Structural analysis and second-order non-linear optical activity of urea hydrogen peroxide adduct

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Received 8 August 2005; revised 27 December 2005; accepted 3 April 2006

Urea hydrogen peroxide adduct is synthesized and characterized using UV and IR spectra. Second harmonic generation (SHG) efficiency has been determined experimentally in this adduct using pulsed Nd: YAG laser at 1064 nm wavelength. The efficiency is higher in the adduct as compared to urea. Geometry of the molecule was optimized using Austin Model 1 (AM1) semi-empirical technique. Our computations suggest two conformers of the adduct, both having no center of symmetry. Complete geometry of the molecule and the dipole moment calculations have been reported. It is concluded that increased dipole moment of one of the conformers of the adduct is responsible for the enhanced SHG efficiency of the adduct.

Keywords: Urea hydrogen peroxide adduct, Hydrogen bonding, Dipole moment, Second harmonic generation

1 Introduction

Non-linear optics (NLO) has been recognized as a promising field to support new and emerging technologies of opto-electronics and photonics. Synthesis of efficient second-order non-linear optical material found potential use in harmonic generation, electro-optic modulator, optical parametric generation and amplification. Today, organic systems are investigated as an alternative to inorganic species for non-linear optical device application because of their low cost and large non-linear response over a broad frequency range. Investigation of the NLO properties of supramolecules and adduct formed due to self-assembly of two or more molecular components has been a topic of considerable recent interest. Hydrogen bonding, electrostatic interactions, π-π bonding and van der-Waals forces have been employed to explain the behaviour of such molecules. Recently, a neutron diffraction study of the adduct formed between 1,2 diamino ethane and benzoic acid has been reported by Adam et al. It has been found that urea also forms adduct with hydrogen peroxide which provide a good means for stabilizing H₂O₂. The urea-H₂O₂ adduct, UHP (1:1) has been found extremely useful as an oxidizing agent, since it can be used in non-aqueous media. A preliminary study reveals that NLO behaviour of UHP is better than urea, reflecting that the ground state polarization or degree of charge separation in the adduct increases due to the presence of H₂O₂. This observation helps one to identify the bonding between H₂O₂ and urea molecules. To the best of our knowledge, there is no report on the structure elucidation and NLO properties of UHP. The present problem was therefore undertaken with a view (a) to get the optimized structure of UHP employing semi-empirical molecular orbital method and (b) to investigate the NLO behaviour of this molecule to confirm its structure.

2 Experimental Details

2.1 Synthesis and characterization

Urea hydrogen peroxide (1:1) crystals were prepared by mixing 1 mole of urea and 1 mole of H₂O₂ in aqueous solution and slow cooling of the solution. The needle shape transparent white crystals thus obtained were washed with toluene. Electronic spectra of UHP were recorded on a Shimadzu UV 160 A spectrometer and is reproduced in Figure 1. IR spectra of UHP and urea were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. Geometry optimization of adduct molecule was performed by AM1 semi-empirical method. The H₂O₂ content of the adduct was determined following the technique described by Vogel.
2.2 Second harmonic generation analysis

In order to measure the properly optimized output intensity, it is always desirable that the crystal should be cut at a particular axis with respect to the optic axis of the crystal. However, in the present measurement scheme, we could not follow this method due to the fine needle shape nature of the UHP crystals. We used the powder of the crystal for the SHG measurements. The SHG measurement was performed using 15 ns pulsed Nd: YAG laser at 1064 nm wavelength. In the experimental set-up used for the study of SHG, the incident beam was split into 95:5 ratio. The 95% fundamental was focused on the polycrystalline sample, while the 5% intensity of the fundamental beam was used as a reference beam to normalize the fluctuations of the incident laser. The second harmonic (SH) radiation at 532 nm obtained at the output was filtered using a SH separator to remove the fundamental input radiation. SHG was detected by a photomultiplier tube (PMT); Model No. RCA-931A, which is connected to 100 MHz digital storage oscilloscope (DSO). The change in the intensity of the second harmonic as a function of the intensity of the fundamental was experimentally measured and is shown in Figure 2. The SH intensity in UHP is stronger than that in urea under identical experimental conditions (Fig. 2). The reason for this enhancement may be explained on the basis of increased optical absorption at 1.06 μm wavelength in the complex under consideration.

2.3 Geometry optimization

The urea moiety is very simple in structure but provides a particularly useful block in supramolecular chemistry. A urea derivative in solid state associates via intermolecular bifurcated NH...O=C hydrogen bonds (Figure 3) and these paired hydrogen bonds afford robust and highly directional intermolecular joints. However, in gaseous state, intramolecular hydrogen bonding can be neglected and two forms of UHP are possible due to hydrogen bonding of urea with s-trans (UHPT) and s-cis (UHPC) conformers of H₂O₂. Both conformers have no center of symmetry and are expected to produce second harmonics. The latter configuration happens to be cyclic. Their optimized geometry is shown in Figure 4 (a and b), respectively. We optimized geometry of UHP by Hyper Chem Software using semi-empirical method,
3 Results and Discussion

IR spectra of UHP and urea reveal that both spectra overlap with each other in band position as well as in intensities. Absence of any additional band in the
spectra suggests very weak association in the two molecules. Similar conclusion can be drawn from the UV spectra reproduced in Figure 1. Hydrogen bonding seems to be too weak to be detected by IR. The analysis of \( \text{H}_2\text{O}_2 \) in UHP (1:1) confirms the presence of \( \text{H}_2\text{O}_2 \) in the adduct.

Atomic charges of various atoms in urea, UHPT and UHPC are shown in Table 2. In these structures nitrogen atom of the urea molecule acquires a positive charge. Further, self-assembly of the adduct is possible due to weak intermolecular forces. The presence of positive charge on N weakens the stability of the crystal due to repulsive forces permitting easy dissociation of the hydrogen peroxide from the adduct and its availability as \( \text{H}_2\text{O}_2 \) in chemical reactions.

Hydrogen bonding occurs between a proton donor group \( \text{D-H} \) and a proton acceptor group \( \text{A} \). \( \text{D} \) can be an electronegative atom O, N, S, P, Se and X (F, Cl, Br, I) or C and \( \text{A} \) is a lone electron pair of an electronegative atom, or a \( \pi \)-electron orbital of a double and triple bond.

\[ \text{D}^+ \text{---H}^+ \cdots \cdots \text{A}^- \]

Generally, a hydrogen bond can be characterized as a proton shared by two lone electron pairs. When one hydrogen atom interacts with two acceptor atoms, it is called bifurcated hydrogen bonding. Increasing the dipole moment of the donor and the electron pair on the acceptor result in an increasing strength of the hydrogen bonding.
proportional to the square of the permanent dipole moment. The SHG measurement results as shown in Figure 2 which shows that the intensity output of the SH signal is stronger than that of urea. Between UHPT and UHPC, UHPC is expected to give stronger signal compared to UHPT because of its high dipole moment. This confirms the dominance of UHPC structure of urea-H₂O₂ adducts over its UHPT configuration in solid state.

Acknowledgement
The authors are thankful to Prof P K Sen, for encouragement and fruitful discussions. They gratefully acknowledge the contribution of S Saxena in the preparation of the sample.

References
7 Laha S C & Kumar R, J Catalysis, 204 (2001) 64.