

# Reinvestigation of Hydrogen Bond Effects on the Polarizability and Hyperpolarizability of Urea Molecular Clusters

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The oriented-gas model based on the additivity hypothesis is widely used in predicting the macroscopic nonlinear optical susceptibility of a molecular crystal from molecular (hyper)polarizability calculations. Here, we argue that the intermolecular hydrogen bond interactions will break the additivity relationship for the first hyperpolarizability of urea hydrogen-bonded clusters on the basis of our high-level *ab initio* studies. The calculations at the HF level without electron correlation correction result in the underestimation of the hydrogen bond effect on the first hyperpolarizabilities to about 15% in the urea case. On the other hand, both HF and MP2 results show the additivity of linear polarizability of urea clusters. We hope that the study will be helpful to the areas of molecular design and simulation of novel nonlinear optical materials.

## I. Introduction

Computational chemistry is becoming increasingly valuable in designing, modeling, and screening novel nonlinear optical (NLO) materials.<sup>1</sup> The polarizability ( $\alpha$ ) and hyperpolarizability ( $\beta$ ,  $\gamma$ , ...) of a microscopic moiety (a molecule, a cluster, an oligomer, etc.), which characterize the NLO properties of the corresponding bulk material, have been extensively studied by a great variety of computational chemistry methods.<sup>2</sup> Nowadays  $\alpha$ ,  $\beta$ , and  $\gamma$  of a medium size molecule in the gas phase could be computed to a satisfactory accuracy within the first-principle theoretical framework under the following conditions: (a) Sufficiently large basis sets extended with additional diffuse functions are used. (b) Electron correlation effects are included e.g. to the second-order Möller–Plessett level (MP2) of accuracy. (c) Vibrational polarization effects are included. (d) Frequency-dependent dispersion is taken into account. In addition to conventional *ab initio* methods, density functional theory (DFT) has been applied to the calculations of  $\alpha$ ,  $\beta$ , and  $\gamma$  recently, which is promising to study the complicated larger size molecular systems.<sup>3,4</sup>

In contrast to the fast growing understanding of  $\alpha$ ,  $\beta$ , and  $\gamma$  at molecular level, the detailed knowledge of how to derive the crystalline susceptibilities ( $\chi^{(1)}$ ,  $\chi^{(2)}$ ,  $\chi^{(3)}$ , ...) is still lacking and continues to be a challenge to scientists. Since molecular crystals have only weak intermolecular interactions (typically within hundreds of kJ/mol) induced by weak van der Waals forces, hydrogen bonds, and internally induced electrostatic forces, the

additivity model has been applied to molecular crystals. The molecular interactions are completely neglected in this model, and the molecular polarizability ( $\alpha$ ) and the first hyperpolarizability ( $\beta$ ) are treated independently and are added up with molecular orientation being taken into account (the so-called oriented-gas model).<sup>5</sup> This model is so widely used in estimating macroscopic susceptibility that it is even adopted for non-molecular crystals.<sup>6,7</sup>

The validity of the additivity model has been in doubt for quite some time. In 1982, using INDO semiempirical theory and *ab initio* method, Zyss and co-workers examined the oriented-gas model by calculating  $\beta$  values of urea monomer and dimer clusters.<sup>8</sup> Since a urea crystal has relatively strong intermolecular hydrogen bonds (approximately a few hundreds kJ/mol), if the urea crystal had fitted well in the additivity framework, the model would be trustworthy in the estimation of NLO susceptibility of molecular crystals. They concluded that the model was questionable and the hydrogen bonds influenced the magnitude of the  $\beta$  values. Dirk et al. drew similar conclusions on again urea crystals that the intermolecular interaction played an important and nonnegligible role by PPP semiempirical methods.<sup>9</sup> Doubting the semiempirical results, Perez and Dupuis extended the urea dimer to trimer cluster calculations with the use of extensive basis sets and the first-principle *ab initio* method.<sup>10</sup> Their calculations have shown that hydrogen bond effects on the (hyper)polarizability of urea clusters might not be as significant as thought. Hamada however reported in 1996 the calculations of the hyperpolarizability of an interacting 2-methyl-4-nitroaniline (MNA) molecular pair using *ab initio* methods and pointed out that the intermolecular

