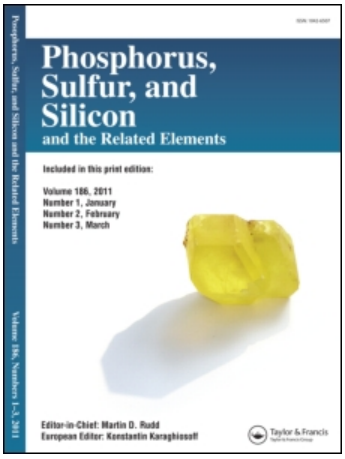

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Effective Atomic Charges and Bonding Character of Y=P-Orbitals in Four-Coordinated Phosphorus Compounds Studied by Photoelectron Spectroscopy Data

L. N. Alexeiko[a]; V. I. Vovna[a]; V. V. Gorchakov[a]; V. I. Kiiarchenko[a]
[a] Physico-Technical Research Institute, Far-East State University, Vladivostok, USSR

To cite this Article Alexeiko, L. N. , Vovna, V. I. , Gorchakov, V. V. and Kiiarchenko, V. I.(1990) 'Effective Atomic Charges and Bonding Character of Y=P-Orbitals in Four-Coordinated Phosphorus Compounds Studied by Photoelectron Spectroscopy Data', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 229
To link to this Article: DOI: 10.1080/10426509008040763
URL: http://dx.doi.org/10.1080/10426509008040763

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 229
Reprints available directly from the publisher
Photocopying permitted by license only

EFFECTIVE ATOMIC CHARGES AND BONDING CHARACTER OF Y=P-ORBITALS IN FOUR-COORDINATED PHOSPHORUS COMPOUNDS STUDIED BY PHOTOELECTRON SPECTROSCOPY DATA

L.N.ALEXEIKO, V.I.VOVNA, V.V.GORCHAKOV, and V.I.KHARCHENKO
Physico-Technical Research Institute, Far-East State University, 27 Octyabrskaya Str., Vladivostok 690600, USSR

Effective atomic charges in $Y=PX_3$-molecules (Y=O or S for X=F, Cl, Me, OMe; Y=BH_3, CH_2, NH for X=Me) were calculated from gas-phase core-electron chemical shifts ΔE utilizing the equations set

$$\Delta E_A = k_A q_A + \sum_{B \neq A} \cdot \frac{q_B}{R_{AB}} + 1 \qquad (I)$$

The applied calculations which take into account the surrounding atoms potentials (molecular potential) does not confirm the high electronegativity of atom S in $S=PX_3$. This contradicts with the widely accepted method of linear correlations of ΔE_A with atomic charge q_A. The slight alteration of ΔE_P while substituting O by S in $Y=PMe_3$, is due to compensation of charges in the first and second member in the equation for ΔE. It has been shown that the universal proportional coefficient between ΔE_P and q_P cannot be found in case of phosphorus compounds. Values of charges q_P obtained by this method and by the method of MNDO are in linear correlation. The significance of accounting of P3d--orbitals occupancy in k_P-selection is discussed. Comparison of ΔE(OIs) with ionization potential of $O2p_\Pi$-electrons in ONX_3 (X=F, Me) reveals the antibonding character of $O2p_\Pi$-orbitals in nitrogen compounds. In phosphorus compounds, due to p_Π-d_Π-interaction, these orbitals are bonding.

(I) Siegbahn K., Nordling C., Fahlman A., e.a. Electron Spectroscopy. - Moscow: Mir, 494 p.p., (1971).