Theoretical Study of Hydrogen Bonding Interaction in Nitroxyl (HNO) Dimer: Interrelationship of the Two N−H···O Blue-Shifting Hydrogen Bonds

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The hydrogen bonding interactions of the HNO dimer have been investigated using ab initio molecular orbital and density functional theory (DFT) with the 6-311++G(2d,2p) basis set. The natural bond orbital (NBO) analysis and atom in molecules (AIM) theory were applied to understand the nature of the interactions. The interrelationship between one N−H···O hydrogen bond and the other N−H···O hydrogen bond has been established by performing partial optimizations. The dimer is stabilized by the N−H···O hydrogen bonding interactions,which lead to the contractions of N−H bonds as well as the characteristic blue-shifts of the stretching vibrational frequencies ν(N−H). The NBO analysis shows that both rehybridization and electron density redistribution contribute to the large blue-shifts of the N−H stretching frequencies. A quantitative correlations of the intermolecular distance H···O (r(H···O)) with the parameters: ρ at bond critical points (BCPs), s-characters of N atoms in N−H bonds, electron densities in the σ^*(N−H), the blue-shift degrees of ν(N−H) are presented. The relationship between the difference of ρ ($|\Delta\rho|$) for the one hydrogen bond compared with the other one and the difference of interaction energy (ΔE) are also illustrated. It indicates that for r(H···O) ranging from 2.05 to 2.3528 Å, with increasing r(H···O), there is the descending tendency for one ρ(H···O) and the ascending tendency for the other ρ(H···O). r(H···O) ranging from 2.3528 to 2.85 Å, there are descending tendencies for the two ρ(H···O) with increasing r(H···O). On the potential energy surface of the dimer, the smaller the difference between one ρ(H···O) and the other ρ(H···O) is, the more stable the structure is. As r(H···O) increases, the blue-shift degrees of ν(N−H) decrease. The cooperative descending tendencies in s-characters of two N atoms with increasing r(H···O) contribute to the decreases in blue-shift degrees of ν(N−H). Ranging from 2.05 to 2.55 Å, the increase of the electron density in one σ^*(N−H) with elongating r(H···O) weakens the blue-shift degrees of ν(N−H), simultaneously, the decrease of the electron density in the other σ^*(N−H) with elongating r(H···O) strengthens the blue-shift degrees of ν(N−H). Ranging from 2.55 to 2.85 Å, the cooperative ascending tendencies of the electron densities in two σ^*(N−H) with increasing r(H···O) contribute to the decreases in blue-shift degrees of ν(N−H).

1. Introduction

Hydrogen bond is an important type of noncovalent interaction that is present in many chemical and biological systems.[1] A sound knowledge of hydrogen bond is fundamental to understand chemical structures, enzyme catalysis, material properties, self-assembly phenomena, and functions of molecular and biological devices and machines. Therefore, considerable amount of experimental and theoretical researches has been conducted concerning the structural, spectroscopic and energetic issues of diverse hydrogen bonds.[2−8] Most hydrogen bonds are of the X−H···Y type, where X is an electronegative atom and Y is either an electronegative atom having one or more lone electron pairs or a region of excess electron density like an aromatic π-system.[9] Recently, a new type of intermolecular bond, termed blue-shifting hydrogen bond, which is accompanied by X−H bond contraction and a blue-shift of the X−H bond stretching frequency, continues to receive significant experimental and theoretical attention.[10−20] The blue-shifts of C−H bonds have been widely studied. The N atom is more electronegative than the C atom is and the N−H bond is a better proton donor than the C−H bond is. The phenomenon of N−H···Y blue-shifting H-bonds is very interesting. Both Hobza and Li et al. have predicted a blue-shifted or improper blue-shifting N−H···F H-bond existing in the NHF_2···HF complex at MP2/6-31G** and MP2/6-311+G** levels, respectively.[4,21] Unexpectedly, Lu and the co-workers have predicted a red-shift for the normal N−H···F H-bond in this complex at the B3LYP/6-31+G**, B3LYP/6-311+G**, and B3LYP/6-311++G (3df, 3pd) levels.[22] In a very recent theoretical investigation, red-shifts for the N−H vibrational frequencies in the $NHF_2\cdots(HF)_n$ and $NH_2F\cdots(HF)_n$ ($1 < n < 3$) complexes were obtained at the MP2/cc-pvdz level by Karpfen when N−H···F hydrogen bonds were formed.[23] To the best of our knowledge, the data on the large blue-shifts of N−H stretching vibrational frequencies upon the hydrogen bond formation is still limited.

