Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Halogen-like properties of Al_{13} cluster mimicking astatine

Supporting Information

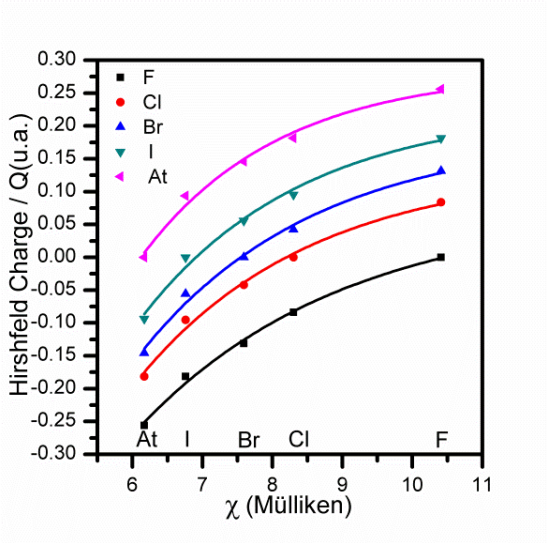
Bertha Molina[a], *Jorge R. Soto**[a], *and Jorge J. Castro*[b]

[a]Facultad de Ciencias, Universidad Nacional Autónoma de México, Apdo. Post. 70-646, 04510 México D.F., México.

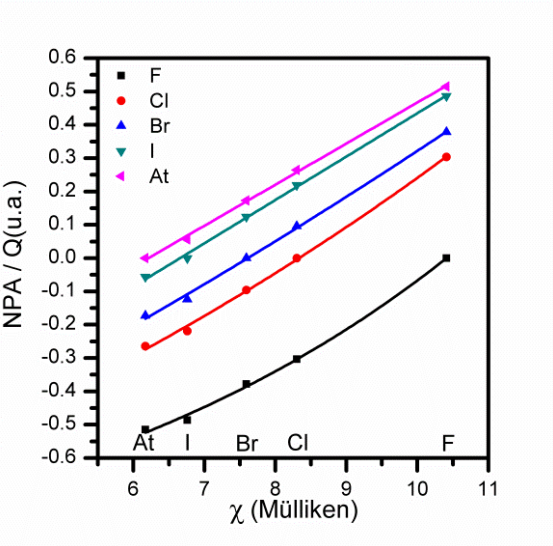
[b]Departamento de Física, CINVESTAV del IPN, Apdo. Post. 14-740, 07000 México D.F., México.

E-mail: mlnbrt@ciencias.unam.mx, jrsoto@unam.mx, jjcastro@fis.cinvestav.mx

1) Comparative study of the Hirshfeld (HPA) and Natural (NPA) population analysis for the diatomic molecules XY with X halogen (F-At) and Y halogen (F-At) or alkaline (Li-Cs).



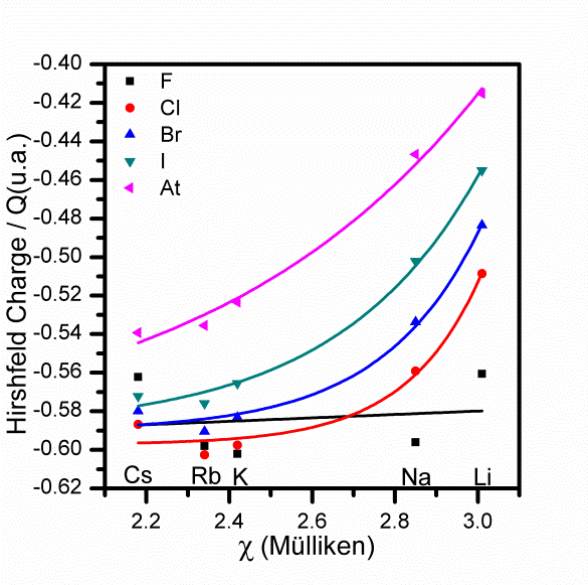
(a)



