The effect of intermolecular interactions on the electric dipole polarizabilities of nucleic acid base complexes

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ABSTRACT

In this Letter, we report on the interaction-induced electric dipole polarizabilities of 70 Watson–Crick B-DNA pairs (27 adenine–thymine and 43 guanine-cytosine complexes) and 38 structures of cytosine dimer in stacked alignment. In the case of hydrogen-bonded Watson–Crick base pairs the electrostatic as well as the induction and exchange-induction interactions, increase the average polarizability of the studied complexes, whereas the exchange-repulsion effects have the opposite effect and consistently diminish this property. On the other hand, in the case of the studied cytosine dimers in stacked alignment the dominant electrostatic contribution has generally much larger magnitude and the opposite sign, resulting in a significant reduction of the average polarizability of these complexes. As a part of this model study, we also assess the performance of recently developed LPol-ds reduced-size polarized basis set. Although being much smaller than the aug-cc-pVTZ set, the LPol-ds performs equally well as far as the excess polarizabilities of the studied hydrogen-bonded complexes are concerned.

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1. Introduction

Much attention has been devoted to analyzing various properties of nucleic acid base complexes in the past and there are still many vital issues to be addressed that facilitate an enormous interest in this subject (cf. [1–4] and references cited therein). The main rationale behind studying structure and stability of DNA (and its model fragments) is mainly due to its biological functions (see, for example, [5–7]). However, recently DNA became also a very interesting material for nanoelectronics and molecular nanotechnology. In fact, this aspect has been extensively studied because of various DNA features including high flexibility, self-assembly, self-recognition and self-replication [8]. Nucleic acids can also be used as a template to align other molecules (due to their ability to form stable aggregates with nanoparticles and proteins [9]) and thus they might serve as parts of assemblies used as molecular switches, memory devices or transistors [10–13]. Successful attempts have been reported to apply DNA as a component in materials of nonlinear optical activity [14–16] and also for holographic inscription [17]. Moreover, DNA potential to serve as a chiral template for second-order nonlinear optical materials has been

recently demonstrated by Wanapun et al. [18]. Also the linear optical properties of organic dyes, such as photoabsorption and photoemission, are affected by the presence of DNA [19,16].

In general, the (non)linear optical response of such hybrid systems is a result of quite complex interplay of various factors. They include the excess (hyper)polarizabilities resulting from interactions among host/guest and guest/guest molecules. This is particularly important in the case of photoactive dyes intercalated into DNA. Our ultimate goal is to describe linear and nonlinear optical (L&NLO) properties of various assemblies of photoactive systems incorporated into DNA. In an attempt to make a step towards understanding of these properties in DNA-based hybrid systems, in this Letter we focus on investigations of the origins of interaction-induced polarizabilities in nucleic acid base pairs.

In particular, we analyze 70 Watson–Crick B-DNA pairs (27 adenine–thymine and 43 guanine-cytosine complexes) and 38 structures representing the cytosine dimer in stacked alignments. All structures have been extracted from the available crystallographic data. The complexes in question, in the very same conformations, have been recently studied by some of us with an eye towards the origins of intermolecular interactions [20,21]. Although the static electric properties of isolated nucleic acid bases have been quite extensively studied [22,23], to the best of our knowledge there is only one study devoted to excess electric properties of nucleic acid base pairs published by Seal et al. [24]. In that paper the authors

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reported only the rough estimates of the first hyperpolarizability obtained within a two-state approximation. In our study, we report on comprehensive *ab initio* results of interaction-induced properties and their partitioning into physically meaningful components. In doing so, we follow here an approach proposed originally by Heijmen and Moszyński [25] which has been applied only to relatively small atomic and molecular dimers [25–27] and trimers [28].

2. Computational details

The total interaction energy of a dimer, calculated by a supermolecular approach using the second-order Møller–Plesset perturbation theory (MP2), is partitioned into the Hartree–Fock (HF) and the electron correlation interaction energy components:

$$\Delta E^{MP2} = \Delta E^{HF} + \Delta E_{corr}^{MP2}. \tag{1}$$

The HF term can be partitioned into the Heitler–London (HL) and the delocalization (ΔE_{del}^{HF}) energy components. The former involves the electrostatic interactions of unperturbed monomer charge densities, $\epsilon_{el}^{(10)}$, as well as the associated exchange repulsion ΔE_{ex}^{HL} and can be calculated after Löwdin [29] as a difference between the expectation value of the Hamiltonian, defined as a sum of the free-monomer Hamiltonians $\mathcal{H}_i$ and $\mathcal{H}_j$ and the intermolecular perturbation $\mathcal{V}_{ij}$, for the wavefunction given as an antysymmetrized Hartree product of monomers' wavefunctions and the sum of monomer energies:

$$\Delta E^{HL} = N_{ij}^{HL} \langle \mathcal{A}\Psi_i\Psi_j \mid \mathcal{H}_i + \mathcal{H}_j + \mathcal{V}_{ij} \mid \mathcal{A}\Psi_i\Psi_j \rangle - \left(E_i^{HF} + E_j^{HF} \right) \tag{2}$$

where N_{ij}^{HL} is the normalization constant. The delocalization term is estimated as a difference between the HF and the HL interaction energies and encompasses the induction and the associated exchange effects due to the Pauli exclusion principle:

$$\Delta E^{HF} = \Delta E^{HL} + \Delta E_{del}^{HF} = \epsilon_{el}^{(10)} + \Delta E_{ex}^{HL} + \Delta E_{del}^{HF}. \tag{3}$$