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In the previous study, Peters has reported the hydrogen bonding interactions of the HNO dimer at MP2 employing 6-31+G** level, obtaining its optimized geometries and vibrational frequencies but did not pay much attention to the blue-shifts of N−H stretching vibrational frequencies, and did not provide the origin of the blue-shifts.[24] Performing further studies is necessary to confirm the blue-shifts of N−H stretching vibrational frequencies and obtain more data to explain the origin of these blue-shifts. Moreover, it is apparent that there are two hydrogen bonds of the HNO dimer. One hydrogen bond change has effect on the other one. The interrelationship between one hydrogen bond and the other one remains unanswered.

In the present work, we focus on the origin of the blue-shifting N−H···O hydrogen bonds and the interrelationship between one hydrogen bond and the other one. It is confirmed that the HNO dimer simultaneously exhibits two blue-shifts of N−H bonds using ab initio molecular orbital and density functional theory with the 6-311++G(2d,2p) basis set. AIM and NBO analysis are carried out to provide the origin of N−H blue-shifts. The interrelationship between one hydrogen bond and the other one is illustrated by establishing a quantitative correlations of the $r(\mathrm{H}\cdots\mathrm{O})$ with parameters: ρ at BCPs, s-characters of N atoms, electron densities in the $\sigma^*(\mathrm{N-H})$, the blue-shift degrees of $\nu(\mathrm{N-H})$, and the correlation of the difference of ρ ($|\Delta\rho|$) with the difference of interaction energy (ΔE).

2. Computational Details

The hydrogen bonding interactions of the HNO dimer were investigated using Becke's three parameter hybrid functional in conjunction with Lee, Yang, and Parr's correlation functional (B3LYP) and second-order Møller−Plesset perturbation (MP2) methods in conjunction with the 6-311++G(2d,2p) basis set. The effect of the counterpoise (CP) correction method, which was advocated by Hobza et al., on the BSSE in the calculations of geometric optimizations, vibrational frequencies, and interaction energies has been taken into account.[25,26] Furthermore, the interaction energies were estimated at G2MP2 level.

Both AIM and NBO analysis were performed at the MP2/6-311++G(2d,2p) level.[27,28] AIM theory of Bader,[27] was used to analyze the bonding characteristics, which is based on the topological analysis of the electron density and its Laplacian. The analysis went further with those obtained by means of NBO theory of Weihnhold and co-workers.[28] The partial optimized parameters were obtained at the MP2/6-311++G(2d,2p) level. All calculations were carried out using the Gaussian03 package.[29]

3. Results and Discussion

3.1. Geometries, Frequencies, and Interaction Energies. Peters found two stable structures of the HNO dimer at the MP2/6-31+G** level. They were five-membered and six-membered cyclic structures upon the hydrogen bond formation using the MP2/6-31+G** optimization.[24] However, in the present work, there is one imaginary vibrational frequency for the five-membered cyclic structure at the B3LYP level employing different basis sets and MP2 employing 6-311+G** and 6-311++G** basis sets; therefore, it will not be discussed hereafter. Geometric characteristics, vibrational frequencies, and interaction energies of the dimer are summarized in Table 1. The optimized structure of the dimer is depicted in Figure 1.

