse electric field. The work of Benichou et al.[4] showed that the trend of the polarizability *per* atom of small lithium clusters differs from those of small sodium and potassium clusters.

Several theoretical calculations have been carried out for the static dipole polarizability of alkali-metal clusters.[6-15] The early calculations, which were based on variants of the jellium model within the framework of density functional theory (DFT), have been reasonably successful in explaining qualitatively the trend in the size dependence of polarizability.[6] However, the calculated polarizabilities were found to be smaller than the corresponding experimental

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values, perhaps due to the fact that the jellium model does not incorporate the effects of discrete atoms in the clusters. Subsequently, calculations have been carried out by considering the actual geometrical arrangement of the metal atoms in the clusters using DFT with different types of pseudopotentials as well as all-electron correlated methods.[7-15] These studies have mainly demonstrated that the theoretically evaluated polarizability values deviate from the experimental polarizability values significantly (often underestimated by an amount of 20-30%). Although the effect of temperature has been ascribed to one of the reasons for the deviation of the calculated values from the corresponding experimental values, it is important to note that the large discrepancy present in the previous theoretical calculations can be due to the fact that the effect of electron correlation has not been taken into account effectively and most of the reported values were obtained by the DFT based methods. In addition, the effect of many-electron correlations has also been studied using second- and fourth-order Møller-Plesset perturbation theory (MP2 and MP4, respectively) methods and single, double and perturbative triple-excitation coupled-cluster (CCSD and CCSD(T), respectively) for smaller ones.

In general, it is now a well-established fact that a large basis set is required for an accurate calculation of the polarizability and the effect of additional polarization and diffuse functions in the basis set is quite considerable.[16] Most calculations so far reported in the literature have used the Sadlej basis set, which is known to be a reasonable basis set, particularly for the molecular response property calculations and/or the standard split-valence basis sets (6-311G along with diffuse and polarization functions). However, for alkali-metal clusters, there are no systematic studies on the polarizability dependence with the use of different methods (e.g., Hartree-Fock (HF), DFT and MP2) in conjunction with a hierarchical sequence of basis sets.

Jorge and co-workers[17,18] presented all-electron segmented contracted double, triple and quadruple zeta valence qualities plus polarization functions (XZP, X = D, T and Q, respectively) basis sets for the atoms from H to Ar. These sets were augmented with diffuse functions with the purpose of having a better description of electron affinity, polarizabilities, hydrogen bonding and optical rotation. They were designed as AXZP.[17,19]

The main objective of this article is to utilize for the first time a hierarchical sequence of basis sets (AXZP, X = D, T and Q) to determine accurately static dipole polarizabilities of lithium and sodium clusters (Li_n and Na_n, n = 2, 4, 6, and 8) from their optimized equilibrium geometries. The convergence of the mean dipole polarizability ($\bar{\alpha}$) and polarizability anisotropy ($\Delta\alpha$) with respect to the basis

set enlargement and electron correlation corrections are examined. At the HF, DFT, MP2 levels, the $\bar{\alpha}$ and $\Delta\alpha$ complete basis set (CBS) limits are estimated and compared with theoretical and experimental data previously reported in the literature. This study is expected to deepen the understanding of the electric property of metal clusters and may also enunciate the best calculation procedure at these levels of theory as well as to provide benchmark theoretical results to calibrate future calculations on dipole polarizabilities of alkali-metal clusters.

Methodology

All calculations are performed with the Gaussian 09 quantum chemistry package.[20] The B3LYP[21,22] functional in combination with ADZP[17] basis set are used for the geometry optimizations of the lithium and sodium clusters. To check the stabilities of the geometries on the potential energy surface, the harmonic vibrational frequencies are also calculated at the same level. From these optimized geometries, the HF, MP2, and B3LYP methods as implemented in Gaussian 09 code along with the AXZP (X = D, T and Q)[17,19] basis sets are employed on polarizability calculations. In the MP2 calculations, the full correlation energy correction for the lithium clusters is used, whereas for the sodium clusters, only the 1s orbital is frozen.

