

Second hyperpolarizability of the lithium salt electride Li–H₃C₄N₂...Na₂

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INTRODUCTION

Molecular systems with excess electrons have attracted great interest because of their intriguing properties. Electrides are compounds that have been extensively investigated since they have electrons with very diffuse character, which usually leads to large values of the polarizability and hyperpolarizabilities. Recently Ma et al.¹ proposed a new molecule with extraordinary first hyperpolarizability, the lithium salt electride. Calculations performed at the MP2 level showed that replacing a hydrogen atom of the pyridazine for a lithium increases the first hyperpolarizability from 5 to 859 au. This property is further increased to the extraordinary value of 1.4×10^6 au when this molecule is doped with two sodium atoms, yielding the lithium salt electride Li–H₃C₄N₂...Na₂. In this work we complement the work of Ma et al.¹ providing information on the second hyperpolarizability of this system.

METHODS

We have calculated the electronic and vibrational contributions for the second hyperpolarizability of the lithium salt electride. The electronic part was computed through coupled cluster cubic response theory² implemented in the DALTON program at the HF, CCS and CCSD levels. The vibrational corrections were obtained at the MP2 level through two methods: the perturbation theoretical method of Bishop and Kirtman (BKPT)³ and variational methodology (VAR) developed in a previous work⁴ to treat anharmonic systems.

RESULTS AND DISCUSSION

With objective of evaluate the role played by the electronic correlation effects we computed the dynamic second hyperpolarizability related to the

dc-Kerr effect at the HF, CCS and CCSD levels. The static value computed at the CCSD level was 1.1×10^9 au. Dynamic results obtained showed that there is a strong dependence of the computed values in relation to the correlation treatment, indicating that accurate results only could be obtained in a more sophisticated level than CCSD. Results for others nonlinear optical processes were obtained and will also be presented.

The computed values for the vibrational corrections show that the term $[\alpha^2]$ corresponds to little more than 10% of the electronic contribution while the term $[\mu\beta]$ is practically zero. Comparisons between the results obtained by perturbative and variational procedures showed large discrepancies.

CONCLUSIONS

The extremely large value of the second hyperpolarizability of the lithium salt electride, even compared to similar systems, reinforces the statement of Ma et al.¹ that the lithium salt electride has potential for application in nonlinear optics.

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