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A Study of the Effect of Protonation on the Electronic Structure of the Diatomic Molecules BF, CO and N_2

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Using non-empirical calculations the changes in the three diatomic systems BF, CO and N_2 on protonation have been studied.

Protonation energies and changes in interatomic distances and stretching force constants of the systems have been interpreted in terms of differences in electronic structure of the diatomic molecules, using a description with localized orbitals.

Introduction

Protonation reaction of hydrocarbons, aldehydes, ketones and carboxylic acids have been subject to several studies. The experimental work is usually carried out in strongly acidic media [1–5]. For a number of protonated systems, the geometry and stability were investigated with the help of non-empirical calculations [6, 7].

The theoretical study of the protonation of first row diatomic molecules is especially interesting because in these systems the influence of the protonation on the electronic structure of the system can be investigated in detail. Several calculations have been performed on HCO^+ [8, 9] and HN_2^+ [9] and as a result of these calculations the geometry and energy of these systems are fairly well established. From experiments data are available on the heat of formation of HCO^+ [10, 11] and of HN_2^+ [11].

In the present paper we intend to investigate the changes, that occur in the electronic structure of the diatomic molecules BF, CO and N_2 on protonation. We will try to understand the effects that give rise to the changes in geometry as found in the calculations. For these studies we made use of a set of calculations performed with a slightly modified version of the IBMOL program [12] (LCAO–MO–SCF method). The basis set used is listed in Table 1 and a discussion of the choice of this basis set is found in Ref. [8].

Results and Discussion

The electronic structure of the diatomic molecules BF, CO and N_2 allows several possible protonated forms, i.e. $[\mathrm{H{-}A{-}B}]^+$, $[\mathrm{A{-}B{-}H}]^+$ and $\left[\mathrm{A}\underset{\mathrm{H}}{\text{———}}\mathrm{B}\right]^+$.

In all cases the linear form with the hydrogen atom attached to the atom of smaller Z-value of the A–B molecule appeared to be most stable, i.e. $[\mathrm{H{-}B{-}F}]^+$, $[\mathrm{H{-}C{-}O}]^+$ and $[\mathrm{H{-}N{-}N}]^+$ [8, 9]. For these systems we optimized the H–A and the A–B distances.

Table 1. *Gaussian basis functions*[a] *(orbital exponents)*

	B	C	N	O	F	H
1*s*	2.7004	3.9683	5.4782	7.2327	9.2271	0.2015
	9.9362	14.602	20.158	26.610	33.952	1.3325
	44.087	64.789	89.438	118.07	150.64	
	292.59	462.97	593.57	783.56	999.76	
2*s*	0.08160	0.1272	0.1820	0.2480	0.3244	
2*s*′	0.21454	0.3345	0.4785	0.6521	0.8529	
2*p* (*x*, *y*, *z*)	0.15669	0.2628	0.39285	0.5300	0.6591	
2*p*′ (*x*, *y*, *z*)	0.63337	1.0622	1.5879	2.1422	2.8097	

[a] The 1*s* orbitals of B, C, N, O and F are contracted according to $G(1s) = 0.50907\, g_1 + 0.47449\, g_2 + 0.13424\, g_3 + 0.01906\, g_4$.

The total energies of the diatomic molecules, given in Table 2, are not very good compared with energies that are computed with the help of a Slater basis [13]. This can be ascribed to the inadequate behaviour of our small set of Gaussian Type Functions near the nuclei. In the region of bond formation, however, the description with Gaussian Type Functions is reasonably good [14]. From the total energies we calculate the following protonation energies: 185 kcal/mole for BF, 153 kcal/mole for CO and 134 kcal/mole for N_2. The protonation energies for CO and N_2 may be compared with those calculated by Forsén and Roos [9], who found 142.4 kcal/mole for CO and 123 kcal/mole for N_2, using an extended basis set with polarization functions. (All these numbers are without zero point vibration energy correction.) We see that the differences between the two calculations are the same for CO and N_2 and that both differences are smaller than 10%. We may consider this as an example for the other properties connected with bond formation. These properties are more reliable than total energies and the changes between different systems are quite accurate, as among others a comparison with the data given in Ref. [9] shows.

Table 2 furthermore shows that the calculated distances in the diatomic molecules do not differ more than a few percents from the experimental values. The values of ΔR_{AB}, the change in the internuclear distance R_{AB} on protonation are also given in Table 2. In accordance with Forsén and Roos we find no significant

Table 2. *Computed*[a] *total energies, energies of protonation and interatomic distances (in a.u.) and stretching force constants (in mdyne/Å)*

	E	ΔE_{prot}	R_{A-B}	ΔR_{A-B}	k_{AB}	R_{A-H}
BF	−122.998		2.370 (2.38)		12.5 (7.9)	
HBF^+	−123.294	0.295	2.318	−0.052	15.3	2.266
CO	−111.858		2.169 (2.14)		24.0 (19.0)	
HCO^+	−112.103	0.243	2.143	−0.026	26.2	2.106
N_2	−108.148		2.115 (2.07)		29.9 (23.0)	
HN_2^+	−108.364	0.213	2.117	+0.002	30.5	1.983

