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LECTURE

"Analysis of bonding patterns in molecular systems exhibiting partial biradical character"

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Analysis of bonding patterns in molecular systems exhibiting partial biradical character

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A quantitative scale of the biradical charater ($0 \leq \beta \leq 1$) of a molecular system based on a Multi-Reference Configuration Interaction (MRCI) wavefunction is introduced and used to analyze its underlying electronic structure and bonding pattern. Triatomic ions in the FX_2^+ series, where X = O, S, Se, Te and Po are the terminal atoms, were found to exhibit unusually high biradical characters ($0.76 < \beta < 0.92$), the largest among the homologous, 18 valence electron molecules CX_2^{2-}, NX_2^-, X_3 and OX_2 (X = O, S, Se, Te and Po). The concept of biradical character was further used to investigate the bonding mechanism in ozone (O_3) and its sulfur-substituted analogues, SO_2, OS_2, and S_3. We demonstrate that the binding in these molecules can be described by a mixture of a closed shell structure with one and a half bond between the central and terminal atoms and an open-shell structure with a single bond and two lone electrons on each terminal atom. The analysis of the MRCI wavefunctions provides a simple measure of the relative mixture of the two bonding scenarios, yielding a biradical character of 3.5% for OSO, 4.4% for SSO, 11% for S_3, 18% for O_3, 26% for SOO, and 35% for SOS. Our analysis further offers an explanation for the different O-O, S-O and S-S bond lengths and singlet-triplet splittings of these species, the stabilization of OSO and SSO over the SOO and SOS isomers as well as the (X-YZ) relative binding energies (X=S, O), all based on their different biradical character.