

VALENCE-HOLE ELECTRON CONFIGURATIONS: A NEW GLOBAL ELECTRONIC STRUCTURE PARADIGM FOR C₂ AND BEYOND

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The global electronic structures of C₂ ¹Π_g and ³Π_g states, up to the energy of the first symmetry-allowed C(2s2p³)+C(2s²2p²) dissociation channel, are modeled using a diabatic state interaction picture. The experimental observations (*v*=0-8 of C¹Π_g; *v*=0-12 of d³Π_g and e³Π_g, and five *v* levels of the coupled 3, 4³Π_g states) are reproduced with an average residual of 0.3 cm⁻¹. The key concept behind the diabatization is the valence-hole electron configurations, for which an electron in the anti-bonding 2σ_u orbital is excited to a higher energy orbital. For C₂, when this electron is excited to a bonding orbital (i.e. 3σ_g/2π_u←2σ_u), the valence-hole configuration is the lowest energy configuration within a given symmetry manifold. These valence-hole configurations have a nominal bond-order of three, and correlate to the excited C(2s2p³)+C(2s²2p²) channel with 2p←2s electron promotion in one of the carbon fragments. A *diabatic* valence-hole state with bond-order of three is expected to have a high dissociation energy, and in our model, it dissociates into the lowest symmetry-allowed C(2s2p³)+C(2s²2p²) channel. As *R* increases, this deeply-bound valence-hole state crosses several other low-lying electronic states (derived from the 2σ_u²2σ_g² configuration), all of which dissociate into the low-energy C(2s²2p²)+C(2s²2p²) channels without 2p←2s promotion. The curve-crossings between the valence-hole and the 2σ_u²2σ_g²-type states in C₂ are analogous to the ionic (A⁺B⁻)/covalent (AB) curve crossings in more ionic species. In both cases, the electronic structure landscape of the low-lying valence states is systematically disrupted due to their curve crossings with a single diabatic state (valence-hole or A⁺B⁻). We believe that the valence-hole state is an important but hitherto neglected feature in the electronic structure model. The C₂ molecule offers a perfect platform to study the role of valence-hole states in causing fundamental changes of the global electronic structure landscape. The valence-hole-induced curve crossings in C₂ occur at much lower excitation energy than the analogous ones in N₂, CO, NO, and O₂. The effects from these curve crossings are gloriously and uniquely sampled in the molecular constants of low-lying states of C₂.