On the Origins of Large Interaction-Induced First Hyperpolarizabilities in Hydrogen-Bonded π-Electronic Complexes

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# On the Origins of Large Interaction-Induced First Hyperpolarizabilities in Hydrogen-Bonded π-Electronic Complexes

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Ⓢ Supporting Information

ABSTRACT: In this article we elucidate the origins of interaction-induced linear and nonlinear electro-optic properties of model hydrogen-bonded π-electronic complexes. In particular we report on contributions due to various interaction energy terms to excess dipole moments ($\Delta\mu$), electric dipole polarizabilities ($\Delta\alpha$), and first hyperpolarizabilities ($\Delta\beta$), focusing on the latter. The analysis of intermolecular interaction-induced electric properties is performed for selected model systems including quasi-linear dimers of urea, diformamide, 4-pyridone, 4-nitroaniline, and the complex of hydrogen fluoride with nitroacetylene. The nature of intermolecular interactions as well as of the $\Delta\mu$ and $\Delta\alpha$ is very similar in all studied complexes. However, partitioning of $\Delta\beta$ into physically well-defined components reveals that the origins of this term, the magnitude of which is often comparable to the hyperpolarizabilities of isolated monomers, are different in each case. Our results indicate that, even though hydrogen bonding usually diminishes the nonlinear response of interacting species, the first hyperpolarizability of complexes with the nitro group acting as a proton acceptor is substantially increased, essentially due to field-induced changes of electrostatic interactions between subsystems. However, in the remaining complexes the origins of $\Delta\beta$ are much more involved. Even though at large intermolecular separations the origins of interaction-induced electric properties are essentially due to the field-induced electrostatic and induction interactions, in the vicinity of van der Waals minimum the overlap effects cannot be neglected since they may substantially alter the predicted excess properties or even determine their magnitude and sign. On the other hand the $\Delta\beta$ contribution due to dispersion interactions is usually negligible. Interestingly, the values of interaction-induced first hyperpolarizability in some cases depend strongly on the intermolecular separation in the vicinity of equilibrium geometry.
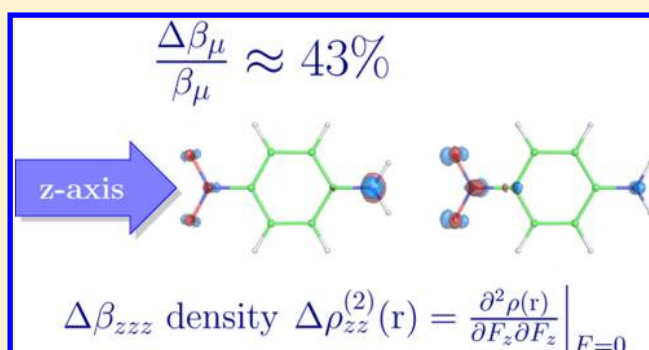
INTRODUCTION

Studies of the nonlinear electric properties of organic compounds are becoming increasingly important due to their relevance in the design of new organic electro-optic materials. In principle the bulk properties of such materials can be related to molecular (hyper)polarizabilities through the local field factors and the orientational order parameters.[1] However, the molecular properties themselves are often substantially influenced by intermolecular interactions in bulk.[2]

These effects are, in fact, the origins of the collision-induced absorption and light scattering[3,4] and were extensively studied in this context both experimentally and theoretically.[5−7] The theoretical investigations of response electric properties of atomic and molecular aggregates could be traced to the seminal works of Silberstein on molecular refractivity.[8,9] The later subject has been thoroughly investigated by Buckingham et al.[10−12] and Hunt et al.,[13−18] and in the past few decades a number of relevant ab initio studies appeared.[7,19−33] These, however, were usually limited to relatively small van der Waals complexes, and although the ab initio studies of aggregates of organic chromophores are still scarce, particularly large

attention has been paid to hydrogen-bonded π-electronic complexes[34−55] and molecular crystals.[56−59]

It should be noted that hydrogen bonding itself does not necessarily enhance nonlinear response. In fact, the opposite is much more likely since it stabilizes primarily the ground state and, thus, enlarges the energy gap between the ground and excited states.[40] The utility of hydrogen bonding lies rather in its directional properties and its ability to enforce an acentric supramolecular self-assembly, like for instance in the extensively studied donor-π-acceptor (D-π-A) aggregates.[40,60−63] Nevertheless, the influence of hydrogen-bonding interactions on the overall response of π-electronic complexes is clearly an interesting and largely unexplored subject. Particularly intriguing are very large magnitudes of interaction-induced first hyperpolarizabilities which seem to be a distinguishing feature of these systems.[35,37,38,42] Thus in this article we wish to elucidate the origins of these effects using the recently proposed

approach that allows the interaction-induced electric properties to be partitioned into contributions arising from various interaction energy terms.[53]