The mean value and anisotropy for the dipole polarizabilities are defined by the following equations:

$$\bar{\alpha} = (\alpha_{zz} + \alpha_{xx} + \alpha_{yy})/3,$$
$$\Delta\alpha = (1/2)^{1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2},$$
respectively   (1)

In this study, it was used the most popular extrapolation form

$$Y_R(X) = Y_R(\infty) + A\,X^{-3}, \tag{2}$$

which forms the basis for the CBS model of Helgaker and co-workers.[23,24] $Y_R(X)$ is the property computed at the inter-nuclear distance R and X denotes the highest angular function of the basis sets used in the extrapolation. $Y_R(\infty)$ is the property value in the complete basis set limit. A is a fitting parameter without physical significance. Since there are two unknown quantities in equation 1, [$Y_R(\infty)$ and A], at least two consecutive basis sets are needed for extrapolation. Restricting ourselves to this requirement, two member groups (X-1, X) were used in our hierarchical sequence of basis sets, namely: ADZP and ATZP or ATZP and AQZP.

Results and Discussion

Equilibrium geometries

The optimized ground state structures of lithium and sodium clusters up to 8 atoms obtained with the B3LYP/ADZP procedure are shown in Table 1. The spin multiplicities are singlets for the even numbered clusters. As expected, for similar equilibrium structures, the lithium bond lengths are always shorter than the corresponding sodium ones. Our obtained B3LYP results show a general topological agreement with those reported in previous theoretical works.[12,14,15,25,26] For example, for Li_8, it was obtained a capped centered trigonal prism (CTP) and for Na_8, a dicapped octahedron (DCO) (Figure 1).

Table 1. Optimized B3LYP/ADZP bond lengths d_{ij} (Figure 1) for Li_n and Na_n clusters (n = 2, 4, 6, and 8). The symmetries are given in parentheses

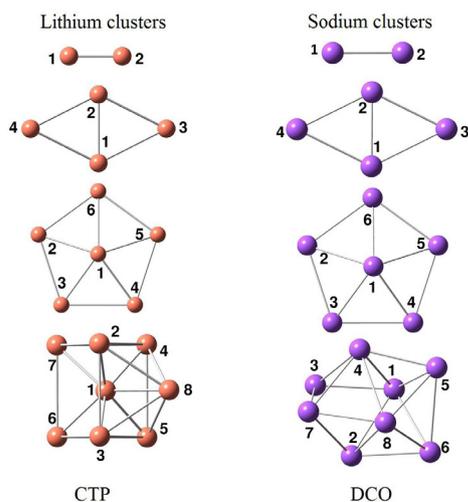|	Cluster
$Li_2 = (D_{\infty h})$	$Na_2 (D_{\infty h})$
$d_{12} = 2.7152$ Å	$d_{12} = 3.048$ Å
$Li_4 = (D_{2h})$	$Na_4 (D_{2h})$
$d_{12} = 3.008$ Å; $d_{24} = 2.578$ Å	$d_{12} = 3.504$ Å; $d_{24} = 3.059$ Å
$Li_6 = (C_{5v})$	$Na_6 = (C_{5v})$
$d_{12} = 2.804$ Å; $d_{26} = 3.178$ Å	$d_{12} = 3.327$ Å; $d_{26} = 3.613$ Å
$Li_8 (C_{2v})$ (CTP)	$Na_8 = (C_{2v})$ (DCO)
$d_{12} = 2.546$ Å; $d_{16} = 2.590$ Å; $d_{18} = 2.606$ Å	$d_{18} = 4.702$ Å; $d_{65} = 3.738$ Å; $d_{54} = 3.331$ Å; $d_{37} = 3.734$ Å

Figure 1. Optimized B3LYP/ADZP equilibrium geometries of lithium and sodium clusters considered for the polarizability calculation.

For the lithium dimer, the bond length predicted by all-electron DFT calculations, *viz.*, LSD/TZ94+p,[25] NLSD/TZ94+p,[25] CCSD/cc-pwCVQZ[26] and CCSD(T)/cc-pwCVQZ[26] are 2.80, 2.80, 2.678 and 2.674 Å,

respectively, while the bond length predicted by the present work (B3LYP/ADZP) is 2.715 Å, which compares well with the experimental value of 2.673 Å.[27] It seems that LDA (local density approximation) overestimates bond lengths as compared to those corresponding to other functionals. For the case of tetramer, the geometrical parameters predicted by the all-electron B3LYP/ADZP calculation are in satisfactory agreement with the CCSD(T)/cc-pwCVQZ ones (2.987 and 2.632 Å).[26] For the other higher membered clusters, the present results are in agreement with those reported by Jones *et al.*[25]

