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Ultrafast optical nonlinearity, electronic absorption, vibrational spectra and solvent effect studies of ninhydrin

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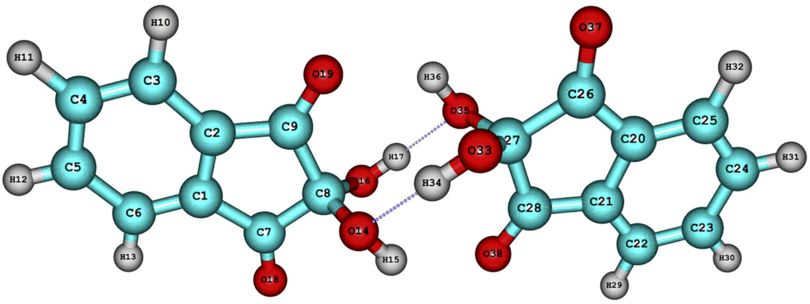
HIGHLIGHTS

- Ninhydrin single crystal was grown by slow evaporation solution growth method.
- FT-Raman and FT-IR spectra of the nonlinear optical material ninhydrin have been recorded and analyzed.
- The hydrogen bonding and the possible interactions were also calculated by using NBO analysis.
- Nonlinear optical absorption of the sample has been studied by open-aperture z-scan technique.

GRAPHICAL ABSTRACT



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ABSTRACT

FT-IR, FT-Raman and UV–Vis spectra of the nonlinear optical molecule ninhydrin have been recorded and analyzed. The equilibrium geometry, bonding features, and harmonic vibrational wavenumbers have been investigated with the help of B3LYP density functional theory method. A detailed interpretation of the vibrational spectra is carried out with the aid of normal coordinate analysis following the scaled quantum mechanical force field methodology. Solvent effects have been calculated using time-dependent density functional theory in combination with the polarized continuum model. Natural bond orbital analysis confirms the occurrence of strong intermolecular hydrogen bonding in the molecule. Employing the open-aperture z-scan technique, nonlinear optical absorption of the sample has been studied in the ultrafast and short-pulse excitation regimes, using 100 fs and 5 ns laser pulses respectively. It is found that ninhydrin exhibits optical limiting for both excitations, indicating potential photonic applications.

Introduction

In recent years, organic nonlinear optical (NLO) crystals have become more attractive and versatile than their inorganic counterparts due to their large electro-optic coefficients with low frequency dispersion and high nonlinearity [1]. There is a considerable interest in the synthesis of new conjugated organic materials with large optical nonlinearities for photonic and electro-optic applications including telecommunications, optical computing, optical storage and optical information processing [2–7]. When acceptor and donor moieties are placed at the terminal position of the conjugated backbone, both linear and nonlinear optical properties are increased significantly due to the correlated and highly delocalized π-electron states. The molecular polarizability and hyperpolarizability coefficients are found to increase superlinearly with increase in conjugation length between the donor and the acceptor. The strength of donor and acceptor groups as well

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as the order of their stacking along the backbone also play important roles in determining the magnitude of the NLO efficiency [8]. A vast majority of organic NLO crystals absorb light in the blue region, and for some of them the cut-off wavelength exceeds 450 nm. This results in reduced conversion efficiency of second harmonic generation due to self-absorption, when using a semiconductor laser in the 800 nm region for excitation [9,10]. Hence, recently there has been a vigorous search for new organic NLO materials with blue light transmittance [11,12]. Ninhydrin is one such organic material in which two hydroxyl groups are attached to the same carbon atom. It has a high melting point. Ninhydrin is an important analytical tool in various fields including soil biology [13], chemistry [14], agriculture [15], medicine [16], forensic [17], food sciences [18,19], and pharmacology [20]. It is used as a potential material for micro molar determination of human serum albumin based on chemiluminescence [21], and in antimicrobial activity [22]. The crystal structure [23], growth, characterization and second order NLO properties of the title compound have already been reported [24].

In the present study we report for the first time the experimental investigations of the absorptive nonlinearity of ninhydrin in the ultrafast and short-pulse excitation regimes. Optical nonlinearity is studied by the open aperture z-scan technique employing 100 fs and 5 ns laser pulses respectively. Detailed vibrational spectral investigations of ninhydrin dimer molecule (Fig. 1) using scaled quantum mechanical (SQM) force field technique based on density functional theory (DFT) calculations is also reported. Natural bond orbital analysis (NBO) is used to explain electron charge transfer through inter molecular hydrogen bonding. Conformational changes occurring from solid state to solution are evidenced by the comparison of X-ray diffraction results and DFT quantum chemical calculations, as well as by the vibrational spectra obtained in both physical states.

