Complexes Pairing Hypohalous Acids with Nitrosyl Hydride. Blue Shift of a NH Bond That Is Uninvolved in a H-Bond

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Correlated calculations are used to analyze the interaction between nitrosyl hydride (HNO) and hypohalous acids (HOF, HOCl, and HOBr). Two minima are located on the potential energy surface of each complex, in both of which HOX acts as proton donor. Donation to the N atom of HNO makes for a more strongly bound complex, as compared to the OH··O bond in the secondary minimum. Binding energies of the global minimum are about 22 kJ/mol, as compared to 18 kJ/mol for the secondary structure; there is little sensitivity to the identity of the halogen atom. Whereas the covalent OH bond of HOX stretches and shifts to the red upon complexation, the NH bond of HNO, whether involved in a H-bond or not, behaves in the opposite manner.

1. Introduction

Over the years, it had become conventional wisdom that the A−H covalent bond stretches, and its vibrational frequency shifts to the red and intensifies, when it participates in a A−H···B hydrogen bond.[1,2] The early appearances of opposite behavior[3−6] were dismissed as either misinterpretation of data or as evidence that there was no H-bond present. In the past decade or so, however, such “blue-shifting”, “improper”, or nonconventional H-bonds have been recognized as a real phenomenon, whose existence is not as rare as once believed.[7−10] The most common of these H-bonds seems to be associated with a CH donor, particularly when the C atom is sp^3-hybridized.[11−18] While first conjectured to represent an entirely new sort of molecular interaction, evidence has accumulated that these blue-shifting entities are indeed H-bonds, whose behavior in other respects mimics that of the more frequently observed red-shifting systems.[19−29]

Blue-shifting does not appear to be limited to CH donors. Despite the greater electronegativity of nitrogen, and its participation in mostly red-shifting H-bonds, a number of exceptions to this rule have been observed of late, wherein the NH··X H-bond shifts the NH stretching frequency to the blue. The HNO molecule is a principal example, forming a blue-shifting H-bond with such proton acceptors as HNO,[30] CH_3-CHO,[31] $HFSO_2$,[32] and even when interacting with the π-electron cloud of alkynes like acetylene.[33] The halogens are generally considered as among the weakest of proton acceptors. It was therefore surprising to find that the NH bond shifts to the blue[34] even when HNO donates a proton to the halogen atoms of the hydrogen halides CH_3X (X = F, Cl, Br). It becomes of interest then to inquire whether the halogen atom can participate in blue-shifting H-bond in other environments as well.

Continuing our recent study[34] regarding theoretical evidence for a NH··XC blue-shifting hydrogen bond in complexes pairing HNO with monohalomethanes, the present work alters the proton acceptor to HOX (X = F, Cl, Br). This work reports the first observation of a case where a N−H donor interacts with the halogen of an O−X acceptor group, thereby shifting its stretching frequency to the blue. Bearing in mind that the HOX species could be easily formed in the atmosphere (e.g., through reactions between the $X^\bullet$ and $OH^\bullet$ radicals), and that halogen-including species in the atmosphere are known to react with ozone, the complexes in the present study may be of genuine importance in understanding the processes that balance ozone concentrations in the upper atmosphere. The importance of HNO to pollution formation, energy release in propellants, and fuel combustion[35] broadens the interest to other facets of atmospheric chemistry as well. Despite the potential importance of these complexes, there is available in the literature neither theoretical nor experimental data regarding the interaction of HNO with any of the hypohalous acids. The present work thus reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of these complexes for the first time.

2. Computational Details

Calculations were performed using the Gaussian 03 system of codes.[36] The geometries of the isolated HOX and HNO molecules and their complexes were fully optimized at the MP2/cc-pvtz level. The modified GDIIS algorithm was implemented in searches for stationary points.[37] Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of vibrational frequencies. The counterpoise (CP) procedure[38,39] was used to correct this quantity for basis set superposition error (BSSE). Additional computations identified minima on the counterpoise-corrected potential energy surface. The polarized cc-pvtz basis was selected for use here because it has shown itself to be reliable for study of hydrogen bonds and other weak noncovalent interactions.[40]

3. Results and Discussion

A number of different structures were considered as starting points in a search for minima on the surfaces of each complex pairing HNO with HOX. These candidates included those that contain only a single H-bond, and others that contained both

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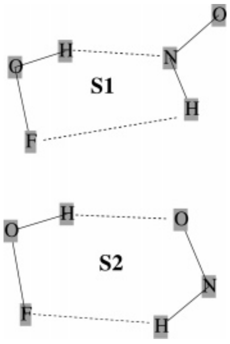

Figure 1. Geometries of optimized structures of complexes pairing HOF and HNO. Complexes in which F is replaced by Cl and Br are similarly arranged.

