MANIFESTATION OF NONADIABATIC EFFECTS IN THE IR SPECTRUM OF PARA-BENZOQUINONE RADICAL CATION

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X-irradiation of an Ar matrix doped with *p*-benzoquinone (PBQ) at 10 K leads to formation of the PBQ radical cation ($PBQ^{\bullet+}$) and radical anion ($PBQ^{\bullet-}$). The IR spectrum of $PBQ^{\bullet+}$ exhibits broad and dense absorption bands in the 2000 cm^{-1} and higher energy region. Another characteristic of the spectrum is the presence of three intense peaks in the lower energy region. Equation-of-motion coupled-cluster calculations have been performed to analyze the spectrum with the quasi-diabatic model Hamiltonian technique. A spectral simulation based on the model Hamiltonian reproduces the observed IR spectrum very well, revealing that the electronic transition to the low-lying excited state, $\tilde{A}\,^2B_{2u} \leftarrow \tilde{X}\,^2B_{3g}$, is severely affected by nonadiabatic interaction of the two states, to which the aforementioned features are attributed. In particular, three b_{1u} fundamental peaks for $\tilde{X}\,^2B_{3g}$ $PBQ^{\bullet+}$ gain large intensities from the electronic transition through the vibronic coupling. On the other hand, transition to another b_{1u} fundamental level (anti-symmetric CO stretch) in the $\tilde{X}$ state has a diminished intensity due to cancellation of the electronic contribution and the usual dipole derivative contribution. Furthermore, this b_{1u} level is significantly scrambled with nearby vibronic states of b_{2u} symmetry, which accounts for the weak broad band experimentally observed in the 1560–1600 cm^{-1} region.