J. Phys. Chem. A **2007,** *111,* 4431−4435

Theoretical Evidence for a NH···XC Blue-Shifting Hydrogen Bond: Complexes Pairing Monohalomethanes with HNO

Mohammad Solimannejad*

Quantum Chemistry Group, Department of Chemistry, Arak University, 38156-879 Arak, Iran

Steve Scheiner*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Received: March 1, 2007; In Final Form: March 23, 2007

Correlated ab initio calculations are used to analyze the interaction between nitrosyl hydride (HNO) and CH_3X (X = F, Cl, Br). Three minima are located on the potential energy surface of each complex. The more strongly bound contains a NH···X bond, along with CH···O; CH···O and CH···N bonds occur in the less stable minimum. Binding energies of the global minimum lie in the range of 11−13 kJ/mol, and there is little sensitivity to the identity of the halogen atom. Unlike most other such hydrogen bonds, the NH covalent bond in this set of complexes becomes shorter, and its stretching frequency shifts to the blue, upon forming the NH···X hydrogen bond. The amount of this blue shift varies in the order F > Cl > Br.

1. Introduction

The importance of noncovalent intermolecular interactions in many areas of contemporary chemical physics has been demonstrated in numerous studies of such systems.[1] Among all noncovalent interactions, the hydrogen-bonding types are particularly significant. A large number of studies devoted to the hydrogen-bonding phenomenon have been published from both experimental and theoretical viewpoints.[2,3] 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.[4,5] These hydrogen bonds are of great interest for a number of reasons, including the proton transfers that can take place within them.[6−8]

Recently, a new type of intermolecular bond, commonly designated as a blue-shifting hydrogen bond, characterized by X−H bond contraction and a blue shift of the X−H bond stretching frequency, continues to receive a good deal of experimental and theoretical attention.[9−19] The majority of these blue-shifting hydrogen bonds contain a C−H group as the donor, but there have been a small number of exceptions observed, such as the N−H donor. Given the small number of observations of the latter, it is perhaps not surprising that the pattern remains inconsistent. For example, some calculations in 2002[20,21] predicted that the NH bond of F_2NH will shift to the blue when bound to FH, but to the red if hydrogen-bonded to either OH_2 or NH_3.[20] In contradiction to this finding, 3 years later Lu and co-workers[22] computed the opposite trend of a red shift for F_2NH···FH at the DFT level with three different basis sets. Consistent with the latter DFT data, another investigation in that same year found red shifts for the N−H stretching frequencies in the $F_2NH\cdots(FH)_n$ and $FNH_2\cdots(FH)_n$ ($1 < n < 3$) complexes, this time at the MP2/cc-pvdz level;[23] yet at the same time the stretching frequency shifts to the blue when N is replaced with its P and As congeners. When the halogen acceptor is changed to oxygen, Yang et al. noted[24] that the NH stretch shifts to the blue, in contradiction to the earlier finding of a red shift for NH···O bonds.[20] Liu et al. also observed blue shifts in the NH···O hydrogen bonds of the HNO dimer;[25] the N−H bond also shifts to the blue when interacting with the π-bond of ethylene.[26] In summary, one is left with a number of results, some in apparent contradiction with one another, and certainly with no obvious patterns. In an effort to help clarify the situation, this work considers the HNO molecule as a proton donor, allowing it to interact with CH_3X, where X = F, Cl, or Br. This work reports the first observation of a case where a N−H donor interacts with the halogen of a C−X acceptor group and thereby shifts its stretching frequency to the blue.

From a more practical perspective, noncovalently bonded complexes of CH_3X (X = F, Cl, Br) are of prime importance in atmospheric chemistry as many of the processes that degrade ozone involve halogen-containing species. In particular, methyl chloride and methyl bromide are important atmospheric trace gases (tropospheric mixing ratios of 12 and 600 pptv, respectively) that contribute directly to stratospheric ozone depletion.[27] It is important to stress that CH_3X species could be easily formed in the environment—important sources of CH_3Cl include oceanic emissions, biomass burning, tropical forests; tropical plants may also be important sources of natural CH_3Br.[28] At the same time, HNO is important in processes such as pollution formation, energy release in propellants, and fuel combustion.[29] Therefore complexes that combine HNO with CH_3X are of paramount interest in the field of atmospheric chemistry. Despite the potential importance of these complexes there is available in the literature neither theoretical nor experimental information regarding the interaction of HNO with any of the monohalomethanes. The present work thus reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of these complexes.

