Chemical Physics Letters 633 (2015) 241–246

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Second hyperpolarizabilities of the lithium salt of pyridazine $Li–H_3C_4N_2$ and lithium salt electride $Li–H_3C_4N_2\cdots Na_2$

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ARTICLE INFO

Article history:
Received 16 March 2015
In final form 12 May 2015
Available online 9 June 2015

Keywords:
Electrides
Hyperpolarizabilities
Vibrational corrections

ABSTRACT

This Letter reports static and dynamic second hyperpolarizabilities of the lithium salt of pyridazine $Li–H_3C_4N_2$ and lithium salt electride $Li–H_3C_4N_2\cdots Na_2$. The results show strong dependence of the computed values with respect to the electron correlation treatment. The static value obtained at the CCSD level with the aug-cc-pVDZ basis set for the $Li–H_3C_4N_2\cdots Na_2$ is 1.1×10^9 au. This extremely large value of the second hyperpolarizability reinforces the potential of this system for application in nonlinear optics.

1. Introduction

Electrides are materials in which electrons, in a stoichiometric concentration, behave as anions. Previous works indicated that excess electrons in crystalline electrides are trapped in cavities and interact through connecting channels, and that many of the properties of these materials can be understood based on the structures of the cavities and channels [1–5]. These materials have been pointed as potential for applications because of their unusual chemical, electrical, optical and magnetic properties, being the main operational barriers related to thermal instability and sensitivity to air and moisture [1–5]. Matsuishi at al. [6] reported the synthesis of a single-crystal electride that is stable at the room temperature and can be exposed to air. The electron anions are localized in cavities but can migrate throughout the crystal, by hopping to neighbouring cavities, enhancing the electronic conductivity. Measurements of magnetic susceptibility and conductivity indicated that the interactions between the spins of neighbouring electron anions are antiferromagnetic, forming diamagnetic electron pairs or singlet bipolarons [6].

Molecules and clusters with excess electrons have also attracted great interest. Electrides and alkalides are two classes of these compounds that have been theoretically and experimentally investigated. In electrides, the anionic sites are occupied solely by electrons. The mechanism in these systems is the formation of a cation and a loosely bound excess electron when an alkali metal atom is placed in the presence of a ligand [7–9]. In alkalides, the anionic sites are alkali metal anions. In these systems an alkali atom is polarized by a ligand becoming a cation. The excess electron is transferred to other alkali atom (more distant from the ligand) to form an alkali anion [10,11]. Recently alkaline-earth-doped compounds with excess electrons, exhibiting alkalide or electride features, have also been investigated as possible units to build nonlinear optical devices [12,13].

The diffuse character of the excess electrons existing in electrides and alkalides usually leads to large values of the hyperpolarizabilities, which is a desirable characteristic for applications in nonlinear optics. Static first hyperpolarizabilities of several of these systems has been computed through the finite-field approach using the Möller–Plesset perturbation theory, coupled cluster or density functional theory methods [7–11,13–20]. Dynamic first hyperpolarizabilities have also been calculated at the CPHF level while correlated dynamical values have been estimated through multiplicative correction [12,21–23]. Second hyperpolarizabilities of molecules with excess electrons have been less studied. Garcia-Borràs et al. [24] investigated the first and second hyperpolarizabilities of five molecules with electride characteristics using second-order Möller–Plesset perturbation theory and density functional theory methods. The static and dynamic vibrational contributions for the hyperpolarizabilities were computed by means of the nuclear relaxation method [25] and the results obtained showed that these corrections are in general important.

A new molecule with extraordinary first hyperpolarizability was designed by Ma et al. [26]. Calculations performed at the MP2 level showed that the value of this property is increased from 5 to 859 au when one hydrogen atom of the pyridazine is replaced by one lithium atom, becoming the lithium salt of pyridazine. Furthermore, the first hyperpolarizability is increased to 1.4×10^6 au

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http://dx.doi.org/10.1016/j.cplett.2015.05.067
0009-2614/

when the lithium salt of pyridazine is doped with two sodium atoms, yielding a lithium salt electride. The frequency-dependent first hyperpolarizability was computed at the CPHF level and estimated at the MP2 level by means of multiplicative correction. This Letter aims to provide information on the second hyperpolarizability of these systems, since to our knowledge there is no published work on this regard. For comparison, we report results for the lithium salt of pyridazine Li–$H_3C_4N_2$ and lithium salt electride Li–$H_3C_4N_2 \cdots Na_2$.

