Diabatic Valence-hole States:
"Putting Humpty Dumpty together again"

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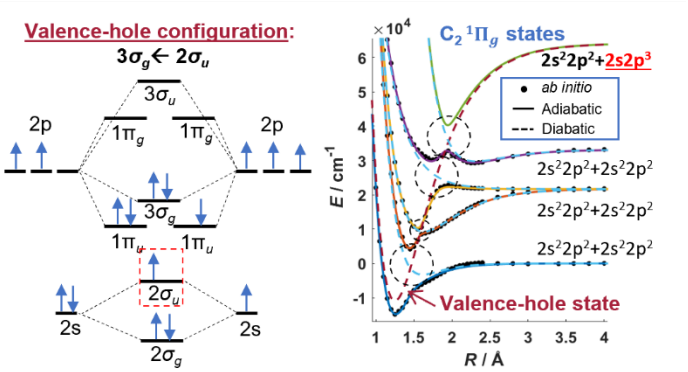
Diatomic molecules are fundamental in shaping our intuitive understanding of electronic structure theory. Despite their structural simplicity, chemical binding mechanisms (i.e., from R_e to dissociation) are well understood only for a few lowest energy electronic states, even for the C/N/O diatomic species. Pervasive configuration interactions and lumpy adiabatic potentials are prominent features of most electronically excited states. Interpretation of energy level structure and spectroscopic patterns becomes increasingly challenging for these higher energy states, because of the reduced utility of simple concepts such as bond order and correlation diagrams.



In this work, the extensive web of avoided-crossing patterns in multiple electronic symmetry manifolds of the C_2 ($^1\Pi_g$, $^3\Pi_g$, $^1\Sigma_u^+$, $^3\Sigma_u^+$), CN($^2\Sigma$), N_2 ($^1\Pi_u$, $^3\Pi_u$), Si_2 ($^3\Pi_g$) and SiC ($^3\Pi$) molecules is modeled by a global diabatization scheme. The key concept of the model is the existence of "valence-hole" configurations, e.g., $2\sigma_g^2 2\sigma_u^1 2\pi_u^4 3\sigma_g^1$ for C_2, that derive from an electron promotion from the nominally anti-bonding $2\sigma_u$ molecular orbital, i.e., $3\sigma_g(5\sigma) \leftarrow 2\sigma_u(4\sigma)$ for C_2, Si_2, CN, and SiC, and $1\pi_g \leftarrow 2\sigma_u$ for N_2. These valence-hole configurations have a nominal bond order of 3 or higher and correlate with separated-atom configurations with a 2p←2s promotion in one of the atomic constituents. The diabatic picture uncovers the profound, disruptive impact of the valence-hole configurations on the global electronic structure and unimolecular dynamics of all five species studied here. The strongly-bound diabatic valence-hole state crosses multiple weakly-bound or repulsive states that are composed of electron configurations with a $2\sigma_g^2 2\sigma_u^2$ valence-core. These curve-crossings of diabatic potential curves result in an interconnected network of many avoided-crossings among multiple electronic states.

The valence-hole configuration is a previously neglected feature in the intuitive electronic structure models of the electronically excited states. The validity of the global valence-hole diabatization scheme is demonstrated by its ability to reproduce the unusual energy level structure of the extensively studied C_2 $^3\Pi_g$, CN $^2\Sigma$, and N_2 $^3\Pi_u$ electronic states. In all three systems, high-resolution data are available for multiple vibrational levels of at least three different electronic states. Rydberg-valence and Rydberg-Rydberg interactions are successfully incorporated into our global fit model for the N_2 $^3\Pi_u$ states. In the case of the C_2 $^3\Pi_g$ and N_2 $^3\Pi_u$ states, the model also reproduces the observed predissociation lifetimes that are strongly dependent on both the electronic and vibration-rotation character of the associated levels.