Ab Initio Study of the Interaction Hyperpolarizabilities of HCN−HF and HNC−HF Complexes

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The effects of the intermolecular interaction on dipole moment (μ), the mean (α) and anisotropy ($\Delta\alpha$) of the polarizability, and the first and second hyperpolarizabilities (β and γ, respectively) of HCN−HF and HNC−HF complexes have been calculated in finite-field approach. The augmented correlation-consistent basis sets x-aug-cc-pVXZ (x = s, d, t; X = D, T, Q) are employed to study the effects of the basis sets. Using the d-aug-cc-pVTZ basis set, we calculated the electric properties at the coupled-cluster theory with single and double substitutions and perturbatively linked triple excitations, CCSD(T) level. The electron correlation effects for those electric properties are discussed. The value of each electric property calculated for HCN−HF is less than that for HNC−HF. The $\mu = 2.2918$ au, $\alpha = 23.186$ au, $\Delta\alpha = 14.393$ au, $\beta = -6.03$ au, and $\gamma = 2553.4$ au for HCN−HF; $\mu = 2.3338$ au, $\alpha = 24.383$ au, $\Delta\alpha = 14.875$ au, $\beta = 7.60$ au, and $\gamma = 3049.3$ au for HNC−HF. The electric properties coming from the interaction parts are as follows: $\mu_{\text{int}} = 0.3908$ au (17.1%), $\alpha_{\text{int}} = 0.181$ au (0.8%), $\Delta\alpha_{\text{int}} = 4.300$ au (29.9%), $\beta_{\text{int}} = 6.02$ au (−99.8%), and $\gamma_{\text{int}} = -492.0$ au (−19.3%) for HCN−HF; $\mu_{\text{int}} = 0.4080$ au (17.5%), $\alpha_{\text{int}} = -0.084$ au (0.3%), $\Delta\alpha_{\text{int}} = 5.041$ au (33.9%), $\beta_{\text{int}} = -7.20$ au (−94.7%), and $\gamma_{\text{int}} = -931.7$ au(−30.6%) for HNC−HF. The estimated electron correlation corrections are $\beta_{\text{corr}} = 6.59$ au and $\gamma_{\text{corr}} = 549.2$ au for HCN−HF and $\beta_{\text{corr}} = -9.49$ au and $\gamma_{\text{corr}} = 1056.5$ au for HNC−HF.

Introduction

The theory of electric hyperpolarizability is currently of great interest[1−3] because it is relevant to the interpretation and description of nonlinear optical phenomena. Considerable progress has been achieved toward understanding the nature of nonlinear optical phenomenon, and ab initio theory has played a significant role in this progress. Ab initio calculations on the first or second hyperpolarizabilities of many individual molecules have been reported.[3−9] With the improvement of the experimental and theoretical techniques, the interest in the interaction hyperpolarizabilities has increased in the past few years.[10−22]

Recently, the research on intermolecular hyperpolarizability has gained attention widely. The studies of the interaction hyperpolarizability of some small van der Waals clusters have already been carried out. The clusters involve the following: He_2, He_3, and Ne_2;[13] Ar_2 and He_2;[14−16] $(H_2O)_2$;[17] H_2−H_2, Ne−HF, Ne−FH, He_2, Ar_2, and Kr_2;[18] Ar−HF.[22] The researched systems are dimers containing inert gases and saturated molecules. For the system with π-bond, it is less reported in the interaction hyperpolarizability by high-level ab initio calculations. Because it has been reported that the π-bond is one of the factors important for influencing nonlinear optical properties of organic molecules,[23] the interaction hyperpolarizability for the system with π-bond should be a meaningful project.

The hydrogen-bonded complex HCN−HF has been extensively studied by experimental[24−31] and theoretical methods.[32−43] This complex is linear with the HF molecule behaving as a proton donor and the HCN molecule as the proton acceptor;[30,33,35,36] in this complex, HF lies directly along the direction of the N lone pair.

Recently, increasing attention has been directed at the complexes that involve the participation of the carbon in hydrogen bonds.[44,45] The bonds in which the carbon acts as the hydrogen acceptor are usually classified as “unconventional”. A recent theoretical study focused on the complexes of HCN and the other isomer of HCN, hydrogen isocyanide (HNC), in which the C atom acts as a proton acceptor.[45] Hydrogen isocyanide has been observed in low-temperature matrixes[46] and also in the gas phase.[47]

In this paper, the electric hyperpolarizabilities of HCN−HF and HNC−HF have been calculated with the augmented correlation-consistent basis sets in finite-field approach. Incidentally, the lower-order quantities (dipole moment and polarizability) should be mentioned. In addition, the effects of the intermolecular interaction on the electric properties of HCN−HF and HNC−HF are calculated with the counterpoise correction.

