

## HYDRATION EFFECTS ON ELECTRONIC AND VIBRATIONAL STRUCTURE OF PHENOXYL RADICALS AND THEIR PARENT ANIONS

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The effects of hydrogen bonding and solvent reaction field on the electronic structure of the phenoxyl radicals, studied by time-resolved Raman spectroscopy and Density Functional Theory, will be discussed by the example of *p*-aminophenoxyl radical ( $\text{H}_2\text{NPhO}^\cdot$ ). Calculations predict the dipole moment of the radical in its ground electronic state ( $^2\text{B}_1$ ) to increase by  $8(\pm 2)$  Debye and the difference between the CN and CO bond-lengths to decrease by  $\sim 0.05 \text{ \AA}$  from gas phase to aqueous solution. This profound hydration effect converts the structure and chemical properties of the radical from a substituted phenoxyl radical in the gas phase to a semiquinone-like radical in water. Two very weakly absorbing excited electronic states of  $^2\text{A}_2$  symmetry have been identified in the 340-390 nm region, which borrow transition moment from closely strongly allowed electronic states of  $^2\text{B}_1$  symmetry at lower ( $\sim 440 \text{ nm}$ ) and higher ( $\sim 320 \text{ nm}$ ) energies. The experiment and theory are combined to estimate the CO and CN bond lengths in  $\text{H}_2\text{NPhO}^\cdot$  as  $\sim 1.263 \text{ \AA}$  and  $\sim 1.34 \text{ \AA}$ , respectively, in liquid water and  $\sim 1.245 \text{ \AA}$  and  $\sim 1.37 \text{ \AA}$  in the gas phase.