A STUDY OF THE HYDROXYCYCLOHEXADIENYL RADICAL ABSORPTION USING TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY

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Thus far there has been little understanding of the vibrational spectra, structure and electronic absorption of hydroxycyclohexadienyl radicals in water. They are primary chemical species formed on interaction of radiation with aqueous solutions containing aromatic molecules. We have applied time- resolved resonance Raman (TR-RR) spectroscopy to structurally identify isomers of cyclohexadienyl radicals formed in the pulse radiolysis, using aqueous benzoate solutions as a model system. An early ESR study ((Eiben, K; Fessenden, R.W.; *J. Phys. Chem.* **1971**, *75*, 1186-1201) has shown that a mixture of three benzoate hydroxycyclohexadienyl radical isomers: ortho-, meta- and para- are formed upon electron irradiation of N_2O saturated benzoate solution. Their collective transient absorption is believed to exhibit a single broad band in the near UV region (λ_{max} = 330 nm, ϵ_{330} = 3800 $M^{-1}cm^{-1}$). To extract the single isomeric contribution to this collective absorption, we applied TR-RR at various wavelengths within the broad transient absorption range looking for the characteristic indication of each individual isomer. Raman signals of various para-substituted benzoates were also collected to aid in the vibrational studies of the aforementioned benzoate hydroxycyclohexadienyl radicals.