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interactions considerably influenced the  $\beta$  values of the MNA pair.<sup>11</sup> However, neither the above two reports of Perez and Hamada considered electron correlation effects in their studies. As a matter of fact, many studies on the hyperpolarizability of single isolated molecules have shown the importance of electron correlation effects on the calculations of  $\beta$  and  $\gamma$  values.<sup>12,13</sup> The question is, if we take electron correlation effects into account, whether the additivity model works for a supermolecular system like a hydrogen-bonded urea cluster. Furthermore, the urea clusters in the above-mentioned studies are relatively small for a credible verification of the validity of the additivity model. The nearest-neighbor configuration of the urea clusters (a septimer cluster in this study) would be good enough for the verification since the influence of the second neighboring interactions on the properties of the central molecule is most likely much weaker.

Motivated by the above questions, we adopt in this paper the supermolecular model to calculate the polarizability  $\alpha$  and the first hyperpolarizability  $\beta$  of urea clusters from a monomer, a dimer, trimers, and pentamers to a septimer which has the nearest-neighbor configuration by using the first-principle methods at different computational levels. We wished that the results could verify the validity or invalidity of the additivity model in the presence of both electron correlation effects and hydrogen bond interactions.

The next section presents the computational methods, i.e., ab initio and DFT for  $\alpha$  and  $\beta$  values of the various sizes of hydrogen-bonded urea clusters. We described the schemes and accuracy levels adopted in various calculations. The calculated results were first presented for a urea monomer at different computational methods and accuracy levels. We found that the finite field (F-F) method with  $f = 0.001$  au is suitable for the numerical evaluation of  $\alpha$  and  $\beta$  values of the ab initio study. The numerical values at the HF level have been compared to the results at MP2 and the higher correlation level of CCD. And we found that DFT results of urea monomer at the GGA/LB94/VI level have a large discrepancy compared to the conventional correlation methods. We then turned to the supermolecular calculations up to a septimer cluster on  $\alpha$  and  $\beta$  at the HF/6-31++G(d, p) level and up to a pentamer at the MP2/6-31++G(d, p) level, discussed the effects of electron correlation and hydrogen bond interactions on  $\alpha$  and  $\beta$  values, and evaluated the additivity relationship in the urea case. Finally, we drew our conclusions.

## II. Computational Methods

The spatial geometries (bond lengths and angles, etc.) of all urea clusters concerned in this paper were taken from the measured X-ray crystalline data including the intermolecular distances and hydrogen bond lengths.<sup>14</sup> The C=O bond length is 1.243 Å, C–N is 1.351 Å, N–H<sub>1</sub> is 0.995 Å, N–H<sub>2</sub> is 0.998 Å, and the –N–C–N bond angles are 117°. The hydrogen bond lengths in the urea clusters vary from 3.018 to 3.076 Å in the different cluster configurations. Using measured geometries avoids the possible structural deviations from a smaller cluster to a larger one if the structural optimizations are performed. The molecular structures of urea clusters from a monomer to a septimer and the molecular orientations are shown in Figure 1. All the configurations of the urea clusters preserve  $C_{2v}$  symmetry. Thus, the nonzero components of the linear and first hyperpolarizabilities of the urea clusters are  $\alpha_{xx}$ ,  $\alpha_{yy}$ ,  $\alpha_{zz}$  and  $\beta_{xxx}$ ,  $\beta_{yyy}$ , and  $\beta_{zzz}$ , respectively. The ab initio calculations were performed by the Gaussian 98 package<sup>15</sup> while the DFT calculations were performed by the Amsterdam Density Func-

tional (ADF) Program 2000.<sup>16</sup> The calculated static  $\beta$  values were compared to the EFISH (electric-field-induced second-harmonic generation) measurement done in water solution by Ledoux and Zyss.<sup>17</sup>