COMPUTATIONAL METHODS

In this work we assumed a methodology that was thoroughly described and tested in our recent study;[53] thus, in this section we will only outline the most important aspects. In short, the interaction-induced electric properties can be defined as excess properties of a complex AD (we will use label "A" to denote proton acceptor and "D" for proton donor):

$$\Delta P_{AD} = P_{AD} - (P_A + P_D) \tag{1}$$

If such a complex is embedded in an external electric field, the interaction energy and all of its components become field dependent and the interaction-induced dipole moment ($\Delta\mu$), polarizability ($\Delta\alpha$), and first hyperpolarizability ($\Delta\beta$) can be estimated as consecutive derivatives of the interaction energy or of the sum of its contributions.[19,21,53]

$$\Delta E(F) = \Delta E(0) - \Delta\mu_i F_i - \frac{1}{2}\Delta\alpha_{ij}F_i F_j \tag{2}$$

$$-\frac{1}{6}\Delta\beta_{ijk}F_i F_j F_k - ... \tag{3}$$

where

$$\Delta P_{ij...n} = -\left(\frac{\partial^n \Delta E}{\partial F_i \partial F_j ... \partial F_n}\right)_{F_i=F_j=...=F_n=0} \tag{4}$$

The required field-dependent intermolecular interaction energies were calculated at the second-order Møller−Plesset perturbation theory (MP2) level and were partitioned using the hybrid variational-perturbational scheme.[64−67] Essentially, in this type of analysis the total interaction energy obtained in the supermolecular approach is partitioned into a selection of interaction terms analogous to the ones defined in state-of-the-art symmetry-adapted perturbation theory (SAPT).[68]

$$\Delta E^{MP2} = \underbrace{\underbrace{\Delta E_{el}^{(10)} + \Delta E_{ex}^{HL}}_{\Delta E^{HL}} + \Delta E_{del}^{HF}}_{\Delta E^{HF}} + \underbrace{\Delta E_{el,r}^{(12)} + \Delta E_{disp}^{(20)} + \Delta E_{ex}^{(2)}}_{\Delta E_{corr}^{MP2}} \tag{5}$$

The total ΔE^{MP2} interaction energy is partitioned into the Hartree−Fock (HF) and the electron-correlation components ΔE_{corr}^{MP2}. The HF term encompasses the electrostatic interaction of unperturbed monomer charge densities ($\Delta E_{el}^{(10)}$), the associated exchange repulsion (ΔE_{ex}^{HL}), and the charge-delocalization (ΔE_{del}^{HF}) energy due to induction and exchange-induction effects, whereas the electron-correlation contribution includes the second-order dispersion interaction ($\Delta E_{disp}^{(20)}$), the electron-correlation correction to the first-order electrostatic interaction ($\Delta E_{el,r}^{(12)}$), and the remaining electron-correlation effects ($\Delta E_{ex}^{(2)}$) due to the uncorrelated exchange-dispersion and electron-correlation corrections to the Hartree−Fock exchange repulsion.[65,66] The dimer-centered basis set is consistently adopted in all calculations, and hence, the interaction energy and all of its components are basis set superposition error (BSSE) free due to the full counterpoise correction.[69]

The interaction energies and interaction-induced properties of the studied complexes at equilibrium geometries were estimated using MP2/aug-cc-pVTZ method. The same method was used to optimize the equilibrium geometries of smaller complexes, whereas in the case of 4-nitroaniline and 4-pyridone

dimers MP2/aug-cc-pVDZ method was used for that purpose. The conclusions of the recent studies[42,51,53,70] as well as the results of our exploratory calculations performed for the studied systems (see the Supporting Information) indicate that the MP2/aug-cc-pVTZ method should provide at least semi-quantitative accuracy of the studied properties which is sufficient for the purpose of this study. In the case of relaxed potential energy surface scans we used a more approximate MP2/aug-cc-pVDZ method for both constrained geometry optimization and calculation of properties which should provide qualitatively correct results.

