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The theoretical calculations of vibrational spectra of guanidine selenate and guanidinium sulphate. Determination of direction of transition dipole moments by two methods: oriented gas model and changes in displacement eigenvectors computed by DFT method

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Abstract

For guanidinium selenate and guanidinium sulphate the energy was 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.

Keywords: Guanidinium; DFT; RHF; Transition dipole moment; Oriented gas model; PED

1. Introduction

The formal symmetrical classification of the observed bands in the polarized vibrational spectra called as factor group analysis can be applied to vibrational measurement, but it is only formal classification and in real experiment this approximation is not sufficient. The complete set of polarised spectra can be correlated with X-ray crystallographic data on the basis of the oriented gas model approximation [1,2]. In this model we assume that (1) the vibrations are localized in the characteristic groups of three atoms (i.e. two bonds) and (2) the transition dipole moments (TDM) of the vibrations are parallel to the axes of the orthogonal system coupled to the group. The directional cosines of such orthogonal system with respect to the experimental system *XYZ* are identical as those for a sum (ν_s, δ), for a difference (ν_{sym}, ρ) and for a dot products (ω) of the unit vector (directional cosines) of the bonds whose (stretching) vibrations may be coupled.

This oriented gas model was applied in a lot of experimental works in our laboratory. In many cases the agreement between theoretical calculation of TDM and experimental polarized vibrational spectra is very good. The best conformity is observed in directional behavior of stretching hydrogen bond vibration [3–7]. In the other experimental works the some discrepancies are emphasized. The oriented gas model was used in the case of $Na_5H_3(SO_4)_4 \cdot H_2O$ single crystal. In this work the polarization features of in-plane bending vibration of hydrogen bond does not correspond to that predicted in TDM calculation [8]. The seriously doubts connected with bands assigned to the wagging ωCOOH mode (their polarization do not correspond to that predicted in calculation) were described [9]. The pretty good agreement between experimental spectra and theoretical calculation is observed in the case of $Cs_5H_3(SeO_4)_4 \cdot H_2O$ crystal for almost all bands except the bands assigned to antisymmetric stretching vibrations of water molecule where this band should be polarized parallel to *X*-axis only, but appears in experimental spectra to be polarized parallel to *Y* and *X* axes [10].

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According to these doubts a new way for calculation of TDM is proposed. This 'dynamic' calculation seems to be faster than other methods 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. Of course, the next problem will be connected with transformation of *XYZ* systems: from theoretical to experimental, but in this work the comparison of two computational methods (described as 'static' and 'dynamic') will be carried out for equilibrium theoretical geometries, only.

2. Experimental

The optimized equilibrium structures, harmonic frequencies, infrared intensities for guanidinium selenate and sulphate compounds were calculated by the density functional triply-parameter hybrid model DFT/B3LYP. The Restricted Hartree–Fock (RHF) method was used. 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 an all atoms).

The normal coordinate analysis has been carried out for both molecules according to the procedure described and recommended by Fogarasi and Pulay [11]. The non-reducible set of 42 internal coordinates has been used. The frequencies of stretching and bending vibration were scaled by 0.9614. This scaling factor was determined in previous studies of similar chemical system by DFT methods [12].

All calculations were performed with GAMESS program [13], version from 12 December of 2003 (R2) compiled under Linux operating system. This job was executed on PC Cluster consisting 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 oriented gas model of Kastler and Rousset [14] 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 the dipoles interact strongly in crystals. Even in a crystal with a relatively low refractive index the induced polarization can 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. [15] to a number of crystals. More recently it was has adapted for the measurement of eigenvectors of lattice vibrations [16,17]. In these applications, the polarizability derivative with respect to the librational coordinates of the molecules is required. For the calculations of eigenvectors it is necessary to have as much accuracy as possible to obtain the polarizability derivative. It is also interesting, for its own merit, to see what the effect of inclusion of the Coulomb interaction will be. It is the reason that this work was undertaken.

The traditional 'static' calculations of transition dipole moment are performed for calculated optimized equilibrium structures or for X-ray crystallographic data in Cartesian coordinate system [18]. 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 the oriented gas approximation the vibrations are localized in the characteristic groups consisting 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 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:

$$\cos X_1 = \frac{B_X - A_X}{R}, \qquad \cos Y_1 = \frac{B_Y - A_Y}{R},$$

$$\cos Z_1 = \frac{B_Z - A_Z}{R}$$

and for B and C atoms:

$$\cos X_2 = \frac{C_X - B_X}{R}, \qquad \cos Y_2 = \frac{C_Y - B_Y}{R},$$

$$\cos Z_2 = \frac{C_Z - B_Z}{R}$$

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

$$\text{sum}_x = \cos X_1 + \cos X_2, \qquad \text{sum}_y = \cos Y_1 + \cos Y_2,$$

$$\text{sum}_z = \cos Z_1 + \cos Z_2$$

$$\text{dif}_x = \cos X_1 - \cos X_2, \qquad \text{dif}_y = \cos Y_1 - \cos Y_2,$$

$$\text{dif}_z = \cos Z_1 - \cos Z_2$$

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 (ν_{sym}, ρ) and for a dot products (ω) of the unit vector (directional cosines) of the bonds whose (stretching) vibrations may be coupled. The direction of TDM for