The basis set used in the ab initio calculations was 6-31++G-(d, p), the standard 6-31G Gaussian basis set extended by a set of d polarization functions on the heavy atoms (C, N, O), a set of p polarization functions on hydrogens, and diffuse functions on all the elements (C, O, N, H). Two types of ab initio calculations have been performed. For a monomer, besides the numerical F-F calculations and analytic coupled-perturbed HF (CPHF) calculations at the HF level, we performed the numerical F-F calculations at both the MP2 level and the coupled cluster with double substitutions (CCD) level for  $\alpha$  and  $\beta$  values. The other type of calculation is supermolecular calculations up to a septimer at HF levels and up to a pentamer at the MP2 level by using the F-F method. Due to the limitation of our computer resources it is impractical to perform the MP2 level calculation to a septimer cluster.

The TDDFT calculations were performed only for a monomer urea cluster for comparison with the conventional ab initio calculations by using the ADF RESPONSE module<sup>18</sup> for the analytic  $\alpha$  and  $\beta$  values. We made use of the VI basis set group, an unrestricted triple- $\xi$  frozen-core STO basis set extended with two polarization functions and diffuse functions with LB94 exchange-correlation (XC) functions<sup>19</sup> at general gradient approximation (GGA).

The results are summarized in Table 1.

## III. Results and Discussion

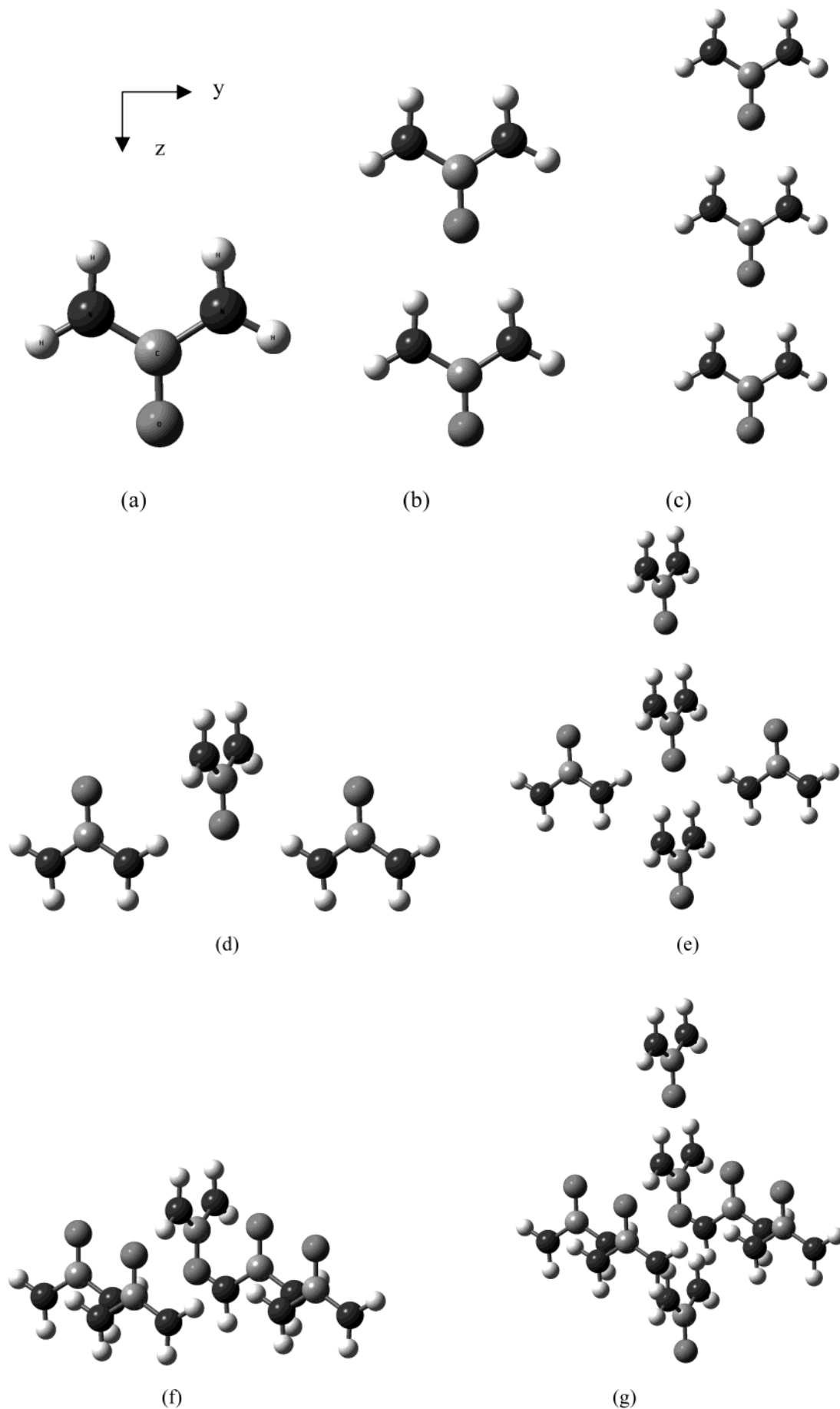
### A. Monomer Cluster. A.1. Analytic and Numeric Results.

