Correction

A Model for the Chemical Bond; *J. Chem. Educ.* 2004, *81*, 427–435

Readers have pointed out some errors and omissions in my paper "A Model for the Chemical Bond" *(1)*. The following comments are given as a Correction, and should amend in part and complete the discussion given in ref *1*.

It was not made adequately clear that the simple model in ref *1* includes only the leading "exchange-overlap" contribution to bond energy *(2),* whereas other quasi-classical electrostatic effects and higher-order Coulombic distortion and dispersion effects were ignored.

1. Deviations from the expected trend suggested in the left column of page 430 of ref *1* for Li_2^+ and Li_2 [$|D_e|$ is 29.7 kcal mol^{-1} for Li_2^+, 24.2 kcal mol^{-1} for Li_2 *(3)*] are mostly due to these second-order distortion effects and to the dependence of the βs on the overlap S, as a deeper analysis shows *(3)*, so that may not be unexpected to occur at this level of the theory.

2. We observe that there is no relationship whatever between bond energies and experimentally observed UV photoelectron spectra. The βs of ref *1* are purely empirical parameters (different for 1σ or 2σ or 1π), assumed *equal* along the series,[1] in terms of which *the bond energy*[2] *is simply assumed to depend on the relative number of electrons filling bonding and antibonding relevant MOs either σ or π.* So, the bottom part of Figure 6 must be interpreted only in relation to the dependence of the bond energy on the number of π electrons along the series. It is not claimed to have any spectroscopic significance, when often *small* energy differences between low lying electronic states [about 2 kcal mol^{-1} for C_2 between $^1\Sigma_g^+$ and $^3\Pi_u$ *(4)*] may be of difficult evaluation even for sophisticated ab initio calculations.

3. The experimental bond energy results $|D_e|$ of the bottom part of Table 1 in ref *1* must be updated as follows with values taken from ref *4*:

C_2^+	124.6 kcal mol^{-1}	C_2	145.8 kcal mol^{-1}
N_2^+	204.1 kcal mol^{-1}	N_2	228.4 kcal mol^{-1}
O_2^+	156.4 kcal mol^{-1}	O_2	120.2 kcal mol^{-1}
F_2^+	78.5 kcal mol^{-1}	F_2	38.3 kcal mol^{-1}

The corresponding bond lengths are unchanged, to the figures reported in Table 1, except for F_2^+ = 1.32 Å and F_2 = 1.31 Å. The substance of the discussion in ref *1* is left essentially unaltered: it is observed that there is a strict correlation between bond lengths and bond energies and the number of π electrons along the series. This is an experimental observation, which is qualitatively followed by the simple model proposed in ref *1*.

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Notes

1. Therefore, the βs do not depend in any way on the kind of atom or on the internuclear distance *R*.

2. Bond energy is a complicated, *small* difference between *very large* quantities such as the molecular energy and the sum of the atomic energies of the constituent atoms.

Literature Cited

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