BROAD SHAPE RESONANCE EFFECTS IN CaF RYDBERG STATES

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Results of *ab-initio* R-matrix calculations [a] indicate the presence of a broad shape resonance in electron-CaF^+ scattering for the $^2\Sigma^+$ electronic symmetry near the ionization threshold. The properties of this shape resonance are analyzed using the adiabatic partial-wave expansion of the scattered electron wavefunction introduced by Le Dourneuf et. al. [b] The qualitative aspects of the shape resonance are explained by an adiabatic approximation on the electronic motion. Mulliken's rule for the structure of Rydberg state wavefunctions [c] specifies that, except for an $(n^*)^{-3/2}$ scale factor, every excited state wavefunction within a Rydberg series is build on an innermost lobe that remains invariant in shape and nodal position as a function of excitation energy. Mulliken's rule implies a weak energy dependence of the quantum defects for an unperturbed molecular Rydberg series, which is given by the Rydberg-Ritz formula.
This zero-prder picture is violated by a single $^2\Sigma^+$ CaF Rydberg series at all Rydberg state energies ($n^* \geq 5$, increasingly with n^*) below the ionization threshold, under the broad width of the shape resonance. Such a violation is diagnostic of a *global* "scarring" of the Rydberg spectrum, which is distinct from more familiar *local* level perturbations.

[a] Altunata et. al. J. Chem. Phys. 123, 084319(2005).
[b] Le Dourneuf et. al. J. Phys. B, 15, L685(1982)
[c] R.S. Mulliken, J. Am. Chem. Soc. 86, 3183(1964).