TABLE 1: Characteristics of HNO Dimer at the B3LYP and MP2 Levels Employing the 6-311++G(2d,2p) Basis Set

	B3LYP/6-311++G(2d,2p)	MP2/6-311++G(2d,2p)
$r(\mathrm{O4}\cdots\mathrm{H1})$/Å	2.3948	2.3528
$r^{\mathrm{CP}}(\mathrm{O4}\cdots\mathrm{H1})$/Å	2.4206	2.4226
$r(\mathrm{O3}\cdots\mathrm{H6})$/Å	2.3948	2.3528
$r^{\mathrm{CP}}(\mathrm{O3}\cdots\mathrm{H6})$/Å	2.4206	2.4226
$\Delta r(\mathrm{N2-H1})$/Å	−0.0051	−0.0041
$\Delta r^{\mathrm{CP}}(\mathrm{N2-H1})$/Å	−0.0050	−0.0040
$\Delta r(\mathrm{N5-H6})$/Å	−0.0051	−0.0041
$\Delta r^{\mathrm{CP}}(\mathrm{N5-H6})$/Å	−0.0050	−0.0040
$\Delta\nu_1$/cm^{-1}	+96	+86
$\Delta\nu_1{}^{\mathrm{CP}}$/cm^{-1}	+92	+81
$\Delta\nu_2$/cm^{-1}	+86	+78
$\Delta\nu_2{}^{\mathrm{CP}}$/cm^{-1}	+82	+75
ΔE^{std}/kcal mol^{-1}	−1.42	−2.25
ΔE^{CP}/kcal mol^{-1}	−1.15	−1.54

[a] Key: Δr, the differences of r(N−H) in the dimer compared with those in the monomer; $\Delta \mathrm{v}_1$, the differences of N1−H2, N5−H6 symmetric stretch in the dimer compared with those in the monomer; $\Delta \mathrm{v}_2$, the differences of N1−H2, N5−H6 asymmetric stretch in the dimer compared with those in the monomer.

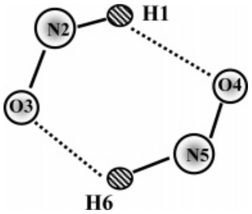

Figure 1. Optimized structure of the dimer at the MP2/6-311++G-(2d,2p) level.

According to Table 1, it becomes evident that there are contractions of N−H bonds compared with the HNO monomer, employing the standard and CP calculations.The contracting degrees of N−H bonds obtained by the DFT method are a little larger than those obtained by the MP2 method. The CP-corrected $r(\mathrm{H1}\cdots\mathrm{O4})$ and $r(\mathrm{H6}\cdots\mathrm{O3})$ bonds are a little longer than the uncorrected ones. As far as the H-bond type prediction is concerned, all results indicate that both N2−H1 and N5−H6 vibrational frequencies are blue-shifted in the dimer. Moreover, the blue-shift degrees of $\nu(\mathrm{N-H})$ obtained by standard calculations are a little larger than the CP-corrected ones. On the basis of these analyses, it can be confirmed that the dimer possesses two blue-shifts on hydrogen bond formations: N2−H1···O4 and N5−H6···O3. It should be pointed out that both N−H vibrational frequencies display very large blue-shifts (about 100 cm^{-1}).

With respect to the hydrogen bonding interaction, it is necessary to carry out the BSSE correction of the interaction energies. As shown in Table 1, the uncorrected interaction energies are −1.42 (B3LYP) and −2.25 kcal mol^{-1} (MP2) and the corrected ones are −1.15 (B3LYP) and −1.54 kcal mol^{-1} (MP2). The interaction energy obtained at the MP2/6-311++G-(2d,2p)-CP level is in reasonable agreement with that obtained at the G2MP2 level (−1.74 kcal mol^{-1}).

3.2. NBO Analysis. To get more information on the blue-shifts of N2−H1 and N5−H6 vibrational frequencies, NBO analysis has been carried out at the MP2/6-311++G(2d,2p) level. The corresponding results are listed in Table 2.