NH••O and OH••O. There were two separate minima identified in each case. The principal intermolecular interaction within the more stable of the two, S1, contains a OH••N H-bond, while S2 contains an OH••O bond (Figure 1). Both structures contain what appears at first sight might be a secondary NH••X bond, but this interaction is likely very weak. In particular, the H••X interatomic distance is quite long for S2, between 2.3 Å for X = F and 2.8 Å (X = Br), beyond the range normally considered for an NH••X H-bond of moderate strength.[2,7,18,41,42] The weakness of the interaction is further exacerbated by a deviation of the θ(NH••X) angle by some 45° from linearity. The geometries in the S1 structure are even worse with regard to any sort of possibly stabilizing NH••X H-bond.

The binding energies of the various complexes are reported in Table 1. Minima were located on both the standard potential energy surface and also within the context of a counterpoise-corrected surface. Adding the counterpoise correction to the geometry optimized on the non-corrected surface yielded interaction energies, ΔE, within 0.1−0.3 kJ/mol of the same quantities obtained for the minima obtained on the fully corrected surface. The OH••N H-bond of structure S1 appears to be a bit stronger than the OH••O interactions of S2, by some 3−4 kJ/mol. There is little sensitivity to the nature of the halogen atom, although the Br derivative is slightly less weakly bound than those for which X = F or Cl. These same patterns hold true when zero-point vibrational energies are incorporated or when ΔH is evaluated at 298 K.

Some of the salient geometrical parameters optimized for these complexes are displayed in Table 2. First with regard to the OH••Y (Y = N,O) H-bond length, this quantity is slightly shorter in the S2 structure, even though this complex is somewhat more weakly bound than is S1. On the other hand, the quantities in parentheses in Table 2 indicate this discrepancy largely evaporates when counterpoise corrections are included in the geometry optimization. The intermolecular OH••Y distance is fairly insensitive to the nature of the halogen X atom. The θ(OH••Y) angle lies in the 158°−168° range for all complexes considered and is smallest for X = F. The reason for disregarding the NH••X interaction as contributing significant stability to the complex is emphasized by the long separations and nonlinearities in Table 2.

The last rows of Table 2 report the changes in certain internal bonds within the two subunits that result from complexation. The stretches of the OH bond of HOX amount to 10−11 mÅ in the S1 structures, and are somewhat smaller, in the 6−8 mÅ range, for S2, consistent with a slightly weaker H-bond in the latter case. Despite its failure to participate in a strong H-bond, the NH bond of HNO undergoes a contraction of 3−5 mÅ when either the N or the O atom acts as proton acceptor. One last interesting observation involves the N−O bond of HNO. This bond contracts a small amount in S1 when the N atom acts as proton acceptor, but elongates when this function is served by O in S2.

The harmonic vibrational frequencies, on both standard and counterpoise corrected potential energy surfaces (PESs), are reported in Tables 3 and 4, respectively, for the S1 and S2 complexes. These values are not very sensitive to the nature of the halogen, consistent with the behavior of the binding energies in Table 1. The greater binding energy of S1 relative to S2 is reflected by the generally higher intermolecular frequencies of the former structure.

Some of the most interesting and enlightening aspects of the vibrational analysis are contained in Tables 5 and 6, which focus upon changes in the frequencies of the monomers when the complex is formed. In both sets of complexes, the OH stretching frequencies of HOX are shifted to the red. The magnitude of this shift is greater for the OH••N H-bond of S1 as compared to S2's OH••O interaction. This trend is consistent with both the larger stretch of the OH bond in S1, as well as its greater interaction energy. The NH bond of HNO, on the other hand, undergoes a considerable blue shift in both S1 and S2, more than 100 cm^{-1} in one case. This observation is consistent with the contraction of this bond indicated in Table 2. However, it is perhaps puzzling in that the NH bond does not participate directly in a H-bond in S1, and any such interaction in S2 would be quite weak.

