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The equilibrium structures, vibrational spectra, NLO and directional properties of transition dipole moments of diguanidinium arsenate monohydrate and diguanidinium phosphate monohydrate The theoretical DFT calculations

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Abstract

For diguanidinium arsenate monohydrate and diguanidinium phosphate monohydrate the energies were minimized and the theoretical vibrational frequencies and potential energy distribution (PED) were calculated by density functional method. The 6-31++G(d,p) basis set was used. The assignment of the bands has been made on the basis of the calculated PED.

For calculated equilibrium geometries two methods for determination of direction of transition dipole moments (TDM) were used. The oriented gas model was used for calculation of "static" TDM and from the other side the "dynamic" approximation of TDM by analysis of changes in internal coordination during characteristic vibrations was performed.

The restricted Hartree–Fock (RHF) methods were used for calculation of the hyperpolarizability for both investigated molecules. The theoretical results are compared with experimental value of β.
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Keywords: Guanidinium; DFT; RHF; Transition dipole moment; Oriented gas model; PED; Hyperpolarizability

1. Introduction

The density functional theory (DFT) [1] has been accepted by the ab initio quantum chemistry community as a popular approach for the computation of molecular structures, vibrational frequencies and energies of chemical reactions. The B3LYP method was found to predict the geometrical parameters in better agreement with reliable experimental results, than other DFT methods [2]. Many studies have shown that DFT methods are successful in predict ion of vibrational frequencies, too.

Some complexes of the amino acids or similar molecules (for example: guanidinium) with organic and inorganic salts appear to be promising for optical second harmonic generation (SHG). The crystals display interesting physical and chemical properties, exhibiting phase transitions with ferroelectric, anti-ferroelectric and ferroelastic behaviors.

In this work the DFT method was used for calculation geometrical parameters of two isostructural compounds: monohydrate diguanidinium arsenate [3] and monohydrate diguanidinium phosphate [4,5]. The crystals were investigated as new materials with organic cations and inorganic ions, which can be used in NLO studies. Both crystals belong to noncetrosymmetric crystallographic space group. For these compounds the non-zero β hyperpolarizability were found [6].

The time dependent Hartree–Fock calculation of NLO properties and dipole moments of the investigated complexes are performed and discussed with experimental values of β.

The second purpose of this work is the detailed investigation of vibrational frequencies and PED analysis. The clear-cut assignment of all the characteristic bands has been made on the basis of the calculated potential energy distribution, PED. This part of work will be helpful in design of new chemical compounds with detailed specific expectations.

According to the detailed PED analysis the new way for calculation of transition dipole moment is proposed. The "dynamic" calculation seems to be faster than other method

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(oriented gas model) and more precise. In real (experimental) vibrational spectra there are often the coupled vibrations and "true" oriented gas model is not appropriate. The preliminary quantum calculation of vibrational spectra and PED analysis and following calculation of TDM from coordinates of displacement eigenvectors should be in the better agreement with experiment.

2. Experimental

The *optimized equilibrium structures*, harmonic frequencies, infrared intensities for diguanidinium arsenate monohydrate and diguanidinium phosphate monohydrate compounds were calculated by the density functional triply-parameter hybrid model DFT/B3LYP. The 6-31++G(d,p) basis set have been employed (the valence triple-ξ basis set, augmented by d-polarization functions on carbon and nitrogen; p-polarization functions on hydrogen atoms and enlarged by diffuse functions on all atoms).

The *normal coordinate analysis* has been carried out for both molecules according to the procedure described and recommended by Fogarasi and Pulay [7]. The nonreducant set of 81 internal coordinates has been used. The frequencies of stretching and bending vibration were scaled by 0.98. This scaling factor was determined for similar chemical system previously studied by DFT methods [8].

