On the Non-Classical Contribution in Lone Pair-π Interaction: IQA perspective

Zahra Badri[a]*, Cina Foroutan-Nejad[a], Jiri Kozelka[b,c], Radek Marek[a,d]*

[a] CEITEC – Central European Institute of Technology, Masaryk University, Kamenice 5/A4, CZ-625 00, Brno, Czech Republic

[b] Université Paris Descartes, UMR 8601 CNRS, 45, rue des Saints-Pères, 75270 Paris, France

[c] Department of Condensed Matter Physics, Faculty of Science, Masaryk University Kotlářská 2, CZ-611 37 Brno, Czech Republic

[d] Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5/A4, CZ-625 00 Brno, Czech Republic

* To whom correspondence should be addressed

Email: zbadri@mail.muni.cz, radek.marek@ceitec.muni.cz

Table S1. The difference in atomic-basin charges induced by complexation, Δq, in atomic units for all three motifs of **3**-H_2O.

	C	N	$H_\pi{}^*$	F	O	$H_W{}^*$	water
t_1-**3**·$\mathbf{H_2O}$	C1/6	+0.0074		−0.0098	−0.0042	+0.0156	+0.0114
	C2/3/4/5	+0.0003		−0.0017			
t_2-**3**·$\mathbf{H_2O}$	C1	+0.0074		−0.0093	−0.0096	+0.017	+0.0074
	C2	+0.0026		−0.0025			
	C3	+0.0137		−0.0045			
	C4/5/6	−0.0023		−0.0026			
p-**3**·$\mathbf{H_2O}$	C1/4	+0.0092		−0.0036	−0.0156	+0.0152	−0.0004
	C2/3/5/6	+0.0035		−0.0045			

* H_π and H_W correspond to hydrogen atoms of the ring and both hydrogen atoms of water molecule, respectively.

Table S2. The magnitude of atomic charges of atoms in the complex in atomic unit.

		C	N	H_π*	F	O	H_W*
1·H₂O	C1	+1.1514		+0.1762		−1.2145	+0.6102
	C3/4	+0.4391		+0.1481			
	N2/5		−1.2533	+0.4991			
2·H₂O	C1/2	+1.0917		+0.0772		−1.1948	+0.5986
	N6/7		−0.5794				
	N8/9		−0.5909				
p-3·H₂O	C1/4	+0.6815			−0.6754	−1.1939	+0.5967
	C2/3/5/6	+0.6743			−0.6759		
t₁-3·H₂O	C1/6	+0.6785			−0.6812	−1.1810	+0.5962
	C2/3/4/5	+0.6731			−0.6741		
t₂-3·H₂O	C1	+0.6759			−0.6804	−1.1888	+0.5981
	C2	+0.6756			−0.6746		
	C3	+0.6887			−0.6772		
	C4/5/6	+0.6692			−0.6747		
4·H₂O	C1/2	+1.8937			−0.6881	−1.1983	+0.6023
	C3	+1.8872			−0.6875		
	N10/12	−1.2043					
	N11	−1.2096					
5·H₂O	C(H)	+0.0880		+0.0984		−1.2014	+0.6011
	C(CN)**	+0.1126					
	(C)-CN**	+0.9511					
	(C)-CN**		−1.1562				

* H_π and H_W correspond to hydrogen atom of the ring and hydrogen atom of water molecule, respectively.

** The bold font in C-CN corresponds to the particular atom which it's property has been reported.

Table S3. Inter-atomic interaction energy, contributions of inter-atomic exchange-correlation energy, electrostatic contribution, and delocalization index as well as primary (E_{int}^{prim}), secondary (E_{int}^{sec}) and fragment-based (E_{int}^{Tot}) for complexes t_1–**3**·H$_2$O and t_2–**3**·H$_2$O. Energy in kcal·mol^{-1} and DI in au.

