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# Bonding/antibonding Character of "Ione Pair" Molecular Orbitals from their Energy Derivatives; Consequences for experimental Data

Patrick Chaquin<sup>1</sup>, Franck Fuster<sup>1</sup> and François Volatron<sup>1</sup>

Correspondence to Patrick Chaquin (E-mail : chaquin@lct.jussieu.fr)

<sup>1</sup> P. Chaquin, F. Fuster, F. Volatron Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, F-75005 Paris, France E-mail: chaquin@lct.jussieu.fr

#### Abstract

The derivative of molecular orbitals (MO) energies with respect to a bond length (dynamic orbital force, DOF) is used to estimate the bonding/antibonding character of valence MOs along this bond, with a focus on lone pair MOs, in a series of small molecules: AH (A = F, Cl, Br), AH<sub>2</sub> (A = O, S, Se) AX<sub>3</sub> (A = N, P, As; X = H, F) and H<sub>2</sub>CO. The HOMO DOF agrees with the calculated variation of bond length and force constant in the corresponding ground state cation, and of bond length variation by protonation. These results also agree with available experimental data. It is worthy to note that the p-type HOMOs in AH and AH<sub>2</sub> are found bonding. The lone pair MO is bonding in NH<sub>3</sub>, while it is antibonding in PH<sub>3</sub>, AsH<sub>3</sub>, and AF<sub>3</sub>.

### Introduction

#### How to define the bonding/antibonding character of a MO?

The bonding/antibonding character can be based on essentially two criteria, energy or force, with different possible definitions on these criteria.

The IUPAC Gold Book<sup>1</sup> prefers the energy point of view, a bonding MO being characterized by "an increase in the total bonding". This generally corresponds also to a MO energy lower than the mean energy of the AOs constituting this MO. These definitions involve the whole molecule. Nevertheless, for the chemist, it is important to characterize local MO properties, i.e. their bonding/antibonding character along a bond, or more generally with respect to geometrical parameters. From this point of view one can consider that a MO is bonding along a given bond if its occupancy increases the bond dissociation energy.

Other definitions are based on force concepts. A MO will be said bonding if its electrons exert an attractive force on the nuclei of concern. For this purpose, a useful guideline is provided by the "Berlin function" f(x, y, z) which performs a partition of the space into bonding and antibonding areas.<sup>2</sup> With the notations of Scheme 1, for a diatomic molecule AB, the forces  $F_{eA}$  and  $F_{eB}$  exerted by an electron density  $\rho$  on nuclei A and B are (Eq. 1) :

$$F_{eA} = F_{eB} = -\frac{1}{2} \int \left[ \frac{Z_A}{r_A^2} \cos \theta_A + \frac{Z_B}{r_B^2} \cos \theta_B \right] \rho dv = -\frac{1}{2} \int f(x, y, z) \rho(x, y, z) dv$$
(1)



Scheme 1. Forces acting in a diatomic molecule AB

The bonding/antibonding zones are thus characterized by a positive/negative value of the function f. They are separated by a non-bonding surface given in Fig. 1 for a symmetrical A<sub>2</sub> molecules and the unsymmetrical HF one.



**Figure 1.** Bonding (f > 0, yellow) and antibonding (f < 0 dark blue) zones for diatomic A<sub>2</sub> and HF molecules.

On this basis, the total electron density is decomposed into MO densities and thus into additive orbital forces which quantify their bonding character.<sup>3, 4, 5</sup>

Another concept of "orbital forces" was proposed by Tal and Katriel <sup>6</sup>. It is built up from the MO energy derivatives with respect to nuclear coordinates. According to the Koopmans theorem<sup>7</sup>, the MO energy can be expressed as Eq. 2:

$$\varepsilon_i = E^0 - E_i^+ \qquad (2)$$

where  $E^{\circ}$  is the Hartree-Fock (H-F) energy of a neutral species and  $E_i^+$  the energy of the frozen orbital cation resulting from the removal of one electron from the *i*<sup>th</sup> spin-orbital  $\phi_i$ . For a diatomic molecule, the derivative with respect to the internuclear distance *R* yields (Eq. 3):

$$\frac{d\varepsilon_i}{dR} = \frac{dE^0}{dR} - \frac{dE_i^+}{dR} \qquad (3)$$

At the equilibrium value  $R_e$  of the neutral species,  $dE^0/dR = 0$  and (Eq. 4):

$$\left(\frac{d\varepsilon_i}{dR}\right)_{R=R_e} = -\left(\frac{dE_i^+}{dR}\right)_{R=R_e} \quad (4)$$

Eq. 4 means that if  $\varepsilon_i^i = d\varepsilon_i/dR$  is positive, the ion energy  $E_i^*$  tends to decrease by lengthening R which characterizes a bonding  $\phi_i$  MO.