For the sodium dimer, the bond distances obtained with two different levels of computation[12] are equal to 3.017 Å with VWN/TZVP and 3.096 Å with BP86/TZVP. It should be noted that the TZVP set was optimized for gradient-corrected functionals. The experimental value is 3.078 Å,[27] in good agreement with the B3LYP/ADZP bond distance (3.048 Å). Values of 3.02 (PW86/A2-DZVP) and 3.054 Å (B3LYP/6-3111G*) were reported by Sophy *et al.*[14] and by Chandrakumar *et al.*,[15] respectively.

The ground state structure of Na_4 is a D_{2h} rhombic structure. The B3LYP results (3.503 and 3.064 Å) reported[15] agree very well with ours, whereas the agreement worsens when it is compared with the BP86 (3.542 and 3.100 Å)[12] and PW86 (3.45 and 3.03 Å)[14] ones. It clearly shows the dependence between geometry and used functional.

The equilibrium geometry of the hexamer is a C_{5v} pentagonal pyramid. Once again, for the Na_6 cluster, the agreement between the B3LYP/ADZP and 6-3111G* (3.320 and 3.610 Å)[15] bond lengths is good, whereas the BP86 (3.379 and 3.619 Å) and VWN (2.290 and 3.481 Å) results[12] are larger and smaller than ours, respectively. It is known that LDA values are considerably smaller than the results from other functionals. Our results add credence to this.

The equilibrium geometry of the octamer has rather compact structure with C_{2v} symmetry. In the literature, there is a controversy about the symmetry of Na_8. Previous DFT calculations reported C_{2v}[13,14] as well as D_{2d}.[12] But, an extensive theoretical study[28] about the electronic structure of alkali-metal clusters confirms C_{2v} to be the most stable structure of the octamer.

Static polarizability and polarizability anisotropy

In principle, a large size basis set for the calculation of polarizability is needed to describe these effects, and it is the main reason for the high computational expense.[16,19] However, Jorge and co-workers[29,30] working with cyclic molecules and even carbon cage fullerenes verified

that a basis set of double zeta quality is enough to give polarizability results close to the complete basis set limits. With this in mind, our group decided to perform a similar study on alkali-metal clusters.

Mean static dipole polarizability and polarizability anisotropy are calculated from the optimized minima structures (Table 1). For the calculations of $\overline{\alpha}$ and $\Delta\alpha$, the clusters were oriented with their permanent dipole moments along the z axis pointing in the positive z direction. The calculations of the static mean polarizabilities and the polarizability anisotropies for the lithium and sodium clusters have been performed using the HF, MP2 and B3LYP methods along with the hierarchical sequence of AXZP (X = D, T and Q) basis sets.[17,19] MP2 level calculations are done for benchmarking our results. The obtained results of $\overline{\alpha}$ and $\Delta\alpha$ are collected in Tables 2 and 3, respectively. For comparison, experimental[3,13,31] data, when available in the literature, are also reported. It may be noted that the experimental study of Tikhonov *et al.*[31] reported polarizabilities mainly for the higher membered sodium clusters and hence only a few of their results are included in Table 2. It is clear that there is considerable disagreement among the various experimental results and reproducible experimental results have been reported for only a few clusters. For the sodium clusters, the values provided by Knight *et al.*[3] and by Rayane *et al.*[13] are quite different from each other. The experimental error in the earlier work

was in the range of 12% whereas the error present in the most recent experimental values[31] is estimated to be a few atomic units *per* atom and, hence, the accuracy of the results will change drastically as the cluster size grows.[3,13,25] The objective of the theoretical calculations of polarizability using a number of procedures (method/basis set) as well as estimates of the CBS limits is to standardize the most suitable procedure for polarizability calculations.

As can be seen in Table 1, Li–Li bonds are shorter than Na–Na bonds. A large part of the decrease in polarizabilities observed from Na_n to Li_n clusters (Tables 2 and 3) is due to the decrease in bond length. This decrease induces an increase of the valence electron density in the cluster. The origin of these differences is the screening due to 2s2p electrons that occurs on sodium clusters. In addition, it should be mentioned here that the above affirmative makes sense because the polarizabilities of the Li and Na atoms are nearly equal (experimental values:[13] 163.85 and 159.39 a.u., respectively).