Theory and Computational Strategy

In the presence of an applied electric field, the energy of a system is a function of the field strength. Hyperpolarizabilities are defined as the coefficients in the Taylor series expansion of the energy in the external electric field.[48] When the external electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu_i F_i - \frac{1}{2}\alpha_{ij} F_i F_j - \frac{1}{6}\beta_{ijk} F_i F_j F_k - \frac{1}{24}\gamma_{ijkl} F_i F_j F_k F_l + \cdots \quad (1)$$

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where μ_i, α_{ij}, β_{ijk}, and γ_{ijkl} are the components of dipole moment, polarizability, the first hyperpolarizability, and the second hyperpolarizability, respectively. For a system of linear (C_∞) symmetry, the static electric properties (μ, α, β, and γ) may be specified by their μ_z, α_{xx}, α_{zz}, β_{xxz}, β_{zzz}, γ_{xxxx}, γ_{zzzz}, and γ_{xxzz} components.

In this paper, the components of the electric properties (μ, α, β, and γ) are calculated in a finite-field approach. A detailed presentation of the finite-field approach may be found elsewhere.[49,50] Here, the following notations will be used:

$$D(0,0,F_z) = E(0,0,-F_z) - E(0,0,F_z)$$

$$S(F_x,0,0) = 2(E(F_x,0,0) - E^0)$$

$$S(0,0,F_z) = E(0,0,-F_z) + E(0,0,F_z) - 2E^0$$

$$C(F_x,0,F_z) = E(F_x,0,F_z) - E(F_x,0,0) - F(0,0,F_z) + E^0$$

The independent components are then computed as

$$\mu_z = [\sigma^3 D(0,0,F_z) - D(0,0,\sigma F_z)]/[2(\sigma^3 - \sigma)F_z]$$

$$\alpha_{xx} = [S(\sigma F_x,0,0) - \sigma^4 S(F_x,0,0)]/[(\sigma^4 - \sigma^2)F_x{}^2]$$

$$\alpha_{zz} = [S(0,0,\sigma F_z) - \sigma^4 S(0,0,\sigma F_z)]/[(\sigma^4 - \sigma^2)F_z{}^2]$$

$$\beta_{xxz} = [C(-F_x,0,-\sigma F_z) - C(F_x,0,\sigma F_z)]/(F_x{}^2 \sigma F_z)$$

$$\beta_{zzz} = \{3[D(0,0,\sigma F_z) - \sigma D(0,0,F_z)]\}/[(\sigma^3 - \sigma)F_z{}^3]$$

$$\gamma_{xxxx} = \{12[\sigma^2 S(F_x,0,0) - S(\sigma F_x,0,0)]\}/[(\sigma^4 - \sigma^2)F_x{}^4]$$

$$\gamma_{zzzz} = \{12[\sigma^2 S(0,0,F_z) - S(0,0,\sigma F_z)]\}/[(\sigma^4 - \sigma^2)F_z{}^4]$$

$$\gamma_{xxzz} = \{-2[C(-F_x,0,-\sigma F_z) + C(F_x,0,\sigma F_z)]\}/(\sigma^2 F_x{}^2 F_z{}^2)$$

The strength of the applied electric field used in this investigation is $F_x = F_y = F_z = 0.009$ au, and the parameter σ is $^4/_3$.

In addition to the preceding components, we also compute the mean and the anisotropy of the polarizability and the mean first and second hyperpolarizabilities defined as

$$\alpha = (2\alpha_{xx} + \alpha_{zz})/3 \tag{2}$$

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx} \tag{3}$$

$$\beta = {}^3/_5(\beta_{zzz} + 2\beta_{xxz}) \tag{4}$$

$$\gamma = (8\gamma_{xxxx} + 3\gamma_{zzzz} + 12\gamma_{xxzz})/15 \tag{5}$$

In this investigation, we have employed the augmented correlation-consistent basis sets [x-aug-cc-pVXZ (x = s, d, t; X = D, T, Q)] developed by Dunning and co-workers.[51-55] All properties are computed by the coupled-cluster techniques, CCSD(T) method.