[a] In parenthesis the experimental values.

change in the N–N distance on protonation of N_2. However, the results of Table 2 show that the bond distance R_{AB} in BF and CO is shortened when the proton is attached to the atom of smaller Z-value and that the value of ΔR_{AB} is the largest for BF, which is the most asymmetric diatomic molecule of the series. As can be seen, the trend found for the protonation energy ($\Delta E_p(BF) > \Delta E_p(CO) > \Delta E_p(N_2)$) agrees with the trend found for the decrease in bond distance.

For the diatomic systems, the stretching force constants calculated from E_{tot} vs R curves may be compared with the experimental values. The values are not very accurate but for reasons given above we expect that the changes in the stretching force constants on protonation are significant. This means that in protonated N_2 the N–N stretching force constant will be nearly the same as in the N_2 molecule, while in CO and BF the stretching force constant becomes larger on protonation. Here too the largest change is found in BF.

In Table 3 the gross atomic charges and atom atom overlap populations [15] are summarized. We see that within this approximation for the atomic charge (Mulliken) the atoms of the diatomic systems are about neutral. Table 4 shows the differences in gross atomic charge and in orbital population on protonation. Both sets of numbers indicate how the incoming proton affects the charge distribution of the diatomic system.

In general the electrons of the diatomic molecule shift towards the proton. In the σ-system the changes are larger for the atom adjacent to the proton and rather small for the other atom. The influence of the proton on the σ-electron distribution is of the same order of magnitude for the three protonated systems. This is not the case for the change in the π-electron system. Here the shift in the

Table 3. *Gross atomic charges and overlap populations*

	BF	HBF^+	CO	HCO^+	N_2	HN_2^+
q_A	−0.04	0.56	0.03	0.33	0.0	0.08
q_B	0.04	0.19	−0.03	0.22	0.0	0.43
q_H	—	0.25	—	0.45	—	0.49
$p(\sigma_{A-B})$	0.239	0.513	−0.009	0.165	−0.175	0.085
$p(\pi_{A-B})$	0.405	0.436	0.762	0.794	0.902	0.864
p_{A-B}	0.644	0.949	0.753	0.959	0.727	0.949
p_{A-H}		0.719		0.628		0.551

Table 4. *Changes in gross atomic charges and in orbital populations on protonation*

	BF/HBF^+	CO/HCO^+	N_2/HN_2^+
Δq_A	0.60	0.30	0.08
Δq_B	0.15	0.25	0.43
q_H	0.25	0.45	0.49
$\Delta n(\sigma_A)$	−0.66	−0.50	−0.42
$\Delta n(\sigma_B)$	−0.09	−0.05	−0.09
$n(s_H)$	0.75	0.55	0.51
$\Delta n(\pi_A)$	0.06	0.20	0.34
$\Delta n(\pi_B)$	−0.06	−0.20	−0.34

symmetrical π-electron system of N_2 is rather large. The π-electrons of BF however are asymmetrically distributed. They are largely located on fluorine and, due to the strong electronegativity of fluorine, they are not inclined to move away form the fluorine. The final gross atomic charges of Table 3 are analogous to those of important Valence Bond structures of the type $H^+A^-B^+$ for protonated N_2 but not for protonated BF and CO.

With the values of Tables 3 and 4 we only get information about the overall changes in the electron distributions. A more detailed picture of the changes in electronic density can be obtained from electron density difference maps [16]. Fig. 1 shows the difference in electron density between $[H\text{–}A\text{–}B]^+$ and AB along

