

Linear and nonlinear optical polarizabilities in supramolecular aggregates: Effects of hydrogen bonding and dipolar interactions

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Abstract

We consider linear hydrogen halide chains, $(\text{HX})_n$, $\text{X}=\text{F}$, Cl and Br , with varying chain length, n , to compare the role of hydrogen bonding strengths in controlling the optical response functions of linear aggregates. We find that while for weakly H-bonded linear chains, the 1st hyperpolarizabilities (β) increase with the increase in the number of monomers in the aggregates, for strong H-bonding species like HF chains, the β shows a remarkable contrast with a maximum at the small chain limit with reduction thereafter with increase in chain length. This behavior is compared with that of a pure dipolar aggregate like $(\text{CO})_n$. The weak H-bonded species follow the trends similar to that of such dipolar aggregates. Additionally, we have considered the H-bonded linear chains as bridges between two terminal components for charge-transfer molecular one-dimensional devices, $\text{NH}_2-(\text{HF})_n-\text{NO}_2$. In contrast to the traditional π -conjugated species, $\text{NH}_2-(\text{CH}=\text{CH})_n-\text{NO}_2$, we find that such linear H-bonded chains have very poor charge-transfer abilities. We report that strong H-bonding by itself is a negative parameter for nonlinear optical response functions at the supramolecular level, although, the directional properties of the H-bonds can be utilized for material integration. We show that it is the long-range supramolecular forces together with H-bonding at the intermediate energy scale at certain special geometries, which brings in a favorable situation for better optoelectronic applications.

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1. Introduction

Designing materials exhibiting large off-resonance nonlinear optical responses is an area of intense research for the last few decades. There has been a lot of interest at the molecular scale where the electronic and structural aspects have been investigated for the optimization of their optical properties [1]. The π -conjugated organic molecules [2] are one of the most promising materials at the molecular scale because of the delocalized π -electrons over a large part of the molecule that allows easy polarization due to shining of light [3].

However, a clear understanding is unavailable for the multi-molecular aggregates at the supramolecular scale, since the interactions governing the aggregate stability have many different length scales. As a result, with the knowledge of the optical properties of the molecules, *a priori* prediction at the supramolecular level like crystals, thin-films or poled polymers

has not been possible. This is primarily due to the lack of information about the interactions between the individual molecules. In most assemblies, weak intermolecular forces like the H-bonding, dipole–dipole interactions, π -stacking (for aromatic molecules), control the overall structure and stability of these macromolecules [4,5]. These weak interactions are extremely important in defining the symmetry elements present in these materials. While pure dipole–dipole interactions lead to a centrosymmetric arrangement for polar molecules, H-bonding can orient molecules in a linear noncentrosymmetric fashion thereby making them suitable for good NLO device integration. Thus, the subtle balance between these forces govern the optoelectronic properties of macromolecules [6]. Fine tuning these interactions however requires extensive research [7].

While, dipole–dipole interactions has effects on NLO properties of aggregates through excitonic splitting [8], the role of H-bonding governing the NLO properties have not been properly investigated. The strength of the hydrogen bonding is generally understood on the basis of its partition into various contributions like the electrostatic energy, exchange repulsion energy, polarization energy and charge-transfer energy [9].

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Out of these, the charge-transfer (CT) effect is very important in controlling the NLO responses as it increases the transition dipole moment from the ground state to the optically active states. The CT salts are known to have large off-resonance NLO properties [10]. Although, the charge-transfer efficiency in hydrogen bonding seems to be quite small, it should depend on many factors including the strength of H-bond. Whether other electrostatic forces play any role in governing NLO properties, is yet to be investigated.

Though there have been a few efforts to model the NLO properties of molecular aggregates like in dimers, trimers etc. [11,12], the role of the H-bonding on NLO properties has not been investigated properly to date [13]. H-bonding has mostly been considered in literature as a mere stitch that brings the molecules together. H-bonding being an electrostatic interaction must lead to electronic effects as well. But the important question in the context of NLO is whether the H-bonding interactions are capable of influencing the excited electronic states as well.

In this article, we critically examine the effect of H-bonding on second order polarizabilities (β) for a series of linear molecular assemblies. We have chosen the model system HX ($X = \text{F}, \text{Cl}, \text{Br}$) for our analysis. HX provides a nice variation of the strength of bonding between the molecules, ($\text{HF} > \text{HCl} > \text{HBr}$); while HF chain has the strongest H-bonding, interactions in HBr chain is seemingly dipole–dipole type. Additionally, we have also considered pure dipolar aggregates such as linear CO chain. The HF chain shows a large deviation from the dipolar aggregates and provides a clear signature for the H-bonding effects. Weakly H-bonded systems like HCl and HBr chains, in contrast have similarities with the pure dipolar chain. β for the conventional D- π -A systems have been compared with the D-(HF) $_n$ -A system. D-(HF) $_n$ -A is a poor molecular electronics material and is very little polarizable. These linear hydrogen-bonded chains serve as a model for molecular crystal systems like that in urea (U), paranitroaniline (PNA) and 2-methyl-4-nitroaniline (MNA).