These orbital forces are not additive since the total H-F energy is not the sum of occupied MO energies. The term of "dynamical orbital forces" (DOF) was proposed by Averill and Painter for these derivatives because they arise from electron removing (whereas the additive Bader orbital forces appear as "static orbital forces").<sup>8</sup> These forces are closely related to the Mulliken's criterion of the "bonding power" of an electron.<sup>9</sup>

Because canonical MOs are delocalized on the whole molecule, a given MO can be more or less bonding along a given bond and antibonding along another one. These characters can be evaluated by calculating the energy derivative (DOF) with respect to each bond by a finite difference of length. In most of cases, a small variation of one bond length, typically a few  $10^{-3}$  Å, has a negligible effect on the other internal coordinates and the resulting DOF can be regarded as a reliable measure of the local (on a given bond) bonding/antibonding character.

Because Eq. 4 involves the neglect of MO relaxation and correlation energy, the question arises if the DOF correctly predicts the variation of geometry (and eventually of other properties) following the ionization. At least, one can expect that this quantity reflects a trend which indicates the sign of this variation. As a matter of fact, this assumption has been fully validated in a recent work<sup>10</sup>, in which were reported the DOFs of the valence shell MOs of a panel of 19 diatomic species and of HCN, HNC and CH<sub>3</sub>CN, focusing our attention on the "lone pairs" MOs of some coordinating species.

Very few works have been devoted to the study of canonical MO derivatives<sup>11,12,13</sup>. Tal and Katriel <sup>6</sup> have determined the bonding/antibonding character of the MOs of diatomic homonuclear molecules of the Li-F period. Also, the variation of the DOFs of selected MOs along a reaction coordinate (RC) highlights the nature of the reorganization of these MOs and what stage of the RC it occurs. Moreover, the shape of the DOF curves reveals the existence and precise location of MO avoided crossings.<sup>14</sup> Because Kohn-Sham MO energy also approximate ionisation energy<sup>15</sup>, its derivative was used successfully by several authors as a criterion of bonding character.<sup>8, 16,17</sup>

In this work, we will focus on the MOs associated to "lone pairs" of small molecules AH (A = F, Cl, Br), AH<sub>2</sub> (A = O, S, Se), AH<sub>3</sub>, AF<sub>3</sub> (A = N, P, As) and H<sub>2</sub>CO. It has been already pointed out that "lone pair" and "non-bonding pair" are not synonymous and, using the localization procedure of Ciolkowski, Chesnut<sup>18</sup> showed that the participation to bonding in some of the preceding molecules is approximately 10-15%. From a qualitative point of view, most of time no "visual" criterion, based on the presence or not of nodal surfaces cutting the bond, can be used to decide whether such MOs are more or less bonding or antibonding. The results will be compared with the variation of observable physical data upon ionization and protonation involving these lone pairs: bond lengths, vibration frequencies and forces constants, computed at a reliable level, and experimental available results.

# **Calculation details**

Calculations of MO energy derivatives (Dynamic Orbital Forces, DOF) have been performed at the HF/6-311G<sup>\*\*</sup> level, and for sake of comparison, at the B3LYP/6-311G<sup>\*\*</sup> level, after optimization of geometrical parameters at the same level. The derivatives are computed by finite difference of the length of equivalent bonds by 2-3.10<sup>-3</sup> Å. In a previous work<sup>10</sup> it was stated that that higher level basis sets do not improve significantly the DOF values. The DOFs have been visualized using red (antibonding)/blue (bonding) arrows, whose thickness is proportional to their value in percent of the maximum DOF of the occupied MOs.