The importance of hyperconjugation and electron density transfer (EDT) from lone electron pairs of the Y atom to the X−H antibonding orbital in the X−H···Y system is well-documented.[28] In general, such interaction leads to an increase in population of X−H antibonding orbital. The increase of electron density in X−H antibonding orbital weakens the X−H bond, which leads to its elongation and constrains the blue -shift of the X−H stretching frequency. Hobza proposed that electron density redistribution is also related to the contraction of X−H bond. [10,30] Recently, it has been reported that the change of

TABLE 2: NBO Analysis of the HNO Monomer and HNO Dimer at the MP2/6-311++G(2d,2p) Level

	HNO monomer	HNO dimer
$E^{(2)}$ $n_1(O4) \rightarrow \sigma^*$ (N2−H1)/kcal mol^{-1}		0.53
$E^{(2)}$ $n_2(O4) \rightarrow \sigma^*$ (N2−H1)/kcal mol^{-1}		0.84
$E^{(2)}$ $n_1(O3) \rightarrow \sigma^*$ (N5−H6)/kcal mol^{-1}		0.53
$E^{(2)}$ $n_2(O3) \rightarrow \sigma^*$ (N5−H6)/kcal mol^{-1}		0.84
$E^{(2)}$ $n_2(O3) \rightarrow \sigma^*$ (N2−H1)/kcal mol^{-1}	17.59	15.19
$E^{(2)}$ $n_2(O4) \rightarrow \sigma^*$ (N5−H6)/kcal mol^{-1}	17.59	15.19
$E^{(2)}$ $n_1(N5) \rightarrow \sigma^*$ (N2−H1)/kcal mol^{-1}		0.06
$E^{(2)}$ $n_1(N2) \rightarrow \sigma^*$ (N5−H6)/kcal mol^{-1}		0.06
σ^* (N2−H1)/e	0.02852	0.02664
σ^* (N5−H6)/e	0.02852	0.02664
q(H1)/e	0.26371	0.29152
q(H6)/e	0.26371	0.29152
sp^n(N2−H1)	$sp^{3.98}$	$sp^{3.75}$
% s-char	19.98	20.95
sp^n(N5−H6)	$sp^{3.98}$	$sp^{3.75}$
% s-char	19.98	20.95

electron density in the σ^*(X−H), compared with monomer, is a combination of two effects for the Z (or Z−W)−X−H···Y(or Y−U) H-bond:[31] hyperconjugation (n(Y) or σ(Y−U) $\rightarrow \sigma^*$(X−H)) increasing electron density in the σ^*(X−H) while the decrease in the n(Z) or σ(Z−W) $\rightarrow \sigma^*$(X−H) interaction of the dimer due to the electron density redistribution decreases electron density in the σ^*(X−H). By examination of Table 2, the electron densities in both σ^*(N2−H1) and σ^*(N5−H6) of the dimer decrease, implying that the electron density redistribution exceeds hyperconjugation. The decreases of electron densities in the σ^*(N−H) strengthen the N2−H1 and N5−H6 bonds, which contribute to the blue-shifts of the corresponding stretching vibrational frequencies.

The chemical perspective has been suggested to explain "proper" and "improper hydrogen bonding": the hyperconjugation (n(Y) $\rightarrow \sigma^*$(X−H)) can be balanced by the increase in s-character and polarization of the X−H bond.[32] The authors have shown that the X−H bond strengthening effect is an increase in s-character of X hybrid orbital in the X−H bond, which is a direct consequence of Bent's rule. According to this rule, the atom tends to maximize the amount of s-character in hybrid orbital with the larger amount of p-character toward more electronegative substituents. As a result, a decrease in effective electronegativity of hydrogen in an X−H bond leads to an increase in the s-character of the X hybrid orbital and results in the corresponding X−H bond polarization's increasing. As listed in Table 2, the change in the electronic structure of the dimer is an increase of positive charge on H1 atom, which leads to the increase in the N2−H1 bond polarization. It results in a simultaneous increase in the s-character of the nitrogen hybrid orbital in the N2−H1 bond, which contributes to the contraction of the N2−H1 bond. Similarly, the variation in the electronic structure of the dimer is an increase of positive charge on the H6 atom, which results in an increase in the N5−H6 bond polarization. It leads to the increase in the s-character of the nitrogen hybrid orbital in the N5−H6 bond, which strengthens the N5−H6 bond.