	A...B	$E_{inter-atomic}$	E_{XC}	E_{Cl}	DI
t_1–**3**·H$_2$O	O...C1/6	−92.2	−2.8	−89.4	0.0272
	O...C2/5	−63.1	−0.2	−62.9	0.0038
	O...C3/4	−51.0	−0.1	−51.0	0.0011
	E_{int}^{prim}	**−412.6**	**−6.2**	**−406.4**	**0.0642**
	O...F7/12	+88.1	−4.0	+92.1	0.0401
	O...F8/11	+59.4	0.0	+59.4	0.0005
	O...F9/10	+47.3	0.0	+47.3	0.0002
	H$_W$*... R	+4.1	−1.3	+5.4	0.0139
	E_{int}^{sec}	**+431.5**	**−9.3**	**+409.8**	**0.0955**
	E_{int}^{Tot}	**−18.9**	**−15.5**	**−3.4**	**0.1597**
t_2–**3**·H$_2$O	O...C1	−93.5	−3.5	−90.0	0.0318
	O...C2	−66.7	−0.5	−66.2	0.0063
	O...C3	−89.2	−2.7	−86.5	0.0257
	O...C4	−52.9	−0.1	−52.8	0.0013
	O...C5	−61.5	−0.2	−61.3	0.0038
	O...C6	−51.4	−0.1	−51.3	0.0013
	E_{int}^{prim}	**−415.2**	**−7.1**	**−408.1**	**0.0702**
	O...F7	+88.7	−4.5	+93.2	0.0414
	O...F8	+63.2	−0.1	+63.3	0.0010
	O...F9	+83.2	−2.5	+85.7	0.0260
	O...F10	+49.4	0.0	+49.4	0.0002
	O...F11	+58.1	0.0	+58.1	0.0005
	O...F12	+48.1	0.0	+48.1	0.0002
	O...F	+390.7	−7.1	+397.8	0.0693
	H$_W$*... π	+386.2	−0.2	+386.4	0.0027
	H$_W$*... F	−380.0	−1.0	−379.0	0.0103
	H$_W$*... R	+6.2	−1.2	+7.4	0.0130

E_{int}^{sec}	+433.5	−8.2	+405.2	0.0823
E_{int}^{Tot}	−18.2	−15.3	−2.9	0.1525

* R and H_w correspond to sum of all atoms of the π-system (lp-acceptor) and hydrogen atoms of water molecule, respectively.

If we compare primary interactions in three $3 \cdot H_2O$ motifs, we notice that in all of them, O…π interaction is attractive and the electrostatic contributions are large that are compensated by large repulsive electrostatic contribution due to unfavorable O…F interactions. However, p-$3 \cdot H_2O$ benefits more from both exchange-correlation and electrostatic contribution in its primary interaction. Moreover, the exchange-correlation contribution varies more compared to the electrostatic contribution by comparing the first motif (p-$3 \cdot H_2O$) with the two tilted motifs. It changes about two times more than electrostatic component. In p-$3 \cdot H_2O$ structure, the exchange-correlation contribution of O…C interactions are generally larger than those in t-$3 \cdot H_2O$ structures except for two carbons C1 and C6 in t_1–$3 \cdot H_2O$ and C1 and C3 in t_2–$3 \cdot H_2O$ motifs close to the water. It suggests that exchange-correlation contribution is affected more by distance compared to the electrostatic component. Those large attractive electrostatic contributions of primary interaction in all conformers are considerably compensated by the repulsive O…F interactions. As it has pointed out in the previous section, the PES of $3 \cdot H2O$ is quite flat and all complexes have very close interaction energies; nevertheless the t_2–$3 \cdot H_2O$ is about 0.3 and 0.2 kcal.mol^{-1} more stable than p-and t_1–HFB·H_2O complexes. Furthermore, t_1-$3 \cdot H_2O$ and t_2-$3 \cdot H_2O$ generally benefit more from the exchange-correlation contribution compared with the p-$3 \cdot H_2O$. A close look at the results shows that the large exchange-correlation contribution in the tilt structures mostly originated from O…F interactions. Consequently, if we only consider the primary

interaction which should be considered as a lone pair-π interaction, we can suggest more efficient lone pair-π interaction for the p-**3**·H_2O structure compared to tilted complexes.