RESULTS AND DISCUSSION

As model hydrogen-bonded π-electronic systems we have selected quasi-linear dimers of urea (U⋯U), diformamide (D⋯D) and complex of nitroacetylene with hydrogen fluoride (FH⋯NA) all bonded via bifurcated hydrogen bonds that are often found in molecular crystals of D-π-A complexes. We have also chosen two complexes representative of D-π-A systems, namely the dimers of 4-pyridone (4P⋯4P) and 4-nitroaniline (4N⋯4N). The geometrical parameters of all studied complexes were optimized assuming quasi-linear C_{2v} symmetry with the principal symmetry axis coincident with the z-axis of Cartesian coordinate system (see Figure 1). The choice of axial symmetry is particularly convenient for analysis of the vector component of interaction-induced first hyperpolarizability.
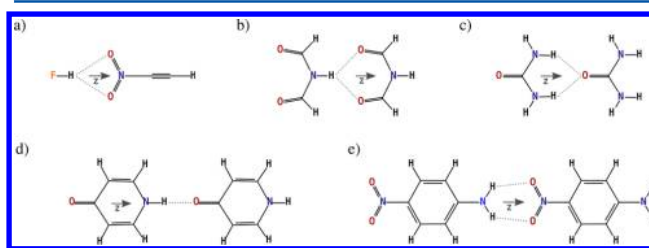

Figure 1. Structures and orientations of the studied complexes: (a) hydrogen fluoride−nitroacetylene dimer (FH⋯NA), (b) urea dimer (U⋯U), (c) diformamide dimer (D⋯D), (d) 4-pyridone dimer (4P⋯4P), and (e) 4-nitroaniline dimer (4N⋯4N).

Although in this paper we intend to focus on the interaction-induced first hyperpolarizabilities, it is relevant to discuss first briefly the nature of the intermolecular interactions as well as the interaction-induced dipole moments and polarizabilities. The field-free ΔE^{MP2} interaction energy terms are shown in Table 1. The total interaction energy strength varies from moderate, found in FH⋯NA (which is comparable to ΔE of water dimer) to quite strong obtained for 4-pyridone dimer. However, the origins of interactions in all studied complexes are rather similar with dominating contribution from the first-order electrostatic term that is further strengthen by charge-delocalization and dispersion interactions. The contribution of the latter two terms is, in fact, almost equally important as $\Delta E_{el}^{(10)}$ since the electron-correlation effects quench the electrostatic contribution by diminishing its magnitude (cf. ($\Delta E_{el,r}^{(12)}$) and by increasing the exchange-repulsion (cf. $\Delta E_{ex}^{(2)}$).

The interaction-induced dipole moments and their partitioning are shown in Table 2. Due to axial symmetry of the studied complexes, the only nonvanishing vector component of dipole moment is the one along principal symmetry axis. Mutual interactions enhance polarity of the interacting species what is reflected in substantially increased magnitudes of the total

Table 1. Intermolecular Interaction Energies and Their Components for the Studied Complexes at Their Equilibrium Geometries[a]

		ΔE^{HF}			ΔE_{corr}^{MP2}		
	ΔE^{MP2}	$\Delta E_{el}^{(10)}$	ΔE_{ex}^{HL}	ΔE_{del}^{HF}	$\Delta E_{el,r}^{(12)}$	$\Delta E_{disp}^{(20)}$	$\Delta E_{ex}^{(2)}$
FH⋯NA	−16.4	−17.1	10.6	−5.8	−0.1	−7.4	3.3
U⋯U	−40.6	−55.5	37.4	−15.2	4.5	−20.4	8.5
D⋯D	−44.5	−60.8	34.5	−14.8	9.7	−24.3	11.3
4P⋯4P	−51.5	−65.8	46.0	−25.5	6.1	−21.4	9.0
4N⋯4N	−27.5	−35.9	23.6	−7.8	2.1	−17.3	7.8

[a]Calculations were performed using the aug-cc-pVTZ basis set. All values are in kJ/mol.