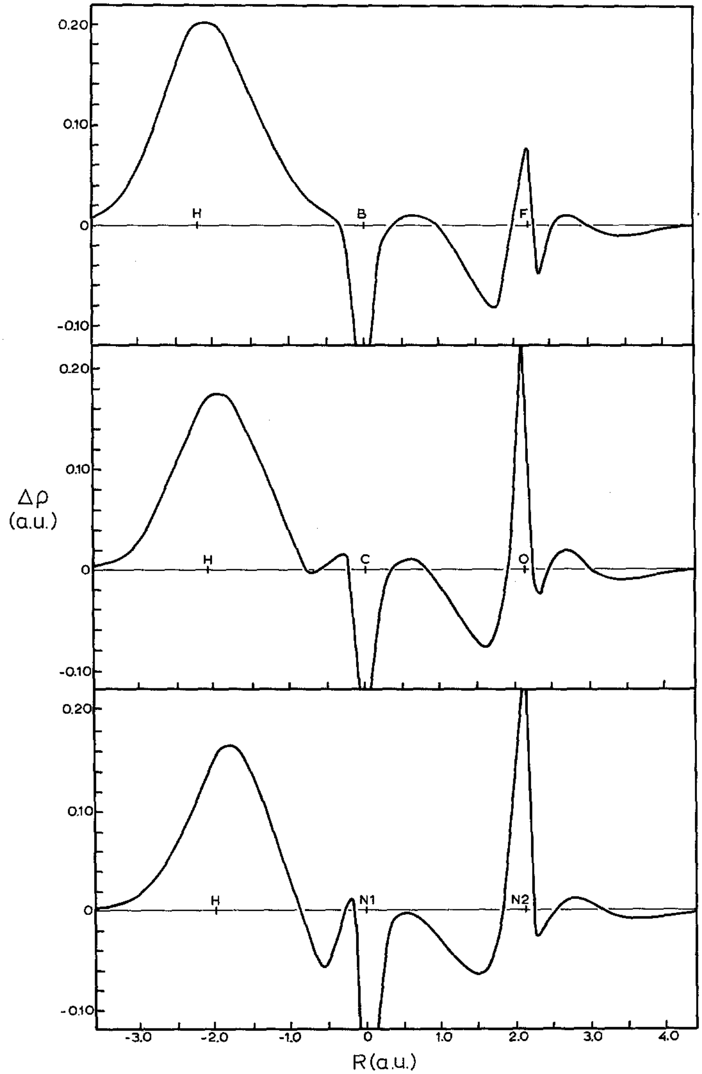

Fig. 1. Electron density difference along the molecular axis for HBF^+/BF, HCO^+/CO and HN_2^+/N_2

Table 5. *Orbital-orbital overlap populations*

System	Localized orbital	A–B (diatomic)	A–B (protonated)	A–H
	σ(B–F)	0.44	0.49	−0.01
BF	B*lp*/σ(B–H)	−0.16	0.01	0.73
HBF^+	F*lp*	−0.04	0.01	0.00
	π(B–F)	0.20	0.22	
	σ(C–O)	0.57	0.50	0.01
CO	C*lp*/σ(C–H)	−0.25	0.05	0.62
HCO^+	O*lp*	−0.33	−0.38	0.00
	π(C–O)	0.38	0.40	
	σ(N–N)	0.64	0.52	−0.01
N_2	N1*lp*/σ(N–H)	−0.40	0.04	0.58
HN_2^+	N2*lp*	−0.40	−0.46	−0.02
	π(N–N)	0.45	0.43	
	σ(C–O)	0.57	0.50	−0.04
CO	O*lp*/σ(O–H)	−0.25	−0.01	0.55
COH^+	C*lp*	−0.33	−0.34	−0.03
	π(C–O)	0.38	0.31	

the molecular axis of the various systems. Of course this figure gives only information about the σ-electron densities. Although the electron density difference along the axis looks rather complicated, it supports the picture outlined above. It also reveals that the shift of electrons towards the hydrogen can be found back in the separate molecular orbitals, e.g. even in the lone pair orbital at the F, O or N2 atoms.

In order to be able to discuss the results in terms of localized bonds the Hartree-Fock one electron functions were transformed into a set of localized orbitals, following the Uniform Localization procedure of Magnasco and Perico [17]. The orbital-orbital overlap populations calculated for these localized molecular orbitals are shown in Table 5. For comparison, we have included the values for linear $[COH]^+$. An analysis of this table shows for the diatomic systems the σ_{AB} overlap population to be built up from positive terms arising from the σ bonding orbital and negative terms arising from the lone pairs. On protonation at the atom of smaller Z-value A the lone pair on this atom moves away from the A–B bonding region and its negative contribution to the A–B overlap population disappears. Consequently the σ_{AB} overlap population becomes larger.

We further see from Table 5 that the changes in the π-electron density are as expected. For BF and CO the electron distribution becomes more symmetric and the overlap population becomes larger. For N_2 the electron distribution becomes asymmetric and the overlap population smaller. However, the changes in the π-overlap population are much smaller than the changes in the σ-overlap population. Therefore the strengthening of the A–B bond on protonation at the atom of smaller Z-value must in the first place be ascribed to changes in the σ-electron distribution.

Conclusion

Protonation of the diatomic molecules BF, CO and N_2 is most likely to occur at one of the lone pairs, because in that case not only the lone pair is stabilized but also the A–B σ-bond becomes more stable. If the proton is attached to the atom of smaller Z-value the π-bond also becomes stronger and therefore both effects work in the same direction. This may contribute to the relatively large protonation energy found for $[HBF]^+$ and $[HCO]^+$. It also results in a small A–B distance and in a considerable change in the A–B stretching force constant. In the case of $[HNN]^+$ and $[COH]^+$ the π-electron distribution becomes more asymmetric on protonation and the π-bond becomes weaker. In these cases the σ- and π-effects work in an opposite direction. For these systems we find a low energy of protonation. Furthermore the A–B distance hardly changes in $[HNN]^+$ and becomes larger in $[COH]^+$.

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