Interestingly, both the HNO and CH_3X molecules may act as simultaneous hydrogen bond donors and acceptors,[25,26,30,31] leading to a wealth of potential minima to be considered, not

---

* Corresponding authors. E-mail: m-solimannejad@araku.ac.ir; scheiner@cc.usu.edu.

10.1021/jp071695u CCC: $37.00

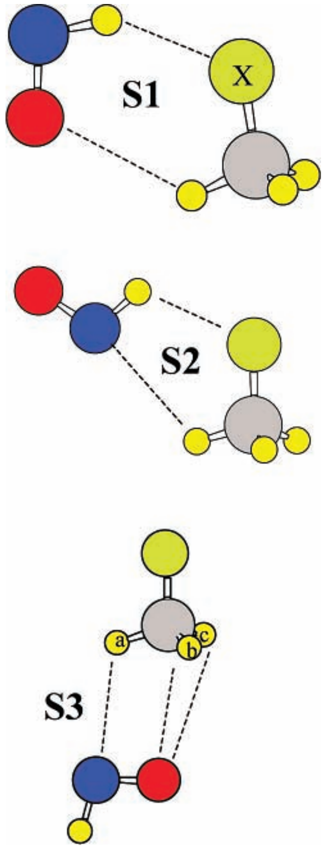

Figure 1. Geometries of optimized structures of complexes pairing CH_3X (X = F, Cl, Br) with HNO.

the least of which are cyclic structures. Of more fundamental interest, these complexes contain a variety of different weak hydrogen bonds, namely, NH···X and CH···O. The absence of any conventional, stronger hydrogen bonds, e.g., OH···O, allows an unobstructed view of these weaker interactions and, in particular, examination of the relative strengths of each such hydrogen bond. The cyclic nature of the complexes allows one to consider how these weak interactions affect one another when they occur simultaneously.

2. Computational Details

Calculations were performed using the Gaussian03 system of codes.[32] The geometries of the isolated CH_3X and HNO molecules and their complexes were fully optimized at the MP2 level, using both the aug-cc-pvdz and 6-311+G(d,p) basis sets. The modified GDIIS algorithm was implemented in searches for stationary points.[33] Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of vibrational frequencies. The counterpoise (CP) procedure[34,35] was used to correct for basis set superposition error (BSSE).

3. Results and Discussion

Three separate minima were identified in the potential energy surface of each complex pairing HNO with CH_3X. As may be seen in Figure 1, all three minima contain more than one interaction that could fairly be categorized as a hydrogen bond. In the two most strongly bound complexes, the HNO donates a proton to the halide atom. In S1 the O atom of HNO accepts a proton from the methyl group of CH_3X, while it is the N atom that accepts the proton in S2. Interaction energies are reported in Table 1 with two different basis sets, for purposes of comparison and consistency. The aug-cc-pvdz set is somewhat larger, and it is probably more reliable than is 6-311+G(d,p). Results with the larger set indicate that the S1 arrangement is preferred over S2 by about 2 kJ/mol, regardless of the nature of the halogen. With regard to the identity of the halogen, there is an interesting oscillation of the results. That is, whereas Br forms the stronger complex with respect to ΔE, it is the X = F complex that is more strongly bound after removal of basis set superposition error; however, the situation reverses once again after zero-point vibrations are included. The 6-311+G(d,p) basis set more consistently shows X = F to be the most strongly bound S1 complex. Perhaps most importantly, both basis sets agree that S1 is of lower energy than S2, and that the counterpoise-corrected interaction energy of either S1 or S2 is most negative for X = F.

S3 is considerably more weakly bound, involving neither the HNO proton nor the halogen atom in any interaction. The binding is due instead to cohesive attractions between the three methyl protons and the O and N atoms of HNO. These forces are weaker than the NH···X hydrogen bond of S1 and S2, with a total interaction energy roughly half that of the latter two structures. Since the halogen is not directly involved, it is not surprising to observe that the binding energy of S3, after counterpoise correction, is some 5.8 kJ/mol with the larger basis set, virtually invariant to the identity of the X atom. Similar invariance is noted with 6-311+G(d,p), albeit the S3 geometry does not appear to be a true minimum for X = Cl.

