Communications

Lone-Pair-Lone-Pair Repulsion in the Halogen Molecules

Sir:

A simple molecular orbital treatment of the diatomic homonuclear halogens, in which the overlap integral is ignored when estimating the resonance integral, leads to the conclusion that the antibonding π^* level is raised above the atomic p level as much as the bonding π level is lowered below that level. This result is equivalent to having the eight π electrons of an X_2 molecule occupy four strictly nonbonding lone-pair orbitals. However, if the overlap integral is included in the treatment, it is found that the antibonding level is raised more than the bonding level is lowered,[1] resulting in a net π-antibonding interaction, or "lone-pair-lone-pair repulsion". One would expect the pπ-pπ overlap integral of F_2 to be much greater than that of the other halogen molecules, and the corresponding high lone-pair-lone-pair repulsion has been proposed as an explanation of the extraordinary weakness of the F-F bond.[2-5] However, other plausible explanations of the weak F-F bond have been proposed[2,6-11] and no direct experimental proof of extraordinarily high lone-pair-lone-pair repulsion in F_2 has been demonstrated.

It has recently been shown that, by combining the results of valence and core photoelectron spectroscopy, the energies of molecular orbitals relative to the energies of strictly nonbonding atomic orbitals (corrected for the effects of potential and relaxation energy) can be determined.[12,13] We here report the results of applying this method to the data for both the homonuclear and the heteronuclear diatomic halogens.

By using both core and valence ionization potentials, it is possible to evaluate the ionization potentials that atomic orbitals (in molecules) would have if they were nonbonding. These localized orbital ionization potentials (LOIPs), the π and π^* ionization potentials, and the differences, Δ, between the average of the π and π^* ionization potentials and the LOIP values are presented in Table I.[14-16] A Δ value of zero corresponds to no lone-pair-lone-pair repulsion; a negative value indicates lone-pair-lone-pair repulsion. In the case of the homonuclear molecules, the only Δ value that is definitely negative (with the ±0.1-eV uncertainty of the method taken into account) is that of F_2. We believe that these data constitute the first unequivocal evidence for lone-pair repulsion in F_2. Other effects may contribute to the weakness of the F-F bond, but clearly lone-pair repulsion is very significant.

In the case of the heteronuclear molecules, the Δ values were calculated by using the average LOIPs for the two atoms. For ClF, Δ is slightly negative, suggesting weak lone-pair repulsion, and for ICl, there is no lone-pair repulsion. The positive Δ value for IBr has no obvious rationale and suggests experimental error; it would be worthwhile to reinvestigate the spectra of IBr.

Table I. LOIPs, Ionization Potentials, and Δ Values for Halogens and Interhalogens (eV)

molecule	LOIP[a]	IP(π)[b]	IP(π^*)[b]	Δ
F_2	17.94	18.80	15.84	−0.62
Cl_2	13.12	14.42	11.61	−0.10
Br_2	11.85	12.85	10.68	−0.08
I_2	10.35	11.21	9.51	0.01
ClF	15.09[c]	17.06[d]	12.79[d]	−0.16
ICl	11.56[c]	12.88	10.24	0.0
IBr	10.59[c]	12.09	9.99	0.45

[a] See ref 14 and 15. [b] Except as noted, from: Potts, A. W.; Price, W. C. *Trans. Faraday Soc.* 1971, *67*, 1242. [c] Average LOIP for the two halogen atoms of the interhalogen. [d] DeKock, R. L.; Higginson, B. R.; Lloyd, D. R.; Breeze, A.; Cruickshank, D. W. J.; Armstrong, D. R. *Mol. Phys.* 1972, *24*, 1059.

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Registry No. F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; ClF, 7790-89-8; ICl, 7790-99-0; IBr, 7789-33-5.

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Syntheses and Structures of a One-Dimensional Palladium(II)-Palladium(IV) Mixed-Valence Complex and Its Parent Palladium(II) and Palladium(IV) Complexes with 1,4,8,11-Tetraazacyclotetradecane

Sir:

One-dimensional M(II)-M(IV) mixed-valence complexes of Pt, Pd, and Ni have attracted much interest from the viewpoint of the chemistry and physics of low-dimensional compounds.[1] Crystal structures of some of these complexes, mostly of Pt, have been reported.[2] In this study, we have

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