

SPECTROSCOPIC STUDIES OF THE  $\tilde{A}$ - $\tilde{X}$  ELECTRONIC SPECTRUM REVEAL BOTH THE STRUCTURE AND DYNAMICS OF  $\beta$ -HYDROXYETHYLPEROXY RADICAL

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The jet-cooled  $\tilde{A}$ - $\tilde{X}$  origin band absorption spectra of the  $G_1G_2G_3$  conformer of four  $\beta$ -hydroxyethyl-peroxy ( $\beta$ -HEP) isotopologues,  $\beta$ -HEP ( $\text{HOCH}_2\text{CH}_2\text{OO}$ ),  $\beta$ -DHEP ( $\text{DOCH}_2\text{CH}_2\text{OO}$ ),  $\beta$ -HEP- $d_4$  ( $\text{HOCD}_2\text{CD}_2\text{OO}$ ),  $\beta$ -DHEP- $d_4$  ( $\text{DOCD}_2\text{CD}_2\text{OO}$ ), have been recorded by a cavity ringdown apparatus with a laser source linewidth  $\sim 70$  MHz in the near IR region. The spectra of all four isotopologues have been analyzed and successfully simulated with an evolutionary algorithm, confirming the cyclic structure of the conformer responsible for the observed origin band. In addition, rotational constants in both the  $\tilde{X}$  and  $\tilde{A}$  states and the orientation of the transition dipole moment have been determined. The broadened linewidth of the absorption spectrum ( $\Delta\nu > 2$  GHz) is due to the shortened lifetime of the  $\tilde{A}$  state following its internal conversion back to the  $\tilde{X}$  state. The variation of lifetime with deuteration suggests that the hydroxyl hydrogen is involved and the process likely occurs along the reaction path for conversion between the peroxy and peroxide isomers.

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