The second order electron correlation term, ΔE_{corr}^{MP2}, includes the second order dispersion interaction, $\epsilon_{disp}^{(20)}$, as well as the electron correlation correction to the first order electrostatic interaction, $\epsilon_{el,r}^{(12)}$, and the remaining electron correlation effects ($\Delta E_{ex}^{(2)}$):

$$\Delta E_{corr}^{MP2} = \epsilon_{el,r}^{(12)} + \epsilon_{disp}^{(20)} + \Delta E_{ex}^{(2)}. \tag{4}$$

The latter term accounts mainly for the uncorrelated exchange-dispersion and electron correlation corrections to the Hartree–Fock exchange repulsion [30,31]. The $\epsilon_{el}^{(10)}$ and the $\epsilon_{disp}^{(20)}$ terms are obtained in the standard polarization perturbation theory, whereas the $\epsilon_{el,r}^{(12)}$ term is calculated using the formula proposed by Moszyński et al. [32]. The indices in parenthesis denote perturbation orders in intermolecular interaction operator and intramonomer correlation operator, respectively. In order to account for higher-order electron correlation effects, this scheme can be extended to higher orders of perturbation theory or augmented with the supermolecular electron correlation corrections estimated using the coupled-clusters approach.

If a molecular complex is embedded in an external uniform electric field, interaction energy and all of its components become field dependent. For interaction-induced tensorial property $\Delta P_{ij...n}$ (dipole moment, polarizability, first- and second hyperpolarizabilities, etc.) one obtains:

$$\Delta P_{ij...n} = -\left(\frac{\partial^n \Delta E}{\partial F_i \partial F_j \ldots \partial F_n} \right)_{F_i=F_j=\cdots F_n=0}. \tag{5}$$

The required derivatives can be estimated in a numerical differentiation procedure, commonly referred to as the finite field (FF) approach, which can be combined with any *ab initio* method. In this study, we use the Rutishauser–Romberg scheme [33] to compute

numerical derivative given by Eq. (5). In case of interaction-induced polarizabilities the diagonal tensor elements can be computed using:

$$\Delta \alpha^{p,k} = \frac{4^p \cdot \Delta \alpha^{p-1,k} - \Delta \alpha^{p-1,k-1}}{4^p - 1} \tag{6}$$

where p is the iteration number and k is related to the distance from $\Delta E(F = 0)$. The values of $\Delta \alpha^{0,k}$ are determined from finite-difference expression for the second derivative of interaction energy ($\Delta E^{(2)}(F)$) or its components ($\Delta E_i^{(2)}(F)$):

$$\Delta E_i^{(2)}(F) \approx \delta^{(2,k)} = \frac{\Delta E_i(-2^k F_h) + \Delta E_i(2^k F_h) - 2\Delta E_i(F = 0)}{(2^k F_h)^2} \tag{7}$$

where F_h is an electric field step equal 0.001 a.u.

In all calculations the aug-cc-pVDZ correlation-consistent basis set was used [34–36]. However, in order to establish the basis set extension effects we calculated the contributions to the interaction-induced diagonal polarizability of AT dimer using a selection of other correlation-consistent basis sets (cc-pVXZ and aug-cc-pVXZ, where X = D,T) as well as the recently developed polarized LPol-ds basis set [37]. The LPol-ds set is the smallest among the LPol-n (n = ds, dl, fs, fl) property-oriented basis sets, designed for accurate studies of linear and non-linear molecular electric properties. High level of saturation of LPol-n sets with respect to polarization effects induced by external electric field makes them also reliable for calculation of interaction-induced properties. They were developed using method based on the studies of analytic dependence of Gaussian-type orbitals (GTOs) on the external oscillating electric field [38]. Polarized set is obtained from some source set of GTOs through addition of multiple first- (all LPol-n sets) and second-order (LPol-fs and -fl sets) polarization functions. Their contraction coefficients are obtained by simple scaling of the corresponding contraction coefficients in the valence orbitals. Quality of the final set depends strongly on the choice of initial set of functions, and thus the LPol-n sets were developed from the fully optimized large [13s8p] ([10s] in the case of hydrogen) basis sets of van Duijneveldt [39]. To further increase basis set flexibility, the source set was augmented with one diffuse s- and one diffuse p-type function (one s-type function in the case of hydrogen atom). Final LPol-ds set was contracted to the form [14s9p6d/6s5p3d] ([11s6p/4s3p] for hydrogen).

In order to elucidate the relations among the various components of interaction energy and interaction-induced electric properties, in this Letter we use both the Pearson's and the Spearman's rank correlation coefficients [40]. The latter coefficient can be estimated as: $\rho = 1 - 6\sum_i d_i^2 / n(n^2 - 1)$, where d_i is the difference between the ranks of each observation for the pair of compared quantities, and n is the number of observations (in this case number of studied complexes in each set). The advantage of using the Spearman's rank is that it does not assume a normal distribution for the compared quantities and it is based on the order of their rising magnitudes rather than their values.

All calculations have been performed using a modified version of the GAMESS (US) program [41].

3. Results and discussion

Regarding evaluation of interaction-induced electric polarizabilities and hyperpolarizabilities in hydrogen-bonded complexes, a considerable improvement of results is observed when using large Dunning's basis sets [34–36] augmented with diffuse functions. However, due to the size of such sets their use makes the calculations unfeasible for larger complexes [42,43,28]. On the other hand, it has been previously shown that the LPol-n sets are competitive to the larger all-purpose sets of Dunning in the case of