The numerical static  $\alpha$  and  $\beta$  values at HF/6-31++G(d, p) listed in Table 1 are very close to the analytic ones, which indicates that the intensity of external field,  $f = 0.001$  au, introduced in our F-F calculations is well suited and, under this finite external field, the F-F method could well reproduce the analytic results. Therefore, we used the F-F method with  $f = 0.001$  au in the all following numerical  $\alpha$  and  $\beta$  calculations. The flexibility of the numerical F-F calculations made it feasible to evaluate the hyperpolarizability of a large-size molecular urea cluster at both HF and MP2 levels.

**A.2. HF Results and MP2 and CCD Results.** It has been pointed out that electron correlation effects are very important for molecular (hyper)polarizabilities. From Table 1,  $\alpha$  values at the MP2 level are evenly 13% larger than those at the HF level indicating the electron correction effect enhances the  $\alpha$  values. However, the different  $\beta$  components have different variations. The  $\beta_{xxx}$  components are almost doubled going from the HF level to the MP2 level. The  $\beta_{yyz}$  component at the MP2 level are slightly larger than that at the HF level, while the  $\beta_{zzz}$  component at the MP2 level are slightly smaller than that at the HF level. It is obvious that electron correlation correction has a significant contribution to  $\alpha$  and  $\beta$  values of a single urea molecule.

CCD calculations with a higher level of electron correlation approximation have been performed as well for  $\alpha$  and  $\beta$  values. Both  $\alpha$  and  $\beta$  values obtained at the CCD level are close to those at the MP2 level. As the CCD computation is very time-consuming, very expensive, and does not provide more new results compared to those at MP2 level, we will in the following supermolecular cluster calculations only perform MP2 calculations from a dimer to a pentamer.

To compare the calculated results to EFISH measurements,  $\beta_z$  was introduced, where  $\beta_z = \beta_{xxx} + \beta_{yyz} + \beta_{zzz}$ . No significant



**Figure 1.** Geometric structures of molecular urea clusters: (a) monomer; (b) dimer; (c) linear trimer; (d) transverse trimer; (e) pentamer I; (f) pentamer II; (g) septimer.

**TABLE 1: Ab Initio and TDDFT Static Results of the Polarizabilities and the First Hyperpolarizabilities (au) of the Urea Monomer at Different Computational Accuracy Levels**

	ab initio					expt
	HF		MP2	CCD	TDDFT: LB94/VI	
	analytic	numeric				
$\alpha_{xx}$	20.7	20.7	23.4	22.6	24.5	
$\alpha_{yy}$	29.8	29.8	34.1	32.6	41.0	
$\alpha_{zz}$	33.2	33.2	37.7	36.5	41.1	
$\beta_{xxz}$	16.2	16.2	30.0	27.5	19.4	
$\beta_{yyz}$	-52.9	-52.9	-61.4	-64.8	-23.4	
$\beta_{zzz}$	61.4	61.4	55.2	58.2	98.1	
$\beta_z$	24.7	24.7	23.8	21.0	94.1	38–66

