

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

KRZYSZTOF PIECH, THOMAS BALLY, *Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland*; TAKATOSHI ICHINO and JOHN F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712*.

X-irradiation of an Ar matrix doped with *p*-benzoquinone (PBQ) at 10 K leads to formation of the PBQ radical cation (PBQ^{•+}) and radical anion (PBQ^{•-}). The IR spectrum of PBQ^{•+} 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^{•+} 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.