The geometry of neutral molecules, positive ions and protonated species were computed at the CCSD(T)/cc-pVTZ level. Vibration frequencies and force constants were computed at the B3LYP/cc-pVTZ level. The GAUSSIAN 09 series of program<sup>19</sup> was used.

# **Results and discussion**

# Molecules HF, HCl and HBr

The results are gathered in Table 1. The DOFs of the valence shell are visualized in Figure 2 in the case of HF.



**Figure 2**. DOF of valence shell MOs of HF. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of maximum DOF

The Table 1 indicates that  $1\sigma$  and  $2\sigma$  usually referred as  $\sigma$  bonding MO and sp lone pair MO respectively are almost equally bonding. The  $\pi$  MOs, usually described as "purely non-bonding" have in fact a marked bonding character. This character is partly due to the presence of empty p MOs of hydrogen in an extended basis set. Nevertheless, even at the STO-3G level, this character remains (0.011 au for HF), though the overlap with the 1s AO of hydrogen is zero. It means that the pure atomic p density on atom A is intrinsically bonding, i.e. exerts an attractive force on the H nucleus. It can be understood qualitatively from Figure 1: the non-bonding surface does not divide equally the 2p density which can be seen slightly more localized in the bonding region.

**Table 1.** Molecules HF, HCl and HBr: DOFs (au) of valence MOs at the H-F(B3LYP) levels; bond lengths (Å) of neutral R(AH), cationic R(AH<sup>+</sup>) and protonated R(AH<sub>2</sub><sup>+</sup>) species; vibration frequency (cm<sup>-1</sup>) and force constant of neutral v(AH) and cationic v(AH<sup>+</sup>) species.<sup>a</sup> 6-311 G<sup>\*\*</sup> <sup>b</sup> CCSD(T)/cc-pVTZ; <sup>c</sup> B3LYP/ cc-pVTZ; <sup>d</sup> experimental values from the NIST database (ref. 20)

	HF	HCI	HBr
MO		DOF H-F(B3LYP) <sup>a</sup>	
1σ	0.201 (0.167)	0.103 (0.082)	0.085 ( <i>0.063</i> )
2σ	0.212 (0.118)	0.111 (0.067)	0.093 ( <i>0.058</i> )
<b>π(HOMO)</b>	0.056 ( <i>0.047</i> )	0.013 ( <i>0.013</i> )	0.008 (0.008)
		Bond lengths <sup>b</sup>	
R(AH)	0.9173	1.2772	1.4129
R(AH <sup>+</sup> )	1.0023	1.3175	1.4451
$\Delta R_{ion}$ (calc)	0.0850	0.0403	0.0322
$\Delta R_{ion}$ (exp) <sup>d</sup>	0.097	0.040	0.034
R(AH <sub>2</sub> <sup>+</sup> )	0.9617	1.3068	1.4370
$\Delta R_{prot}$	0.0444	0.0296	0.0241
	Stretching	vibration frequency (f	force constant) <sup>c</sup>

	Stretching vi	Stretching vibration frequency (force constant) <sup>c</sup>		
ν(AH)	4088.0 (10.42)	2936.8 (5.26)	2620.5 (4.13)	
ν(AH⁺)	2992.3 (5.58)	2616.8 (4.18)	2372.9 (3.39)	
$\Delta v_{ion}$ (calc)	-1095.7	-320	-247.6	
$\Delta v_{ion}$ (exp) <sup>d</sup>	-1225.	-318.	-207.	

The bonding character of  $\pi$  MOs agrees with the calculated bond lengths of neutral and cationic (<sup>2</sup> $\pi$ ) species: in each case the cation HF<sup>+</sup>, HCl<sup>+</sup>, HBr<sup>+</sup> exhibit a bond lengthening ( $\Delta R_{ion} > 0$ ) with respect to the neutral molecule. As also expected, the ionization results in a decrease of the vibration frequency and force constant. The protonation results also in a bond lengthening, but less marked than in ionization: it can be viewed essentially as a partial electron removing from one  $\pi$  MO because the HAH<sup>+</sup> angle is close to 90° (111° for A= F, 94° for A = Cl and 92° for A = Br). Experimental results available in the NIST database<sup>20</sup>, reported in Table 1, agree with the bonding character of the HOMO, with an increase of the bond length and a decrease of the vibration frequency, close to calculated values. Also, an increase of the bond length from 0.917 Å to 0.961 Å has been observed in H<sub>2</sub>F<sup>+</sup>.<sup>21</sup>

We can note that the B3LYP DOF values are in qualitative agreement with H-F ones and close to them for the HOMO, but may differ significantly in some other cases.