The electron correlation correction for the electric property, P, is defined as

$$P_{\text{corr}} = P_{\text{CCSD(T)}} - P_{\text{HF}} \tag{6}$$

where $P_{\text{CCSD(T)}}$ is the property calculated by CCSD(T)/d-aug-cc-pVTZ and P_{HF} is the value by HF/d-aug-cc-pVTZ method.

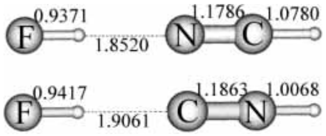

Figure 1. Geometry structures of HCN−HF and HNC−HF complexes.

TABLE 1: The Electric Properties (au) of HCN−HF with Nine Kinds of Basis Sets at the MP2 Level of Theory

basis set	μ	α	$\Delta\alpha$	β	γ
aug-cc-pVDZ	2.2943	22.074	14.914	−6.16	1687.6
d-aug-cc-pVDZ	2.2921	23.020	13.830	0.62	2299.6
t-aug-cc-pVDZ	2.2922	23.030	13.807	0.60	2389.1
aug-cc-pVTZ	2.2978	22.684	14.136	−5.01	1997.0
d-aug-cc-pVTZ	2.2967	23.011	13.765	−0.77	2446.5
t-aug-cc-pVTZ	2.2964	23.016	13.767	−1.12	2539.6
aug-cc-pVQZ	2.3012	22.838	13.883	−2.78	2178.1
d-aug-cc-pVQZ	2.3014	22.947	13.752	−0.66	2445.3
t-aug-cc-pVQZ	2.3013	22.946	13.751	−0.63	2654.3

The counterpoise (CP) correction[56] is employed in the computation of the interaction static electric properties. Thus,

$$P_{\text{int}} = P(\text{A}-\text{B}) - P(\text{A}-\text{X}) - P(\text{X}-\text{B}) \tag{7}$$

P(A−B) is the property of the complex A−B. P(A−X) is the calculated value of property P for subsystem A in the presence of the ghost orbitals of subsystem B, and P(X−B) is the calculated value of property P for subsystem B in the presence of the ghost orbitals of subsystem A.

The optimized structures of the HCN−HF and the HNC−HF have been obtained by the MP2/aug-cc-pVDZ method. The structures and related geometrical parameters are shown in Figure 1. All calculations were performed with the Gaussian 98 program package.[57]

Results and Discussion

1. Electron Properties. The electron properties are calculated with nine kinds of augmented correlation-consistent basis sets x-aug-cc-pVXZ (x = s, d, t; X = D, T, Q) at MP2 level for HCN−HF complex to study the basis set effect and choose the suitable basis set. The calculated results are shown in Table 1. In Table 1, the MP2 results of μ are stable, and the smallest value (d-aug-cc-pVDZ, 2.2921 au) is only 0.4% lower than the largest value (d-aug-cc-pVQZ, 2.3014 au). Figures 2 and 3 depict the trends in α and $\Delta\alpha$ for the two sets of basis set (XZ and x-aug) dependencies. The XZ dependence of α and $\Delta\alpha$ varies significantly with the number of diffuse functions. The aug-cc-pVXZ series sharply increases for α and sharply decreases for $\Delta\alpha$, and the d-aug-cc-pVXZ, t-aug-cc-pVXZ series of α and $\Delta\alpha$ slightly change and show obvious convergence. This indicates that the *f* and *g* functions have rather small effects in the calculations on the polarizabilities of HCN−HF if two or more diffuse functions are included in the set. The relative importance of diffuse functions for α and $\Delta\alpha$ can be seen form the x-aug dependence, Figures 2b and 3b. The effects decrease with the increase of the basis set quality. For the DZ and TZ series, at least two diffuse functions are necessary for the accurate determinations of α and $\Delta\alpha$. For the QZ series, α increases only 0.5% and $\Delta\alpha$ decreases only 0.9% from aug-cc-pVQZ to d-aug-cc-pVQZ.