Some of the key geometrical parameters optimized for these complexes are displayed in Table 2. Considering first the H···X hydrogen bonds in S1 and S2, it is first clear that this distance elongates as one progresses from F to Cl to Br, in line with the increasing size of the halogen atom. More importantly, for any one halogen atom, this hydrogen bond is shorter for S1 than for S2, by anywhere between 0.17 and 0.26 Å. The other hydrogen bond in these two structures, between the methyl H and the O (S1) or N (S2) atom is also consistently longer for the S2 geometry than for S1, by about 0.1 Å. The strengths of the shorter hydrogen bonds in S1 are likely reinforced by the lesser angular distortion. The angularities of these hydrogen bonds are closer to the linear value of 180° in S1, particularly in the case of the NH···X angles, wherein the hydrogen bond in S1 is more linear than that in S2 by 30−40°.

The next few rows of each section of Table 2 report how some of the internal bond lengths in the two monomers are affected by the formation of the complex. The Δr(NH) values are all negative, indicating that this hydrogen bond contracts upon complexation. Such a contraction in a N−H covalent bond is extremely rare; this bond normally lengthens when a hydrogen bond is formed. It may be noted that the degree to which the NH bond contracts is largest for X = F and smallest for X = Br. The next row in Table 2 illustrates that a contraction occurs as well in the hydrogen-bonding C−H bond, albeit to a much lesser extent. The succeeding rows show that the internal C−X bond of the methyl halide, and the N═O bond of HNO, both elongate when the hydrogen bond is formed.

The H···O,N hydrogen bond lengths in the S3 complex are generally longer than in S1 and S2. Those involving the O atom as acceptor are 3.0 Å or longer; these bonds grow longer as the halogen progresses from F to Cl to Br. The bonds involving the N atom are much shorter, and obey the opposite trend, shortest for Br. The next three rows document the shortening of the three methyl C−H bonds, most notably for the proton that interacts with the N atom.

TABLE 1: Binding Energies (kJ mol^{-1}) and Enthalpies for the Association of CH_3X (X = F, Cl, Br) with HNO

	MP2/ aug-cc-pvdz				MP2/ 6-311+ G(d,p)		
X	ΔE	$\Delta E^{cp\ a}$	$\Delta E_0{}^{b}$	ΔH(298 K)	ΔE	$\Delta E^{cp\ a}$	$\Delta E_0{}^{b}$
				S1			
F	−15.54	−12.42	−11.26	−9.37	−15.10	−11.00	−10.73
Cl	−15.87	−11.47	−11.72	−9.86	−13.93	−8.27	−10.17
Br	−17.50	−11.29	−13.24	−11.45	−13.27	−8.80	−9.57
				S2			
F	−13.53	−10.53	−10.00	−7.74	−12.36	−9.45	−8.77
Cl	−13.87	−10.01	−10.64	−8.26	−13.08	−7.44	−8.93
Br	−15.15	−9.84	−12.02	−9.51	−12.59	−7.95	−8.60
				S3			
F	−9.53	−5.81	−5.86	−4.01	−7.01	−4.63	−4.48
Cl	−9.70	−5.82	−6.30	−4.21	*c*	*c*	*c*
Br	−9.10	−5.74	−6.70	−4.47	−6.98	−4.35	−4.75

[a] ΔE^{cp} refers to the interaction energy after counterpoise correction, ΔE + CC. [b] ΔE_0 represents energy of complexation including CC + ZPE. [c] S3 is not a minimum on the MP2/6-311+G** surface for X = Cl.

TABLE 2: Intermolecular Distances (*R*, in Å), Angles (*θ*, in degree), and Changes in Internal Bond Lengths (Δ*r*, in mÅ) Occurring upon Formation of Complexes, Computed at MP2/aug-cc-pvdz Level