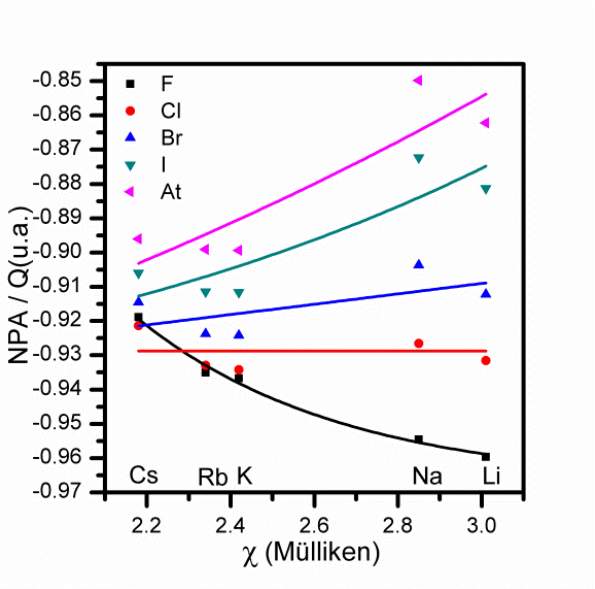
(b)

Figure S1. Interhalogen electron population analysis (PA) as a function of the Mülliken electronegativity. (a) Hirshfeld (HPA); (b) Natural (NPA).

Interhalogen: For HPA, the exponential fit is better than the linear one.
Exponential: ($0.98 < r < 1$); linear ($0.87 < r < 0.93$).
For NPA, the exponential fit is better than the linear one.
Exponential: ($r \sim 1.0$); linear ($0.98 < r < 1.0$).



(a)



(b)

Figure S2. Alkali halide electron population analysis (PA) as a function of the Mülliken electronegativity. (a) Hirshfeld (HPA); (b) Natural (NPA).

Halogen-alkaline: For HPA, the exponential fit is better than the linear one.
Exponential: ($0.95 < r < 0.99$); with the exception of F.
For NPA, no correlation is found, except for F; however it presents a behavior contrary to what is expected as a function of the difference in C

The exponential fit is consistent with the fact that Li and Na, having the largest electronegativity, should correspond to the lowest transferred charge, whereas K, Rb and Cs to higher transferred charge. This shows that in general the HPA provides a better description for halogen-halogen and halogen-alkaline diatomic systems. Since we are interested in the PA and how it correlates with, for both alkaline and halogens adatoms on Al_{13} and its halogen-like behavior, we select the HPA to model the transferred charge to the Al_{13} cluster.

Our result is consistent with previous studies favoring the Hirshfeld population analyses over Mülliken, NPA and others. Fonseca Guerra et al.[1] performed a charge analysis of several biological, organic and inorganic molecules and showed that Hirshfeld analysis yield chemically meaningful charges as compared to other schemes, which predict charges not compatible with chemical intuition. They also found a non-linear behavior as a function of the electronegativity. Roy et al.,[2-3] based their preference on the fact that Hirshfeld's partitioning technique is the only population analysis scheme that produces non-negative condensed Fukui functions. HPA has also been the base of many studies since Nalewajski and Parr, based on theoretic information theory, provide a theoretical foundation of the Hirshfeld's stockholder partitioning technique.[4] See also the review by Geerlings et al.[5]

(1) C. F. Guerra, J. W. Handgraaf; E. J. Baerends; F. M. Bickelhaupt, *J. Comput. Chem.,* 2004**, 25**, 189.
(2) R. K. Roy; K. Hirao; S. *J.* Pal, *Chem. Phys.,* 2000, **113**, 1372.
(3) R. K. Roy; K. Hirao; S. Krishnamurty; S. Pal, *J. Chem. Phys.,* 2001, **115**, 2901.
(4) R. F. Nalewajski; R. G. Parr, *Proc. Natl. Acad. Sci. U. S. A,.* 2000**, 97**, 8879.
(5) P. Geerlings; F. De Proft; W. Langenaeker, *Chem. Rev.,* 2003**, 103**, 1793.