On the basis of the analysis, for the dimer, the changes of electron density in the σ^*(X−H) and s-character of the X hybrid orbital in X−H bond compared with the monomers are crucial to the elongation and contraction of X−H bond. The decreases of the electron densities due to the electron density redistribution in the σ^*(N2−H1) and σ^*(N5−H6) and the increases in s-characters of N2 and N5 atoms strengthen the N2−H1 and N5−H6 bonds. Both contribute to the blue-shifts of N2−H1 and N5−H6 vibrational frequencies.

3.3. Interrelationship between One N—H···O Hydrogen Bond and the other N—H···O Hydrogen Bond. It is evident that there are two blue-shifting hydrogen bonds of the dimer: N2−H1···O4 and N5−H6···O3. One hydrogen bond change has an effect on the other one. The interrelationship between one N−H···O hydrogen bond and the other N−H···O hydrogen bond has been established by performing partial optimizations. It is analyzed by using relaxed H1···O4 distance scan where all geometric variables are allowed to optimize except for the H1···O4 distance, ranging from 2.05 to 2.85 Å. Quantitative correlations of intermolecular distance H1···O4 (*r*(H1···O4)) with the parameters ρ at BCPs, s-characters of N atoms, electron densities in the σ^*(N−H), and the blue-shift degrees of ν(N−H) are presented. On the potential energy surface, the characteristics of the symmetric structure are defined as r_0, ν_0, ρ_0, and ΔE_0, whereas others are defined as r_i, ν_i, ρ_i and ΔE_i. The relationship between the difference of $\rho(|\Delta\rho| = |\rho(\text{H1}\cdots\text{O4}) - \rho(\text{H6}\cdots\text{O3})|)$ and the difference of interaction energy ($\Delta E = \Delta E_i - \Delta E_0$) is illustrated.

3.3.1. AIM Analysis of the Interrelationship between One Hydrogen Bond and the Other One. According to the topological analysis of electron density in the theory of AIM, ρ is used to describe the strength of a bond. The $\nabla^2\rho$ is used to characterize the bond. Where $\nabla^2\rho < 0$, the bond is the covalent bond, as $\nabla^2\rho > 0$, it is the closed-shell interaction and belongs to the ionic bond, hydrogen bond or van der Waals interaction. For the symmetric structure, the $\nabla^2\rho_0$(O4···H1) and $\nabla^2\rho_0$(O3···H6) of the dimer obtained by performing AIM are 0.042 and 0.042 au, which indicate they are the closed-shell interactions. The corresponding ρ_0(O4···H1) and ρ_0(O3···H6) are 0.011 and 0.011 au, which are the largest among all the structures. Figure 2 illustrates the correlations of ρ(H1···O4) with *r*(H1···O4) (Figure 2(a)), of ρ(H6···O3) with *r*(H1···O4) (Figure 2(b)). ρ_0 and r_0 are denoted as dot points. Two different tendencies in the two correlations have been observed. Since the increase in distance (*r*(H1···O4)) results in reduced orbital overlap and the corresponding electron density (ρ(H1···O4)) decreases, ρ(H1···O4) decreases with increasing *r*(H1···O4) (Figure 2(a)). Whereas the correlation of ρ(H6···O3) with *r*(H1···O4) is different. There is the ascending tendency in ρ(H6···O3) with increasing *r*(H1···O4), ranging from 2.05 to 2.3528 Å inversely, ranging from 2.3528 to 2.85 Å, there is a descending tendency in ρ(H6···O3) with increasing *r*(H1···O4) (Figure 2(b)). In contrast, from 2.05 to 2.3528 Å, the less ρ(H1···O4) is, the more ρ(H6···O3) is. From 2.3528 to 2.85 Å, ρ(H1···O4) decreases with ρ(H6···O3) decreasing.