# Molecules $H_2O$ , $H_2S$ and $H_2Se$

The results are gathered in Table 2. The DOFs are visualized for  $H_2O$  in Figure 3.



Figure 3. Molecule H<sub>2</sub>O.Graphical representation of H-F DOFs of valence shell MOs. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of maximum DOF

The  $1a_1$  and  $1b_2$  MOs correspond to the  $\sigma$  bonds of AH<sub>2</sub>; they appear with almost equal bonding character. The  $2a_1$  MO is associated to the sp lone pair and is also bonding, but significantly less than the corresponding ones in AH molecules. Like in the AH species, the HOMO is essentially a p AO of atom A, nevertheless slightly bonding in H<sub>2</sub>O and very slightly bonding in H<sub>2</sub>S and H<sub>2</sub>Se. This character agree with the lengthening of the A-H bonds in cations AH<sub>2</sub><sup>+</sup> (<sup>2</sup>B<sub>1</sub>) and protonated AH<sub>3</sub><sup>+</sup> species as well as a decrease of both (in-phase and out-of-phase) stretching vibrations frequencies agree with the bonding character of the HOMO of these species: the  $a_1$  and  $b_2$  modes of H<sub>2</sub>O at respectively 3652 cm<sup>-1</sup> and 3757 cm<sup>-1</sup> drops to 3213 cm<sup>-1</sup> and 3259 cm<sup>-1</sup> in H<sub>2</sub>O<sup>+</sup>;<sup>20</sup> similarly the  $a_1$  mode of H<sub>2</sub>S (2615 cm<sup>-1</sup>) and H<sub>2</sub>Se (2345 cm<sup>-1</sup>) slightly decreases in H<sub>2</sub>S<sup>+</sup> (2496 cm<sup>-1</sup>) and H<sub>2</sub>Se<sup>+</sup> (2267 cm<sup>-1</sup>) respectively<sup>20</sup>.

Also, an increase of the bond lengths is observed by protonation of  $H_2O$  (from 0.958 Å to 0.974 Å)<sup>22</sup> and of  $H_2S$  (from 1.336 Å to 1.359 Å)<sup>23</sup>.

**Table 2**. Molecules  $H_2O$ ,  $H_2S$  and  $H_2Se$ : DOFs (au) with respect to A-H length of valence MOs at the H-F(B3LYP) levels; bond lengths (Å) of neutral R(AH<sub>2</sub>), cationic R(AH<sub>2</sub><sup>+</sup>) and protonated R(AH<sub>3</sub><sup>+</sup>) species; vibration frequencies (cm<sup>-1</sup>) and force constants of neutral v (AH<sub>2</sub>) and cationic v(AH<sub>2</sub><sup>+</sup>) species <sup>a</sup> 6-311 G<sup>\*\*</sup> <sup>b</sup> CCSD(T)/cc-pVTZ; <sup>c</sup> B3LYP/ cc-pVTZ.