Table 2. Longitudinal Dipole Moments (μ_z) of the Studied Complexes (AD) and of the Constituent Monomers (A and D) along with the Total Interaction-Induced Contribution ($\Delta\mu_z$) and Its Partitioning into Terms Arising from Various Interaction Energy Components[a]

					$\Delta\mu_z^{HF}$			$\Delta\mu_{z,corr}^{MP2}$		
	$\mu_{z,AD}^{MP2}$	$\mu_{z,A}^{MP2}$	$\mu_{z,D}^{MP2}$	$\Delta\mu_z^{MP2}$	$\Delta\mu_{z,el}^{(10)}$	$\Delta\mu_{z,ex}^{HL}$	$\Delta\mu_{z,del}^{HF}$	$\Delta\mu_{z,el,r}^{(12)}$	$\Delta\mu_{z,disp}^{(20)}$	$\Delta\mu_{z,ex}^{(2)}$
FH⋯NA	2.332	1.322	0.715	0.295	0.254	−0.014	0.041	0.016	0.000	−0.002
U⋯U	4.086	1.724	1.705	0.657	0.516	−0.005	0.114	0.022	−0.006	0.016
D⋯D	5.106	2.189	2.190	0.726	0.587	0.045	0.116	−0.045	−0.025	0.049
4P⋯4P	6.756	2.761	2.761	1.233	0.921	0.045	0.267	−0.031	−0.017	0.048
4N⋯4N	6.349	2.713	2.733	0.902	0.740	−0.039	0.162	0.039	0.000	0.001

[a]All values are in au.

Table 3. Isotropic Average Polarizabilities (α_0) of the Studied Complexes (AD) and of the Constituent Monomers (A and D) along with the Total Interaction-Induced Contribution ($\Delta\alpha_0$) and Its Partitioning into Terms Arising from Various Interaction Energy Components[a]

					$\Delta\alpha_0^{HF}$			$\Delta\alpha_{0,corr}^{MP2}$		
	$\alpha_{0,AD}^{MP2}$	$\alpha_{0,A}^{MP2}$	$\alpha_{0,D}^{MP2}$	$\Delta\alpha_0^{MP2}$	$\Delta\alpha_{0,el}^{(10)}$	$\Delta\alpha_{0,ex}^{HL}$	$\Delta\alpha_{0,del}^{HF}$	$\Delta\alpha_{0,el,r}^{(12)}$	$\Delta\alpha_{0,disp}^{(20)}$	$\Delta\alpha_{0,ex}^{(2)}$
FH⋯NA	47.21	41.32	5.52	0.37	0.24	−0.47	0.36	0.31	0.13	−0.20
U⋯U	75.71	37.21	36.96	1.48	1.26	−1.22	0.94	0.39	0.41	−0.30
D⋯D	83.53	41.42	41.56	0.55	0.88	−1.51	1.09	0.40	0.54	−0.85
4P⋯4P	154.93	73.46	73.57	7.90	5.12	−1.62	2.18	1.35	0.47	0.40
4N⋯4N	231.22	107.98	108.02	15.22	7.83	−1.53	3.48	3.88	0.68	0.88

[a]All values are in au.

dipole moments of the studied complexes. The relative ratios of the interaction-induced dipoles to the corresponding total dipole moment range from about 13% to 18%. Their origins are purely electrostatic in nature with only a minor contribution from charge-delocalization term and virtually negligible remaining components. This is rather expected result since interaction-induced dipole moments reflect simply the changes of charge densities of the interacting species upon interaction and, in fact, could be calculated from the difference densities between the interacting and noninteracting systems.[44,71]

In Table 3 we report the isotropic average polarizabilities of the studied complexes and of their constituents, calculated according to eq 6, as well as the corresponding interaction-induced contributions and their analysis.

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{6}$$

The origins of interaction-induced polarizabilities are slightly more complicated even though they also seem to be dominated by the first-order electrostatic term. In general, the intermolecular interactions tend to increase polarizability of the studied systems. Although the $\Delta\alpha_{0,el}^{(10)}$ alone predicts with qualitative accuracy the effect of intermolecular interactions, in this case it is rather due to cancellation of higher-order terms of

comparable magnitude. Particularly in the smaller complexes with bifurcated hydrogen bonds the exchange-repulsion effects ($\Delta\alpha_{0,ex}^{HL}$) quench entirely the associated first-order electrostatic contribution. Thus, considering the negligible electron-correlation correction the incremental polarizabilities of smaller complexes are dominated by induction and exchange-induction effects represented by the $\Delta\alpha_{0,del}^{HF}$ term. Recently we have reached similar conclusions in the case of Watson−Crick base pairs; however, the electron-correlation effects in that case were much more pronounced.[72] Only in the larger dimers of 4-pyridone and 4-nitroaniline the $\Delta\alpha_{0,ex}^{HL}$ term is much smaller than $\Delta\alpha_{0,el}^{(10)}$ and the latter is indeed a leading contribution. What is interesting is that all of the electron-correlation corrections in D-π-A complexes enforce the incremental polarizability, with the largest contribution due to electron-correlation correction to the first-order electrostatic term ($\Delta\alpha_{0,el,r}^{(12)}$). Nonetheless, the overall relative influence of intermolecular interactions on isotropic average polarizability of the studied complexes is generally small (much smaller than in the case of $\Delta\mu_z$ or $\Delta\beta_\mu$) and ranges from less than 2% in the smaller complexes up to about 5−7% in 4-pyridone and 4-nitroaniline dimers.