	F	Cl	Br
	S1		
R(H···X)	2.180	2.648	2.752
R(O···H)	2.638	2.519	2.509
θ(NH···X)	147	146	146
θ(CH···O)	128	142	143
Δr(NH)	−6	−4	−3
Δr(CH)	−2	−1	−1
Δr(CX)	10	7	3
Δr(ON)	4	3	3
	S2		
R(H···X)	2.354	2.910	2.956
R(N···H)	2.728	2.609	2.609
θ(NH···X)	117	107	114
θ(CH···N)	117	131	135
Δr(NH)	−5	−4	−3
Δr(CH)	−1	−0.9	−0.5
Δr(CX)	8	7	4
Δr(ON)	2	0.9	1
	S3		
R(N···H$_a$)	2.713	2.630	2.617
R(O···H$_b$)	2.975	3.119	3.138
R(O···H$_c$)	2.992	3.120	3.138
Δr(CH$_a$)	−1.5	−1.3	−1.5
Δr(CH$_b$)	−0.6	−0.3	−0.4
Δr(CH$_c$)	−0.6	−0.3	−0.4
Δr(ON)	0.8	0.7	0.5

TABLE 3: Unscaled Harmonic Vibrational Frequencies (cm^{-1}) Computed for S1 Complexes at MP2/aug-cc-pvdz Level

	X = F	X = Cl	X = Br
	ONH		
N−O stretch	1469	1466	1466
ONH bend	1590	1586	1588
N−H stretch	3117	3082	3074
	CH_3X		
C−X stretch	1011	738	627
bending motions	1185	1036	978
	1187	1040	983
	1462	1364	1327
	1486	1470	1463
	1495	1478	1471
CH stretch	3098	3109	3111
	3213	3228	3235
	3224	3241	3284
	intermolecular		
	23	24	25
	54	62	54
CH···O stretch	74	75	80
	101	108	108
NH···X stretch	154	138	138
ONH torsion	164	163	184

TABLE 4: Changes in Selected Vibrational Frequencies (cm^{-1}) Occurring within S1 ONH···CH_3X Complexes

	F	Cl	Br
	ONH		
N−H stretch	+112	+77	+69
ONH bend	+21	+17	+19
	CH_3X		
CH symmetric stretch	+8	+4	+3
C−X stretch	−25	−12	−6

The harmonic vibrational frequencies for the most strongly bound S1 complexes are reported in Table 3. The intramolecular modes are reported first, followed at the lower part of the table by the intermolecular vibrations. The higher NH···X stretching frequencies, as compared to the CH···O stretches, confirm the supposition that the former represent stronger bonds. These frequencies are not very sensitive to the nature of the halogen, consistent with the behavior of the binding energies in Table 1. Some of the most interesting aspects of the vibrational analysis are contained in Table 4, which focuses upon changes in the frequencies of the monomers when the complex is formed. Both the NH and CH stretching frequencies that describe the proton donors are shifted to the blue. The blue shift of the NH stretch is opposite to the normally observed red shift, but is consonant with the contraction noted above for its equilibrium bond length. In both the NH and CH cases, the amount of the blue shift diminishes upon going from F to Cl to Br.

Our recent calculations[31] considered the methyl halides and the complexes which they formed with the OOH radical, differing in only one atom from the HNO partner molecule here. The OOH···CH_3X complexes which are similar to the S1 structure here were bound by some 20−24 kJ/mol, nearly twice as strong an interaction as the HNO complexes. Moreover, the OH···X bonds were roughly 0.3−0.4 Å shorter than the NH··X bonds considered here, consistent with the stronger bonding of HOO. Some other properties that are consistent with the weaker interaction of HNO are the lesser stretch of the C−X bond in CH_3X, and its accompanying smaller red shift, as well as the lesser blue shift in the C−H stretching frequency. One point of distinction, and a notable one, is that the O−H covalent bonds of OOH were stretched and manifested a red shift, while

TABLE 5: Properties Calculated for ONH···CH_3F Complexes at B3LYP Level with Two Different Basis Sets[a]

	aug-cc-pvdz		6-311+G(d,p)	
	without CC	with CC	without CC	with CC
		S1		
ΔE^{cp},[b] kJ/mol	−9.69	−9.70	−11.38	−11.40
R(NH···F)	2.232	2.245	2.181	2.203
R(CH···O)	2.790	2.805	2.798	2.817
Δr(NH), mÅ	−6	−6	−7	−7
Δr(CH), mÅ	−2	−2	−2	−2
$\Delta \upsilon$(NH), cm^{-1}	104	102	125	122
$\Delta \upsilon$(CH), cm^{-1}	24	25	29	28
		S2		
ΔE^{cp},[b] kJ/mol	−7.54	−7.57	−8.94	−8.92
R(NH···F)	2.363	2.377	2.287	2.327
R(CH···N)	2.960	3.052	3.123	3.073
Δr(NH), mÅ	−6	−5	−6	−6
Δr(CH), mÅ	−1	−1	−1	−1
$\Delta \upsilon$(NH), cm^{-1}	90	85	112	105
$\Delta \upsilon$(CH), cm^{-1}	16	17	19	19
		S3		
ΔE^{cp},[b] kJ/mol	−2.53	−2.61	−2.97	−3.03
$R(CH_a\cdots N)$	2.909	3.232	3.158	3.227
$R(CH_b\cdots O)$	3.237	3.276	3.144	3.263
$\Delta r(CH_a)$, mÅ	−1	−1	−1	−1
$\Delta \upsilon(CH_a)$, cm^{-1}	14	11	14	13