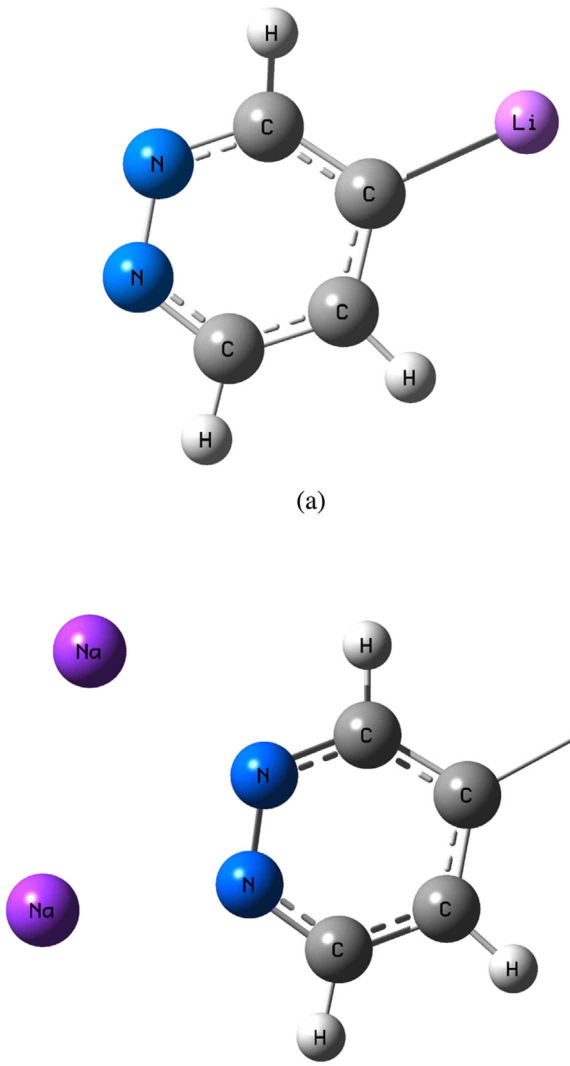
2. Computational details

The calculations of the electronic contributions to the second hyperpolarizabilities of the systems studied here were performed through coupled cluster cubic response theory [27] implemented in the DALTON program [28]. This methodology allows to compute hyperpolarizabilities including simultaneously electron correlation and dispersion (frequency dependence) effects. We did calculations at the SCF, CCS, CC2 and CCSD levels [29] using the aug-cc-pVDZ, d-aug-cc-pVDZ and aug-cc-pVTZ basis sets [30,31]. For comparison, we also performed density functional theory calculations using the B3LYP functional. We explored the frequency dependence of the hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$, $\gamma(-2\omega;\omega,\omega,0)$, $\gamma(-\omega;\omega,\omega,-\omega)$ and $\gamma(-\omega;\omega,0,0)$, which are related to the third harmonic generation (THG), dc-second harmonic generation (dc-SHG), intensity dependent refractive index (IDRI) and dc-Kerr effect (dc-K) nonlinear optical processes, respectively. For simplicity, we report only the mean second hyperpolarizability, defined as $\bar{\gamma} = \sum_{ij}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})/15$ for THG, dc-SHG and IDRI, and $\bar{\gamma} = \sum_{ij}(3\gamma_{ijij} - \gamma_{ijji})/10$ for dc-K [32]. In the static limit, both expressions reduce to $\bar{\gamma} = \sum_{ij}\gamma_{iijj}/5$.

We also present results for static vibrational corrections to the second hyperpolarizability of the lithium salt of pyridazine Li–$H_3C_4N_2$. As in the previous work on the first hyperpolarizability, these corrections were obtained at the MP2 level through two methods: the perturbation theoretical method of Bishop and Kirtman (BKPT) [33–35] and a variational methodology (VAR) [36] developed to treat anharmonic systems. We followed the partition of the vibrational correction in zero-point vibrational average (zpva) and pure vibrational (pv) corrections, but as the zpva correction is small for the first hyperpolarizability [36] and its calculation would involve high computational cost, we did not compute this part here. The general expression for the pv correction to the second hyperpolarizability is given by $\gamma^{pv} = [\alpha^2] + [\mu\beta] + [\mu^2\alpha] + [\mu^4]$. In this Letter we have implemented the BKPT approximation up to first general (electrical + mechanical) order of perturbation, so that the pv correction is given by $\gamma^{pv} = [\alpha^2]^{0,0} + [\mu\beta]^{0,0} + [\mu^2\alpha]^{1,0} + [\mu^2\alpha]^{0,1}$, where the expressions to compute the square brackets which appear in these expressions are provided elsewhere [32–35]. The variational methodology was implemented as in the previous work [36], including derivatives of the electric properties up to second order and derivatives of the energy up to third order. The vibrational wave functions were written as combinations of M-modes functions which are product of single-mode harmonic-oscillator functions in which the sum of the single-mode quantum numbers is no more than 3 [36,37].

3. Results and discussion

The results reported in this Letter for the second hyperpolarizability were obtained on geometries optimized at the MP2 level using aug-cc-pVDZ basis sets through Gaussian 09 program [38] (see Figure 1). The geometrical parameters optimized for the Li–$H_3C_4N_2$ were reported in the previous work [36]. The results obtained for the bond distances N–N, C–Li, N···Na, and Na···Na in the Li–$H_3C_4N_2 \cdots Na_2$ were 1.349, 2.033, 2.550 (2.622), and 3.222 Å, respectively. These values are slightly larger than those reported by Ma et al. [26] at the same level of calculation using a different basis set. The optimized bond angles CNNa and NNNa were 137 (123) and 105° (118°), where values in parenthesis refers to the Na atom closest to the Li atom.



(a)

(b)

Figure 1. Structure of the (a) lithium salt of pyridazine Li–$H_3C_4N_2$ and (b) lithium salt electride Li–$H_3C_4N_2 \cdots Na_2$.

Results for the static second hyperpolarizabilities of lithium salt of pyridazine and lithium salt electride, computed by different methods and using different basis sets, are shown in Table 1. For Li–$H_3C_4N_2 \cdots Na_2$ (Li–$H_3C_4N_2$) the aug-cc-pVDZ, d-aug-cc-pVDZ and aug-cc-pVTZ basis sets comprise a total of 242 (188), 335 (263) and 491 (391) basis functions, respectively. Due to computational limitations, we did not perform calculations for the lithium salt electride at the CCSD level using the largest basis set.

We start the analysis by the lithium salt of pyridazine. The large discrepancies between results obtained at different levels are visible. The SCF values correspond to only 40% of the CCSD results when the two smallest basis sets are used and nearly 50% when the analysis is based on results obtained using the largest basis set. The CCS results are only slightly larger than the SCF ones and much smaller than the CCSD reference values. The CC2 and B3LYP values are nearly twice larger than the corresponding CCSD values.