In the case of the first hyperpolarizability, the relevant tensor invariant in the limit of static fields is the vector component of

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Table 4. Vector Components of First Hyperpolarizabilities (β_z) of the Studied Complexes (AD) and of the Constituent Monomers (A and D) along with the Total Interaction-Induced Contribution ($\Delta\beta_z$) and Its Partitioning into Terms Arising from Various Interaction Energy Components[a]

	$\beta_{z,AD}^{MP2}$	$\beta_{z,A}^{MP2}$	$\beta_{z,D}^{MP2}$	$\Delta\beta_z^{MP2}$	$\Delta\beta_z^{HF}$			$\Delta\beta_{z,corr}^{MP2}$		
					$\Delta\beta_{z,el}^{(10)}$	$\Delta\beta_{z,ex}^{HL}$	$\Delta\beta_{z,del}^{HF}$	$\Delta\beta_{z,el,r}^{(12)}$	$\Delta\beta_{z,disp}^{(20)}$	$\Delta\beta_{z,ex}^{(2)}$
FH···NA	79.0	57.9	−9.7	30.8	26.0	−13.4	10.2	15.7	2.6	−10.3
U···U	−34.2	−27.3	−34.5	27.6	12.0	−12.3	14.7	19.4	0.6	−6.8
D···D	−97.3	−80.1	−85.7	68.5	−30.2	55.5	0.2	−31.8	−19.1	94.0
4P···4P	92.0	70.0	39.5	−17.5	−61.0	12.2	−9.1	76.6	1.2	−37.4
4N···4N	3798.4	1096.9	1063.8	1637.7	666.9	−62.3	304.2	563.6	12.7	152.5

[a]Except for 4-pyridone, where the aug-cc-pVDZ basis set was found to assure a better numerical accuracy of the interaction-induced terms, all remaining results were obtained in the aug-cc-pVTZ basis set. All values are in au.
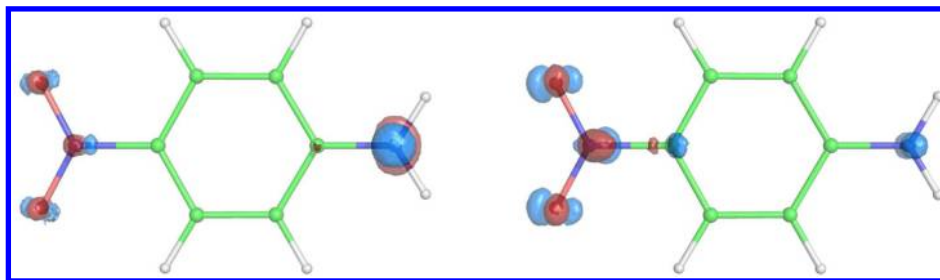

Figure 2. Interaction-induced longitudinal first hyperpolarizability ($\Delta\beta_{zzz}$) density of the 4-nitroaniline dimer calculated at the MP2/aug-cc-pVDZ level. The hyperpolarizability isodensity contours were plotted for ± 4 au/bohr^3. Red indicates an increase and blue a decrease of hyperpolarizability density.

the first hyperpolarizability tensor in the direction of the permanent dipole moment (β_μ). In the case of systems having a rotational symmetry axis, it can be calculated as a projection of the β tensor on that axis (in our case z-axis):[73]

$$\beta_\mu = \beta_z = \frac{3}{5}(\beta_{zzz} + \beta_{yyz} + \beta_{xxz}) \tag{7}$$

