The $B$ ($\frac{1}{2}$) and $C$ ($\frac{3}{2}$) ion-pair excited states of XeF are coupled by the rotational Hamiltonian, producing perturbations in the rotational structure of $B \rightarrow X$ ($\Sigma^+$) transitions involving $v'$ levels < 5. A number of $v' - v''$ bands in the $B \rightarrow X$ emission spectrum of the single isotopomer $^{136}$Xe$^{19}$F are analyzed by a deperturbation model to yield improved spectroscopic descriptions of the low-$v$ regions of the $B$ and $C$ states. The $C$ state lies 797 cm$^{-1}$ below the $B$ state, with $R_e = 2.473$ Å. The electronic perturbative coupling element for $B$–$C$ interactions is 6% below the simple Hund's case $c$-based prediction and just 3% greater than an estimate obtained from a more elaborate case-$a$ approach.