variation is found among the  $\beta_z$  values at the different accuracy levels with a order of  $\beta_z(\text{HF}) > \beta_z(\text{MP2}) > \beta_z(\text{CCD})$ . The  $\beta_z$  value obtained from the EFISH measurement in water solution is  $(0.45 \pm 0.12) \times 10^{-30}$  esu, which ranges from  $0.33 \times 10^{-30}$  to  $0.57 \times 10^{-30}$  esu (38–66 au).<sup>17</sup> The calculated results at various accuracy levels roughly agree to the measurements, but they are all underestimated.

By using the additivity model, we obtained the NLO susceptibilities of a urea crystal,  $d_{XYZ}$ ,

$$d_{XYZ} = N(\beta_{yyz} - \beta_{xxz})$$

where  $N$  is the density of the unit cell of a urea crystal,  $6.57 \times 10^{21} \text{ cm}^{-3}$ . The theoretical  $d_{XYZ}$  values are  $-3.9 \times 10^{-9}$  esu at the HF level,  $-5.2 \times 10^{-9}$  esu at the MP2 level, and  $-5.19 \times 10^{-9}$  esu at the CCD level. The experimental  $d_{XYZ}$  value measured by Halbout et al. is  $3.4 \times 10^{-9}$  esu.<sup>20</sup> The difference in sign between the measurement and calculation comes from an opposite choice of the  $z$ -axis. The calculated values at all computational levels are overestimated. The deviations between the calculated results and measured value is not significant, but it seems that  $d_{XYZ}$  at HF level is closer to the measurement than that at CCD level, which is completely unreasonable due to the lack of consideration of intermolecular hydrogen bond interactions.

**A.3. TDDFT Results.** Table 1 also lists the TDDFT static results of  $\alpha$  and  $\beta$  values at the GGA/LB94/VI computational level. It is surprising to see that the TDDFT results are very different from the ab initio MP2 results. The  $\alpha$  values at the GGA/LB94/VI level increase within 17% percent over the corresponding MP2 values, while the  $\beta$  values are greatly different; e.g.,  $\beta_{xxz}$  is two-thirds in magnitude of the MP2 result and  $\beta_{yyz}$  is about one-third of that from the MP2 calculation, while  $\beta_{zzz}$  is about one times larger than that of MP2. It is seems that even to a small molecule in the gas phase such as a urea monomer, TDDFT results have a large discrepancy compared to the conventional ab initio/MP2(CCD) results, particularly for hyperpolarizability. Further DFT studies with an improved computational scheme are expected.<sup>21,22</sup> By using the additivity

model, TDDFT results yielded the  $d_{XYZ}$  value of  $-2.4 \times 10^{-9}$  esu, which underestimates the measurement.

**B. Urea Supramolecular Clusters and Hydrogen Bond Effects.** In this subsection, we turn to the supramolecular urea clusters from a dimer, trimers (linear and transverse configurations) and pentamers (two kinds of configuration) to a septimer. The septimer cluster has the nearest-neighbor configuration, i.e. a central urea molecule with six analogue urea molecules around it, just like is the case in the real crystalline structure. The supramolecular model is an effective way to account for intermolecular interactions. The supramolecular results are then compared to those derived from the additivity model to analyze the deviation of the additivity model and hydrogen bond effects.

In Table 2 we list the numerical results of the static  $\alpha$  and  $\beta$  values at HF/6-31++G(d, p) with the percentage deviations from the additivity rule. In Table 3 the MP2 numerical results of the static  $\alpha$  and  $\beta$  values at the 6-31++G(d, p) level with the percentage deviations from the additivity model are listed.