In Table 4 we report the total and interaction-induced vector components of first hyperpolarizabilities for all studied complexes. Perhaps the most striking observation is that the interaction-induced contribution ($\Delta\beta_z^{MP2}$) has a comparable magnitude to the properties of isolated monomers. As we have already mentioned in the Introduction this effect seems to be a distinguishing feature of all hydrogen-bonded π-electronic systems and was reported before by several research groups including our.[35−38,40,42,53] The total excess electric properties of some of the studied complexes have also been estimated before at various levels of theoretical approximation.[34−36,39,40,42,44,74,75] The common observation for all of these studies was a large magnitude of the interaction-induced first hyperpolarizability which, as expected, usually diminished the nonlinear response of a complex with respect to isolated subsystems. Interestingly, the opposite effect was observed for aggregates of 4-nitroaniline. However, due to the size of this system so far this conclusion was supported only by rather approximate results obtained from the two-states model or Hartree−Fock calculations.[35,40,75] Nonetheless, the MP2/aug-cc-pVTZ results reported in Table 4 are qualitatively consistent with the HF/6-31+G(d,p) results of Moliner et al.,[35] who reported 3197.1 au for β_μ of the 4-nitroaniline dimer and 892.4 au for the monomer. We should also note that our MP2/aug-cc-pVTZ estimates of β_μ for both 4-nitroaniline molecules at the geometries they assume in the dimer are close to the experimentally determined gas-phase value of 1072 ± 44 au[76] and the state-of-the-art coupled-cluster response theory result

of Hammond and Kowalski, who obtained the value 1041.7 au for the experimental crystal-phase geometry at the CCSD/aug-cc-pVDZ level.[77] Our analysis indicates that the huge interaction-induced effect is primarily electrostatic in origin, as the sum of $\Delta\beta_{z,el}^{(10)}$ and $\Delta\beta_{z,el,r}^{(12)}$ accounts for nearly 76% of the total increment given by $\Delta\beta_z^{MP2}$, while the $\Delta\beta_{z,ex}^{HL}$ and $\Delta\beta_{z,ex}^{(2)}$ terms cancel each other out. The effect of electrostatic interactions is further enforced by significant charge-delocalization contribution. The plot of the longitudinal component of the first hyperpolarizability density defined[71] as $\Delta\rho_{zz}^{(2)}(\mathbf{r}) = ((\partial^2\rho(\mathbf{r}))/(\partial F_z^2))|_{F=0}$ is shown in Figure 2. It indicates that the largest changes of β tensor upon interaction are localized within the nitro and amine groups forming the hydrogen bonds.