So as to examine the question of a putative NH••X H-bond, the electron density was analyzed via the AIM procedure.[43] Within the S2 complex, a critical point was noted in the density in the region where it would be anticipated for an NH••X bond. Two of the eigenvalues are negative, and one positive, also consistent with a H-bond. The density at the pertinent NH••X bond critical point is equal to 40−53% of the same quantity within the stronger OH••O H-bond. Likewise, the Laplacian of this density at this point in the NH••X bond is equal to 35% that of the OH••O bond. These observations would indicate that there is indeed an NH••X H-bond present in S2, albeit a weak one. It may be that an otherwise weak bond is strengthened somewhat by positive cooperativity[1,2,44,45] effects, originating in the presence of the OH••O H-bond in this structure.

Given the appearance of an NH••X H-bond in S2, if not in S1, additional calculations were carried out to unambiguously rule out such an interaction. So as to more strictly guarantee the absence of this H-bond, the HOX molecule was rotated by 180° around the H−O axis, thereby maximizing the NH•••X separation, while leaving intact the OH••Y H-bond. In this modified geometry, the contraction of the NH bond in the S1 configuration was barely affected. In S2, on the other hand, the contraction was reduced from 4 to 5 mÅ, down to 1−2 mÅ. Likewise, the blue shift of this same bond is reduced by only 12−16% in S1, but the pivoting of HOX around its O−H bond in S2 very substantially reduces the blue shift, by 45−68%. This same reorientation has only modest effects upon the energetics. The S1 structures were destabilized by only 2−3 kJ/mol. In the case of S2 where there seems to be a weak NH••X H-bond, this rotation raised the energy of the complex by 5−8 kJ/mol, roughly 20−30% of the total interaction energy. Of course, this rise in energy cannot be attributed solely to the NH••X interaction, but it does suggest this bond is a source of some stability.

One can conclude that there is likely a weak NH••X H-bond in S2. The rupture of this bond reduces, but does not eliminate, the contraction of the covalent NH bond and its blue shift.

TABLE 1: Binding Energies and Enthalpies (kJ mol^{-1}) for the Association of HOX (X = F, Cl, Br) with HNO on Standard and CP-Corrected PES

	standard PES				CP-corrected PES		
X	ΔE	$\Delta E^{\mathrm{cp}\,a}$	$\Delta E_0{}^b$	ΔH(298 K)	ΔE	$\Delta E_0{}^b$	ΔH(298 K)
				S1			
F	−27.78	−21.95	−14.27	−14.79	−22.14	−14.83	−15.10
Cl	−27.58	−22.22	−14.58	−15.01	−22.42	−15.27	−15.40
Br	−27.21	−21.56	−15.91	−14.38	−21.76	−14.65	−14.65
				S2			
F	−25.72	−18.79	−10.12	−11.19	−19.04	−11.03	−11.77
Cl	−23.67	−18.45	−10.62	−11.22	−18.25	−10.91	−11.27
Br	−23.40	−17.40	−9.80	−10.27	−17.69	−10.60	−10.80

[a] ΔE^{cp} refers to the interaction energy after counterpoise correction, ΔE + CC. [b] ΔE_0 represents energy of complexation including CC + ZPE.

TABLE 2: Intermolecular Distances (*R*, Å), Angles (*θ*, deg), Dihedral Angles (*φ*, deg), and Changes in Internal Bond Lengths (Δ*r*, mÅ) Occurring upon Formation of Complexes Computed at MP2/cc-pvtz Level (Values in Parentheses Computed for CP-Corrected PES)

	F	Cl	Br
		S1	
R(OH··N)	1.952(1.994)	1.936(1.986)	1.945(1.996)
R(NH··X)	3.056 (3.285)	3.592(3.605)	3.685(3.745)
θ(OH··N)	158(162)	166(167)	166(168)
θ(NH··X)	79(73)	71(73)	70(72)
φ(XOH··N)	0.0(0.0)	14(−0.2)	19(11)
Δ*r*(OH)	10(9)	11(10)	11(10)
Δ*r*(NH)	−4(−4)	−4(−4)	−3(−4)
Δ*r*(NO)	−3(−2)	−3(−2)	−3(−2)
		S2	
R(OH··O)	1.911(1.969)	1.924(1.984)	1.941(2.004)
R(NH··X)	2.283(2.377)	2.726(2.798)	2.820(2.923)
θ(OH··O)	160(159)	166(164)	167(166)
θ(NH··X)	134(132)	133(132)	134(132)
Δ*r*(OH)	8(7)	8(6)	8(6)
Δ*r*(NH)	−5(−5)	−4(−4)	−4(−3)
Δ*r*(NO)	3(3)	3(2)	3(2)
Δ*r*(OX)	4(3)	−3(−3)	−5(−5)