A brief look at Table 2 offers some general trends. As expected, the $\overline{\alpha}$ value increases with the system size. For the hierarchical sequence of all-electron basis sets, one can observe that the results decrease or increase monotonically with the basis set size enlargement and that the largest difference between adjacent results occurs from ADZP to ATZP. Except for a few cases, the convergence is essentially achieved at the AQZP level and, in these cases,

Table 2. Theoretical and experimental mean static dipole polarizabilities ($\overline{\alpha}$) of lithium and sodium clusters

Procedure	Li_2 ($D_{\infty h}$) / a.u.	Li_4 (D_{2h}) / a.u.	Li_6 (C_{5v}) / a.u.	Li_8 (C_{2v}) / a.u.	Na_2 ($D_{\infty h}$) / a.u.	Na_4 (D_{2h}) / a.u.	Na_6 (C_{5v}) / a.u.	Na_8 (C_{2v}) / a.u.
HF/ADZP[a]	207.11	349.31	511.89	565.896	269.50	525.92	727.09	851.50
ATZP[a]	205.28	348.31	509.23	562.391	270.61	529.24	729.87	852.68
AQZP[a]	205.11	348.19	509.06	562.268	270.55	529.76	729.96	852.53
CBS-HF[b]	204.99	348.10	508.94	562.178	270.51	530.14	730.03	852.47
MP2/ADZP[a]	209.16	347.56	519.06	575.53	263.74	515.24	717.07	823.01
ATZP[a]	206.90	344.83	513.86	567.56	261.37	511.28	712.20	815.86
AQZP[a]	204.71	341.79	510.09	564.56	257.97	506.85	705.32	[c]
CBS-MP2[b]	203.12	339.56	507.34	562.38	255.48	503.62	700.30	812.85[d]
B3LYP/ADZP[a]	199.65	351.66	497.06	552.954	231.78	481.51	651.26	748.71
ATZP[a]	198.95	351.05	494.71	548.168	230.27	481.70	650.87	747.25
AQZP[a]	198.83	350.95	494.45	[c]	230.75	482.69	[c]	[c]
CBS-B3LYP[b]	198.74	350.88	494.26	546.15[d]	231.10	483.41	650.71[d]	746.64[d]
Experimental[e]	221.07	327.15	359.14	559.29	265.24	565.58	754.42	901.14
Experimental[f]	–	–	–	–	251.90	538.62	816.62	868.75
Experimental[g]	–	–	–	–	264.54	–	–	955.57

[a]Present investigation, basis sets generated in references 17 and 19. [b]Present investigation, $\overline{\alpha}$ value obtained from 2 point fits (ATZP and AQZP) to equation 2. [c]Convergence failure in the SCF process. [d]Present investigation, $\overline{\alpha}$ value obtained from 2 point fits (ADZP and ATZP) to equation 2. [e]From reference 13. [f]From reference 3. [g]From reference 31.

Table 3. Theoretical polarizability anisotropies (Δα) of lithium and sodium clusters

Procedure	Li_2 ($D_{\infty h}$) / a.u.	Li_4 (D_{2h}) / a.u.	Li_6 (C_{5v}) / a.u.	Li_8 (C_{2v}) / a.u.	Na_2 ($D_{\infty h}$) / a.u.	Na_4 (D_{2h}) / a.u.	Na_6 (C_{5v}) / a.u.	Na_8 (C_{2v}) / a.u.
HF/ADZP[a]	76.59	259.23	306.23	10.51	129.02	465.04	438.65	79.51
ATZP[a]	75.08	261.12	305.45	9.92	126.68	462.94	435.86	77.80
AQZP[a]	74.25	260.70	305.05	9.87	125.31	463.29	435.46	77.28
CBS-HF[b]	73.64	260.39	304.76	9.84	124.31	463.544	435.157	76.90
MP2/ADZP[a]	102.56	260.64	316.83	20.87	152.77	462.56	436.73	106.42
ATZP[a]	97.22	258.48	313.52	21.60	148.02	454.16	430.68	105.93
AQZP[a]	95.51	255.62	311.47	21.54	146.73	452.79	427.22	[c]
CBS-MP2[b]	94.27	253.62	309.97	21.50	145.78	451.78	424.70	105.73[d]
B3LYP/ADZP[a]	96.92	298.22	311.67	14.42	136.33	467.15	410.82	109.52
ATZP[a]	94.95	299.17	310.41	15.30	135.16	465.37	408.84	109.11
AQZP[a]	94.37	298.70	309.99	[c]	133.96	466.11	[c]	[c]
CBS-B3LYP[b]	93.95	298.35	309.68	15.67[d]	133.08	466.66	408.00[d]	108.94[d]

