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Optical nonlinearity and charge transfer analysis of 4-[(E)-2-(2,4,6-Trinitrophenyl) ethylidene] benzonitrile adsorbed on silver nanoparticles: Computational and experimental investigations

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ABSTRACT

The search for a potential nonlinear optical (NLO) material has led to the investigation of an organic compound 4-[(E)-2-(2,4,6-Trinitrophenyl)ethylidene]benzonitrile (TEB), which has a possibility of enhancing the NLO properties by the charge transfer mechanism if metal atoms are adsorbed on it. The experimental characterization of TEB is done using Fourier Transform Infrared (FT-IR), FT-Raman, Ultraviolet–visible (UV–Visible), Photoluminescence (PL), Thermogravimetric/Differential Thermal Analysis (TG/DTA) and Z-scan techniques. The third order NLO properties evaluated using Z-scan technique proves that the material can be used as a good optical limiter. TEB is attached with silver atoms and the theoretical studies including geometry optimization, NBO analysis and hyperpolarizability calculations are carried out. The TEB molecule with silver atoms adsorbed is found to have increased hyperpolarizability values. The charge transfer from the metal atom to the nitrile group of the molecule is evident from the Surface Enhanced Raman Scattering (SERS) spectra using the silver nanoparticles.

1. Introduction

The synthesis of materials having good nonlinear optical (NLO) response attracts greater attention due to their potential photonic applications [1,2]. The third order NLO materials are used in diverse fields for optical power limiting, bio-imaging, nanophotonics, ultrafast optical switches and other optoelectronic devices, which makes the design and synthesis of such materials more important [3,4]. Organic NLO materials, when compared to inorganic materials, are found to have properties such as higher nonlinear optical coefficients, ease of fabrication, high laser damage threshold and relatively low cost [5]. The quantum computational techniques give insight into the behaviour of the molecules in terms of the bonds for interaction and can be used for designing and developing materials of desired properties with low cost and less effort. These methods use theories varying from ab initio to density functional theories (DFT) with different basis sets to match with the systems under consideration [6–8]. The present work is concentrated on the characterization of an organic NLO material 4-[(E)-2-(2,4,6-Trinitrophenyl)ethylidene] benzonitrile (TEB) which was originally synthesized [9] for using it as an organometallic ligand for iron-phosphine complexes that can increase the NLO activity. A ligand rich in π electrons can extend π-conjugation and increase charge transfer leading to greater values of β hyperpolarizability [10]. The previous studies reveal that the co-ordination through CN functional group of nitrile ligand permits π backdonation from metal d orbitals with π* orbitals of CN group, leading to an extension of π electron system between the metal and the ligand [11–13]. These facts are being checked in the present study using the theoretical and experimental means.

Since the synthesis and X-ray diffraction studies of the ligand molecule are already reported [9], a detailed study regarding the third order NLO properties along with the vibrational spectroscopic characteristics are carried out in the present study. The effect of adsorption of metal atoms to the TEB molecule is studied theoretically and also experimentally by adsorbing silver atoms to the molecule.

2. Experimental/theoretical methods

2.1. Synthesis and crystal growth

The compound (TEB) is synthesized as per the details given by Borger et al. [9].

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2.2. FT-IR, FT-Raman, UV–Vis, photoluminescence, thermal and Z-scan studies

The FT-IR spectrum of TEB was recorded using a Perkin Elmer spectrophotometer with 1 cm^{-1} spectral resolution in the wavenumber range from 4000 to 400 cm^{-1} with samples in the KBr technique. The Raman spectrum of the solid compound is recorded using 1064 nm laser between 4000 and 10 cm^{-1} with a Bruker RFS 27 spectrometer with 100 mW laser power and a resolution of 2 cm^{-1}. The UV–Vis absorption spectrum of the sample is recorded in chloroform solution using a JASCO UV–Vis spectrophotometer in the spectral region of 190–1100 nm. Thermogravimetric and differential thermal analyses (TG/DTA) are carried out with the help of the Perkin Elmer instrument in nitrogen atmosphere for a 4.5 mg sample and heating in the range of 50–995 °C at 10 °C/min is supplied. Photoluminescence studies are carried out at room temperature using the Horiba Scientific Inc. spectrophotometer at an excitation wavelength of 350 nm with Xe lamp as the excitation source. The sample in powder form is mixed in chloroform and mounted inside the chamber for the measurements. The open aperture Z-scan method is employed using laser wavelength of 532 nm, pulse width 5000 ps and an average energy of 140 μJ, to study the nonlinear absorption properties of the sample. The sample position is changed from the positive to the negative z direction with respect to the focus of the beam, and the transmittance value is noted for each position.

