There is currently much interest in the production metal halide ions that are both translationally and internally cold. One potential route to the production of rotationally and vibrationally cold ions is excitation of a vibrationally autoionizing state of the neutral molecule. However, the autoionization dynamics of most molecules are difficult to predict since the key parameters that describe the process, the quantum defect derivatives with respect to internuclear distance, are only known for a very small number of molecules. We recently developed a complete quantum defect model for calcium monofluoride (CaF), a prototypical metal halide molecule, that is fully capable of describing all vibrational autoionization processes. Here, we use this model to calculate the distribution of ionic rovibrational states that result from autoionization of Rydberg states of CaF, and discuss the general prospects for the selective preparation of rotationally and vibrationally cold metal halide ions.