[a]Present investigation, basis sets generated in references 17 and 19. [b]Present investigation, Δα value obtained from 2 point fits (ATZP and AQZP) to equation 2. [c]Convergence failure in the SCF process. [d]Present investigation, Δα value obtained from 2 point fits (ADZP and ATZP) to equation 2.

the AQZP mean dipole polarizabilities can be considered good estimates of the CBS limits. Overall, the mean absolute deviations (MADs) from CBS-HF, -MP2 and -B3LYP limits of ADZP, ATZP and AQZP mean dipole polarizabilities are, respectively, 2.39, 0.30 and 0.12 a.u.; 10.72, 6.15 and 2.78 a.u.; 2.06, 0.77 and 0.28 a.u. These results show that the convergences at the HF and B3LYP levels of theory are faster than that at the MP2 level. Besides, on average, the HF and B3LYP/AQZP results are excellent approximations for the CBS limits. But, as the computational time increases significantly going from ATZP to AQZP and as the MADs computed with the former set are not so high, one can consider a basis set of triple zeta valence quality as the best compromise between accuracy and computational cost on the HF and B3LYP polarizability calculations of alkali-metal clusters. It should be noted that MP2/AQZP MAD is at least nine times larger than the corresponding ones obtained with HF and B3LYP. Even so, this procedure can be considered a satisfactory approach for the CBS limit. On the other hand, at any level of theory, MAD increases significantly going from ATZP to ADZP. This should be an alert to use low quality basis set in such calculations. We recall that many static dipole polarizabilities of lithium and sodium clusters reported previously in the literature were obtained with a basis set of double zeta quality.[13]

For polarizability anisotropy, the convergence with respect to basis set quality is very similar to that observed for mean polarizability (Table 3). The current study indicates that except for MP2, the calculated Δα value does not display a significant basis set dependence.

Overall, MADs with respect to the CBS-HF, -MP2 and -B3LYP limits of ADZP, ATZP and AQZP Δα values are, respectively, 2.65, 1.08 and 0.45 a.u.; 6.66, 2.78 and 1.32 a.u.; 1.93, 1.04 and 0.50 a.u. Whereas MADs increase when compared with the corresponding HF and B3LYP ones for $\overline{\alpha}$, the opposite occurs for MP2. Once again, the ATZP and AQZP Δα results can be considered reliable and good approximations for the CBS limits, respectively.

It should be mentioned here that the differences among the CBS limit estimates obtained in this work and the HF and B3LYP mean dipole polarizabilities for the lithium[11] and sodium[15] clusters do not exceed 2.8%.

An analysis of the electron correlation effects can be done comparing the CBS-HF and CBS-MP2 limit estimates displayed in Tables 2 and 3. One can verify that electron correlation has a non-uniform effect on the $\overline{\alpha}$ and Δα values, i.e., it can increase or decrease the corresponding HF value. For the lithium and sodium clusters, differences between non-correlated and correlated $\overline{\alpha}$ values do not exceed 5.0%, while for Δα, this number arrives at 100%. Except for Li_4, the CBS-B3LYP mean dipole polarizabilities are systematically smaller than values deduced from CBS-MP2 (Table 2), whereas, for the Δα values, there is no systematic trend. Moreover, as the values obtained by the two methods can differ significantly among themselves, it is not possible to draw any general conclusion from the above results on the systematic inclusion of the electron correlation effects and to point out the best correlated method to carry out such calculations.

