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A nations's growth is in proportion to education and intelligence spread among the masses. Having this idealistic vision, two great philanthropists late. S.P. Nallamuthu Gounder and Late. Arutchelver Padmabhushan Dr.N.Mahalingam formed an organization called Pollachi Kalvi Kazhagam, which started NGM College in 1957, to impart holistic education with an objective to cater to the higher educational needs of those who wish to aspire for excellence in knowledge and values. The College has achieved greater academic distinctions with the introduction of autonomous system from the academic year 1987-88. The college has been Re-Accredited by NAAC and it is ISO 9001 : 2015 Certified Institution. The total student strength is around 6000. Having celebrated its Diamond Jubilee in 2017, the college has blossomed into a premier Post-Graduate and Research Institution, offering 26 UG, 12 PG, 13 M.Phil and 10 Ph.D Programmes, apart from Diploma and Certificate Courses. The college has been ranked within Top 100 (72nd Rank) in India by NIRF 2021.

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Nonlinear Optical Properties of Superalkali–Metal Complexes: A DFT Study

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ABSTRACT: Density functional theory has been employed to explore the geometry and nonlinear optical properties of Superalkali-metal (SA-M) complexes. The structures have been optimized to analyze the variation in the geometry. The stability of SA-M complex has been studied by dissociation of SA-M complex into superalkali and metal fragments. The energy values indicate that the closed ring structures exhibiting c2v symmetry dominates the stability in FLi_2-M (1) (M=Li, K). The calculated dissociation energy shows that all the complexes are kinetically stable due to the existence of the positive values of De. The Nonlinear optical properties of SA-M species are calculated and analyzed using total static dipole moment (μ**)** mean polarizability (α_0) and hyperpolarizability (β_0) by finite field approach.

Keywords: Superalkali, Dissociation energy, Interaction energy, NLO

1. INTRODUCTION

Nonlinear Optics (NLO) took its beginning in 1875; with the instigation of the interpretation on a quadratic electric field induce alteration in the refractive index of CS2 by Kerr, known as Kerr effect [1]. After the invention of laser, many typical experiments in NLO like Second Harmonic Generation (SHG) by Franken et al. [2] in 1961, Sum Frequency Generation (SFG) through Bass et al. in 1962 and optical alteration by Bass et al.[3] in 1962 are performed. Since then, NLO have become a speedily emergent field in Physics [4]. Vibrational spectroscopic techniques united with quantum chemical computations have newly been used as a successful tool for the investigation of nonlinear optical properties [5,6]. The NLO material is in the midst of the smartest material of time that has capability to change the phase as well as frequency of a laser light passing through it. Based under this capability, different significant applications in optoelectronics, photonics, and optical data storage have been urbanized [7]. The calculation of molecular hyperpolarizability is the input feature that is used to describe new NLO materials [8,9].

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In recent years, a set of research effort has been devoted to second-order nonlinear optical organic materials due to their high potential in photonic applications such as active wavelength filters, optical switches, and modulators for THz wave generation [10]. Nonlinear optical materials play a key role in the future development of nonlinear optics and its impact in technology and industrial applications are admirable [11].

Alkali metals are remarkably good electron donors, tending to form monopositive ions by donation of one electron to an acceptor atom or molecule. In a precursory hypothetical work, Khanna et al. [12] proposed that atomic clusters in way of suitable size and composition could mimic the chemical activities of elements in the periodic table and for this reason, be regarded as “superatoms.” A distinguished subset of superatoms is superalkali, which is characterized by lower ionization potentials (IPs) than those 5.4–3.9 eV of alkali-metal atoms. The hyperlithiated molecules are a main class of superalkali since they frequently exhibit very low IPs [13]. The superalkalies are of enormous importance because they can be used in the synthesis of a novel class of charge-transfer salts in which the resulting anions are created by the species with low electron affinity [14]. In the present study, DFT has been employed to explore the NLO properties of SA-M species.

