Charge-transfer induced large nonlinear optical properties of small Al Clusters: Al$_4$M$_4$ (M=Li, Na and K)

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Abstract

We investigate the linear and nonlinear electric polarizabilities of small Al$_4$M$_4$ (M=Li, Na and K) clusters. Quantum chemical calculations reveal that these compounds exhibit an exceptionally high magnitude of linear and nonlinear optical (NLO) coefficients which are orders of magnitude higher than the conventional π-conjugated systems of similar sizes. We attribute such phenomenal increase to non-centrosymmetricity incorporated in the systems by the alkali atoms surrounding the ring leading to charge transfer with small optical gap and low bond length alternation (BLA). Such a low magnitude of the BLA from a different origin, suggests the possibility that these clusters are aromatic in character and along with the large NLO coefficients they appear to be better candidates for next generation NLO fabrication devices.
The development of materials with large nonlinear optical (NLO) properties is a key to controlling the propagation of light by optical means. In particular, the response of the materials to the application of the electric field has found tremendous applications in designing materials for NLO devices\[1\]. These devices are being used in numerous applications, from lasers to optical switches and optoelectronics. The NLO properties of organic $\pi$-conjugated materials have been studied in great details in the last few decades \[2, 3\]. The second and third order non-linear optical properties, $\beta$ and $\gamma$ for the $\pi$-conjugated polymers increase with the conjugation length (L) roughly as $L^3$ and $L^5$ respectively \[4\]. Therefore, the general strategy to model NLO materials has been to increase the conjugation length. However, there exist an upper limit for every off-resonant susceptibilities \[5\]. Alternatives to these $\pi$-conjugated compounds are yet to be explored theoretically in a detailed fashion. But, with the gaining popularity of various \textit{ab-initio} level methods\[6\], there has been a tremendous impetus in investigating the structure and electronic properties of both homogeneous and heterogeneous small clusters in recent years\[7, 8\].

Small Al$_4$ rings like Al$_4$M$_4$ and their anions Al$_4$M$_5^-$, M=alkali metals, have been a subject of current interest \[9, 10\] because of their unique characteristics and close structural resemblance with the C$_4$H$_4$. However, although C$_4$H$_4$ is an anti-aromatic species, these Al$_4$-clusters are recently reported to be $\sigma$ aromatic\[11\]. Thus, it would be interesting to ask whether these rings are better polarized than their organic counterpart; whether the structural
characteristics has any role in their polarization response functions. Organic π-conjugated systems are stabilized due to π-electron delocalizations, while the inorganic metal complexes reduce their energy through strong charge transfer. There have been no previous efforts to study in details the NLO properties of these all-metal clusters. We describe in the following that these metal clusters offer a unique polarization response due to their ionic character, contrary to conventional π-conjugated systems, leading to large optical coefficients.

We begin our calculations by optimizing the ground state geometries of the Al₄-clusters (Al₄Li₄, Al₄Na₄ and Al₄K₄). All the optimizations have been done using the 6-31G(d,p) basis set. Electron correlation has been included according to the DFT method using Becke’s three parameter hybrid formalism and the Lee-Yang-Parr functionals (B3LYP) available in the GAMESS electronic structure set of codes. Since, we want to compare the optical properties of these small four-membered rings with their organic analogue C₄H₄, we start with a planar initial geometry for the optimizations. We have varied the level of basis set from 6-31G(d,p) to 6-311G+(d) to ensure that these geometries correspond to the minima in the potential energy surface. The final geometries indeed remain independent of the selection of the basis set. Contrary to that of C₄H₄ having a rectangular ring, these Al₄-clusters are found to have a rhomboidal structure with four Al atoms forming a rhombus and the four alkali atoms around the four Al-Al bonds forming four Al-M (Li, Na, K)-Al triangles. One of the diagonals of the Al₄ ring are
also connected by Al-Al bond. The equilibrium geometries are shown in Fig. 1 [1(a), 1(b) and 1(c)].

