# Density functional theory calculations of the molecular structure and the vibrational spectra of bis-tetrapropyl-ammonium hexachloro-dizincate

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ABSTRACT

The molecular structure and vibrational spectra of bis-tetrapropyl-ammonium hexachloro—dizincate in the ground state have been investigated by density functional method (DFT) using the B3LYP method with the LanL2DZ and LanL2MB basis set. Infrared and Raman spectroscopes of the $[N(C_3H_7)_4]_2Zn_2Cl_6$ compound have been measured at room temperature in the frequencies range ($3500-400$ cm$^{-1}$) and ($3500-100$ cm$^{-1}$), respectively. The optimized geometric shows that the calculated values obtained by B3LYP/LanL2DZ basis are in much better agreement with the experimental data than those obtained by B3LYP/LanL2MB. Actually the theoretical vibrational spectra (B3LYP/LanL2DZ) of the title compound have been interpreted by means of potential energy distribution (PED) which is in good agreement with the experimental data. The comparison of the infrared spectrum of the tetrapropyl-ammonium chloride ligand with those of the bis-tetrapropyl-ammonium hexachloro-dizincate compound confirms an increase of the wavenumber in the $[N(C_3H_7)_4]_2Zn_2Cl_6$ compound. This can be explained by an increase of the electrostatic interactions of the $[N(C_3H_7)_4]Cl$ ligand.

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## 1. Introduction

Research in the field of organic—inorganic hybrid compounds is of great interest in chemistry and materials science. The interest in such materials mainly originates from the fact that these compounds represent the combined properties of both organic and inorganic compounds within a single entity. This enables them to exhibit some interesting crystal structures and properties such as second-order nonlinear optical (NLO) response, magnetism, luminescence [1–6]. As a matter of fact, many of these crystals exhibit structural phase transitions caused by the reorientational dynamics of the tetra-alkylammonium groups [7]. This kind of material, generally expressed as $[(C_nH_{2n+1})_4N^+]_xM_yX_z$ (where M = divalent metal, X = halogen and n = 1, 2, 3, 4).

For a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational modes is essential. For this purpose, density functional theory (DFT) approaches, especially those using hybrid functional, have evolved to be powerful and very reliable tool, being now routinely used for the determination of the geometry and various properties of the molecules [8,9]. His advantage is to determine reasonable vibrational frequencies and geometries much superior to the conventional methods [10].

The present research work undertakes the comparison of the calculated results by using the.DFT (B3LYP) approach with the experimental data of the $[N(C_3H_7)_4]_2Zn_2Cl_6$ compound. Its objective is also to find the effect of the LanL2DZ basis set in predicting the structure and vibrational spectra of the title compound. Besides this, the Raman and IR experimental spectra are compared with literature results, and we have discussed the wavenumber differences.

## 2. Method and calculation

The molecular geometry optimization and vibrational frequencies calculations of the complex $[N(C_3H_7)_4]_2Zn_2Cl_6$ compound were performed with the Gaussian 09 program [16] using DFT approaches [11]. The geometry was fully optimized at the density functional level of theory with Becke's three parameter exchange functional [12] combined with the Lee Yang Parr correlation functional [13] (B3LYP) by the LanL2DZ [14] and LanL2MB [15] basis sets.

The main raison for choosing the LanL2DZ and LanL2MB basis is related to a relativistic effect that is essential for heavy elements. On the other hand, it was capable to generate results of a very satisfactory quality in the case of large molecules [17]. The first task of the computational study was to determine the optimized geometry of the bis-tetrapropyl-ammonium hexachloro−dizincate. The second task was to undertake a vibrational frequency analysis with the aid of the calculation of the potential energy distribution (PED) which was completed again using the DFT method. These calculations were determined with the VEDA 4.0 program written by Jamroz [18].

It should be noted that the Raman intensities were not calculated by the Gaussian 09 package, but the Raman activities were transformed into Raman intensities using the RAINT program [19] by the following relationship derived from the basis theory of Raman scattering:

$$I_i = 10^{-12}(\nu_0 - \nu_i)^4 \left(\frac{1}{\nu_i}\right) S_i$$

where: $I_i$ is the Raman intensity, $S_i$ the Raman scattering activity, $\nu_i$ the wavenumber of normal modes and $\nu_0$ denotes the wavenumber of the excitation laser [20].

The calculated wavenumbers of infrared and Raman spectra are usually bigger than the observed wavenumbers. This variation can be explained by the fact that the experimental results belong to the solid phase, whereas the theoretical calculations belong to the gaseous phase. In order to obtain the calculated values in

**Table 1**
The values of scale factors using by (B3LYP/LanL2MB) and (B3LYP/LanL2DZ).

| Regions | LanL2DZ (IR and Raman) | LanL2MB (IR and Raman) |
|---|---|---|
| $0-400$ cm$^{-1}$ | 0.963 | 0.903 |
| $401-1600$ cm$^{-1}$ | 0.977 | 0.943 |
| $2700-3500$ cm$^{-1}$ | 0.950 | 0.859 |

agreement with the experimental values, it is necessary to determine the scaling factors. The scaled factors have applied the following method which is formed by three steps. Firstly, the unscaled vibrational wavenumbers have been calculated and compared with the experimental result. The experimental wavenumbers, based on the literature and later on theoretical vibrational wavenumbers and the potential energy distribution (PED), have been carefully screened to eliminate misassignments and uncertainties in the interpretation of these complex spectra. Fundamentals, which were uncertain or not directly observed, were not used as input data to the scaling procedure. Secondly, we divided the theoretical IR and Raman spectra into three intervals, which are in the range of [0−400 cm$^{-1}$], [401−1600 cm$^{-1}$], and [1601−3500 cm$^{-1}$], respectively. Finally, the values of scale factors have been evaluated by using a least squares optimization between the calculated and the observed fundamental frequencies.

The correlations between the theoretical (LanL2DZ and LanL2MB) and the experimental results for Raman and IR bands in the three regions are shown in Table 1. The vibrational assignments of the title molecule were realized by a comparison with previous research publications works on analogous compounds [21−28], and it is based on the result of the PED calculation for the vibrational modes.

## 3. Results and discussion

### 3.1. Conformational analysis

The bis-tetrapropyl-ammonium hexachloro−dizincate [(C$_3$H$_7$)$_4$N]$_2$Zn$_2$Cl$_6$ crystallizes in the centrosymmetric triclinic system, space group $P\bar{1}$, with the cells dimension: a = 13.736(2) Å, b = 17.044(3) Å, c = 17.334(2) Å, $\alpha$ = 68.30(2)$^\circ$, $\beta$ = 75.14(2)$^\circ$ and $\gamma$ = 84.93(3)$^\circ$. The crystallographic analysis reveals that the asymmetric unit is formed by one and two half of [Zn$_2$Cl$_6$]$^{2-}$ unequivalent dimers and four [N(C$_3$H$_7$)$_4$]$^+$ cation (Fig. 1) [29]. Indeed, the cations are stacked in a regularly cross form and orient



**Fig. 1.** Asymmetric unit of [(C$_3$H$_7$)$_4$N]$_2$Zn$_2$Cl$_6$ sample.