[a] Geometries optimized both without and with counterpoise corrections (CC). [b] ΔE^{cp} refers to the interaction energy after counterpoise correction, ΔE + CC.

the N−H bond of HNO is contracted and its stretching frequency shifted to the blue. Another interesting contrast is the elongation of the ON bond within HON upon complexation, as compared to the shortening of the OO bond of OOH.

From a methodological perspective, there might be some interest in how well weakly bound systems such as these might be treated by density functional methods. A second issue concerns how much the results might be affected if basis set superposition is corrected as part of the geometry optimization process, rather than simply applying the counterpoise correction to the structure optimized on the uncorrected potential energy surface. In order to address these issues, an additional set of calculations was performed for all three of the minima identified on the ONH···CH_3F surface. The currently most popular B3LYP variant of DFT was chosen, and it was applied to both the aug-cc-pvdz and 6-311+G(d,p) basis sets. In both cases, the geometry was fully optimized both with and without counterpoise correction of the surface.

The binding energies displayed in the first row of each section of Table 5 make it immediately clear that the counterpoise correction of the surface during the optimization procedure affects the final quantity hardly at all. Also suffering only very minor changes are the contractions of the N−H and C−H covalent bond lengths, as well as the amounts of the blue shifts of their stretching frequencies. Somewhat more sensitive to counterpoise correction of the surface are the intermolecular distances. In the case of the S1 complex, for example, and with the aug-cc-pvdz basis set, the hydrogen bond lengths stretch by about 0.014 Å as a result of correction of the surface. There is a larger elongation of the CH···N bond in the S2 complex; the CH···N bond in the S3 structure stretches by 0.3 Å underscoring the flatness of this surface. Counterpoise also tends to lengthen the hydrogen bond lengths of the 6-311+G(d,p) geometries, although there are notable differences with the aug-cc-pvdz results. For example, while the CH···N distance in the S2 complex is stretched by 0.09 Å by inclusion of counterpoise directly into the aug-cc-pvdz surface, the effect on this same internuclear distance in the 6-311+G(d,p) complex is a contraction by 0.05 Å.

In terms of a comparison of the DFT with the more reliable MP2 data, the two methods, with either basis set, and with or without correction of the counterpoise procedure, all concur that S1 is the most stable geometry, followed by S2 and then by S3. There is also rough agreement concerning the energy differences; namely, S1 is more stable than S2 by about 2 kJ/mol, which is in turn more stable by some 5 kJ/ mol compared to S3. However, the different methods differ in the quantitative aspects. With the aug-cc-pvdz basis set, the B3LYP estimates of the binding energies are too small by about 3 kJ/mol with all three geometries. Curiously, though, the result is different with the 6-311+G(d,p) basis set, where the B3LYP and MP2 interaction energies are surprisingly close to one another. In fact, it is interesting to note that whereas the MP2/aug-cc-pvdz binding energies exceed the MP2/6-311+G(d,p) values by more than 1 kJ/mol, the reverse is true at the B3LYP level, where the latter basis set provides considerably stronger interaction energies.

Concerning geometric and spectroscopic data, the B3LYP intermolecular hydrogen bond lengths tend to be longer than the MP2 values, but there is solid agreement concerning the effects of the complexation upon the internal bond lengths. The blue shift of the NH stretching frequency of the most stable S1 complex was predicted to be 112 cm^{-1} for the NH bond at the MP2/aug-cc-pvdz level (see Table 4), which is reproduced quite well by the B3LYP/aug-cc-pvdz calculation which provides a value of 104 cm^{-1}. On the other hand, the MP2 blue shift of the CH bond in the same complex of 8 cm^{-1} is strongly exaggerated by the B3LYP approach which estimates this property to be three times higher.