Highly correlated results for the dimer and tetramer mean dipole polarizabilities have been presented in the

literature.[10,11,15,32,33] For Li_2 and Li_4, Chandrakumar *et al.*[11] reported values of 215.62 and 338.34 a.u., respectively, at the CCSD/Sadlej basis set level of theory, in good agreement with our CBS-MP2 results. For Li_4, Maroulis and Xenides[32] obtained $\overline{\alpha}$ = 381.86 a.u. at the CCSD(T)/[15s7p1d] level of theory, which is about 12% higher than ours. Possibly, the reason for such difference is the reduced number of polarization and diffuse functions used by these authors. For the sodium dimer, the MP2 result for $\overline{\alpha}$ is 253.05 a.u.,[33] a result which is obtained from a large basis set ([18s14p9d2f1g]). The CCSD and CCSD(T) results in the same work[33] are 263.70 and 263.28 a.u., respectively, but these results are obtained with a smaller basis set of size [12s9p7d1f]. Jiemchooroj *et al.*[10] determined a CCSD value for $\overline{\alpha}$ using a large basis set of size [19s15p12d6f] and obtained a value of 259.5 a.u., quite close to the basis set limit. It is concluded that the CBS-MP2 result is ca. 1.5% lower than an estimated CCSD result as obtained with a large basis set.[10] For the sodium tetramer, however, even if the quality of the basis sets in the correlated wavefunctions published previously[10,15] does not match that in the dimer calculations,[10,33] a close agreement among CBS-MP2 (503.62 a.u.), CCSD (511.5 a.u.)[10] and CCSD(T)/Sadlej basis set (509.59 a.u.)[15] results for $\overline{\alpha}$ is observed. In summary, the good accordance among the CBS-MP2 values and those obtained from high level calculations adds credence to our results.

The following critical observations are made after comparison of the CBS-B3LYP mean polarizability values with the CBS-MP2 and CBS-HF values. In general, both the CBS-HF and the CBS-MP2 mean polarizability values are closer to the experimental values as compared to the CBS-B3LYP results (Table 2). In fact, certain CBS-HF values are closer to the experimental results than the CBS-MP2 values, which are unexpected, since MP2 is a correlated method, whereas HF theory lacks correlation terms in its energy expression. Also, usually DFT is believed to perform better than the HF theory due to incorporation of the correlation effects. Overall, MADs among the CBS-HF, CBS-MP2, and CBS-B3LYP $\overline{\alpha}$ values from the corresponding experimental data[13] are 37.94, 47.85 and 71.10 a.u., respectively. It may be noted that the temperature effects which are present in the experiments are missing in the above theories, making difficult the comparison between the experimental and theoretical results. Besides, it was expected the mean polarizability values to approach the experimental values as the basis set size increases, but Table 2 shows that it is not always true. On analyzing the results obtained by different basis sets, ADZP, ATZP and AQZP at any level of theory shown in Table 2, it appears that the effect of basis set is very marginal and the deviations are less than 2.3%. These results indicate that the level of theoretical method used is much more important than the size of basis set used in the polarizability calculations of lithium and sodium clusters, which is rather somewhat unusual.

A careful analysis of the experimental polarizability values provided by Rayane *et al.*[13] as well as by Knight *et al.*[3] (for the lithium and sodium clusters) reveals that the polarizability gradually increases from dimer to octamer, although the increment in polarizability in going from Li_4 to Li_6 is predicted to be very small, such a trend has not been observed by any theoretical method shown in Table 2.

Since the source of experimental errors can be due to many factors, the temperature factor alone may not be able to explain the discrepancy between the experimental and theoretical results. In general, the experimental static dipole polarizability is normally measured by the electric field deflection of a supersonic cluster beam and the deflection is characteristic of the number of sodium atoms in the cluster. It should, however, be noted that the measured deflection in the actual experiment is not only due to a single cluster, but also due to the mixture of other higher and lower member clusters which are normally present in the supersonic beam.[3,13,31] Another main source of error might be due to the cluster beam velocity. Since the measured experimental polarizability is directly proportional to the deflection of the beam as well as the cluster beam velocity, any error introduced in these two quantities will change the value of the polarizability considerably. Although the most recent work of Tikhonov *et al.*[31] took care of the above aspects, the accuracies of the measured values are still disputable due to the cluster temperature as well as the applied inhomogeneous electric field.

