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Non-bonded interactions and its contribution to the NLO activity of Glycine Sodium Nitrate – A vibrational approach

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Abstract

Vibrational spectral analysis of the novel nonlinear optical (NLO) material, Glycine Sodium Nitrate (GSN) is carried out using NIR FT-Raman and FT-IR spectroscopy, supported by Density Functional Theoretical (DFT) computations to derive equilibrium geometry, vibrational wave numbers and first hyperpolarizability. The reasonable NLO efficiency, predicted for the first time in this novel compound, has been confirmed by Kurtz–Perry powder SHG experiments. The influence of Twisted Intramolecular Charge Transfer (TICT) caused by the strong ionic ground state hydrogen bonding between charged species making GSN crystal to have the non-centrosymmetric structure has been discussed. The shortening of C—H bond lengths, blue-shifting of the stretching frequencies and intensity variation indicating the existence of 'blue-shift or improper' C—H···O hydrogen bonding. The intense low wavenumber H-bond Raman vibrations due to electron–phonon coupling and non-bonded interactions in making the molecule NLO active have been analyzed based on the vibrational spectral features. The Natural Bond Orbital (NBO) analysis confirms the occurrence of a strong intra- and intermolecular N—H···O and C—H···O hydrogen bonds.

Keywords: NIR FT-Raman; FT-IR; Ionic hydrogen bonds; Nonlinear optics; SHG; First hyperpolarizability; DFT; *Ab initio* computations; Twisted Intramolecular Charge Transfer (TICT); Glycine conformers; Natural Bond Orbital analysis

1. Introduction

Nonlinear optical (NLO) materials are active elements for optical communications, optical switching data storage technology, optical mixing and electro-optic application [1–4]. The development of photonic and optoelectronic technologies rely heavily on the growth of NLO materials with high nonlinear optical responses and the development of novel and more efficient materials [5]. To design and fabricate the NLO materials, much effort is being devoted to understand the origin of nonlinearity in large systems and to relate NLO responses to electronic structure and molecular geometry. The molecular engineering approach has led to better understanding of the relationship between the crystal structure and its optical nonlinearities [6–8]. Chirality [9] and hydrogen bonding [10] are important factors in the design of NLO chromophores since the measurement of bulk NLO properties in the solid state is dependent on a non-centrosymmetric packing environment within the crystal lattice. Molecules in pure organic crystals are often coupled by relatively weak van der Waals forces or hydrogen bonding, resulting in rather poor mechanical properties. In such organic crystals, two requirements to be satisfied are: (i) they are made of highly polarizable molecules, the so-called conjugated molecules, where the asymmetric π electron system of aromatic molecules can easily move between a donor and an acceptor substituent groups that induce a molecular charge transfer and (ii) the molecules are adequately packed to build up a non-centrosymmetric crystal structure that provides non-vanishing second order nonlinear coefficients [11,12]. Metal-organic

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hybrids also offer interesting advantages with respect to both pure organics and pure inorganic materials in that they may be reliably designed by integrating highly predictable structural features, such as hydrogen bonds and coordination bonds, in each of these cases which are used jointly to achieve spatial and dimensional control in organic–inorganic hybrid [13].

Presently, semi organics are being explored, which can share the properties of both organic and inorganic materials, such as high laser damage threshold, optical transparenc and high efficiency. Complexes of amino acids with inorganic salts have been of interest as materials for optical second harmonic generation (SHG), and all amino acids except glycine contain chiral carbon atoms and perhaps crystallize in the non-centrosymmetric space group [8]. Dipolar molecules possessing an electron donor group and an electron acceptor group contribute to large second order optical nonlinearity arising from the intramolecular charge transfer between the two groups opposite nature. Due to this dipolar nature, amino acids have been considered potential candidates for NLO applications [6,8]. Although the salts of amino acids like L-Arginine [14], L-Histidine [15] and L-Proline [7,16] are reported to have NLO properties; the complexes of glycine with inorganic salts are not explored for optical SHG so far, since glycine, the simplest amino acid, does not possess the asymmetric carbon, it is NLO inactive. Out of the number of semi organic single crystals of glycine that have been already reported, most of them are not NLO active [17–19].