	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se
МО		DOF HF(B3LYP) <sup>a</sup>	
1a1	0.283 (0.224)	0.146 (0.111)	0.127 (0.091)
1b <sub>2</sub>	0.294 (0.195)	0.156 (0.107)	0.132 (0.091)
<b>2</b> a <sub>1</sub>	0.098 ( <i>0.038</i> )	0.040 (0.015)	0.032 (0.014)
1b1(HOMO)	0.042 (0.038)	0.003 (0.007)	0.003 (0.005)
		Bond lengths <sup>b</sup>	
R(AH <sub>2</sub> )	0.9595	1.3406	1.4583
R(AH <sub>2</sub> <sup>+</sup> )	1.0012	1.3607	1.4747
<b>∆R</b> <sub>ion</sub>	0.0417	0.0201	0.0164
R(AH <sub>3</sub> <sup>+</sup> )	0.9778	1.3549	1.4688
∆R <sub>prot</sub>	0.0183	0.0143	0.0105
	Stretching vibration frequency (force constant) <sup>c</sup>		
		AH <sub>2</sub>	
ν(a <sub>1</sub> )	3801.0 (8.89)	2685.3 (4.40)	2391.7 (3.44)
v(b <sub>2</sub> )	3901.3 (9.70)	2699.4 (4.46)	2406.2 (3.48)
		AH <sub>2</sub> <sup>+</sup>	
v(a1)	3326.4 (6.80)	2562.8 (4.01)	2324.2 (3.24)
v(b <sub>2</sub> )	3372.3 (7.28)	2565.3 (4.033)	2331.8 (3.27)

#### Molecules NH<sub>3</sub>, PH<sub>3</sub> and AsH<sub>3</sub>

The results are gathered in Table 3.

	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>
MO		DOF HF (B3LYP) <sup>a</sup>	
<b>1a</b> 1	0.280 (0.213)	0.146 (0.106)	0.135 ( <i>0.096</i> )
1e	0.223 (0.146)	0.114 (0.074)	0.098 ( <i>0.065</i> )
<b>2</b> a <sub>1</sub>	0.024 (0.009)	-0.013 ( <i>-0.020</i> )	-0.013 (-0.019)
		Bond lengths <sup>b</sup>	
R(AH <sub>3</sub> )	1.0141	1.4185	1.5098
R(AH <sub>3</sub> <sup>+</sup> )	1.0223	1.4003	1.4833
$\Delta \mathbf{R}_{ion}$	0.0082	-0.0182	-0.0265
R(AH <sub>4</sub> +)	1.0226	1.3966	1.4776
$\Delta \mathbf{R}_{prot}$	0.0085	-0.0219	-0.0322
		Stretching vibration frequency (force constant) <sup>c</sup>	
		AH <sub>3</sub>	
ν(a <sub>1</sub> )	3462.5 (7.25)	2384.8(3.46)	2178.9(2.85)
v(e)	3578.9(8.22)	2392.6(3.51)	2193.3 (2.89)
		AH <sub>3</sub> <sup>+</sup>	
ν(a <sub>1</sub> )	3339.6 (6.62)	2446.8(3.57)	2239.1 (2.98)
ν(e)	3513.7 (8.06)	2523.3(3.95)	2311.7 (3.23)

Table 3. Molecules  $NH_3$ ,  $PH_3$  and  $AsH_3$ : DOF (au) of valence MOs with respect to A-H length at the H-F(B3LYP) levels; bond lengths (Å) of neutral R(AH<sub>3</sub>), cationic R(AH<sub>3</sub><sup>+</sup>) and protonated R(AH<sub>4</sub><sup>+</sup>) species; vibration frequencies (cm<sup>-1</sup>) and force constant of neutral and cationic species.<sup>a</sup> 6-311 G<sup>\*\* b</sup> CCSD(T)/ccpv-TZ; <sup>c</sup> B3LYP/ccpv-TZ

The MOs  $1a_1$  and e, associated to the  $\sigma$  bonds have DOFs of the same order of magnitude. A remarkable point is the fact that the  $2a_1$  MO associated to the lone pair is bonding for NH<sub>3</sub> and antibonding for PH<sub>3</sub> and AsH<sub>3</sub>, which is visualized in Figure 4. Available experimental results agree with the bonding character of the HOMO of NH<sub>3</sub> whose vibration frequency drops in NH<sub>3</sub><sup>+</sup> from 3444 cm<sup>-1</sup> to 3389 cm<sup>-1</sup> (e) and from 3337 cm<sup>-1</sup> to 3177 cm<sup>-1</sup> (a<sub>1</sub>).<sup>20</sup> Protonated species NH<sub>4</sub><sup>+</sup> in Ne matrix absorbs at 3357.5 (e) <sup>24</sup>, very close to NH<sub>3</sub><sup>+</sup>.