Since an increase in value of β_μ upon hydrogen bond formation is rather unusual we decided to investigate yet another π-electronic compound with a nitro group. In order to focus on the properties of the X−H···O$_2$N− motif, we have chosen a complex of nitroacetylene with hydrogen fluoride in which a similar bifurcated hydrogen bond is formed as in the investigated urea dimer. This choice was also partially dictated by the results of our previous studies on fluoroacetylene dimer in which we have found an increase of β_μ magnitude, although in that case it is rather small as it does not exceed 6%. Interestingly, in the complex of nitroacetylene with hydrogen fluoride we observe a substantial increase of β_μ with respect to the sum of isolated monomer properties. Even though in this case the exchange-repulsion terms quench the electrostatic contributions to a large extent, the latter prevail, and the origins of $\Delta\beta_z^{MP2}$ are quite similar to those found in the 4-nitroaniline dimer. The importance of the nitro group in the design of organic electro-optic materials is nowadays well recognized; however, the above findings indicate that it has interesting properties not only as an electron acceptor moiety but also as a proton acceptor.
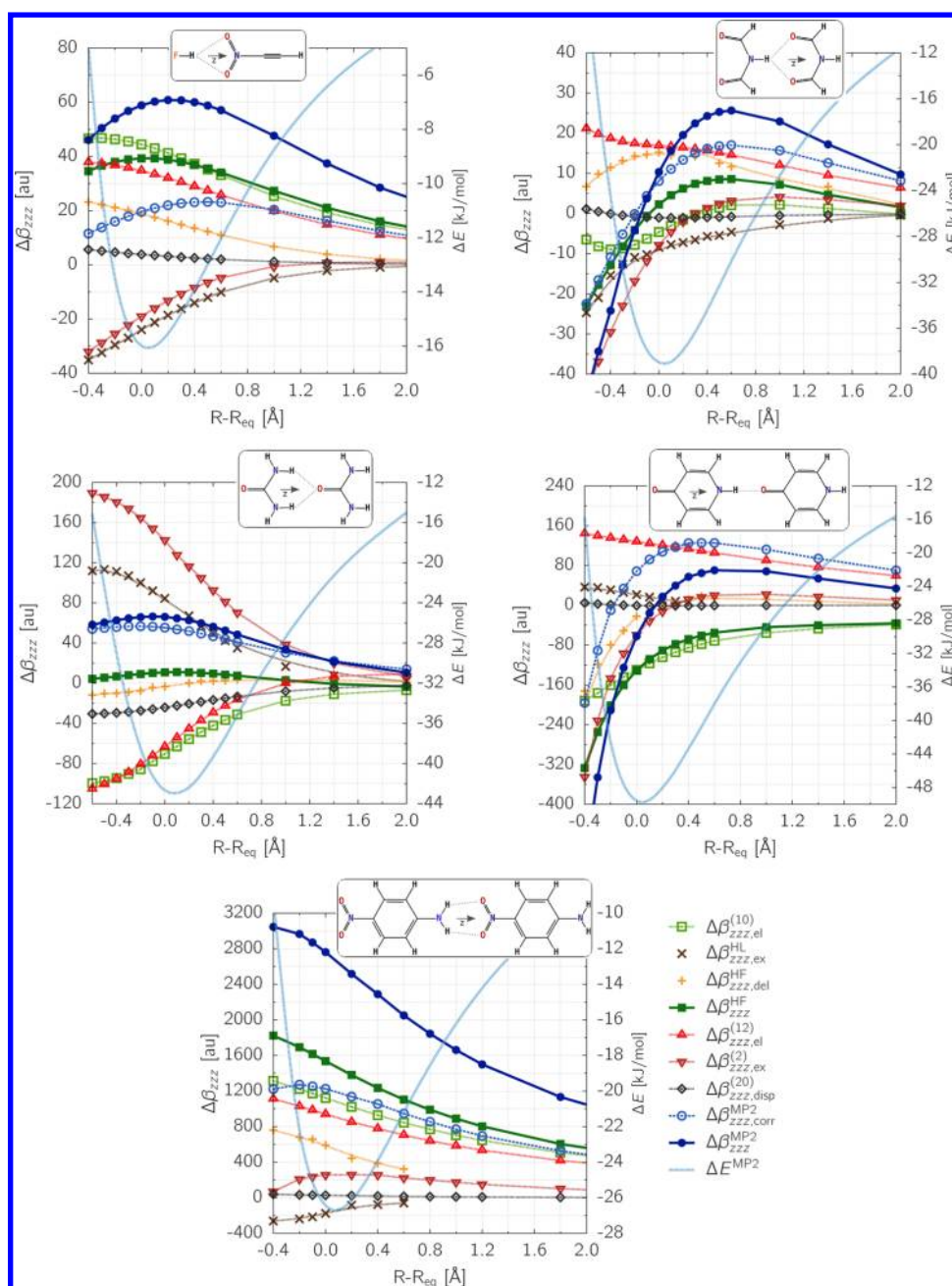
Figure 3. Longitudinal interaction-induced first hyperpolarizabilities ($\Delta\beta_{zzz}$ in au) of the studied complexes and their contributions arising from various interaction energy terms plotted for varying intermolecular separation. The interaction energy curves are also shown for reference. The distances (in Å) are given relative to the equilibrium geometries.

In all of the remaining complexes intermolecular interactions diminish substantially their first hyperpolarizability. However, the origins of this effect seem to be different in each case. The composition of $\Delta\beta_z^{MP2}$ of the urea dimer is quite similar to that of FH···NA, and even though the first order electrostatic term is completely canceled by the corresponding exchange-repulsion term, larger magnitudes of $\Delta\beta_{z,del}^{HF}$ and $\Delta\beta_{z,el}^{(10)}$ compensate for this and the resultant incremental hyperpolarizability is almost the same. Albeit, the properties of isolated urea molecules are opposite to the interaction induced effect and as a consequence of that the first hyperpolarizability of the complex is almost identical to that of isolated monomer. The same is true for the diformamide dimer; however, in this case the origins of this effect are completely different. The contribution from both

electrostatic terms is now opposite than in the previously discussed systems and does not even provide a qualitatively correct prediction of the interaction-induced effect. The latter seems to be primarily due to the exchange-repulsion effects. Interestingly, in this system there is also a significant contribution from dispersion interactions which in the case of other complexes studied here is rather negligible. The first hyperpolarizability of the 4-pyridone dimer is also diminished as a result of intermolecular interactions. In this complex the first-order electrostatic contribution is also negative but so is the total interaction-induced property. Thus, considering the relatively small magnitude of $\Delta\beta_{z,ex}^{HL}$ term, one could argue that $\Delta\beta_{z,el}^{(10)}$ is the key contribution. On the other hand, in this system the corresponding electron-correlation correction

