

DISSOCIATION DYNAMICS OF VIBRATIONALLY EXCITED TRANS-PERP HOONO

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Peroxynitrous acid (HOONO) is formed by the reaction of OH and NO₂ in conjunction with the more stable isomer, nitric acid (HONO₂). Determination of the HOONO binding energy is essential for atmospheric models to correctly budget these two reactive radical species. We have used an infrared pump-ultraviolet probe technique to obtain an accurate measurement of the binding energy of the trans perp (tp) conformer. The OH ($v = 0$) rotational state distribution resulting from vibrational predissociation of tp-HOONO ($2\nu_{\text{OH}}$) was measured by saturated laser induced fluorescence, and found to be consistent with a statistical model. A dissociation energy of 16.2 kcal/mol was obtained from the best fit of the data to a prior distribution, and is complemented by the value inferred from the highest energy channel with observable population. This information, combined with an *ab initio* calculation of 3.4 kcal/mol for the relative conformational stability,^a provides an estimate of 19.6 kcal/mol for the binding energy of the more stable cis-cis (cc) conformer. Additional insight into the decay dynamics is provided by the 0.2 cm⁻¹ linewidth observed in the IR spectrum. A discussion is presented on the likely origin of this homogeneous broadening (corresponding to a 30 ps lifetime) in terms of intramolecular vibrational redistribution (IVR) and unimolecular dissociation.

^aBean, B. D. *et al.*, *J. Phys. Chem. A* **107**, 6974 (2003).