WHAT IS A SIMPLE MOLECULE LIKE CaF DOING IN A PLACE LIKE THIS?

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With only one electron outside of a doubly-closed shell $Ca^{2+}F^{-}$ ion-core, the electronic spectrum of CaF is simple enough to reveal *all* of the important mechanisms for exchange of energy and angular momentum between massive nuclei and light electrons. These mechanisms are encoded in spectra as perturbation matrix elements, autoionization rates, and both direct and *indirect* predissociation rates; however, these are numbers, not ball-and-spring mechanistic pictures. The most compact but global numerical representation of electronic structure and dynamics is the internuclear distance dependent quantum defect matrix, $\boldsymbol{\mu}(R)$. But the elements of the quantum defect matrix are just another way of encoding dynamical mechanisms. It may be possible to understand the complete s∼p∼d∼f set of empirically determined $\boldsymbol{\mu}(R)$ matrix elements based on ligand field theory at short range and ion-core multipole moments at long range. CaF, despite its present advanced stage of spectroscopic characterization, is not without surprises! CaF violates Mulliken's rule about the shapes of the innermost lobes of all Rydberg orbitals: "ontogeny recapitulates phylogeny." This rule is the basis for most of the principal (n) and orbital (ℓ) quantum number scaling rules for which Rydberg states are notorious. A variety of indirect processes mediated by a repulsive $^2\Sigma^+$ valence state are observed, including violations of both the Franck-Condon principle and the standard $\Delta v = 1$ mechanism for vibrational autoionization. A simple wavepacket picture should explain *all* such indirect processes. All of what CaF has taught us about dynamical mechanisms is transferable to more complex molecules.
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