

ELECTRONIC STRUCTURE OF THE $X^1\Sigma^+$ ION CORE OF CaF RYDBERG STATES

STEPHEN COY, JOSHUA H BARABAN, DAVID GRIMES, TIMOTHY J BARNUM, ROBERT W FIELD,
Department of Chemistry, MIT, Cambridge, MA, USA; BRYAN M. WONG, *Department of Chemistry, Uni-*
versity of California, Riverside, Riverside, Ca, USA.

We use ab-initio calculations to examine the electronic structure of CaF^+ , making comparison to the available experimental data and effective potential models. An electron-density-difference plot comparing isolated Ca^{+2} and F^- ions with the CaF^+ ab-initio density shows s-d mixing at Ca, and maintenance of near spherical symmetry at F. This unexpected result is interpreted in terms of the electronic states of Ca^+ . Calculation of the effective charge on F spanning the region of the transition from ionic to dissociating $\text{Ca}^+ \text{F}^0$ locates the transition very near the crossing of the $\text{Ca}^{+2} \text{F}^-$ and $\text{Ca}^+ \text{F}^0$ curves and additionally determines the width of the ionic-bonding transition region. An accurate non-relativistic long or intermediate range effective potential for the CaF Rydberg electron is obtained by choice of origin at the center of polarizability, with inclusion of multipoles through octopole and the use of anisotropic polarizability. The estimates of CaF^+ polarizability from ab-initio and effective potential models predict high anisotropy, with the parallel dipole polarizability, where the atomic dipoles are mutually enhancing, predicted to be about double the perpendicular polarizability, where the atomic dipoles are mutually antagonistic.