

# MULTI-CHANNEL QUANTUM DEFECT THEORY CALCULATION OF VIBRATIONAL AUTOIONIZATION RESONANCE WIDTH OF $v = 1, n^* \approx 14$ CaF RYDBERG STATE

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Vibrational auto-ionization resonance widths ( $\gamma$ ) of  $v = 1, n^* \approx 14$  Rydberg states of CaF are calculated in this work, based on results of a global multi-channel quantum defect fit. The calculation indicates that the  $n.36 p\Pi$  eigen-channel has the shortest vibrational auto-ionization lifetime,  $\sim 10$  ps, which is at least  $4\times$  shorter than the lifetime of all other CaF eigen-channels, in agreement with experimental observations. In addition, the calculation successfully reproduces the experimental observations that  $\gamma$  of the  $14.36 p\Pi^-$  rotational sequence (where the superscript '-' indicates negative Kronig symmetry) are nearly  $N$ -independent, while those of the  $14.36 p\Pi^+$  rotational sequence (where the superscript '+' indicates positive Kronig symmetry) decrease quickly as a function of  $N$ , i.e.  $\gamma(N = 10) \approx \frac{1}{2}\gamma(N = 1)$ . By examining the eigen-channel composition of the two rotational sequences of state of opposite Kronig symmetry, we are able to show that the significantly faster decrease of  $\gamma$  for the  $14.36 p\Pi^+$  rotational sequence is caused by the stronger  $l$ -uncoupling interaction in the positive Kronig symmetry manifold. Based on a valence-precursor model (first suggested by Mulliken), the significantly faster vibrational auto-ionization rate of the  $n.36 p\Pi$  eigen-channel is explained based on the electronic properties of its valence-precursor state, the  $C^2\Pi$  state, for which the electron density is polarized toward the fluorine atom.