2. COMPUTATIONAL DETAILS

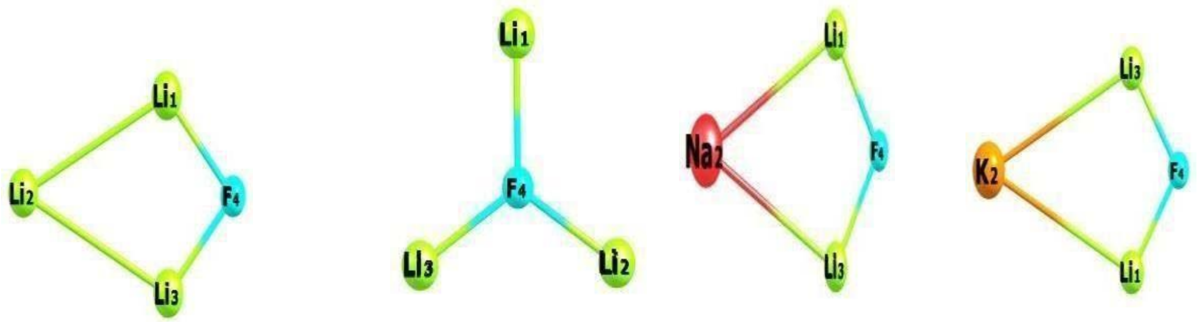
B3LYP/6-311++G(d,p) [15,16] of density functional theory method has been used to optimize the geometries of SA–M complexes. The vibrational frequency analysis has been performed to determine the nature of the stationary points found by geometry optimization. The stability of SA-M complex has been analyzed by dissociation of SA-M complex into SA and M fragments. The NLO properties are calculated and analyzed using total static dipole moment, mean polarizability (α_0) and hyperpolarizability (β_0) by finite field approach. All the calculations have been using Gaussian 03W [17] computational package. The electrostatic potential surface map has been drawn using Molekel 4.3 Software [18].

3. RESULTS AND DISCUSSION

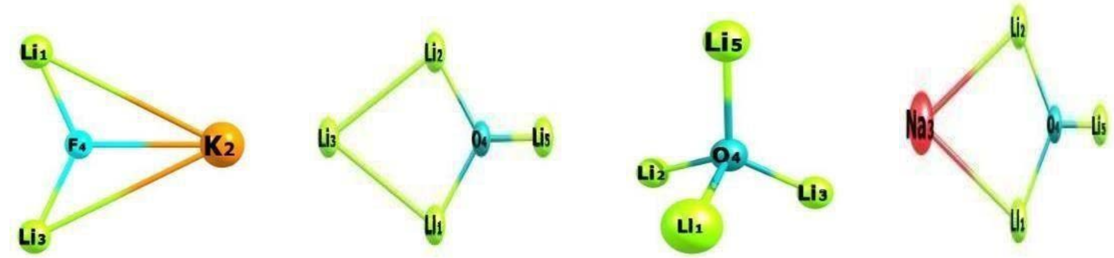
The interaction of superalkali clusters (SA = FLi_2, OLi_3, NLi_4) with metal atoms (M) [Li(R=1.67Å), Na(R=1.90Å) and K (R=2.43Å)] have been studied using B3LYP/6311++G(d,p) level of theory and the optimized SA-M species are shown in Fig.1. The complexes FLi_2 –Li (1), FLi_2 –Na and FLi_2 –K (1) possess c2v symmetry and exhibit a closed ring structure. The complex FLi_2-Li (2) is associated with c2v symmetry and possesses a trigonal planar structure. As the atomic radius of the metal atom and the size of the superalkali clusters increases, the bond length of the metal from superalkali increases consequently.