4. Conclusions

In summary, the complexes pairing HNO with the methyl halides contain three minima, one of which is more weakly bound than the other two, due to the presence of only CH···O or CH···N hydrogen bonds. The global minimum is cyclic in character, bound by roughly 11−12 kJ/mol, and contains a NH···X and a weaker CH···N bond, both of which are angularly distorted. There is not much distinction between X = F, Cl, or Br in terms of total binding energy. Perhaps the most surprising finding is that the N−H covalent bond of HNO is shortened by the interaction, while undergoing a blue shift in its stretching frequency. This behavior is in clear contrast to the complexes pairing CH_3X with OOH, wherein the OH bond of the OOH is stretched and shifts to the red, a more expected trend for such hydrogen bonds.

References and Notes

(1) Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143.
(2) Scheiner, S. *Hydrogen Bonding − A Theoretical Perspective*; Oxford University Press: Oxford, 1997, and references therein.
(3) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
(4) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(5) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 5928.
(6) Scheiner, S.; Duan, X. *Biophys. J.* **1991**, *60*, 874.
(7) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1993**, *115*, 1958.
(8) Duan, X.; Scheiner, S. *J. Mol. Struct.* **1992**, *270*, 173.
(9) Hobza, P.; Špirko, V. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1290.
(10) Mrázková, E.; Hobza, P. *J. Phys. Chem. A* **2003**, *107*, 1032.
(11) Karpfen, A.; Kryachko, E. S. *J. Phys. Chem. A* **2003**, *107*, 9724.
(12) Kryachko, E. S.; Zeegers-Huyskens, Th. *J. Phys. Chem. A* **2001**, *105*, 7118.
(13) McDowell, S. A. C. *J. Chem. Phys.* **2003**, *119*, 3711.
(14) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784.

(15) Kryachko, E. S.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **2003**, *107*, 7546.
(16) Harada, T.; Yoshida, H.; Ohno, K.; Matsuura, H. *Chem. Phys. Lett.* **2002**, *362*, 453.
(17) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.
(18) Fang, Y.; Fan, J. M.; Liu, L.; Li, X. S.; Guo, Q. X. *Chem. Lett*. **2002**, *31*, 116.
(19) Masunov, A.; Dannenberg, J. J.; Contreras, R. H. *J. Phys. Chem. A* **2001**, *105*, 4737.
(20) Hobza, P. *Int. J. Quantum Chem*. **2002**, *90*, 1071.
(21) Li, X. S.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc*. **2002**, *124*, 9639.
(22) Lu, P.; Liu, G. Q.; Li, J. C. *J. Mol. Struct. (THEOCHEM)* **2005**, *723*, 95.
(23) Karpfen, A. *J. Mol. Struct. (THEOCHEM)* **2005**, *757*, 203.
(24) Yang, Y.; Zhang, W. J.; Gao, X. M. *Int. J. Quantum Chem.* **2006**, *106*, 1199.
(25) Liu, Y.; Liu, W.; Li, H.; Liu, J.; Yang, Y. *J. Phys. Chem A* **2006**, *110*, 11760.
(26) Liu, Y.; Liu, W.; Yang, Y.; Liu, J. *Int. J. Quantum Chem*. **2006**, *106*, 2122.
(27) Montzka, S. A.; Butler, J. H.; Hall, B. D.; Mondeel, D. J.; Elkins, J. W. *Geophys. Res. Lett.* **2003**, *30*, Article No. 1826.
(28) Saito, T.; Yokouchi, Y. *Atmos. Environ*. **2006**, *40*, 2806.
(29) Bunte, S. W.; Rice, B. M.; Chabalowski, C. F. *J. Phys. Chem. A* **1997**, *101*, 9430.
(30) Solimannejad, M.; Scheiner, S. *Chem. Phys. Lett.* **2006**, *424*, 1.
(31) Solimannejad, M.; Scheiner, S. *J. Phys. Chem. A* **2006**, *110*, 5948.
(32) Frisch, M. J.; et al. *Gaussian 03*, Revision B02; Gaussian, Inc.: Pittsburgh, PA, 2003.
(33) Csaszar, P.; Pulay, P. *J. Mol. Struct. (THEOCHEM)* **1984**, *114*, 31.
(34) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(35) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 1194.