**Figure 4.** Molecules NH<sub>3</sub>, PH<sub>3</sub> and AsH<sub>3</sub>. Graphical representation of H-F DOFs of the HOMO lone pair. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of the maximum DOF

Again, B3LYP DOF values agree qualitatively with H-F ones though important differences in absolute values. All computed physical properties are consistent with DOF results :  $NH_3^+$  and  $NH_4^+$  exhibit longer bond lengths than  $NH_3$ , while  $PH_3^+$  and  $PH_4^+$  on the one hand,  $AsH_3^+$  and  $AsH_4^+$  on the other hand have shorter bonds than  $PH_3$  and  $AsH_3$  respectively. Similarly, ionisation and protonation result in a decrease of stretching vibration frequencies and force constants for  $NH_3$  and an increase of the

same quantities for  $PH_3$  and  $AsH_3$ . To understand this difference, the corresponding planar structures were studied: the lone pair  $2a_1$  MO is now pure p, and its DOF becomes positive for all three species as it can be seen in Table 4. The corresponding cations have longer bond lengths.

**Table 4.** Planar NH<sub>3</sub>, PH<sub>3</sub> and AsH<sub>3</sub>. DOF of the HOMO  $a_1$  at the H-F level; bond lengths of AH<sub>3</sub> and AH<sub>3</sub><sup>+</sup> species (CCSD(T)/cc-pVTZ.

МО	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>
HOMO DOF a1	0.037	0.005	0.009
R(AH₃)	0.9952	1.3802	1.4595
R(AH₃ <sup>+</sup> )	1.0223	1.3955	1.4752
$\Delta R_{ion}$	0.0271	0.0153	0.0157

The evolution of the bonding character of the lone pair from NH<sub>3</sub> to PH<sub>3</sub> may appear paradoxical. As depicted in scheme 2, this lone pair results, by pyramidalization, from a destabilizing mixing with  $\sigma$  (out-of-phase) and a stabilizing mixing with  $\sigma^*$  (in-phase). Moreover, it has been shown there is a stronger mixing of p with  $\sigma^*$  in PH<sub>3</sub> than in NH<sub>3</sub> and though an increase in the in-phase participation of hydrogens<sup>25</sup>. But, at the same time, due an increase of its s character, the "lone pair" density is repelled out of the A-H bond, in the antibonding force region, a phenomenon which appears in the MOs of Fig. 4.



Scheme 2. Interacting MOs in NH<sub>3</sub> and PH<sub>3</sub> lone-pairs.

A similar evolution could be expected for the sp  $a_1$  "lone pair" in the series  $H_2O-H_2S-H_2Se$ . Indeed, the DOF drops from 0.098 to 0.040 and 0.032 for this MO which remains nevertheless bonding.

#### Molecules NF<sub>3</sub>, PF<sub>3</sub> and AsF<sub>3</sub>

The results are gathered in Table 5. For all three molecules, the  $a_1$  MO associated to the lone pair is strongly antibonding.

	NF <sub>3</sub>	PF <sub>3</sub>	AsF <sub>3</sub>
MO		DOF HF (B3LYP) <sup>a</sup>	
HOMO a <sub>1</sub>	-0.169 (-0.154)	-0.161 (-0.129)	-0.116 (-0.078)
		Bond lengths <sup>t</sup>	)
AF <sub>3</sub>	1.3717	1.5762	1.706
<b>AF</b> <sub>3</sub> <sup>+</sup>	1.2839	1.5051	1.648
$\Delta R_{ion}$	-0.0878	-0.071	-0.058
	Stretching vibration frequency (force constant) <sup>c</sup>		
		AF <sub>3</sub>	
ν(a <sub>1</sub> )	1050.4 (9.90)	871.2 (10.0)	720.0 (6.77)
v(e)	895.6 (7.19)	837.4 (9.38)	686.3 (6.34)
		AF <sub>3</sub> <sup>+</sup>	
ν(a <sub>1</sub> )	988.5 (9.80)	907.6 (10.1)	753.8 (6.90)
v(e)	1234.8 (13.60)	1063.2 (15.4)	798.1(8.81)