While Al$_4$Li$_4$ and Al$_4$K$_4$ have a planar structure ($D_{2h}$), Al$_4$Na$_4$ has a distorted structure, with the four Na atoms arranged in a nonplanar geometry around the planar ring (the Na atoms are distorted by 13 degrees from the plane of Al$_4$ ring). This can be understood by considering the increase in size of the alkali ions and the distances of the ions from the Al$_4$-ring. With the progressive increase in the ionic radii of counterion, Li to K (Li = 0.68 Å, Na = 0.97 Å and K = 1.33 Å), the structures are expected to be distorted and the four alkali atoms should arrange in a non-centrosymmetric geometry around the Al$_4$ ring to minimize steric repulsion. But, the average Al-M distance increases while going from Al$_4$Li$_4$ (2.65 Å) to Al$_4$Na$_4$ (3.00 Å) to Al$_4$K$_4$ (3.35 Å). Although the ionic radii of K ion is more than that of Li and Na, in Al$_4$K$_4$, the four K ions are far separated from the Al$_4$ ring, allowing a planar structure. For Al$_4$Na$_4$, both the ionic radius of Na and the average Al-M distance fall in between Al$_4$Li$_4$ and Al$_4$K$_4$ and thereby minimizes the steric repulsion through distortion.

Also, very close in energy to these planar rhomboidal structures for these Al$_4$-clusters are the capped octahedron structures for the Al$_4$Li$_4$ [2(a)] and Al$_4$Na$_4$ [2(b)] (with $C_{2h}$ symmetry) and a distorted tricycle-like structure for Al$_4$K$_4$ [2(c)]. These geometries are shown in Fig. 2. At the footnote of each structure, the corresponding ground state energies are given. It has however not escaped our attention that previous works on alkali derivatives of Al$_4$-
clusters have predicted more than one unique structures for these systems [14]. This calls for a study to elucidate whether the optical properties for these Al₄-clusters for different geometries are substantially different or are very similar. Hence, both the geometries for each cluster were considered for computing the optical response functions.

These geometries were used to compute the SCF MO energies and then the spectroscopic properties using the Zerner’s INDO method [15]. We have varied the levels of CI calculations, with singles (SCI) and multi-reference doubles CI (MRDCI), to obtain a reliable estimate of the second order optical response. The later method is particularly important since it includes correlation effects substantially. The MRDCI approach adopted here has been extensively used in earlier works, and was found to provide excitation energies and dipole matrix elements in good agreement with experiment [16, 17]. As reference determinants, we have chosen those determinants which are dominant in the description of the ground state and the lowest one-photon excited states [18]. We report the MRDCI results with 4 reference determinants including the Hartree-Fock HF ground state. For each reference determinant, we use 5 occupied and 5 unoccupied molecular orbitals to construct a CI space with configuration dimension of 800 to 900. To calculate NLO properties, we use correction vector method, which implicitly assumes all the excitations to be approximated by a correction vector [19]. Given the Hamiltonian matrix, the ground state wave function and the dipole matrix, all in CI basis, it is straightforward to compute the dynamic nonlinear optic
coefficients using either the first order or the second order correction vectors. Details of this method have been published in a number of papers $^{20, 21, 22}$.

Table 1. shows the bond-length alternation (BLA), $\Delta r$, the optical gap and the average Mulliken charge on the Al$_4$ ring for all the geometries. The $\Delta r$ is defined as the average difference between the bond lengths of two consecutive bonds in the Al$_4$-ring and the optical gap is calculated as the energy difference between the geometry relaxed ground state and the lowest optically allowed state with substantial oscillator strength. This corresponds to the vertical absorption gap. To directly compare the efficiency of these Al$_4$-clusters with the conventional $\pi$ conjugated systems, we calculate the optical properties of the 1,3-cyclobutadiene (C$_4$H$_4$) and benzene (C$_6$H$_6$) at the same level of theory. For the Al$_4$-clusters, there is a substantial amount of charge transfer from the alkali atoms to the Al atoms (negative charge), making them act as donor and acceptor respectively. Such a charge transfer induces polarization in the ground state structure and reduces the optical gap. On the other hand, the C-H bond being perfectly covalent, there is almost no charge transfer in case of C$_4$H$_4$ and C$_6$H$_6$ and thus have a large optical gap due to finite size molecular architecture.