3.1 Interaction Energy

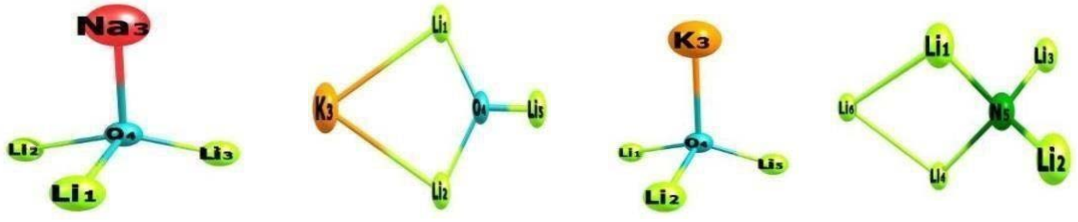
The interaction energy of Superalkali-metal complexes is summarized in Table 1. Interaction energy of -33.9 and -31.2 kcal/mol is noted for FLi_2-Li (1) and FLi_2-Li (2) complexes. The complexes with larger interaction energy are the most stable [19,20]. The complexes follow the stability order: FLi_2-Li (1) > FLi_2-Li (2), FLi_2-K (1) >FLi_2-K (2), OLi_3-Li (1) > OLi_3- Li (2) and OLi_3-Na (2) > OLi_3-Na (1), OLi_3-K (2) > OLi_3- K (1), NLi_4-Li (2) > NLi_4-Li (1), NLi_4-Na (2) > NLi_4- Na (1)



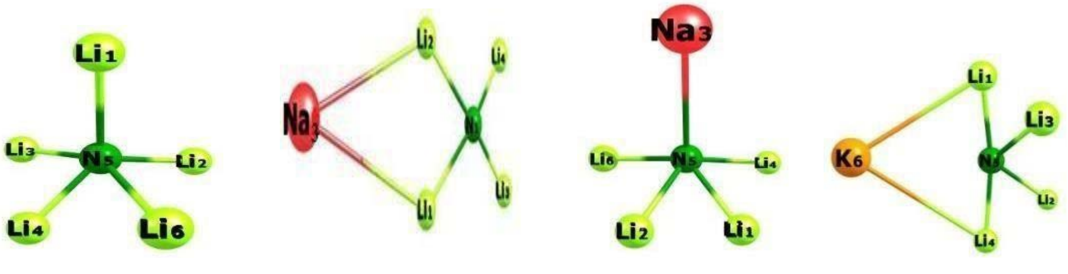
FLi$_2$-Li (1) FLi$_2$-Li (2) FLi$_2$-Na FLi$_2$-K (1)



FLi$_2$-K (2) OLi$_3$-Li (1) OLi$_3$-Li (2) OLi$_3$-Na (1)



OLi$_3$-Na (2) OLi$_3$-K (1) OLi$_3$-K (2) NLi$_4$-Li (1)



NLi$_4$-Li (2) NLi$_4$-Na (1) NLi$_4$-Na (2) NLi$_4$-K

Fig.1. The optimized structures of Superalkali-metal complexes calculated at B3LYP/6-311++G(d,p) level of theory.

3.2 Adiabatic Ionization Energy (Ie_a)

The adiabatic ionization energy (Table 1) are calculated using

$$IE_a = E\ (\text{cation}) - E\ (\text{neutral})$$

The adiabatic ionization energy values of metal atoms increase in the order of Li > Na > K which ranges 4.34-5.39 eV. The IE_a of super alkali clusters ranges 3.60-3.92 eV and the order of adiabatic ionization energy is FLi_2> OLi_3 > NLi_4. In the present study, IE_a of SA-M complex lies between 3.97 and 5.33 eV. It is found that the ionization energy of the SA-M complex decreases with the increase in the atomic radius of metal atoms. This may be due to the increase in bond distance of Superalkali with metal atoms. Further, the calculated IE_a of SA-M complexes are higher than superalkali clusters.

3.3 Dissociation Energy

The stability of hyperalkalized (SA-M) complexes has been analyzed by dissociation of SA-M in to SA and M fragments. The dissociation energies are calculated using

$D_e= E_t\ [M] +E_t\ [SA] -E_t\ [SA\text{-}M]$ and are given in Table 1.

The calculated value shows that all the hyperalkalized complexes are kinetically stable due to the existence of the positive values of D_e. These energies range from 0.832.38eV. Further, when the size of the metal atom increases, the dissociation energy of the Superalkali-metal complex decreases accordingly. As a result the stability of SA-M complex decreases with the increase in the size of the metal atoms. The reason may be due to the increase in bond length between Superalkali and metal atoms. Among all the complexes the maximum dissociation energy is noted for OLi_3-Li (2) and NLi_4-Li (2) and FLi_2-K (2) possess the minimum energy.