For the symmetric structure (r_0(H1···O4)), the difference of ρ $(|\Delta\rho| = |\rho_0(\text{H1}\cdots\text{O4}) - \rho_0(\text{H6}\cdots\text{O3})|)$ is zero. Except in the case of r_0(H1···O4), the symmetric structure was disturbed with the *r*(H1···O4) increasing. Figure 3 describes the correlation of the absolute value of $\Delta\rho$ with ΔE. $|\Delta\rho_0|$ and ΔE_0 are denoted as the dot point in Figure 3. From the figure, the less the absolute value of $\Delta\rho$ is, the less the ΔE is, which indicates the smaller the difference between ρ(H1···O4) and ρ(H6···O3) is, the more stable the structure is.

3.3.2. Correlations of the *r*(H1···O4) with s-Characters of N Atoms, Electron Densities in the σ^*(N—H), the Blue-Shift Degrees of ν(N—H). Figure 4 describes the correlation of the blue-shift degrees of ν(N−H) with *r*(H1···O4). r_0(H1···O4) with Δv_0 are denoted as the dot points. From 2.05 to 2.85 Å, all ν(N−H) values are blue-shifted relative to those in the monomer. It is evident that the blue-shift degrees of ν(N−H) decrease with increasing *r*(H1···O4).

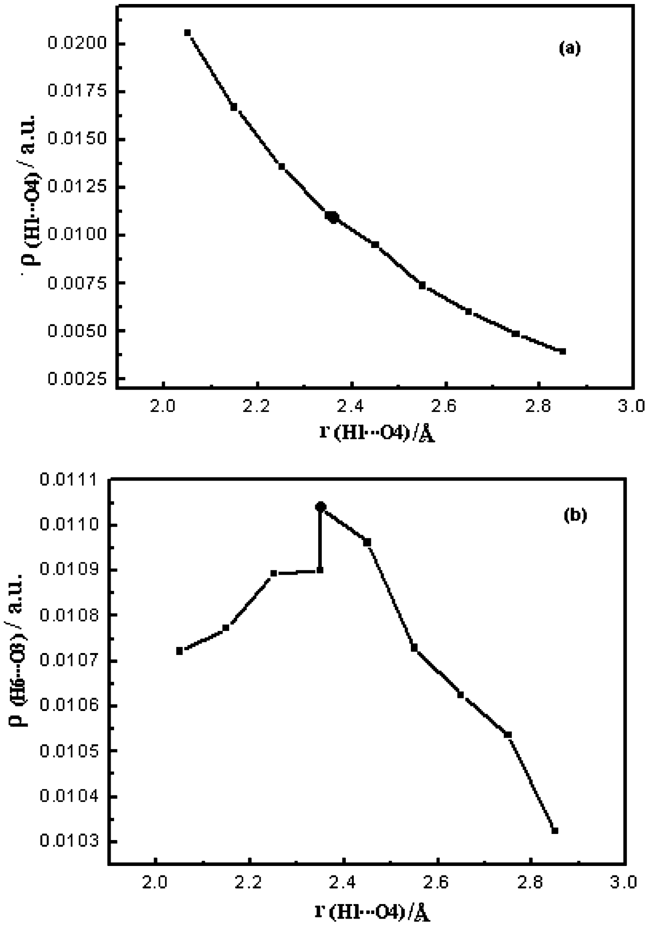

Figure 2. Correlations of *r*(H1···O4) with variations: (a) *ρ*(H1···O4); (b) *ρ*(H6···O3).