Charge transfer stabilizes the system with very small changes in the bond lengths. The chemical hardness, $\eta$, defined as, one half of (ionization potential-electron affinity), decreases as one moves from Li to K. More specifically, the $\eta$ for Li, Na and K are 2.39eV, 2.30eV and 1.92eV respectively $^{23}$. So, the extent of charge transfer from the alkali atom to the Al$_4$-ring should
increase with the decrease in the chemical hardness of the alkali atoms which is evident from Table 1. From Al₄Li₄ to Al₄Na₄ to Al₄K₄, the Mulliken charge on the Al₄-ring increases leading to decrease in the BLA along the series with the exception of Al₄Na₄ [1(b) and 2(b)] which has much lower Mulliken charge on the Al₄-ring. For the Al₄Na₄ [1(b)] as mentioned above, there is a substantial distortion of the Na atoms from the Al₄-ring. For the Al₄Na₄, with C₂ᵥ symmetry [2(b)] even though there is no distortion, the large Al-Na distance reduces the ionicity of the bond. As a result the extent of charge transfer is lesser for Al₄Na₄.

Benzene is aromatic with $\Delta r = 0$. Although BLA can not be regarded as the sole measuring index of aromatic character, the small BLA found for the Al₄-clusters (together with large BLA for the anti-aromatic C₄H₄) tend to suggest that the Al₄-clusters are more like aromatic but most certainly not anti-aromatic species, as has been proposed recently [10]. The distorted Al₄K₄ structure [2(c)] is very interesting. The Al₄-ring is distorted from planarity by 9.5 degrees. Such a distortion arises to minimize the steric repulsion in accommodating four bulky K atoms on a plane, very similar to that of cyclooctatetraene, which undergoes a distortion from planar to tub-shaped geometry to minimize the ring-strain [24]. Thus, this structure of Al₄K₄ is neither aromatic nor anti-aromatic but can be considered to be non-aromatic just like cyclooctatetraene. This is supported by the energies for the structures for Al₄K₄ [1(c) and 2(c)]. The distorted structure is more stable than the planar structure. Thus, the steric repulsion for the four large
K atoms overwhelms the stability of the planar undistorted aromatic Al₄K₄ making the Al₄K₄ cluster non-aromatic.

In Table 2, the magnitudes of the ground state dipole moment, μ₆, the linear(α), and nonlinear (β and γ) polarizabilities for the clusters are reported from the ZINDO calculations. Note that we report the magnitudes for the tumbling averaged $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$, defined as

$$
\bar{\alpha} = \frac{1}{3} \sum_i (\alpha_{ii}) \\
\bar{\beta} = \sqrt{\sum_i \beta_i \beta_i^*}; \quad \beta_i = \frac{1}{3} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \\
\bar{\gamma} = \frac{1}{15} \sum_{ij} (2\gamma_{ijij} + \gamma_{ijji})
$$

where the sums are over the coordinates x, y, z ($i, j = x, y, z$) and $\beta_i^*$ refers to the conjugate of $\beta_i$ vector.