Table 1: Interaction energy E_{int} (in kcal/mol), Adiabatic ionization energy IE_a (in eV) and Dissociation energy D_e (in eV) of Superalkali-metal complexes calculated at B3LYP/6-311++G(d,p) theory.

Species	**Eint**	**IE_a**	**D_e**
FLi_2-Li (1)	-33.9	5.14	1.47
FLi_2-Li (2)	27.9	4.68	1.17
FLi_2-Na (1)	-31.2	5.03	1.36
FLi_2-K (1)	-20.8	4.59	1.15
FLi_2-K (2)	-19.1	4.16	0.83
OLi_3-Li (1)	-96.3	4.48	1.23
OLi_3-Li (2)	-50.5	5.33	2.06
OLi_3-Na (1)	-27.4	4.43	1.16
OLi_3-Na (2)	-35.5	4.70	1.37
OLi_3-K (1)	-23.2	4.08	0.96
OLi_3-K (2)	-31.1	4.02	1.32
NLi_4-Li (1)	-22.8	5.17	1.07
NLi_4-Li (2)	-56.4	4.29	2.38
NLi_4-Na (1)	-24.4	4.35	1.00
NLi_4-Na (1)	-36.8	4.05	0.97
NLi_4-K (1)	-32.5	3.97	0.89

4. NONLINEAR OPTICAL PROPERTIES

4.1 Polarizability (α_o)

The nonlinear optical properties of superalkali-metal complexes are studied by calculating polarizability and hyperpolarizability of SA-M complexes at B3LYP level of theory and the calculated values are given in Table 2. The calculated mean polarizability (α_o) values of SA-M complex ranges from 162.2 to 784.7 a.u. OLi_3-M and NLi_4-M ranges 244.1- 682.3 a.u. and 311.2 - 784.7 a.u., respectively. Evidently, with the increase in atomic radius of metal atom and size of the superalkali, the polarizability of SA-M complex increases successively. Larger size of the superalkali usually possesses more delocalized electron cloud and is expected to exhibit larger polarizability. This has been observed for NLi_4-K among all the SA-M complexes. In earlier studies [21] the polarizability value of SA-M (X= F, Cl) is observed to be 16-136 a.u. and 29-116 a.u. for SA-BF_4 complex which are significantly lower than those of SA-M complexes calculated in the present study. The calculated α_o shows an increasing sequence of

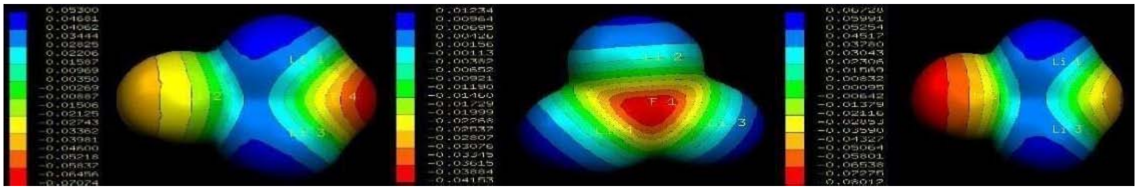
FLi_2-M (Li, Na, K) < OLi_3-M (Li, Na, K) < NLi_4-M (Li, Na, K)

Table 2: Static dipole moment μ (in Debye), Polarizability α_0 (in a.u.) and hyperpolarizability β_0 (in a.u.) of Superalkali-metal complexes calculated at B3LYP/6311++G(d,p) level of theory.