For systems with flat potential energy surfaces (PESs), it is thought that vibrational effects might be important in the calculation of the polarizability.[8] Moullet *et al.*[7] estimated the contributions of vibrational effects to the molecular polarizability of the sodium dimer and trimer in the harmonic approximation. This analysis has shown that vibrational contributions to the molecular polarizability are much smaller for Na_2 and Na_3. Moullet *et al.*[7] have also emphasized that anharmonic effects, neglected in their work, should be even smaller, or at most of the same order of magnitude in the exceptional cases of floppy molecules like Na_3. Recently, Lefebvre and Carrington[34] studied the effect of vibrational and rotational contributions for the static polarizability of Na_3. They computed Na_3 PES and also the electronic dipole moment and polarizability surfaces with the density functional method deMon-KS.[35] Using these surfaces, Lefebvre and Carrington[34] computed the exact field-dependent vibrational energy levels, wavefunctions and polarizabilities. They found that the

sodium trimer vibrational and rotational contributions are very small and cannot explain the discrepancy between experimental and theoretical polarizability of Na_3. The discrepancy between experimental and theoretical sodium cluster polarizability might be due to the presence of different isomers in the experiment. In order to understand the effect of different isomers in the calculation of a $\bar{\alpha}$ for the sodium clusters, Calaminici et al.[12] calculated the mean polarizability of the low-lying isomers found for the Na_3 and Na_6 clusters. Their DFT results show that the effect of different isomers on PESs could be very important for the calculation of the mean polarizability of sodium clusters.

Thus, from the discussions presented in the last two paragraphs, it can be seen that a direct comparison between theory and experiment does not make sense. For that, it is necessary to carry out some corrections in both approaches. As it is not always possible and as CBS-MP2 provides an excellent choice for the response property calculation, it can be used for benchmarking future calculations on electric polarizabilities of alkali-metal clusters.

For Li_2 and Na_2, the experimental values[5] of the mean dipole polarizabilities are very similar to those reported in another work.[36] For these clusters, Tarnovsky et al.[36] proposed $\bar{\alpha}$ = 229.4 ± 20.2 at 948 K and 269.9 ± 20.2 at 676 K, respectively. To compare our value to this finding, it was used a zero-point vibrational correction (ZPVC) (1.10 a.u.) derived in a previous work[32] for Na_2 to estimate the mean dipole polarizability at the ground vibrational state as $\bar{\alpha}$ (υ = 0) = 256.58 a.u. Müller and Meyer[37] obtained the temperature dependence of the mean polarizability. Their findings suggest an increase of theoretical values by 11.8 (for Li_2) and 10.4 (for Na_2). Thus, our group finds CBS-MP2 estimates of $\bar{\alpha}$ ca. 214.9 at 948 K and 267.0 at 676 K, which are inside of the uncertainness bars of the experimental values (229.4 ± 20.2 and 269.9 ± 20.2) measured at the same temperatures by Tarnovsky et al.[36] For Na_2, our estimate is in excellent agreement with that (274.8 at 676 K) obtained from the CCSD(T) calculation reported by Maroulis.[33] For Li_4, whereas the CBS-MP2 mean dipole polarizability is about 3.9% higher than the static experimental value of 326.62 a.u. reported by Benichou et al.[4] in their pioneering work on the dipole polarizability of lithium clusters, the CCSD(T)/[15s7p1d] result (381.86 a.u.)[32] achieves 16.9%. It reinforces the idea that the CBS-MP2 $\bar{\alpha}$ results provided in this work are reliable and that they can be used as benchmark theoretical values to calibrate future dipole polarizability calculations on alkali-metal clusters.

Figure 2 displays the CBS-MP2 estimates of the mean static dipole polarizability for all the studied clusters. From this figure, it is clear that the polarizability of lithium and sodium clusters increases monotonically presenting the expected proportionality with n and that the sodium cluster values are greater than the corresponding ones obtained for the lithium clusters.
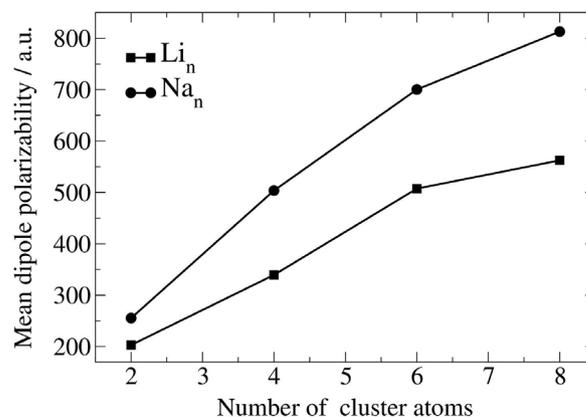

Figure 2. Estimated CBS-MP2 mean dipole polarizability vs. cluster size.