The ground state dipole moment $\mu_G$ and $\bar{\beta}$ are zero for the C₄H₄ and C₆H₆ due to its perfect centrosymmetric geometry, although, the $\bar{\alpha}$ and $\bar{\gamma}$ have finite values. For the Al₄-clusters with the progressive increase in the ionic radii of counterion, the ground state dipole moment increases. Thus, while Al₄Li₄ has no ground state dipole moment, Al₄Na₄ and Al₄K₄ have substantial ground state dipole moment (particularly 1(b) and 2(c) due to their non-centrosymmetric structures discussed above). For Al₄K₄, while the rhomboidal geometry has a very low ground state dipole moment but the distorted tricycle-like structure has a very high dipole moment. Thus, due to the out-of-plane charge transfer, the dipole matrix elements are also larger, resulting in particularly large value for $\bar{\beta}$. For Al₄Li₄ and Al₄Na₄ [2(b)] the
polarization is in the excited state as the ground state dipole moment is zero. However, it is not the case for the insulating C₄H₄ and C₆H₆ which have zero polarization both in the ground and the optical excited states. Thus, $\bar{\beta}$ is zero for C₄H₄ and C₆H₆.

The optically active states are the low-energy states of these metallic clusters and the lowest optical gap is about 0.07 au for Al₄-clusters compared to 0.25 au for the C₄H₄ and C₆H₆. Since the optical coefficients are inversely proportional to the optical gaps and proportional to the dipolar matrices, a large optical gap implies low magnitudes for the optical coefficients. C₄H₄ has the highest magnitude of BLA and optical gap and the least charge transfer on the ring structure, thereby smallest magnitude of $\bar{\gamma}$. On the other hand, although BLA is zero for C₆H₆ due to complete $\pi$-electron delocalization, there is no charge transfer in the finite molecular structure leading to large optical gap and weak polarization. Consequently, $\bar{\gamma}$ is very less also for C₆H₆.

In contrast, the optical coefficients in general are quite large for the Al₄-clusters. For example, the $\bar{\gamma}$ for the Al₄-clusters are roughly $10^4$ times more than that for C₄H₄ and C₆H₆. This is because the $\bar{\gamma}$ is a third order property with 4 dipolar matrices in the numerator and 3 optical gaps in the denominator [26]. The $\bar{\gamma}$ for the Al₄-clusters increases with the increase in the polarization of the Al-M bonds and follows the trend: $\bar{\gamma}$ of Al₄Li₄ < $\bar{\gamma}$ of Al₄Na₄ < $\bar{\gamma}$ of Al₄K₄ (same trend as $\eta$). But, the distorted structures for Al₄Na₄ and Al₄K₄ [1(b) and 2(c)] have less $\bar{\gamma}$ due to less polarization of the Al-M bonds. For C₄H₄ ($\Delta r = 0.245 \text{Å}$), C₆H₆ ($\Delta r = 0.00 \text{Å}$) and linear chain,
(-CH=CH-)$_n$, $n$=3 ($\Delta r$= 0.1 Å) the $\bar{\gamma}$ are 2.21, 2.63 and 192.85 (all in au) per CH bond, respectively. This is in agreement with previous findings that the magnitude of $\gamma$ varies nonlinearity with $\Delta r$ and its maxima occurs at an optimal $\Delta r \neq 0$ [27]. However, for the Al$_4$-clusters, because of strong charge-transfer, the $\bar{\gamma}$ are less sensitive to variation in $\Delta r$ and even for $\Delta r=0.0$ Å (perfect square Al$_4$ ring) and $\Delta r=0.245$ Å (rectangular Al$_4$ ring like C$_4$H$_4$) the $\bar{\gamma}$ are similarly high, as found for the optimized structures. Such charge-transfer induced large NLO is evident for even bulk materials like CsLiB$_6$O$_{10}$ (CLBO) showing significant 4$^{th}$ and 5$^{th}$ harmonic generation [29].

The maximum possible value for the off-resonance $\gamma$(Al$_4$M$_4$) calculated using the Kuzyk’s simple two-state model [5] is about 2825 times more than that for $\gamma$(C$_4$H$_4$). This is in very good agreement with our MRDCI calculations at a low frequency (0.001 au), which predict $\gamma$(Al$_4$M$_4$)/$\gamma$(C$_4$H$_4$) $\approx 10^4$.