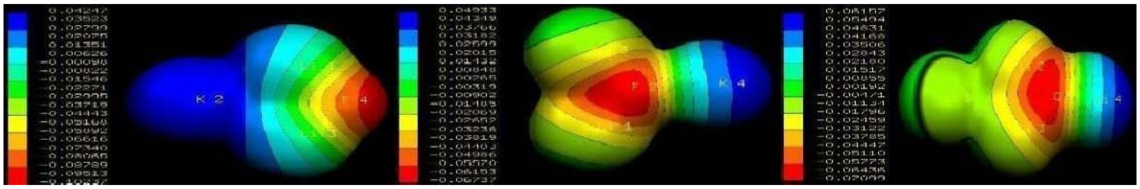
Species	**M**	**α_0**	**β_0**
FLi_2-Li (1)	4.16	174.5	2373.5
FLi_2-Li (2)	1.37	326.4	7093.8
FLi_2-Na (1)	0.65	197.6	2330.3
FLi_2-K (1)	2.05	312.3	54921.9
FLi_2-K (2)	3.93	553.7	60303.9
OLi_3-Li (1)	7.27	244.1	15138.8
OLi_3-Li (2)	1.82	515.4	5013.2
OLi_3-Na(1)	7.21	271.7	15951.7
OLi_3-Na(2)	2.50	553.0	56768.7
OLi_3-K (1)	6.03	393.3	61625.0
OLi_3-K(2)	2.59	682.3	18260.5
NLi_4-Li(1)	6.47	311.2	40307.3
NLi_4-Li(2)	2.08	634.0	42.267.3
NLi_4-Na (1)	6.97	345.0	54793.3
NLi_4-Na (2)	2.54	635.1	58783.0
NLi_4-K (1)	3.74	784.7	49218.5

4.2 Hyperpolarizability (β_o)

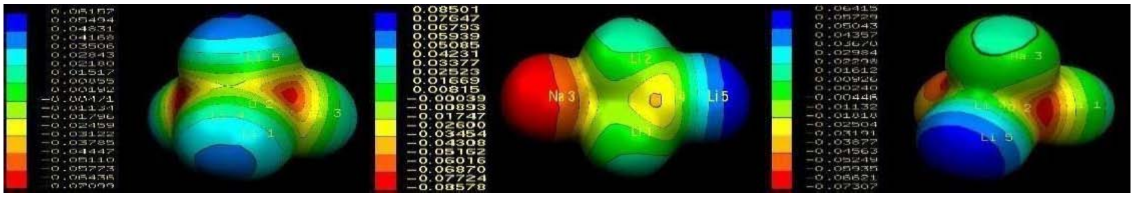
β_o values ranges from 2.3 10^3 a.u. (FLi_2-Na) to 6.1 10^4 a.u. (OLi_3-K). According to the principle of hard soft acids bases (HSAB), the systems with smaller E_{gap} are less hard and more polarisable [22]. For instance, OLi_3-K possesses smaller energy gap and hence higher β_o. It is interesting to note that the SA-M compounds show large NLO responses, with hyperpolarizability ranging from 2330 - 61625 a.u. Earlier, Ying et al. [23] have predicted β_o of Li-F to be 90.2 a.u., respectively. This value suggest that the β_o of superalkali- metal compounds in the present study exhibit large NLO responses compared to the traditional alkali halide. Hyperpolarizability of SA-M complex are comparable to earlier studies reported in previous work, such as Li^+(calix[4]pyrrole)e^- (7326 a.u) [24] and Li^+(calix[4]pyrrole)Na^- (14772 a.u) [25]. This may provide hints to design high performance NLO materials using hyperalkalized compounds. In earlier studies [21], the calculated βo values of SA-BF4 supersalts is 2.8×10^3 a.u. for SA=NLi_4 and BLi_6-SH is limited to 1.7×10^4 a.u for LiF_2. Enhancement of the hyperpolarizability values is the required property of the system to be NLO active.



