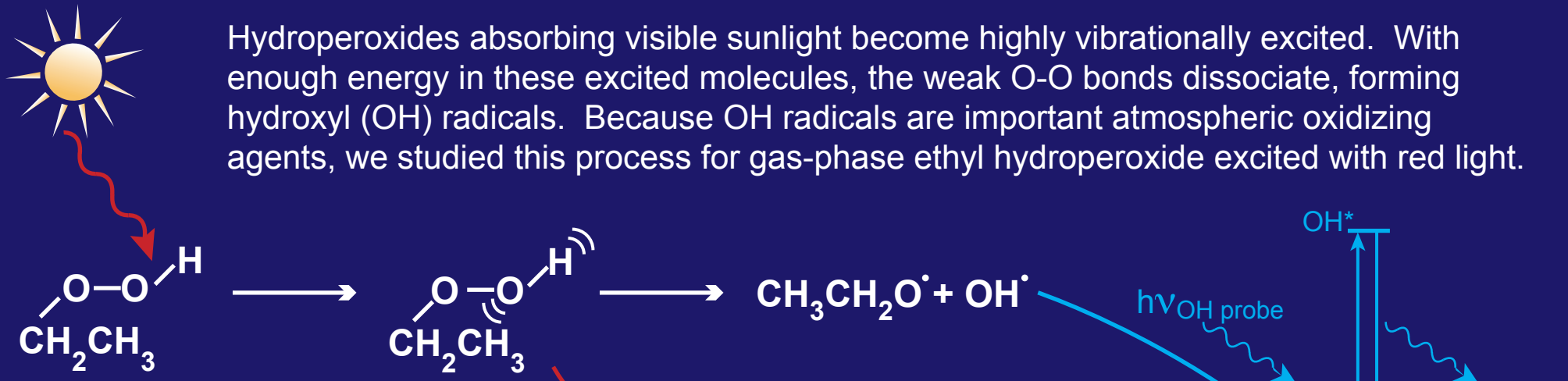
Overtone-initiated chemistry of atmospheric hydroperoxides

Shizuka Hsieh, Chemistry Department, Smith College
Northampton, MA 01063

Hydroperoxides absorbing visible sunlight become highly vibrationally excited. With enough energy in these excited molecules, the weak O-O bonds dissociate, forming hydroxyl (OH) radicals. Because OH radicals are important atmospheric oxidizing agents, we studied this process for gas-phase ethyl hydroperoxide excited with red light.



The experimental absorption spectrum (top left) and calculations (bottom left) show contributions from two ethyl hydroperoxide conformers. The *trans* conformer dominates at room temperature and is ~300 cm^{-1} lower in energy. Dissociation produces OH fragments with rotational distributions (right) that match statistical predictions (lines). Our experimental O-O bond dissociation energy (< 44 kcal mol^{-1}) revises current literature values.