To compare and contrast these clusters with their organic counterparts, we calculate the NLO properties of the well-known $\pi$-conjugated systems, the trans-polyacetylene chain, (-CH=CH-)$_n$, by varying the number of spacers, $n$, from $n$=1 to 6, and thereby extending the length of conjugation from 2.65 au to 29.11 au. The geometries were optimized by the same method as mentioned above. The linear and nonlinear polarizations are calculated at the same frequency (0.001 au). Our calculated values for the optical properties compare fairly well in trends with the experimental results that the linear ($\alpha$) and nonlinear ($\gamma$) optical properties increase steadily with the increase in
the conjugation-length of the chain (see Table 2 and Table 3). For example, for ethylene, $\gamma_{\text{expt}} = 1504.9$ au, for butadiene ($n=2$), $\gamma_{\text{expt}} = 4566.4$ au and for hexatriene ($n=3$), $\gamma_{\text{expt}} = 14950.1$ au [28]. Note that our calculations are done at a lower frequency compared to the laser frequency used in the experiment (0.066 au). However, the magnitudes of all the polarization quantities are much higher for the charge-transfer complex ($\text{Al}_4\text{M}_4$ clusters) compared to the conventional $\pi$ conjugated chains with comparable conjugation length. Only when there are very large number of spacers ($n=5-6$), that the magnitudes become comparable to the much smaller $\text{Al}_4$-clusters. For example, $\gamma[(-\text{CH}=\text{CH})_6] \approx \text{gamma}(\text{Al}_4\text{M}_4)$. ($-\text{CH} = \text{CH} -)_6$ has 12 atoms in conjugation while $\text{Al}_4\text{M}_4$ has only 4. So, as a thumb-rule, one can state that gamma for the Al-atoms in the charge-transfer ring scale three times that for pi-conjugated organic materials.

As discussed, the large NLO properties for $\text{Al}_4\text{M}_4$ is due to the charge transfer from the alkali metals to the $\text{Al}_4$ ring. It will be thus of interest to compare these hetero atomic all-metal clusters with alkylated organic compounds such as lithiated benzene or organolithium and organosodium derivatives like $\text{C}_8\text{H}_6\text{Li}_2$ and $\text{C}_8\text{H}_6\text{Na}_2$. These alkylated organic compounds also exhibit larger NLO coefficients. For example, $\gamma(\text{C}_6\text{Li}_6)/\gamma(\text{C}_6\text{H}_6)=7.3 \times 10^2$ [30]. Similarly, $\gamma(\text{C}_8\text{H}_6\text{Li}_2)/\gamma(\text{C}_8\text{H}_6)=5.5$ and $\gamma(\text{C}_8\text{H}_6\text{Na}_2)/\gamma(\text{C}_8\text{H}_6)=20$ [31].

But, NLO responses for the $\text{Al}_4\text{M}_4$ is much higher than these alkylated organic compounds compared to pure organic materials. Also, there have been previous efforts to calculate the NLO coefficients in inorganic clusters like
GaN, GaP and GaAs. These systems have higher gap than the Al$_4$M$_4$ clusters so the NLO coefficients are smaller.

To conclude, our theoretical study shows that the small four membered Al$_4$-clusters functionalized with various metal cations provide an innovative route for selection of materials with very high nonlinear optical properties. We believe that our study will motivate experiments on these Al-clusters. Some of these compounds have already been well characterized from stable alloys but laser evaporation is not sufficient to stabilize these materials for NLO experiment. One idea will be to stabilize these clusters in a sandwich type geometry by incorporating a suitable transition metal ion or solvents.