Experimental

The sample of ninhydrin in solid form at room temperature was purchased from Sigma Aldrich Chemical Company, USA and was used as such without further purification. Temperature reduction technique was employed to grow single crystal of ninhydrin. Recrystallized salt of ninhydrin was used to prepare saturated solution at 35 °C and the solution was kept in a constant temperature bath having an accuracy of ±0.01 °C. One of the good quality single crystals got from slow evaporation at room temperature was used as the seed crystal. The growth process was initiated at a temperature of 35 °C and the temperature was reduced at a rate of 0.2 °C per day. After a growth period of 10 days, well-developed single crystal of ninhydrin of dimension 11 mm × 10 mm × 7 mm was harvested.

IR, Raman and UV–Vis measurements

FT-IR spectra of the title compound were recorded on Thermo Nicolet Magna 760 FT-IR spectrometer by DRIFTS (*Diffuse Reflectance Infrared Fourier Transform Spectroscopy*) technique. The sample was mixed with KBr and scanned in 400–4000 cm^{-1} wavenumber range (Happ-Genzel apodization, 2 cm^{-1} resolution) using Pike Technology Easi Diff accessory. The FT-Raman spectra of polycrystalline samples and water solution were collected on the same spectrometer equipped with Thermo Nicolet Nexus FT-Raman module. The measurements were carried out in the range of 100–3700 cm^{-1} (Happ-Genzel apodization, 2 cm^{-1} resolution, 1064 nm Nd:YVO_4 laser excitation, 450 mW power at the sample). Both IR and Raman spectra were processed using the OMNIC software [25]. The UV–Vis absorption spectrum of the sample was recorded in water solution using a Shimadzu UV–Vis spectrophotometer in the spectral region of 200–400 nm.

Nonlinear optical studies – z-scan measurement

In z-scan measurements, water solutions of the sample taken in 1 mm cuvettes were irradiated by plane polarized laser pulses. The sample was mounted on a precision translation stage with a step resolution of 100 μm. In two different experiments, ultrafast laser pulses of 100 fs width at 800 nm and short laser pulses of 5 ns width at 532 nm were employed for the measurements. Ultrafast (fs) pulses were obtained from a chirped pulse amplifier laser (TSA-10, Spectra Physics) seeded by a mode-locked Ti:Sapphire laser (Tsunami, Spectra Physics), while the short (ns) pulses were obtained from the second harmonic output of a Q-switched Nd:YAG laser (MiniLite, Continuum). For fs excitation the laser pulse energy used was 26 μJ while for ns excitation it was 73 μJ. The focusing lens is chosen such that the Rayleigh range (z_0) larger than 1.5 mm, so that samples taken in 1 mm cuvettes will satisfy the thin sample approximation [26]. The lasers were essentially run in the single-shot mode using appropriate triggering, with an approximate interval of 3–4 s between successive pulses. This low repetition rate prevents sample damage and cumulative thermal effects in the medium.

Computational details

All *ab initio* molecular orbital calculations were carried out using the Gaussian'09 suite of programs [27]. To determine conformational features of the molecule, the selected degree of torsional freedom, T (C_9—C_8—O_{16}—H_{17}), was varied from −40° to 320° in every 10° and the molecular energy profile was obtained with the B3LYP/6-311G(d,p) method. Initially, the structure of the ninhydrin molecule was optimized, and then the vibrational wavenumbers were calculated with the B3LYP method using 6-

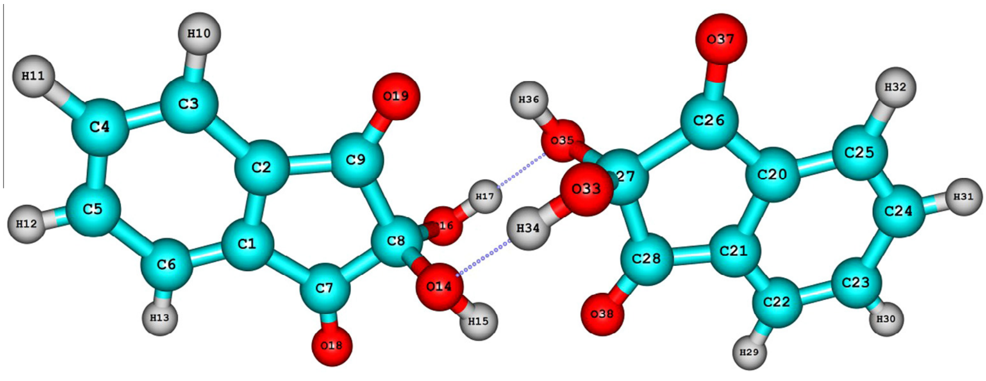

Fig. 1. Optimized structure of ninhydrin dimer.