Table 5. Molecules NF<sub>3</sub>, PF<sub>3</sub> and AsF<sub>3</sub>: DOF (au) of the HOMO  $a_1$  with respect to A-F length at the H-F(B3LYP) levels; bond lengths (Å), stretching vibration frequencies (cm<sup>-1</sup>) and force constants for neutral R(AF<sub>3</sub>) and cationic R(AF<sub>3</sub><sup>+</sup>) species. <sup>a</sup> 6-311 G<sup>\*\* b</sup> CCSD(T)/cc-pVTZ; <sup>c</sup> B3LYP/cc-pVTZ

The graphical representation of this MO in NF<sub>3</sub> shows that it results from an out-of-phase mixing of the sp hybrid of the central atom with 2p AOs of fluorine atoms, *a priori* antibonding; but the density in yellow in Fig. 5, can be viewed as a bonding interaction through the N-F bonds, the balance of which is not self-evident. The antibonding nature of  $a_1$  is clearer for PF<sub>3</sub> and AsF<sub>3</sub>.



Fig. 5.  $a_1$  HOMO lone pairs of NF<sub>3</sub>, PF<sub>3</sub> and AsF<sub>3</sub>

Accordingly, we observe a marked shortening in bond lengths of the corresponding cations. Frequencies and force constants of the e vibration increase in cations. This effect is weak in  $a_1$  vibrations of PF<sub>3</sub> and AsF<sub>3</sub>, and even a weak decrease is observed for NF<sub>3</sub>.

#### Molecule H<sub>2</sub>CO

In Table 6, we report the DOFs corresponding to derivatives with respect to the various atom distances: CO and CH bond lengths and HH distance. In the latter case, this distance variation was obtained by variation of HCH angle, i.e. keeping constant both CO and CH lengths.

**Table 6**. Molecule  $H_2CO$ : DOFs (au) with respect to C-O, C-H and H-H distances at the H-F(B3LYP) levels; bond lengths (Å), stretching vibration frequency (cm<sup>-1</sup>) and force constants for neutral  $H_2CO$ , cationic and protonated  $H_2COH^+$ . <sup>a</sup> 6-311 G\*\* <sup>b</sup> CCSD(T)/cc-pVTZ; <sup>c</sup> B3LYP/cc-pVTZ.

		H <sub>2</sub> C=O	
MO	DOF/R(CO) <sup>a</sup>	DOF/R(CH) <sup>a</sup>	DOF/R(HH) <sup>a</sup>
<b>1a</b> 1(σco)	0.341 ( <i>0.029</i> )	-0.024 (-0.028)	0.005 ( <i>0.012</i> )
2а₁(σ <sub>сн2</sub> )	-0.095 <i>(-0.077</i> )	0.169 ( <i>0.129</i> )	0.025 ( <i>0.044</i> )
<b>1b</b> <sub>2</sub> (σ <sub>CH2</sub> )	0.109 ( <i>0.079</i> )	0.124 (0.088)	-0.031 <i>(-0.055</i> )
3a <sub>1</sub> (n <sub>sp</sub> )	0.140 (0.077)	0.008 (-0.013)	0.025 ( <i>0.039</i> )
<b>1b</b> <sub>1</sub> (π)	0.225 ( <i>0.171</i> )	-0.027 (-0.023)	0.009 (0.013)
2b <sub>2</sub> (n <sub>p</sub> )	-0.074 <i>(-0.029</i> )	0.040 (-0.011)	-3.10 <sup>-4</sup> (0.015)
		Bond lengths <sup>b</sup>	
	R(CO)	R(CH)	R(HH) (HCH)
R(H <sub>2</sub> CO)	1.2095	1.1033	1.8732 (116.2)
<sup>2</sup> b <sub>2</sub> R(H <sub>2</sub> CO <sup>+</sup> )	1.200	1.1135	1.9401 (121.2)
$\Delta R_{ion}$	-0.0095	0.0102	0.067 (5.0)
R(H <sub>2</sub> COH <sup>+</sup> )	1.2520	1.0872	1.9146 (122.9)
		1.0896	
$\Delta R_{prot}$	0.0425	-0.0161	0.0414 (6.0)
		-0.0137	
		Frequencies (force constant) <sup>c</sup>	
	v(CO)	v(CH)	γ <b>(HCH)</b>
H <sub>2</sub> CO	1823.5 (14.41)	a1 2878.5 (5.09)	a1 1536.3 (1.54)
		b <sub>2</sub> 2932.6 (5.68)	
H <sub>2</sub> CO <sup>+</sup>	1708.0 (19.8)	2758.7 (4.64)	1248.0 (0.97)
		2840.9 (5.26)	

The DOFs of the three highest MOs are graphically presented in Fig. 6.