The XZ and x-aug dependencies of the first hyperpolarizability (β) are shown in Figure 4a,b. For the aug-cc-pVXZ series, the β value sharply increases with the increase of the basis set. For the d-aug-cc-pVXZ series, the value of β decreases 1.39 au from d-aug-cc-pVDZ to d-aug-cc-pVTZ and increases 0.11 au

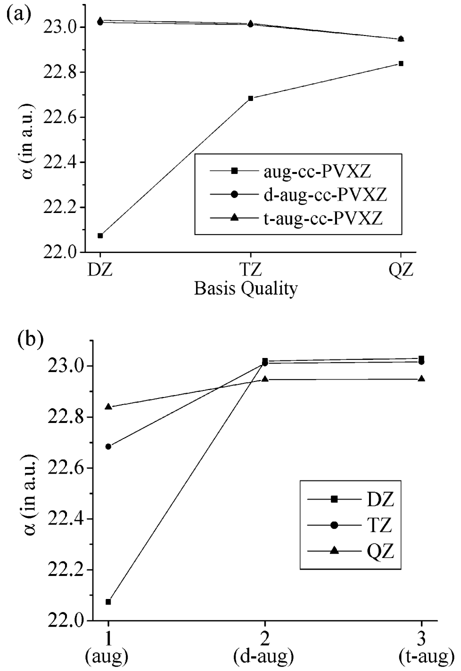

Figure 2. Behavior of the mean polarizability of HCN−HF at MP2 level.

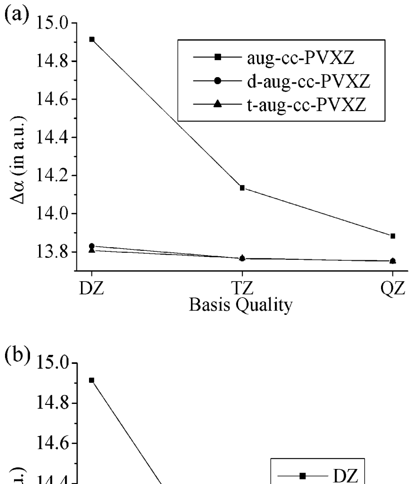

Figure 3. Behavior of the anisotropy of the polarizability of HCN−HF at MP2 level.

from d-aug-cc-pVTZ to d-aug-cc-pVQZ. For the t-aug-cc-pVXZ series, the value of β decreases 1.72 au from t-aug-cc-pVDZ to t-aug-cc-pVTZ and then increases 0.49 au from t-aug-cc-pVTZ to t-aug-cc-pVQZ.

The XZ and x-aug dependencies of the second hyperpolarizability (γ) are shown in Figure 5a,b. For the aug-cc-pVXZ series, the γ value sharply increases and does not show convergence. The d-aug-cc-pVXZ and t-aug-cc-pVXZ series appear to converge regularly. For the d-aug-cc-pVXZ series, the γ value increases 146.9 au from d-aug-cc-pVDZ to d-aug-cc-pVTZ and then decreases only 1.2 au (0.05%) from d-aug-cc-pVTZ to d-aug-cc-pVQZ. For the t-aug-cc-pVXZ series, the γ value increases 150.5 au from t-aug-cc-pVDZ to t-aug-cc-pVTZ and then increases 114.7 au from t-aug-cc-pVTZ to t-aug-cc-pVQZ.

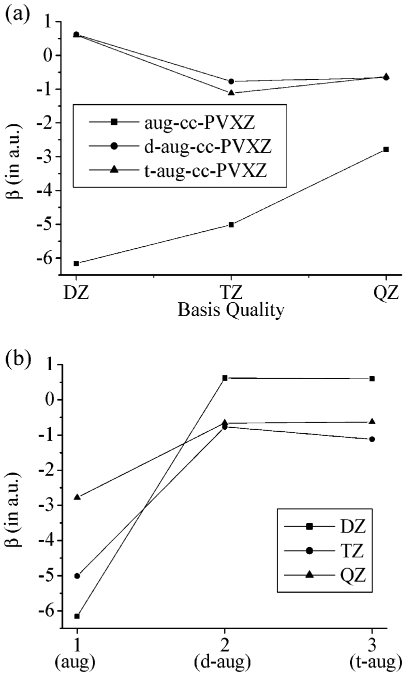

Figure 4. Behavior of the first hyperpolarizability of HCN−HF at MP2 level.

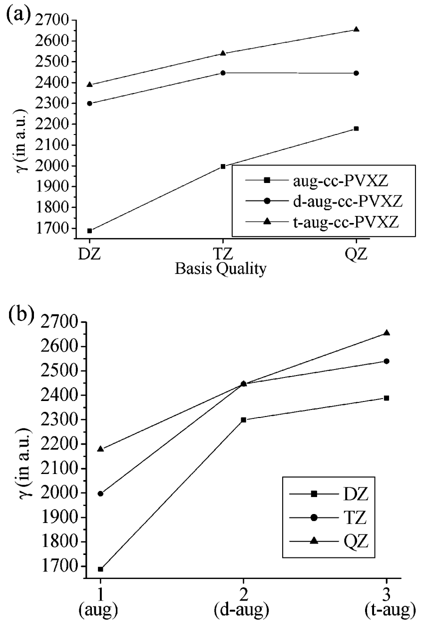

Figure 5. Behavior of the second hyperpolarizability of HCN−HF at MP2 level.