TABLE 3: Unscaled Harmonic Vibrational Frequencies (cm^{-1}) Computed for S1 Complexes at MP2/cc-pvtz Level (Values in Parentheses Are from CP-Corrected PES)

	X = F	X = Cl	X = Br
		HOX	
OX stretch	997(998)	774(774)	669(669)
HOX bend	1513(1509)	1408(1398)	1343(1335)
OH stretch	3605(3624)	3583(3609)	3585(3609)
		HNO	
NO stretch	1505(1502)	1503(1502)	1502(1500)
HNO bend	1570(1574)	1572(1572)	1573(1573)
NH stretch	3100(3094)	3094(3090)	3091(3086)
		intermolecular	
	31(26)	18(7)	22(11)
	51(41)	52(47)	50(44)
	132(118)	98(110)	87(92)
	205(206)	196(205)	190(181)
	234(219)	283(211)	297(250)
	642(615)	641(618)	625(604)

Notably, this same pattern appears in the S1 complex where there is no evidence of an NH··X H-bond at all. Also, this contraction/blue shift is scarcely affected when any possibility of an NH··X interaction is precluded by adjustment of the geometry.

It has been documented already that the NH bond of HNO contracts and shifts to the blue when it is involved in a strong H-bond. One example is the NH··O interaction in HNO dimer[30] where contraction of 4−5 mÅ was observed, along with a blue shift of 75−96 cm^{-1}. The issue here centers around the consequences of a weaker interaction. A previous set of calculations[34] paired HNO with monohalomethanes hydrogen halides, CH_3X (X = F, Cl, Br), which do not contain a strong proton acceptor. These complexes, like those considered here, contain a bent NH··X interaction. A major difference though is that whereas the present complexes also contain a strong OH··Y H-bond, the second H-bond in the HNO··CH_3X pairs consists of a very weak CH··Y interaction. Not surprisingly, then, the interaction energies of the HNO··CH_3X complexes were smaller than those computed here for HNO··HOX, by a factor of roughly one-half. One point of consistency between the two sets of complexes is the behavior of the NH bond of HNO, which undergoes a contraction/blue shift in all cases. When paired with CH_3X, these contractions are in the 3−6 mÅ

TABLE 4: Unscaled Harmonic Vibrational Frequencies (cm^{-1}) Computed for S2 Complexes at MP2/cc-pvtz Level (Values in Parentheses Are from CP-Corrected PES)

	X = F	X = Cl	X = Br
		HOX	
OX stretch	998(1000)	773(774)	668(668)
HOX bend	1502(1486)	1374(1398)	1306(1293)
OH stretch	3648(3676)	3660(3608)	3664(3689)
		HNO	
NO stretch	1497(1500)	1495(1501)	1494(1495)
HNO bend	1604(1602)	1597(1597)	1597(1597)
NH stretch	3137(3121)	3112(3090)	3103(3091)
		intermolecular	
	19(26)	20(7)	23(29)
	124(108)	91(47)	76(69)
	162(151)	140(109)	134(127)
	219(200)	199(204)	192(175)
	285(257)	253(211)	253(230)
	558(516)	541(618)	527(487)

TABLE 5: Changes in Selected Vibrational Frequencies (cm^{-1}) Occurring Within S1 HNO··HOX Complexes (Values in Parentheses Are from CP-Corrected PES)

	F	Cl	Br
		HOX	
OH stretch	−193(−174)	−219(−193)	−215(−191)
OX stretch	+1(+2)	+5(+5)	+7(+7)
HOX bend	+101(+97)	+130(+120)	+136(+128)
		HNO	
NH stretch	+74(+68)	+68(+64)	+65(+60)
NO stretch	+20(+17)	+18(+17)	+17(+15)
HNO bend	−15(−11)	−13(−13)	−12(−12)

TABLE 6: Changes in Selected Vibrational Frequencies (cm^{-1}) Occurring Within S2 HNO··HOX Complexes (Values in Parentheses Are from CP-Corrected PES)

	F	Cl	Br
		HOX	
OH stretch	−150(−122)	−142(−194)	−136(−111)
OX stretch	+2(+4)	+4(+5)	+6(+6)
HOX bend	+90(+74)	+96(+120)	+99(+86)
		HNO	
NH stretch	+111(+95)	+86(+64)	+77(+65)
NO stretch	+12(15)	+10(+16)	+9(+10)
HNO bend	+15(+13)	+12(+12)	+12(+12)

range, consistent with the values obtained here for a HOX partner molecule. Likewise, the change in stretching frequency computed for CH_3X amounted to some 85−125 cm^{-1}, again consistent with the 65−111 cm^{-1} range obtained here.

