

RESONANCE RAMAN SPECTRA OF PROTOTYPE (HYDROXY)CYCLOHEXADIENYL RADICALS IN WATER

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The simplest symmetric cyclohexadienyl radical produced upon H atom addition to benzene was generated pulse radiolytically and characterized vibrationally using Raman scattering in resonance with its first optical absorption band located at 312 nm. After the initial assignment of Raman bands of the intermediate, we performed corresponding studies on its lower symmetry hydroxyl analog, which we also produced by pulsed irradiation using the addition of OH radical to benzene. To assist in band assignments, parallel experiments were performed with benzene-d6 analogs and theoretical calculations of all intermediates' molecular geometries and vibrational frequencies using DFT methodology. Resonance Raman spectrum of cyclohexadienyl radical recorded in 500-4800 cm^{-1} consists of 8 bands which can be assigned in terms of strongly enhanced fundamental ν_3 at 1560 cm^{-1} accompanied by two weakly enhanced fundamentals ν_1 and ν_2 at 556 and 1174 cm^{-1} , respectively, and additional weaker overtones and combinations at 1738, 2131, 2744, 3152 and 4715 cm^{-1} . In deuterated analog radical, all of these bands shift to lower wavenumbers. The first three fundamentals shift by 23, 279, and 40 cm^{-1} . Based on these shifts along with DFT computations ν_1 - ν_3 fundamental vibrations of cyclohexadienyl radical were assigned to CCC bending, CH bending, and C=C stretching ring modes, or 6a, 9a, and 8a in Wilson notation, respectively. Due to the lower symmetry of the hydroxy-cyclohexadienyl radical, its resonance Raman spectrum exhibits a higher number of bands in the same spectral region. The first eight fundamental bands lay below 1700 cm^{-1} , and the remaining combinations and overtones (6 bands) are above. The strongest fundamental ν_7 at 1560 cm^{-1} was assigned to 8a mode (C=C stretching). Weaker fundamentals located at 554, 961, 1176, and 1420 cm^{-1} were assigned to ring modes 6a, 18a, 9a, and 19a, respectively. Moving the laser excitation wavelength around the absorption peak position allowed us to record the excitation profile of recorded vibrations and observe the change of relative intensity pattern in the observed fundamental bands. Based on this observation, we could discuss the nature of the overlapping excited states contributing to the absorption envelope in these types of intermediates.