**B.1. HF/6-31++G(d, p) Results Up to a Septimer.** The calculated  $\alpha$  values are close to those derived from the additivity model. The largest deviation percentage is only 12% ( $\alpha_{zz}$  of linear trimer), and the deviation percentages of the  $\alpha$  components of the nearest-neighbor configuration, the septimer cluster, are all less than 5%. The results show that the average values of  $\alpha$  ( $\alpha_{av}$ ) at HF level follow the additivity model to within a few percent. The  $\beta$  values behave in similar manner. Except for the  $\beta_{yyz}$  component of the linear trimer (18%), all the deviation percentages are below 15%. The quantities of  $\beta_{yyz} - \beta_{xxz}$ , which relate to the evaluations of  $\chi^{(2)}$  values, perfectly fit to the additivity model from the transverse trimer to septimer (within 7%). The results indicate that when  $\alpha$  and  $\beta$  values of the urea clusters are evaluated at the HF level, the additivity model works well and the effects of hydrogen bonds on  $\beta$  values are not serious. Our HF results are close to those of Perez and Dupuis though they only computed urea clusters up to the trimers. However we did not take electron correlation effects into account. As mentioned above, the MP2 calculation might break the additivity rule and bring nonlinearity into the matter.

**B.2. MP2/6-31++(d, p) Results Up to a Pentamer.** We found in Table 3 that  $\alpha$  components of various cluster configurations at MP2 level fit the additivity relationship to within 15%. The largest deviation percentage of  $\alpha_{av}$  is as small as 5%. Linear polarizabilities are mainly due to intramolecular chemical bonds and composing elements rather than intermolecular interactions. According to this,  $\chi^{(1)}$  of the urea crystal can be perfectly estimated by the oriented-gas model in terms of molecular  $\alpha$  values without introducing the local factor, which is conventionally adopted to approximately describe the intermolecular actions. From  $\chi^{(1)}$ , one could estimate the linear optical properties such as the refraction index, which are the key parameters in the Lorentz–Lorenz approximation of the local factor that is widely used in the oriented-gas model for

**TABLE 2: Ab Initio HF/6-31++G(d, p)/F-F Results of the Polarizabilities and the First Hyperpolarizabilities (au) of the Urea Clusters in Different Configurations (1 for Monomer; 2 for Linear Dimer; 3 for Linear Trimer; 4 for Transverse Trimer; 5 for Pentamer I; 6 for Pentamer II; 7 for Septimer Configuration) with Percent Deviations from Additivity Model in Parentheses**

	1	2	3	4	5	6	7
$\alpha_{xx}$	20.8	40.5 (−3)	60.1 (−4)	88.5 (+9)	132.0 (+9)	148.4 (+1)	188.5 (+3)
$\alpha_{yy}$	30.0	58.7 (−2)	87.5 (−3)	70.3 (−2)	125.5 (−5)	122.2 (+7)	181.2 (+4)
$\alpha_{zz}$	33.2	72.5 (+8)	113.2 (+12)	95.8 (−4)	176.8 (+6)	154.7 (−7)	236.7 (+2)
$\alpha_{av}$	28.0	57.2 (+2)	86.9 (+3)	84.9 (+1)	144.8 (+3)	141.8 (+1)	202.1 (+3)
$\beta_{xxz}$	16.3	30.9 (−6)	44.5 (−9)	126.1 (+3)	165.3 (+6)	212.9 (−7)	232.9 (−12)
$\beta_{yyz}$	−52.9	−123.2 (+14)	−195.6 (+18)	−81.4 (5)	−206.3 (+7)	−120.1 (+2)	−249.5 (+10)
$\beta_{zzz}$	61.6	132.6 (+7)	195.1 (+5)	60.9 (−1)	69.8 (+12)	−178.0 (−4)	−65.6 (+6)
$\beta_{yyz} - \beta_{xxz}$	−69.2	−154.1 (+10)	−240.1 (+13)	−207.5 (0)	−371.6 (+7)	−333.0 (−4)	−482.4 (0)



**TABLE 3: Ab Initio MP2/6-31++G(d, p)/F-F Results of the Polarizabilities and the First Hyperpolarizabilities (au) of the Urea Clusters in Different Configurations (1 for Monomer; 2 for Linear Dimer; 3 for Linear Trimer; 4 for Transverse Trimer; 5 for Pentamer I Configuration) with Percent Deviations from Additivity Model in Parentheses**