For the x-aug dependence of γ, the DZ series does not show convergence, while the TZ and QZ series show obvious convergence with the increasing number of the diffuse functions. For example, the γ value increases 449.5 au (22.5%) from aug-cc-pVTZ to d-aug-cc-pVTZ and increases 93.1 au (3.8%) from d-aug-cc-pVTZ to t-aug-cc-pVTZ.

As above, the dependencies of the hyperpolarizabilities (β, γ) on the basis set show that the d-aug-cc-pVTZ is the suitable basis set.

The electric properties of the HCN−HF and HNC−HF calculated with d-aug-cc-pVTZ at six levels of theory [HF, MP2, MP3, MP4, CCSD, and CCSD(T)] are given in detail in Table

TABLE 2: The Electric Properties (au) of HCN−HF and HNC−HF with the d-aug-cc-pVTZ Basis Set

	HCN−HF					HNC−HF				
level of theory	μ	α	$\Delta\alpha$	β	γ	μ	α	$\Delta\alpha$	β	γ
HF	2.4669	22.403	14.185	−12.62	2004.2	2.2566	22.677	13.352	17.09	1992.8
MP2	2.2967	23.011	13.765	−0.77	2446.5	2.4103	24.350	14.442	8.19	2845.9
MP3	2.3273	22.727	14.061	−3.61	2194.6	2.3255	23.746	14.315	11.91	2447.8
MP4(SDTQ)	2.2815	23.371	14.511	−10.01	2550.4	2.3543	24.367	14.535	9.20	2996.6
CCSD	2.3130	22.844	14.178	−3.96	2374.7	2.3255	24.039	14.713	9.02	2759.4
CCSD(T)	2.2918	23.186	14.393	−6.03	2553.4	2.3338	24.383	14.875	7.60	3049.3

TABLE 3: The Interaction Electric Properties (au) of HCN−HF and HNC−HF with the d-aug-cc-pVTZ Basis Set

	HCN−HF					HNC−HF				
level of theory	μ_{int}	α_{int}	$\Delta\alpha_{\text{int}}$	β_{int}	γ_{int}	μ_{int}	α_{int}	$\Delta\alpha_{\text{int}}$	β_{int}	γ_{int}
HF	0.3866	0.043	3.609	2.24	−414.4	0.3749	−0.160	4.113	−5.61	−609.4
MP2	0.3821	0.135	4.118	5.76	−421.6	0.4067	−0.181	4.907	−9.08	−927.9
MP3	0.3875	0.165	4.020	5.51	−368.0	0.3974	−0.101	4.747	−7.08	−811.0
MP4(SDTQ)	0.3897	0.178	4.259	5.07	−419.9	0.4051	−0.180	5.012	−7.46	−854.3
CCSD	0.3870	0.161	4.070	5.54	−428.6	0.4033	−0.096	4.865	−7.14	−881.3
CCSD(T)	0.3908	0.181	4.300	6.02	−492.0	0.4080	−0.084	5.041	−7.20	−931.7
η^a	17.1%	0.8%	29.9%	−99.8%	−19.3%	17.5%	0.3%	33.9%	−94.7%	−30.6%

[a] $\eta = P_{\text{int}}/P$.

2. For the HCN−HF complex, the CCSD(T) results are $\mu = 2.2918$ au, $\alpha = 23.186$ au, $\Delta\alpha = 14.393$ au, $\beta = -6.03$ au, and $\gamma = 2553.4$ au and the MP4 results are $\mu = 2.2815$ au, $\alpha = 23.371$ au, $\Delta\alpha = 14.511$ au, $\beta = -10.01$ au, and $\gamma = 2550.4$ au. For HNC−HF complex, the CCSD(T) results are $\mu = 2.3338$ au, $\alpha = 24.383$ au, $\Delta\alpha = 14.875$ au, $\beta = 7.60$ au, and $\gamma = 3049.3$ au and the MP4 results are $\mu = 2.3543$ au, $\alpha = 24.367$ au, $\Delta\alpha = 14.535$ au, $\beta = 9.20$ au, and $\gamma = 2996.6$ au. Obviously, the MP4 results are quite close to the CCSD(T) results for the electric properties of the two complexes. The correspondence value of the HNC−HF is larger than that of the HCN−HF for each electric property.