A particularly weak sort of interaction occurred when HNO was paired with HCCH. The HNO O atom[33] acts as proton acceptor to HCCH, and its NH is donated to the π system of the alkyne. The total interaction energy is understandably quite small, less than 7 kJ/mol. Even so, the NH bond shrinks by 2 mÅ and exhibits a blue shift of 40 cm^{-1}. When combined[46] with BH_3NH_3, the O atom of HNO acts as proton acceptor to NH, whereas its NH donates a proton to the BH_3 group, in what is commonly termed a dihydrogen (NH··HB) bond. Even though the latter interaction is likely quite weak, especially considering its highly bent nature, the N−H nonetheless undergoes a contraction (7 mÅ) and blue shift (128 cm^{-1}). When superimposed with our own data described above, especially the results computed when a NH··X H-bond is fully ruled out by the geometries involved, one may conclude that the contraction and blue shift of the NH covalent bond is not dependent upon its direct participation in a H-bond, but is frequently the result of an electronic reorganization within the HNO molecule caused by another interaction.

DFT methods have rapidly gained in popularity, but there remains some question as to how well such techniques fare when applied to H-bonded systems. For purposes of comparison and calibration, the most widely used of the DFT methods, B3LYP,[47,48] has been applied to both the S1 and the S2 minima identified on the surfaces of the HNO−HOX complexes, within the context of the same cc-pvtz basis set. To facilitate the comparisons, tables were composed that are the B3LYP analogues of Tables 1−6; these tables are supplied as Tables S1−S6 in the Supporting Information.

In general, the B3LYP approach seems rather suitable to these systems, comparing rather nicely with the MP2 results. There is a tendency for the B3LYP approach to slightly overestimate the binding energy for X = F, and to slightly underestimate the same quantity for Cl and Br, but these errors amount to only 1 or 2 kJ/mol. The principal trend, that S1 is more stable than S2 for all halogen atoms, is correctly reproduced. Geometric data are also good. H-bond lengths are accurate within about 0.02 Å for X = F, but this error climbs as X progresses from F to Cl to Br; angles are correct within 5°. The changes in the r(NH) and r(OH) covalent bond lengths associated with dimerization are all reported correctly with regard to sign, that is, stretching or contracting. On the other hand, there is a tendency for B3LYP to overestimate the magnitudes of these changes, in some cases by a factor as large as 2.

Intramonomer B3LYP vibrational frequencies are slightly smaller than their MP2 correlates, with the exception of the NO stretch in the HNO subsystem, which is exaggerated; intermolecular vibrational frequencies are very close between the two methods. Of greater significance here are the changes in these frequencies that occur when the complexes are formed. B3LYP correctly predicts a red shift for the OH stretch and a blue shift for NH in both S1 and S2; however, these quantities are consistently overestimated. The OH red shift exaggeration is largest for X = F (26−34%) and smallest for X = Br where it is less than 10%. The B3LYP overestimates of the NH blue shift are a bit more severe, consistently in the 25−42% range.

In summary, the complexes pairing HNO with the hypohalous acids contain two minima, in both of which HOX acts as primary proton donor. The more strongly bound of the two contains an OH··N H-bond, slightly stronger than the OH··O bond of the other minimum. The electronic contributions to the binding energies are about 22 kJ/mol for the global minimum and 18 kJ/mol for the secondary minimum. These quantities are reduced to about 15 and 11 kJ/mol, respectively, when Δ*H* is computed at 25 °C. The nature of the halogen, whether F, Cl, or Br, has only a marginal effect upon the energetics of these complexes. The covalent O−H bond of HNO undergoes a stretch and red shift, the magnitude of which is roughly proportional to the interaction energy of each complex. The N−H bond of HNO, on the other hand, is shortened and manifests a blue shift in its stretching frequency. These effects are not attributable to the participation of this proton in a H-bond, but appear instead to be secondary, due to the activity of HNO as proton acceptor, at either the N or the O atom.

Supporting Information Available: Binding energies, intermolecular distances, and vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond. Recent Developments in Theory and Experiments*; North-Holland Publishing Co.: Amsterdam, 1976.

(2) Scheiner, S. *Hydrogen Bonding − A Theoretical Perspective*; Oxford University Press: Oxford, 1997; and references therein.

(3) Pinchas, S. *J. Phys. Chem.* **1963**, *67*, 1862.