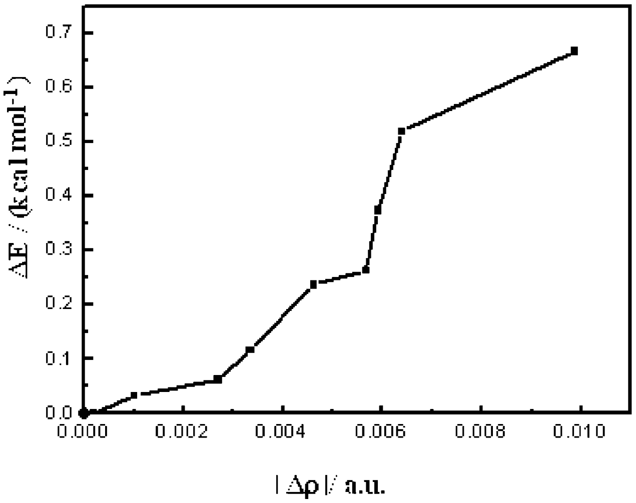

Figure 3. Correlation of the difference of interaction energy (Δ*E*) with the difference of *ρ* (|Δ*ρ*|).

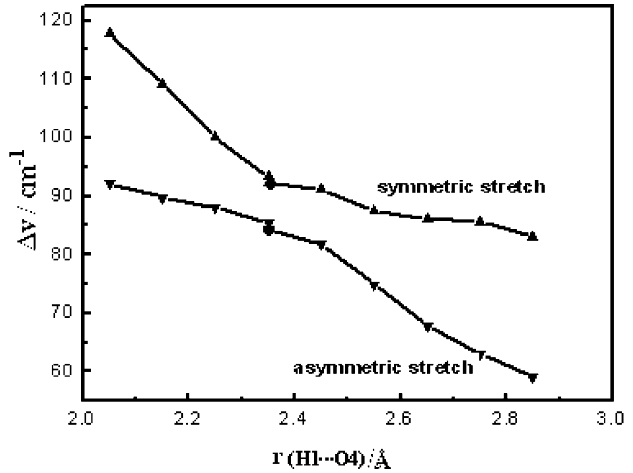

Figure 4. Correlation of the blue-shift degrees of *ν*(N−H) with *r*(H1···O4).

