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Ab initio investigation on the nonlinear optical properties of Cd_nTe_n (n = 1–10) clusters

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ABSTRACT

We report herein the numerical analyses on the nonlinear optical properties of Cd_nTe_n clusters up to decamer unit. A detailed study on the static and frequency dependent response properties of these Cd_nTe_n clusters has been performed employing density functional approximations of different levels. Our investigation reveals that both static and frequency dependent second order hyperpolarizability tensors of these clusters are significantly high (10^3–10^7 a.u.) in magnitude. The first order counterpart is also high for certain cluster size. We observed that the response properties are highly structure-dependent and is particularly noticeable in higher clusters.

1. Introduction

Cadmium telluride clusters (Cd_nTe_n) and quantum dots are recently attracting much attention due to their unique response properties and potential application in some of the modern technological applications like photonic devices and high speed electro-optic device fabrication [1–6]. The Cd_nTe_n clusters and quantum dots are the examples of II–VI semiconductors and are widely used in the design of solar cell, optical-switching and in the field of opto-electronics. It has been highlighted in numerous previous investigations that the response properties of such clusters are characterized by their large nonlinear optical (NLO) coefficients [6–13]. Moreover, some of the contemporary literatures [12–14] reported that NLO parameters of these nanoclusters are higher than that of sulphur and selenium analog. Therefore, these results provide strong impetus for the theoretical explorations of such nanoclusters.

In general response properties under investigation includes elements of linear polarizability tensor, first order hyperpolarizability tensor and second order hyperpolarizability tensor, respectively. The first order hyperpolarizability tensor is described in terms of three frequency dependent components namely second harmonic generation (SHG) [$\beta(-2\omega;\omega,\omega)$], electro-optical Pockels effect (EOPE) [$\beta(-\omega;\omega,0)$], optical rectification (OR) [$\beta(0;\omega,-\omega)$] and the static first order hyperpolarizability [$\beta(0;0,0)$]. In the same way, in addition to the static analogue [$\gamma(0;0,0,0)$] the frequency dependent components of second order hyperpolarizability tensor are third harmonic generation (THG) [$\gamma(-3\omega;\omega,\omega,\omega)$], electro-optical Kerr effect (EOKE) [$\gamma(-\omega;\omega,0,0)$], dc-induced second harmonic generation (dc-SHG) [$\gamma(-2\omega;\omega,\omega,0)$] and intensity dependent refractive index (IDRI) [$\gamma(-\omega;\omega,-\omega,\omega)$] or degenerate four-wave mixing (DFWM). Amongst different response properties, SHG is of great importance [12,13] because of its ability to provide important information on the electronic structure of solids. Theoretical study of SHG in some of the semiconducting materials has been highlighted in recent communications [13]. THG is another important frequency dependent NLO process and can be estimated through sum-over-states (SOS) approach.

Earlier studies have mainly highlighted on the experimental realization of the higher order optical processes in Cd_nTe_n clusters and quantum dots. Third-order nonlinear susceptibilities of colloidal CdTe nanocrystals were measured by Ma et al. [6]. They employed polarization-resolved degenerate four-wave mixing (DFWM) spectroscopy and conjectured that nonlinearity is contributed by anharmonic oscillations of bound electrons of CdTe nanocrystals and surface trap effect. In a separate experimental study, Menezes and co-workers described the method of obtaining CdTe core shell nanocrystals in quantum confinement regime and investigated the structural and optical properties of such nanocrystals [15]. Size dependent complex dielectric spectra of CdTe nanoparticles were observed by Chandra et al. [16]. They reported that average number of electrons participating in the optical transition from valence to conduction band decreases with the reduction in particle size [16]. Chin and his group synthesized highly luminescent CdTe nanocrystals [17]. They also fabricated light emitting diodes

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from CdTe nanocrystals and measured relevant luminescent efficiency. Despite extensive experimental investigations have been carried out on the response properties of Cd_nTe_n clusters, quantum dots and nanocrystals, detailed theoretical analyses on all the hyperpolarizability components of such cluster systems is still very limited. Excepting some of the structural and electronic property study [18–20], there is only one theoretical study based on the optical properties of Cd_nTe_n clusters [14]. In Ref. [14], the authors clearly illustrated that Cd_nTe_n clusters could be used for future nonlinear optical applications. However, their work [14] only describes the importance of static optical coefficients (linear and second order NLO). It is well known that overall optical property of a material is determined both by static as well as frequency dependent response properties; hence a detailed analysis, comprising of both static and frequency dependent NLO coefficients is yet to be performed.