2. Interactions in aggregates

Many NLO active materials like urea, PNA and MNA have a linear arrangement of the chromophores connected by H-bonds. In the crystal, however, they have an anti-parallel stacked environment for these linear H-bonded chains. Therefore, to model the H-bonding effect in a single linear chain, we next consider a linear chain for HX. The bond lengths for HF, HCl and HBr are calculated as 0.950, 1.28093 and 1.42354 Å at B3LYP/aug-cc-pVQZ level. The distance between each HX monomer is kept constant for all chain lengths ($d = 1.87$ Å for HF, $d = 2.665$ Å for HCl and $d = 3.178$ Å for HBr). Fig. 1 shows the linear chains considered with the H-X...H distances. This is the standard average distance that we found from our calculation of the geometry optimized structures of the linear chains.

For an analysis of the energetic associated with these structures, we calculate the binding energies for the clusters using the definition; $\Delta E_{0,n} = nE_0[(\text{HX})] - E_0[(\text{HX})_n]$. All the

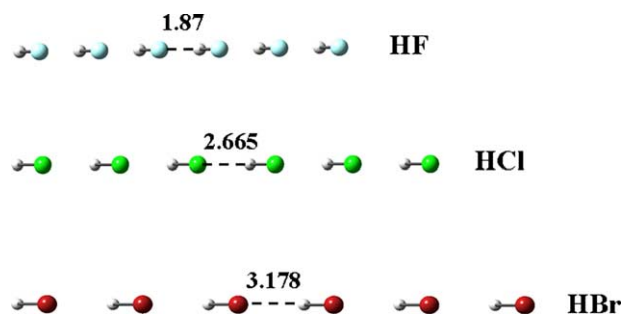


Fig. 1. Structures for the linear chains of HF, HCl and HBr. The distance (in Å) between each monomer is kept constant as shown in the figure.

energies are corrected for zero-point vibrational energy (ZPVE) corrections and the basis set superposition errors (BSSE). BSSE was calculated using the counterpoise correction (CP) scheme [14,15]. We report the results with the CP corrections. Fig. 2 shows the binding energies for the six structures in HF, HCl and HBr at the MP2/6-311++G(d, p) level. The binding energies for the HF chain increases with increase in the cluster size. The binding energy remains almost constant for the HCl chain and for the HBr chain, the binding energy decreases with increase in the chain length. Thus, HF clusters are bound strongest while the HBr clusters are weakly bound.

From Fig. 2, it is evident that while the linear H-bonded chains are stable for HF, for HCl the stabilizations are very small. On the contrary in HBr, the linear chains are unstable and are not sustained by the weak H-bonds. It will thus be interesting to examine the linear and nonlinear optical properties for these three limiting cases of stability in these chains.

For the calculation of the linear (α) and nonlinear (β and γ) optical coefficients, we have followed the finite-field formalism. The finite field approach expands the energy of the system in terms of the static field, F and has been extensively used in literature for accurate calculation of linear and nonlinear

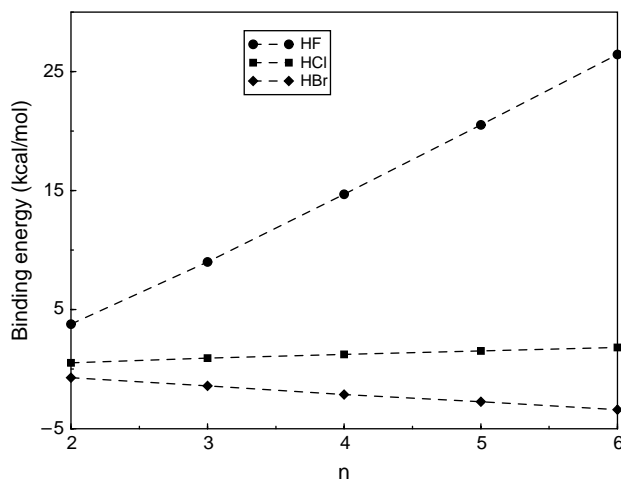


Fig. 2. Variation of binding energy, ΔE for different sizes of clusters for HF, HCl and HBr in linear chains. The reported energies include corrections for BSSE and ZPVE.

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