2.3. For SERS spectrum

The colloidal silver nanoparticles are prepared by the Lee-Meisel method [14], where 18 mg of silver nitrate is mixed in 100 ml of distilled water and boiled while stirring. To the boiled solution, 2 ml of 1% sodium citrate solution is added dropwise and the boiling is continued for one hour. After that, the solution is cooled and used for mixing with TEB in dimethyl sulfoxide (DMSO) solution. The TEB solution of 10^{-5} M and 10^{-6} M, and the silver sol are mixed in two ratios 1:2 and 1:4. They are drop-coated on a glass slide and made to dry for the Raman spectral measurement using LabRAM HR (UV) system with 532 nm wavelength in the range 4000–250 cm^{-1}.

The silver nanoparticles are characterized using the Brookhaven Instruments Corp. ZetaPALS instrument for the measurement of particle size and zeta potential. Zeiss Ultra 55 Scanning Electron Microscope (SEM) is used to find the surface morphology of the nanoparticles.

2.4. DFT, NCA, NBO

In the present work DFT [7] calculations at the B3LYP/cc-pVTZ level of theory are done to compute structural parameters and spectral details using the Gaussian'09 program package [15]. For the hyperpolarizability calculation, the 6-311++G(d,p) basis set is used with the B3LYP exchange correlation functional. The adsorption characteristics of TEB on silver atom and cluster are theoretically investigated with the LANL2DZ basis set.

By the Normal Co-ordinate Analysis (NCA), the percental contributions of internal coordinates to the normal coordinates is obtained using a normalized potential energy distribution (PED). The MOLVIB program [16] is used for the IR and Raman vibrational assignments of the molecule. The Natural Bond Orbital (NBO) analysis is carried out using the NBO 3.1 version [17] as implemented in the Gaussian'09 program and the second order stabilization energies [18] $\Delta E_{ij}^{(2)}$ that depict the strength of the interactions are evaluated.

2.5. Quantum theory of atoms in molecules (QTAIM)

The principles of quantum mechanics can be applied to predict the chemical behavior of the molecules including the strength of the hydrogen bonds using Bader's Theory of Atoms in Molecules [19–21]. For rank three critical points, four signatures are possible and the stable or non-degenerate critical points are represented as (3,−3), (3,−1), (3,+1) and (3,+3), depending on the curvature at the point. The analyses are done using AIMAll program suite [22] which is developed by Todd A. Keith.

2.6. Hirshfeld surfaces

Hirshfeld surfaces [23] are a measure of the space occupied by a molecule in a crystal [24]. It is defined as an isosurface with $w_i(r) = 0.5$. The parameters that we get for the Hirshfeld surfaces from the CrystalExplorer 3.1 [25] software are the normalized contact distance (d_{norm}), the shape index (S) and the curvedness (C), which are defined as [25,26]

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}} \quad (1)$$

$$S = \left(\frac{2}{\pi}\right) \arctan\left[\frac{(\kappa_1 + \kappa_2)}{(\kappa_1 - \kappa_2)}\right] \quad (2)$$

$$C = \left(\frac{2}{\pi}\right) \ln\left[\frac{(\kappa_1^2 + \kappa_2^2)}{2}\right]^{1/2} \quad (3)$$

where d_i is the distance from the surface to the nearest atom interior to the surface, d_e is the distance from the surface to the nearest atom exterior to the surface, r_i^{vdW} is the van der Waals (vdW) radius of the appropriate atom internal to the surface, r_e^{vdW} is the van der Waals (vdW) radius of the appropriate atom external to the surface, κ_1&κ_2 are the principal curvatures of the surfaces.

3. Results and discussion

3.1. Molecular structure analysis

The optimized structure of the TEB molecule is shown in Fig. 1(a). In Table 1, the bond lengths and the bond angles obtained from geometric optimization are compared with the experimental data obtained from the previous work [9] of the compound and also with the theoretical output calculated for Ag- and Ag_3-adsorbed molecule. Since the silver atoms are attached to the TEB molecule through the CN group, variations are expected to the bond lengths and bond angles between the nearest neighbor atoms to the CN group. Due to the interaction between the N_{10} atom and the silver atoms, C_9—N_{10} bond length is increased, while C_3—C_9 bond length is decreased slightly. Almost equal increase of about 0.02^0 in bond lengths is observed for C_2—C_3, C_3—C_4, C_5—C_6 and C_6—C_1 bonds in the ring Ph1, while the CH bonds remain almost the same. The other double bonds in the molecule also got lengthened, while the single bonds remain the same in length. We can see that the silver triangular cluster plane is oriented perpendicular to the plane of the ring Ph1. The bond angle of Ag_{34}-N_{10}-C_9 to be 176.7^0 reveals that the Ag_{34} atom is almost in line with the C_9—N_{10} bond in the case of cluster attachment to the molecule. The length between the silver atoms in the cluster triangle is 2.74 Å which gives an equilateral triangle with bond angles $\sim 60^0$ between them.