(4) Schneider, W. G.; Bernstein, H. J. *Trans. Faraday Soc.* **1956**, *52*, 13.

(5) Trudeau, G.; Dumas, J.-M.; Dupuis, P.; Guerin, M.; Sandorfy, C. Intermolecular interactions and anesthesia: Infrared spectroscopic studies. *Top. Curr. Chem.* **1980**, *93*, 91−125.

(6) Budesinsky, M.; Fiedler, P.; Arnold, Z. *Synthesis* **1989**, 858.

(7) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford: New York, 1999.

(8) Scheiner, S. CH···O Hydrogen Bonding. In *Advances in Molecular Structure Research*; Hargittai, M., Hargittai, I., Eds.; JAI Press: Stamford, CT, 2000; Vol. 6, pp 159−207.

(9) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **2002**, *108*, 325.

(10) Scheiner, S. The CH−O Hydrogen Bond. A Historical Account. In *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; pp 831−857.

(11) Wang, Y.; Balbuena, P. B. *J. Phys. Chem. A* **2001**, *105*, 9972.

(12) Wetmore, S. D.; Schofield, R.; Smith, D. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 8718.

(13) Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A* **1999**, *103*, 6394.

(14) Scheiner, S.; Grabowski, S. J.; Kar, T. *J. Phys. Chem. A* **2001**, *105*, 10607.

(15) Domagala, M.; Grabowski, S. J. *J. Phys. Chem. A* **2005**, *109*, 5683.

(16) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(17) Barnes, A. J. *J. Mol. Struct*. **2004**, *704*, 3 and references therein.

(18) Grabowski, S. J., Ed. *Hydrogen Bonding - New Insights*; Springer: Dordrecht, The Netherlands, 2006.

(19) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.

(20) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639.

(21) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784.

(22) Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695.

(23) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.

(24) Herrebout, W. A.; Delanoye, S. N.; Veken, B. J. v. d. *J. Phys. Chem. A* **2004**, *108*, 6059.

(25) Rutkowski, K. S.; Rodziewicz, P.; Melikova, S. M.; Herrebout, W. A.; Veken, B. J. v. d.; Koll, A. *Chem. Phys.* **2005**, *313*, 225.

(26) Rodziewicz, P.; Rutkowski, K. S.; Melikova, S. M.; Koll, A. *ChemPhysChem* **2005**, *6*, 1282.

(27) Tang, K.; Shi, F. Q. *Int. J. Quantum Chem.* **2006**, *107*, 665.

(28) Yang, Y.; Zhang, W.-J.; Gao, X.-M. *Chin. J. Chem.* **2006**, *24*, 887.

(29) Joseph, J.; Jemmis, E. D. *J. Am. Chem. Soc.* **2007**, *129*, 4620.

(30) Liu, Y.; Liu, W.; Li, H.; Liu, J.; Yang, Y. *J. Phys. Chem. A* **2006**, *110*, 11760.

(31) Yang, Y.; Zhang, W.; Gao, X. *Int. J. Quantum Chem*. **2005**, *106*, 1199.

(32) Liu, Y.; Liu, W.; Li, H.; Liu, J.; Yang, Y.; Cheng, S. *Int. J. Quantum Chem*. **2006**, *107*, 396.

(33) Liu, Y.; Liu, W.; Yang, Y.; Liu, J. *Int. J. Quantum Chem*. **2006**, *106*, 2122.

(34) Solimannejad, M.; Scheiner, S. *J. Phys. Chem. A* **2007**, *111*, 4431.

(35) Bunte, S. W.; Rice, B. M.; Chabalowski, C. F. *J. Phys. Chem. A* **1997**, *101*, 9430.

(36) Frisch, M. J.; et al. *Gaussian 03*, revision B02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(37) Csaszar, P.; Pulay, P. *J. Mol. Struct. (THEOCHEM)* **1984**, *114*, 31.

(38) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(39) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 1194.

(40) Riley, K. E.; Hobza, P. *J. Phys. Chem. A* **2007**, *111*, 8257.

(41) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1993**, *115*, 1958.

(42) Scheiner, S.; Duan, X. *Biophys. J.* **1991**, *60*, 874.

(43) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

(44) Kar, T.; Scheiner, S. *Int. J. Quantum Chem.* **2006**, *106*, 843.

(45) Kar, T.; Scheiner, S. *J. Phys. Chem. A* **2004**, *108*, 9161.

(46) Yang, Y.; Zhang, W. *J. Mol. Struct (THEOCHEM)* **2007**, *814*, 113.

(47) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.