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Table 1: The bond length alternation, $\Delta r$ (in Å), Optical Gap (in au) and the average Mulliken charge ($\Delta q$) on the ring for the clusters from ZINDO calculations.

| Molecule  | $\Delta r$ | Gap  | $\Delta q$ |
|-----------|------------|------|------------|
| Al$_4$Li$_4$ 1(a) | 0.1283 | 0.0819 | -0.592 |
| Al$_4$Li$_4$ 2(a) | 0.1276 | 0.024 | -0.506 |
| Al$_4$Na$_4$ 1(b) | 0.1302 | 0.0909 | -0.174 |
| Al$_4$Na$_4$ 2(b) | 0.1103 | 0.0607 | -0.127 |
| Al$_3$K$_4$ 1(c) | 0.0656 | 0.0663 | -0.634 |
| Al$_3$K$_4$ 2(c) | 0.0649 | 0.0867 | -0.618 |
| C$_4$H$_4$ | 0.245 | 0.2410 | -0.030 |
| C$_6$H$_6$ | 0.000 | 0.2588 | -0.009 |
Table 2: The ground state dipole moment, $\mu_G$, linear polarizability, $\alpha$, 1st hyperpolarizability, $\beta$ and the 2nd hyperpolarizability, $\gamma$, (tumbling average) for the clusters and for trans- polyacetylene chain from ZINDO-MRDCI calculations. The units are in au. ‘n’ is the number of $-CH=CH- \text{units.}$

| Molecule          | $\mu_G$ | $\alpha$   | $\beta$   | $\gamma$   |
|-------------------|---------|------------|-----------|------------|
| Al$_4$Li$_4$ 1(a) | 0.000   | $4.9 \times 10^3$ | 542.5     | $1.91 \times 10^7$ |
| Al$_4$Li$_4$ 2(a) | 0.000   | $5.5 \times 10^3$ | 244.9     | $5.33 \times 10^8$ |
| Al$_4$Na$_4$ 1(b) | 0.076   | $5.9 \times 10^4$ | 8465.2    | $1.09 \times 10^9$ |
| Al$_4$Na$_4$ 2(b) | $8.6 \times 10^{-2}$ | $8.7 \times 10^3$ | 1098.5    | $2.00 \times 10^8$ |
| Al$_4$K$_4$ 1(c)  | 0.004   | $5.4 \times 10^3$ | 79.3      | $2.60 \times 10^4$ |
| Al$_4$K$_4$ 2(c)  | 5.720   | $4.7 \times 10^3$ | $1.2 \times 10^5$ | $1.90 \times 10^7$ |
| C$_4$H$_4$        | 0.000   | $2.9 \times 10^2$ | 0.000     | $4.76 \times 10^3$ |
| C$_6$H$_6$        | 0.000   | $5.4 \times 10^4$ | 0.000     | $8.44 \times 10^4$ |
| (CH=CH)$_n$, n=1  | 0.000   | 136.3      | 0.000     | $2.78 \times 10^4$ |
| (CH=CH)$_n$, n=2  | 0.000   | 421.0      | 0.000     | $4.15 \times 10^4$ |
| (CH=CH)$_n$, n=3  | 0.000   | 852.4      | 0.000     | $6.17 \times 10^5$ |
| (CH=CH)$_n$, n=4  | 0.000   | 1455.2     | 0.000     | $2.82 \times 10^6$ |
| (CH=CH)$_n$, n=5  | 0.000   | 2203.2     | 0.000     | $8.41 \times 10^6$ |
| (CH=CH)$_n$, n=6  | 0.000   | 3074.9     | 0.000     | $2.07 \times 10^7$ |
Figure 1: Equilibrium ground state geometries for Al₄Li₄, Al₄Na₄ and Al₄K₄. The footnote of each structure contains the ground state energies in au.
Figure 2: Equilibrium ground state geometries for the other set of Al$_4$Li$_4$, Al$_4$Na$_4$ and Al$_4$K$_4$, very close in energy to Figure 1. The footnote of each structure contains the ground state energies in au.

$E = -999.8539 \text{ au}$

$E = -1618.9396 \text{ au}$

$E = -3369.3809 \text{ au}$