**Figure 6.** Molecule H<sub>2</sub>CO. Graphical representation of H-F DOFs of valence shell MOs. Blue/red arrows indicate a bonding/antibonding character, with a thickness proportional to the % of the maximum DOF

Some discrepancies appear between HF and B3LYP calculated DOFs. For examples, the  $2b_2$  and  $3a_1$  MOs are found bonding along C-H at HF level and antibonding at B3LYP level.

The HOMO  $2b_2$  is antibonding along CO, in agreement with the shortening of this bond and the increase of force constant upon ionization (the lowering of the frequency is due to an increase of reduced mass in the cation).

Regarding the C-H bonds, the variation by ionization of their lengths and of the force constant of the vibration in which they are involved agree with an bonding character of the HOMO along them, predicted by the B3LYP DOF (but not at the H-F level).

The calculated DOF with respect to H...H distance (i.e. with HCH angle) of the HOMO is near zero at the H-F level and positive (0.015) at the B3LYP one. By ionization, we observe an increase of this distance and a decrease of the forces constants in the  $a_1 \gamma$  mode (in-plane deformation), which agrees with the bonding character found at the B3LYP level.

The effect of protonation is more difficult to discuss because several MOs are strongly perturbed. Regarding for example the variation of CO bond length, we deal with the  $2b_2$  (antibonding) and  $3a_1$  (bonding) associated to each "lone pair" of oxygen, but the  $b_1$  (p) is expected to become more located on oxygen and thus less bonding along CO.

#### **Concluding remarks**

The dynamic orbital force (DOF) appears as a good criterion of the bonding/antibonding character of MOs along a given bond. For canonical H-F MOs, this quantity is the force exerted by electrons on nuclei if one electron occupying a given MO is removed, all other electrons being frozen. Indeed, it allows the prediction, with very few exceptions, of the bond length variation upon ionization and protonation, as summarized in Fig. 7. The relative bond lengths variations by ionization,  $\Delta R/R_e$ , are plotted as a function of the H-F (7a) and B3LYP (7b) DOFs. In the blue areas, both DOF and  $\Delta R/R_e$  are positive, corresponding to a lengthening of bonds by removing an electron from a bonding MO. In the red areas both DOF and  $\Delta R/R_e$  are negative, corresponding to a shortening of bonds by removing an electron from an antibonding MO. A very rough relation appears between  $\Delta R/R_e$  and the Hartree-Fock DOFs. It means that, though these DOFs involve the neglect of MO relaxation and of correlation energy, they provide a reliable predictive index for the variation of experimental data upon ionisation, in confirmation to a previous work mainly devoted to diatomic species<sup>10</sup>. The same relation between  $\Delta R/R_e$  and DOF is observed from B3LYP DOFs, with even a better linear correlation.

From a practical point of view, the DOFs are easy to compute and are stable with respect to the basis set, provided double zeta or higher levels are used.<sup>10</sup> Generally, it is no more the case with the classical overlap population which can be strongly dependant on the basis set, especially with extended ones or when diffuse OAs are included. Another criterion for the MO bonding/antibonding character along a bond A-B consists in comparing the MO energy of the mean energy of the AOs of A and B fragments involved in this MO, which is not straightforward in the practice.



**Figure 7**. Relative bond length variation upon ionization as function of DOF of the removed electron; (a) DOF at the HF level; (b) DOF at the B3LYP level.

The DOFs are also in qualitative agreement with the variation of forces constants in vibration normal coordinates when the molecule is ionized. It is worthy to note that the relatively important bonding character found for the p MOs of halogen hydride is somewhat counterintuitive. Also, it can be surprising at first glance that the "lone pair" of NH<sub>3</sub> is bonding, while those of PH<sub>3</sub> and AsH<sub>3</sub> are antibonding.

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