The *nonlinear optical response* of an isolated molecule in an electric field $E_i(\omega)$ can be presented as a Taylor expansion of the total dipole moment, μ_t, induced by the field:

$$\mu_t = \mu_0 + \alpha_{ij} E_i + \beta_{ijk} E_i E_j + \cdots$$

where α is a linear polarizibility, μ_0 the permanent dipole moment, and β_{ijk} are the first hyperpolarizability tensor components. The NLO response of the material in molecular state can be determined either by computation or by measuring. The values obtained in this way may be different, therefore it is necessary to give an exact definition [9]. In this paper we will consider only the frequency doubling process, i.e. $\beta = \beta(-2\omega, \omega, \omega)$, and we define in a molecule fixed coordinates:

$$\beta_i = \beta_{iii} \frac{1}{3} \sum_{k\_i} (\beta_{ikk} + \beta_{kik} + \beta_{kki})$$

where $i = x$, y or z

$$\beta_V = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

For calculation of the first hyperpolarizability, ab initio quantum chemical methods at RHF level of theory with 6-31++G(d,p) basis set were chosen. The time dependent Hartree–Fock (TDHF) algorithm was used (the TD-DFT methods was not implemented in this version of GAMMES program).

Calculations were performed with GAMESS program [10], version from 12 December 2003 (R2) compiled under Linux operating system. This job was executed on PC Cluster consists of one server node with two 32-bit Intel Xeon processors running at 1.8 GHz and 3 GB RAM, 20 computing nodes with dual 32-bit Intel Xeon processors running at 2.8 GHz and 2 GB RAM, 9 computing nodes with dual 32-bit Intel Xeon processors running at 1.7 GHz and 1 GB RAM.

The *FT-IR powder spectra* were measured as Nujol suspensions using a Bruker IFS-88 spectrometer with a resolution of $2\,\text{cm}^{-1}$. The samples were put between KBr and NaCl windows.

The *oriented gas model* of Kastler and Rousset [11] treats a molecular crystal as a 'frozen' gas in which, under an applied electric field, the induced dipoles on different molecules do not interact. This is an unrealistic approximation as in fact, the dipole interaction is strong in crystals. Even in a crystal with a relatively low refractive index the induced polarization give rise to a field of strength comparable with the applied field. Nevertheless, the oriented gas model has been applied qualitatively in its original form by Kastler and Rousset and Ito et al. [12] to a number of crystals. More recently the authors have adapted it to the measurement of eigenvectors of lattice vibrations [13,14]. In these applications it is the polarizability derivative with respect to the vibrational coordinates of the molecules which is required. For the measurement of eigenvectors in the calculation of the polarizability derivative, it is necessary to have as much accuracy as possible. It is also interesting, for its own merit, to see what the effect of including the Coulomb interaction will be. It is the reasons that this work was undertaken.

The traditional "static" calculations of transition dipole moment are performed for previously calculated optimized equilibrium structures or for X-ray crystallographic data in Cartesian coordinate system [15]. The typical mathematical formulas are used (i.e. sum of difference of vectors or length of segment). The coordinates of three atoms are used (in theory of oriented gas the vibrations are localized in the characteristic groups of three atoms (i.e. two bonds)). For three atoms A, B and C with coordinates $A_x, A_y, A_z, B_x, B_y, B_z$ and C_x, C_y, C_z first the distances (R): A–B and B–C are calculated from the relationship:

$$R = \sqrt[2]{(B_x - A_x)^2 + (B_y - A_y)^2 + (B_z - A_z)^2}$$

and

$$R = \sqrt[2]{(C_x - B_x)^2 + (C_y - B_y)^2 + (C_z - B_z)^2}$$

and for A and B atoms directional cosines are calculated from relationships:

$$\cos x_1 = \frac{B_x - A_x}{R}, \quad \cos y_1 = \frac{B_y - A_y}{R}, \quad \cos z_1 = \frac{B_z - A_z}{R}$$

and for B and C atoms:

$$\cos x_2 = \frac{C_x - B_x}{R}, \quad \cos y_2 = \frac{C_y - B_y}{R}, \quad \cos z_2 = \frac{C_z - B_z}{R}$$

and calculations of sum and difference of two vectors $\overrightarrow{AB}$ and $\overrightarrow{BC}$:

$$\text{sum}_x = \cos x_1 + \cos x_2, \qquad \text{sum}_y = \cos y_1 + \cos y_2,$$

$$\text{sum}_z = \cos z_1 + \cos z_2, \qquad \text{dif}_x = \cos x_1 - \cos x_2,$$

$$\text{dif}_y = \cos y_1 - \cos y_2, \qquad \text{dif}_z = \cos z_1 - \cos z_2$$

according to oriented gas model approximation the directional cosines of such orthogonal system with respect to the system xyz are identical as those for a sum (ν_s, δ), for a difference (a_{sym}, ρ) and for a dot products (ω) of the unit vector (directional cosines)