Glycine has three polymorphic crystalline forms α, β, γ [20,21]. Both α and β forms crystallize in centrosymmetric space groups ruling out the possibility of optical second harmonic generation. But γ-glycine crystallizes in non-centrosymmetric space groups $P3_1$ making it a possible candidate for NLO applications and it is difficult to grow the γ-glycine crystals [22,23]. The thermodynamic stabilities of the three polymorphs of glycine at room temperature are in the order $\gamma > \alpha > \beta$ [24]. It has recently been reported that complexes of the γ-glycine can be efficient in optical SHG with inorganic salt sodium nitrate [8]. Due to their potential applications in photonic devices, bulk NLO properties of materials as well as their dependence on the first hyperpolarizabilities of molecules have evoked a lot of experimental efforts [25–27] and theoretical research [28–30]. The Natural Bond Orbital (NBO) analysis can be employed to identify and substantiate the possible intra- and intermolecular interactions between the units that would form the H-bonded network [31]. Vibrational spectral studies of the molecules can be used to provide deeper knowledge about the relationships between molecular architecture, nonlinear response and hyperpolarizability. NIR FT-Raman spectra combined with quantum chemical computations have recently been effectively applied in the vibrational analysis of drug molecules [32], biological compounds [33,34], natural products [35,36] and NLO active compounds [7,37–39], since fluorescence free Raman spectra and computed results help unambiguous identification of vibrational modes and provide deeper insight into the bonding and structural features of complex organic molecular systems. Glycine Sodium Nitrate (GSN) crystals, being the first complex of glycine reported with NLO property, the vibrational spectral studies of this novel NLO system is taken up, based on NIR FT-Raman and IR spectra along with DFT and MP2 theoretical support to elucidate the relationship between the molecular structural features and NLO properties.

2. Experimental

2.1. Preparation

Glycine Sodium Nitrate (GSN) crystals grown by slow evaporation [40] were subjected to repeated recrystallization and good quality single crystals with size of around 0.6 mm were obtained.

2.2. Crystal structure

GSN (Fig. 1) crystallizes in monoclinic space group Cc with four formula units in unit cell ($Z = 4$) [40]. The cell dimensions are: $a = 14.329(3)$ Å, $b = 5.2662(11)$ Å, $c = 9.1129(18)$ Å, $\beta = 119.10(3)°$. The glycine molecules are seen 'sandwiched' between layers of Na (NO_3) as shown in Fig. 2. Both carboxyl O atoms participate in the hydrogen bonds as acceptors forming head-to-tail hydrogen bonds. Almost linear O—Na—O chains involving carbonyl O atoms run along the $(2 0 \bar{2})$ plane in the [1 0 1] direction. X-ray powder diffraction was used for the identification of the grown crystals of GSN. Usually, the characteristic strong peaks of α-glycine and γ-glycine are expected near 2θ values of 29° and 24°, respectively [41].

2.3. Raman and IR measurements

The NIR FT-Raman spectrum (Fig. 3) of GSN was obtained on a Bruker RFS 100/S FT-Raman Spectrometer

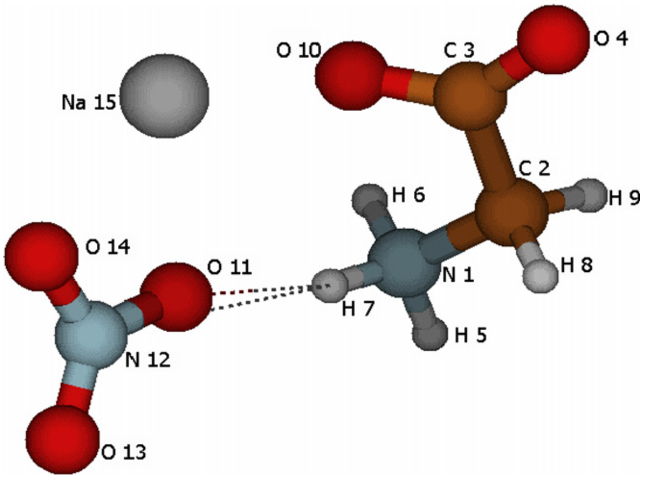

Fig. 1. Optimized molecular structure of GSN.