$\Delta\beta_{z,el,r}^{(12)}$ cancels out the first-order term and the net effect of electrostatic interactions at the MP2 level amounts to 15.6 au. Since the corresponding sum of the exchange-repulsion terms equals −25.2 au we conclude that the origins of $\Delta\beta_z^{MP2}$ are, similarly as in the diformamide dimer, the exchange-repulsion and the charge-delocalization effects. Although in the case of 4-pyridone we decided to show the aug-cc-pVDZ results due to their greater numerical stability, the magnitudes of $\Delta\beta_z^{MP2}$ calculated using both basis sets are virtually identical and amount to −17.5 and −17.8 au, respectively, for the aug-cc-pVDZ and aug-cc-pVTZ sets.

In order to gain more insight into the origins of interaction-induced hyperpolarizabilities of the studied complexes, we calculated the contributions to the longitudinal component ($\Delta\beta_{zzz}$) on the relaxed potential energy surface. This term was always the one most affected by intermolecular interactions. The results are shown in Figure 3. The total interaction-induced property ($\Delta\beta_{zzz}^{MP2}$) in the long-range limit is positive for all studied systems (i.e., the corresponding induced dipole moment is consistent with the polarization of monomers and dimers). It is gradually increasing as the molecules approach each other and in the vicinity of equilibrium geometry (between R_{eq} and R_{eq} + 0.5 Å) goes through a maximum and starts decreasing (the only exception is 4-nitroaniline dimer for which such a maximum occurs at much shorter intermolecular separations). This decrease is particularly steep for urea and 4-pyridone dimers, and it is primarily due to exchange and exchange-correlation effects which lead to the negative values of $\Delta\beta_{zzz}^{MP2}$ at equilibrium geometries. The large slope of the interaction-induced hyperpolarizability in these complexes suggest also a potentially significant vibrational contribution to β. It is also worth noticing that, even though in the long-range limit the electrostatic terms are usually the leading contributions, the corresponding electron-correlation contribution ($\Delta\beta_{z,el,r}^{(12)}$) is at least equally important as the first-order term. Furthermore, there are exceptions like the urea dimer (due to a significant charge-delocalization contribution) or diformamide dimer (due to dominant exchange-repulsion effects).

■ CONCLUSIONS AND OUTLOOK

In this article we have analyzed the origins of interaction-induced linear and nonlinear electro-optic properties of model hydrogen-bonded π-electronic complexes in terms of the intermolecular perturbation theory. The nature of intermolecular interactions as well as of the $\Delta\mu_z$ and $\Delta\alpha_0$ is very similar in all studied complexes. However, partitioning of the $\Delta\beta_\mu$ into contributions arising from various interaction energy terms reveals that the origins of this effect, the magnitude of which is often comparable to that of isolated monomers, are different in each case. Our results indicate that even though hydrogen bonding usually diminishes the nonlinear response of interacting species, the first hyperpolarizability of complexes with nitro group acting as a proton acceptor is substantially increased due to the field-induced changes of electrostatic interactions between subsystems. Nonetheless, in the remaining complexes the nonlinear response of a dimer is substantially reduced with respect to isolated monomers. Moreover, the origins of $\Delta\beta$ are qualitatively different in each case. In the case of the urea dimer, the first hyperpolarizability is diminished due to induction and exchange-induction terms, whereas in diformamide and 4-pyridone dimers the observed reduction is primarily due to exchange-repulsion effects. A general conclusion arising from our results is that, even though at large intermolecular separations the origins of interaction-induced electric properties are essentially due to the field-induced electrostatic and induction interactions, in the vicinity of the van der Waals minimum the overlap effects cannot be neglected since they may substantially alter the predicted excess properties or even determine their magnitude and sign. Surprisingly, our results also indicate that the $\Delta\beta$ contribution due to dispersion interactions is usually negligible. What is interesting, the values of interaction-induced first hyperpolarizability depend in some cases strongly on the intermolecular separation which could indicate potentially large vibrational contributions as well as significant sensitivity to external pressure. Investigations of both of these effects are currently in progress in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results of exploratory calculations justifying the selected methodology. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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