In the present work, we investigate first and second order static as well as frequency dependent hyperpolarizability components of Cd_nTe_n clusters. We use density functional theory (DFT) for the estimation of response properties. Within DFT, four different approximate functionals including coulomb attenuated exchange correlation functional [21] has been used.

2. Computational details

Geometries of the clusters under investigation have been optimized through GAUSSIAN 03 [22] suite of programs using B3LYP

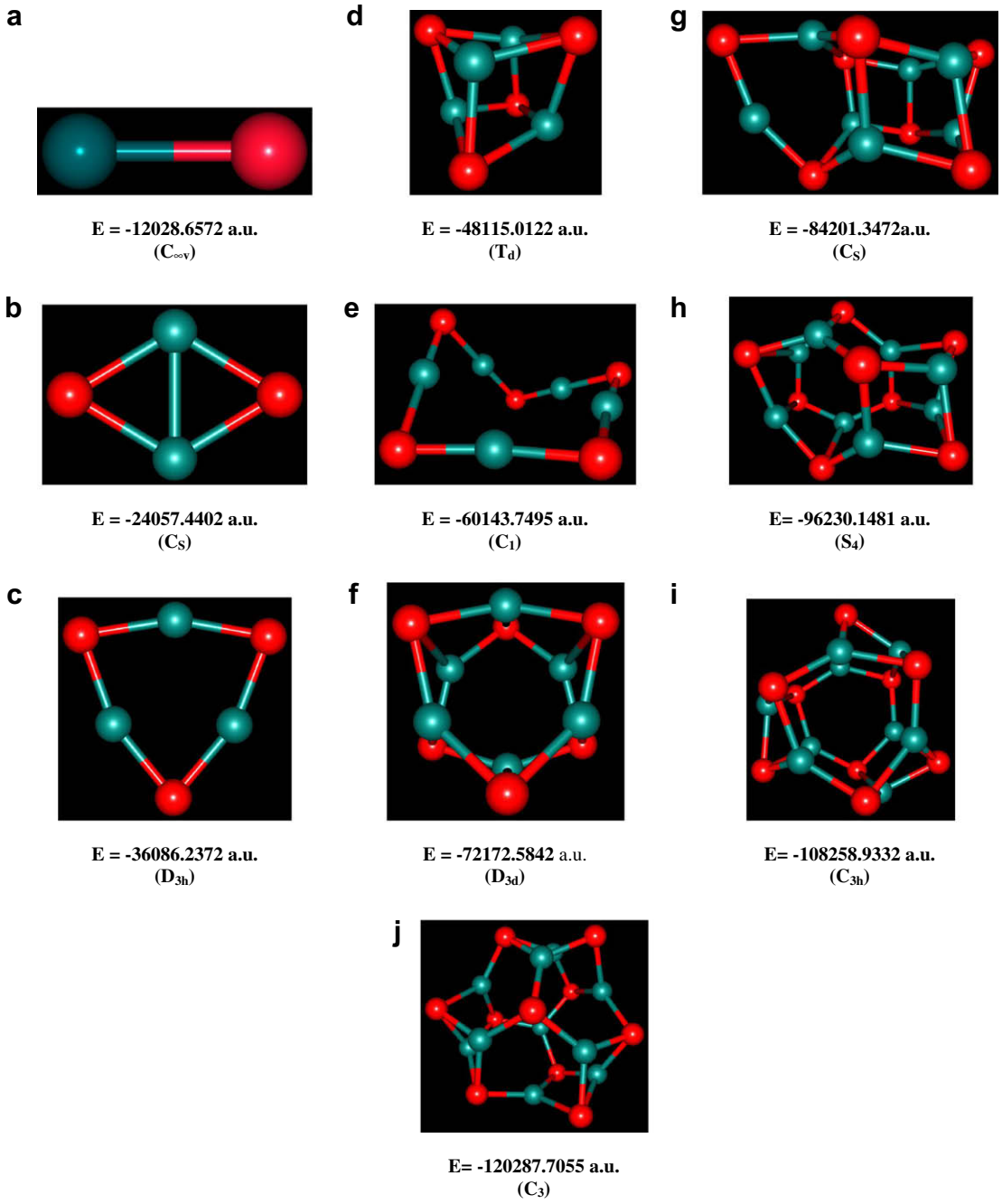

Fig. 1. Optimized geometries of the most stable Cd_nTe_n (n = 1–10) clusters; the footnote of each structure contains the ground state energies in a.u. and point group symmetry.