

# UNIMOLECULAR DISSOCIATION OF PEROXYFORMIC ACID INITIATED BY VIBRATIONAL OVERTONE EXCITATION TO THE $6\nu_{\text{OH}}$ STATE<sup>a</sup>

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Photodissociation is an important loss mechanism for atmospheric hydroperoxides (R-O-OH) leading to the production of OH radicals via the rupture of the weak O-O bond. Photodissociation can either occur through electronic excitation to a repulsive excited electronic state or, alternatively, through unimolecular dissociation on the ground electronic surface. Here we present results from the unimolecular dissociation of peroxyformic acid (PFA) initiated by exciting the molecule in the vicinity of its fifth OH stretching overtone state ( $6\nu_{\text{OH}}$ ) at both 615 and 626 nm. Based on the estimated heat of formation of PFA and its fragments, the O-O bond dissociation energy ( $D_0$ ) in PFA is estimated to be 45.1 kcal/mol. Thus, exciting room temperature PFA molecules at 615 nm and 626 nm is expected to leave the OH + HCO<sub>2</sub> fragments with roughly 3.3 kcal/mol and 2.5 kcal/mol of available energy, respectively. Using laser induced fluorescence (LIF), we have probed the OH fragments from the near threshold unimolecular dissociation and have determined the partitioning of the available energy in to its internal and translational degrees of freedom. These results, along with the insight they provide regarding the unimolecular dissociation dynamics of HC(O)OOH, will be presented.

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