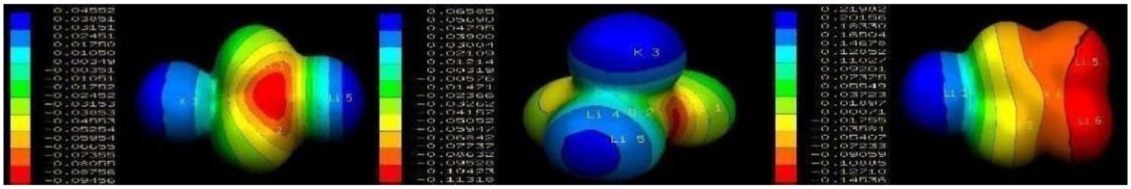
FLi_2-Li (1) FLi_2-Li (2) FLi_2-Na



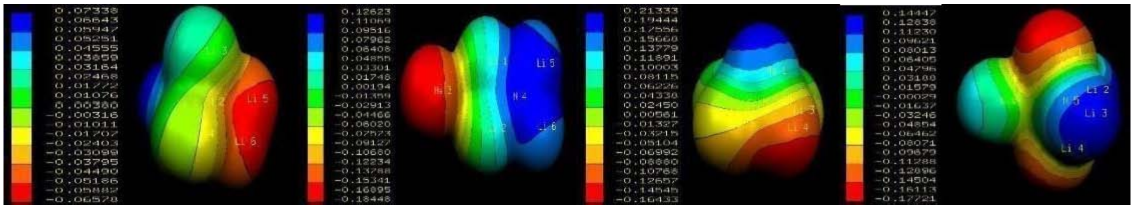
FLi_2-K (1) FLi_2-K (2) OLi_3-Li (1)



OLi_3-Li OLi_3-Na (1) OLi_3-Na (2)



OLi3-K (1) OLi3-K (2) NLi4-Li (1)



NLi_4-Li (2) NLi_4-Na (1) NLi_4-Na (2) NLi_4-K

Fig. 2. Electro static potential surfaces of Superalkali-metal complexes calculated at B3LYP/6-311++G(d,p) level of theory.

4.3 Molecular Electrostatic Potential Surfaces [MEP]

The MEP maps have been drawn for all the Superalkali-metal complexes and are shown in Figure 2, using Molekel 4.3. Areas of low potential (red) are characterized by an abundance of electrons and the areas of high potential (blue) are characterized by a relative absence of electrons. The electrostatic potential increases in the order of red< orange < yellow < green < blue. The red color region is susceptible to electrophilic attack. The blue region represents strong positive region and is prone to nucleophilic attack and green corresponds to a potential half way between the two extremes, red and blue. It is clear from the MEP map that in FLi_2-M complexes, the halogen F and oxygen atom in OLi_3-M complex attains lower potential (red color). This may be due to the larger electronegativity of halogen and oxygen atoms and are susceptible to electrophilic attack. Further, alkali metal atom attains higher potential (blue color) because of their electro positive nature. MEP maps are especially useful to compare the redistribution of charge, and changes in reactive sites, when molecules acquire and loss different functional groups [26].

5. CONCLUSIONS

The superalkali-metal complexes have been studied at B3LYP level of theory using 6311++G(d,p) basis set to analyze the variation in the geometry. The adiabatic ionization energy of SA-M complex decreases with the increase in the atomic radius of metal atoms. This may be due to the increase in bond distance of Superalkali with metal atoms. The calculated dissociation energy values shows that all the SA-M complexes are kinetically stable due to the existence of the positive values of D_e. Further, when the size of the metal atom increases, the dissociation energy of the SA-M complexes decreases accordingly. The non-linear optical properties are studied by calculating static dipole moment, polarizability and hyperpolarizability values. With the increase in atomic radius of metal atom and size of the superalkali, the polarizability of SA-M complex increases successively. The maximum β_0 value may due to the pi-electron cloud movement from donor to acceptor which makes the molecule highly polarized. This has been observed for NLi_4-K among all the SA-M species. It is clear from the MEP map that in FLi_2-M complexes, the halogen F and oxygen atom in OLi_3-M complex attains lower potential. This may be due to the larger electronegativity of halogen and oxygen atoms and are susceptible to electrophilic attack. Further, alkali metal atom attains higher potential because of their electro positive nature. Hence, it is evident that SA-M compounds show large NLO responses which are confirmed through polarizability and hyperpolarizability. This may provide hints to design high performance NLO materials using Superalkalimetal complexes in the future which will have significant applications in optoelectronics, photonics, and optical data storage.

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