	1	2	3	4	5
$\alpha_{xx}$	23.4	45.6 (−1)	67.5 (−4)	102.2 (+10)	151.8 (+2)
$\alpha_{yy}$	34.1	66.9 (−2)	99.6 (−3)	79.7 (−2)	142.1 (+3)
$\alpha_{zz}$	37.7	84.1 (+10)	132.3 (+15)	108.8 (−4)	204.6 (+8)
$\alpha_{av}$	31.7	65.5 (+3)	99.8 (+5)	96.9 (+2)	166.2 (+5)
$\beta_{xxz}$	30.0	57.8 (−4)	83.2 (−8)	160.2 (+5)	232.8 (+9)
$\beta_{yyz}$	−61.4	−154.8 (+21)	−250.6 (+26)	−119.1 (−2)	−279.4 (+13)
$\beta_{zzz}$	55.2	118.2 (+7)	164.1 (−1)	−54.5 (1)	53.0 (−4)
$\beta_{yyz} - \beta_{xxz}$	91.4	−212.6 (+14)	−333.8 (+18)	−279.3 (+2)	−512.2 (+11)

the evaluation of NLO susceptibilities. Thus, the accuracy of the estimation of NLO coefficients could be enhanced by accurately calculating linear polarizabilities at the molecular level. The calculated linear polarizabilities were used to obtain the dielectric constant of urea crystal. The calculated value in terms of  $\alpha$  values of the monomer at the MP2 level is 3.1, which agrees with the measured dynamic value of 3.5.<sup>23</sup>

The conditions are different from those for  $\beta$  values. We found the deviation percentages of 21% ( $\beta_{yyz}$  of dimer) and 26% ( $\beta_{yyz}$  of linear trimer) as listed in Table 3. And the deviation percentages of  $\beta_{yyz} - \beta_{xxz}$  quantities are around 15% for dimer, linear trimer, and pentamer clusters. The effect of weak intermolecular hydrogen bonds on the  $\beta$  values is significant when the electron correlation computation is performed, the MP2 scheme in this case. The deviation percentages of  $\beta_{yyz} - \beta_{xxz}$  quantities are positive without exception indicating that the hydrogen bonds, in the urea case, would enhance the magnitude of the  $\beta_{yyz} - \beta_{xxz}$  quantities. In other word, the  $\chi^{(2)}$  value of the urea crystal would be underestimated without considering electron correlation effects. We have to say that the hydrogen bond interactions play a role in the NLO response and break the additivity relationship in the urea case. The NLO property is not only originated from the constituent individual molecule but also is influenced by the intermolecular interactions.

#### IV. Concluding Remarks

We use high-level ab initio method to calculate static polarizabilities and hyperpolarizabilities of urea molecular clusters at both HF and MP2 levels to justify the validity of the additivity relationship. The results show that the influence of intermolecular interactions on the linear polarizability is very small. Both the calculations at the HF and MP2 levels led to the same conclusion. Linear polarizability fits well to the additivity model, and the influence of intermolecular hydrogen bonds on the superposition of linear polarizability is within 5% in the urea case.

The results show that, at the HF level, the effect of hydrogen bonds on  $\beta$  calculations is underestimated. Only in a computation using the electron correlation approach, the MP2 method in our case, could the intermolecular hydrogen bond influences be described. Similar to the report of Hamada, the intermolecular interactions would enhance the estimated macroscopic susceptibility compared to that from the additivity rule. In urea case, the  $\chi^{(2)}$  value would be underestimated by about 15% without considering electron correlation effects, based on our MP2 calculations. And roughly speaking, this is the quantity of percentage that hydrogen bond interactions would affect the NLO coefficients of a urea crystal.

In summary, intermolecular actions, the hydrogen bonds in the urea case, distinctly affect the  $\beta$  values and  $\chi^{(2)}$  values, which

results in a significant deviation from the additivity relationship. Therefore, the oriented-gas model meets a challenge in  $\chi^{(2)}$  evaluation even for molecular crystals.

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