2. Interaction Electric Properties. The interaction electric properties of HCN−HF and HNC−HF calculated with d-aug-cc-pVTZ at six levels of theory [HF, MP2, MP3, MP4, CCSD, and CCSD(T)] are listed in Table 3. The result obtained at MP2 level is quite close to the MP4 and CCSD(T) results for the two complexes. For HCN−HF, we obtained the following interaction electric properties (with their relative contributions): $\mu_{\text{int}} = 0.3908$ au (17.1%), $\alpha_{\text{int}} = 0.181$ au (0.8%), $\Delta\alpha_{\text{int}} = 4.300$ au (29.9%), $\beta_{\text{int}} = 6.02$ au (−99.8%), and $\gamma_{\text{int}} = -492.0$ au (−19.3%) at CCSD(T) level. For HNC−HF, $\mu_{\text{int}} = 0.4080$ au (17.5%), $\alpha_{\text{int}} = -0.084$ au (0.3%), $\Delta\alpha_{\text{int}} = 5.041$ au (33.9%), $\beta_{\text{int}} = -7.20$ au (−94.7%), and $\gamma_{\text{int}} = -931.7$ au (−30.6%) at CCSD(T) level. This shows that interaction electric properties from intermolecular interaction are large.

For the monomers HCN and HF, the reported electric properties are $\mu = 1.181$ au, $\alpha = 16.74$ au, $\Delta\alpha = 8.38$ au, and $\beta = -2.8$ au[58] for the HCN and $\mu = 0.708$ au,[59] $\alpha = 5.52$ au, $\Delta\alpha = 1.32$ au,[60] and $\beta = -7.6469$ au[61] for the HF. For the HF dimer, the values are $\mu = -1.3076$ au, $\alpha = 10.3449$ au, and $\beta = -3.7368$ au.[61] The β value for the dimer (HCN−HF or HF−HF) is less than the sum of two monomers in one dimer. For the saturated molecules HF dimer, the β value is about $^1/_4$ of the sum of two monomers. For the dimer HCN−HF containing π-bond, the β value is about $^3/_5$ of the sum of two monomers. Recent research on HCN−HCN shows that the β value is about 4 times of the sum of two monomers.[62] Here it primary shows that the π-bond plays an important role on the electric properties for intermolecular interaction systems.

3. Electron Correlation Effects. For HCN−HF and HNC−HF, the contributions of electron correlation effects on the electric properties are −7.1% and 3.4% for μ, 3.5% and 7.5% for α, 1.5% and 11.4% for $\Delta\alpha$, −52.2% and −55.5% for β, and 27.4% and 53.0% for γ, respectively (in Table 4). It is clear that the electron correlation contributions on β and γ are large.

TABLE 4: Electron Correlation Effects (au) for HCN−HF and HNC−HF

	electric properties		interaction electric properties	
	HCN−HF	HNC−HF	HCN−HF	HNC−HF
μ (au)	−0.1751	0.0772	0.0042	0.0331
η^a	−7.1%	3.4%	1.1%	8.8%
α (au)	0.783	1.706	0.138	0.076
η^a	3.5%	7.5%	320.9%	−47.5%
$\Delta\alpha$ (au)	0.208	1.523	0.691	0.928
η^a	1.5%	11.4%	19.1%	22.6%
β (au)	6.59	−9.49	3.78	−1.59
η^a	−52.2%	−55.5%	168.8%	28.3%
γ (au)	549.2	1056.5	−77.6	−322.3
η^a	27.4%	53.0%	18.7%	52.9%

[a] $\eta = P_{\text{corr}}/P_{\text{HF}}$.

For HCN−HF and HNC−HF, the contributions of electron correlation effects on the interaction electric properties amount to 1.1% and 8.8% for μ_{int}, 320.9% and −47.5% for α_{int}, 19.1% and 22.6% for $\Delta\alpha_{\text{int}}$, 168.8% and 28.3% for β_{int}, and 18.7% and 52.9% for γ_{int}, respectively (in Table 4.). The electron correlation contributions of α_{int} and β_{int} are large. It is concluded that the electron correlation contribution is important for the calculations of the electric properties and their interactions.

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