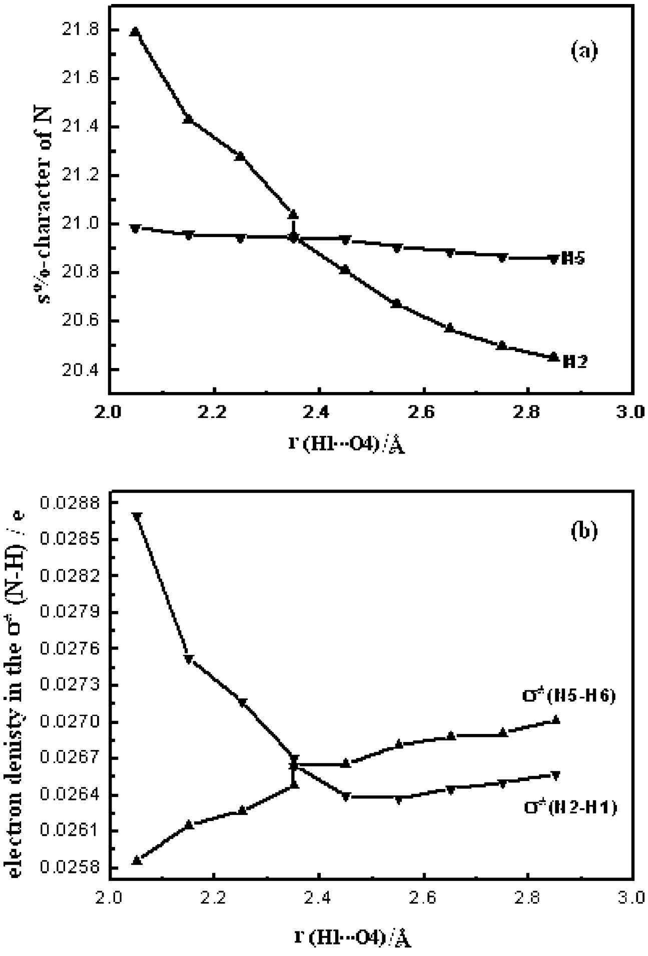

Figure 5. Correlations of *r*(H1···O4) with variations: (a) s-characters in N2 and N5; (b) the electron densities in the *σ**(N2−H1) and *σ**(N5−H6).

From NBO analysis, the blue-shift of *ν*(N−H) is related to the electron density in the *σ**(N−H) and s-character of N atom. The correlations of s-characters of N atoms with *r*(H1···O4), of the electron densities in the *σ**(N−H) with *r*(H1···O4) are illustrated in Figure 5. As depicted in Figure 5(a), the tendency in s-character of N2 as a function of *r*(H1···O4) corresponds with that of N5. The decrease in s-character of N2 is accompanied by a simultaneous decrease in s-character of N5 with elongating *r*(H1···O4), which weaken the N2−H1 and N5−H6 bond-shortening effects based on the Bent's rule and contribute to the decreases in the blue-shift degrees of *ν*(N−H).

Figure 5(b) depicts the correlations between the change of *r*(H1···O4)and the two variations: the electron densities in the *σ**(N2−H1) and *σ**(N5−H6). It is noted that there are different tendencies between the correlations of electron densities in the *σ**(N2−H1) with *r*(H1···O4), and electron densities in the *σ**(N5−H6) with *r*(H1···O4). As *r*(H1···O4) increases, the electron density in the *σ**(N5−H6) increases, which restrains the blue-shift degrees of ν(N−H). However, the electron density in the σ^*(N2−H1) decreases with increasing r(H1···O4) from 2.05 to 2.55 Å, which strengthens the blue-shift degrees of ν(N−H). From 2.55 to 2.85 Å, the electron density in the σ^*(N2−H1) increases accompanied by r(H1···O4) elongating, which constrains the blue-shift degrees of ν(N−H).

Summary

This work deals with the hydrogen bonding interactions of HNO dimer by ab initio and density functional theoretical methods employing the 6-311++G(2d,2p) basis set. The dimer exhibits simultaneously contractions of the N1−H2 and N5−H6 bonds and large blue-shifts (about 100 cm^{-1}) of ν(N−H). From the NBO analysis, electron density redistribution and rehybridization contribute to the blue-shifts of ν(N−H). The interrelationship between one hydrogen bond and the other one is analyzed. r(H1···O4) ranging from 2.05 to 2.3528 Å, ρ(H6···O3) increases with decreasing ρ(H1···O4); inversely, ρ(H6···O3) decreases with decreasing ρ(H1···O4) ranging from 2.3528 to 2.85 Å. The less the difference between ρ(H1···O4) and ρ(H6···O3) ($|\Delta\rho|$) is, the more stable the structure is. There are descending tendencies in the blue-shift degrees of ν(N−H) with increasing r(H1···O4). The cooperative descending tendencies in s-characters of N2 and N5 with increasing r(H1···O4) contribute to the decreases in blue-shift degrees of ν(N−H). Moreover, as r(H1···O4) elongates, the increase of the electron density in the σ^*(N5−H6) restrains the blue-shift degrees of ν(N−H). Ranging from 2.05 to 2.55 Å, the decrease of the electron density in the σ^*(N2−H1) with elongating r(H1···O4) strengthens the blue-shift degrees of ν(N−H). Ranging from 2.55 to 2.85 Å, the electron density in the σ^*(N2−H1) increases, accompanied by r(H1···O4) elongation, which constrains the blue-shift degrees of ν(N−H).

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