The obtained trend of polarizability anisotropy for Li_n (n = 2, 4, 6 and 8) clusters is the same by the three methods. As can be seen in Table 3, it increases going from the dimer up to the hexamer and decreases to the octamer. As the polarizability anisotropy is related to the particular cluster structure, it explains the value obtained for the octamer (Figure 1). Except for Li_4 (at the MP2 level), the electron correlation effect increases the polarizability anisotropy of the lithium clusters.

Observing the clusters Na_2 through Na_8 in Table 3, the polarizability anisotropy value increases from the dimer to the tetramer and decreases to the hexamer and octamer. This trend in the values reflects the clear relation between the cluster structure and the polarizability anisotropy values. It is worth noting that as the cluster structure becomes compact like in the case of the octamer, the polarizability anisotropy value decreases. The value for the octamer is even lower than the value for the dimer which has an open structure. From the tetramer to hexamer, it is seen that the hexamer being a closed structure as against the planar tetramer, it shows a decrease in the polarizability anisotropy value from that of the tetramer. Similar trend was reported by Banerjee et al.[38] studying static polarizabilities on sodium clusters, i.e., they infer that the polarizability anisotropy attains minimum values for magic clusters containing 2 and 8 atoms, and maximum value for cluster with 4 atoms. This tendency is similar to both the SAOP and LDA-XC/(11s9p7d3f) procedures. These results are consistent with the fact that the magic number clusters are more symmetric than the nonmagic ones.

A comparison of the polarizability anisotropy values for all the clusters among the three methods shows that

CBS-HF gives values smaller (for Na_2 and Na_8) and greater (for Na_4 and Na_6) than CBS-MP2. A general trend of the CBS-B3LYP approach giving higher values for the polarizability anisotropy than the CBS-HF approach can be seen except for the hexamer calculations.

It was not possible to compare our results with experiments as there is no experimental measurement of polarizability anisotropy available, but, some theoretical results for sodium clusters were reported. For these clusters, the trends observed in this work are exactly equal to previous works.[12,14] Besides, it should be mentioned that the BP86/Sadlej basis set $\Delta\alpha$ values (geometries optimized at the VWN/DZVP-A2 level)[14] are in good accordance with our reference CBS-B3LYP data. For the VWN and BP86/TZVP-FIP1 results,[12] it does not occur.

Conclusions

By means of density functional techniques, the structures of some even lithium and sodium clusters are optimized and, then, the convergence of HF, MP2 and B3LYP polarizabilities with respect to hierarchical sequence of AXZP (X = D, T and Q) basis sets[17,19] is studied.

In general the theoretical results do not converge to the experimental data with the basis set enlargement, consequently, the HF, MP2 and B3LYP CBS limits of the mean dipole polarizability and polarizability anisotropy are estimated. According to our knowledge, it is the first time that such limits are estimated for alkali-metal clusters. For the most clusters, one verifies that the AQZP polarizabilities are close to the CBS limits. However, for the few compounds whose convergence at the AQZP level has not been achieved, the CBS results must be considered estimates of these limits.

For the dimer and tetramer clusters, the comparison with mean static dipole polarizabilities published previously in the literature and that use high level of theory (CCSD and/or CCSD(T)/large basis set) points out that the MP2 limits reported in this work are reliable and, then, they can be useful to calibrate future calculations on polarizabilities of alkali-metal clusters. For Li_2 and Na_2, the good agreement between theory and experiment obtained after ZPVC and temperature effect added to the CBS-MP2 $\overline{\alpha}$ values augment credence to this. The complete set of s, p, d, f, and g parameters of all basis sets for Li and Na are available through the internet.[39]

Acknowledgements

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