

INFRARED PHOTODISSOCIATION SPECTROSCOPY AND MULTIREFERENCE ANHARMONIC VIBRATIONAL STUDY OF THE HO<sub>4</sub><sup>+</sup> MOLECULAR CATION

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HO<sub>4</sub><sup>+</sup> has been proposed as an astrochemical sink of oxygen but has never been observed.<sup>a</sup> Molecular cations of HO<sub>4</sub><sup>+</sup> and DO<sub>4</sub><sup>+</sup> are produced in a supersonic expansion. They are mass-selected, and their infrared photodissociation spectra are measured with the aid of argon-tagging. Previous theoretical studies have modeled these systems as proton-bound dimers of molecular oxygen.<sup>b</sup> Several conformers were located on the quintet, triplet, and singlet surfaces, differing in energy by, at most, a few thousand wavenumbers; the singlet and triplet conformers have pronounced multiconfigurational character. Our HO<sub>4</sub><sup>+</sup> is formed in a relatively hot environment, and similar experiments have been shown capable of producing multiple conformers in low-lying electronic states.<sup>c</sup> None of the predicted HO<sub>4</sub><sup>+</sup> isomers can be ruled out *a priori* based on energetic arguments. We interpret our spectra with second-order vibrational perturbation theory with resonances (VPT2+K) using quartic force fields based on an economical combination of single- and multi-reference theories. The VPT2+K simulations include the effect of electrical anharmonicity; this is particularly important for transitions involving the shared-proton stretch. Previously unidentified chain structures (H-O-O-O-O) that exist on the singlet and triplet surfaces likely represent the global minima.

<sup>a</sup>Xavier, G. D.; Bernal-Uruchurtu, M. I.; Hernandez-Lamonedea, R., *J. Chem. Phys.* **2014**, 141, 5, 081101.

<sup>b</sup>Xavier, F. G. D.; Hernandez-Lamonedea, R., *PCCP* **2015**, 17, 16023-16032.

<sup>c</sup>Wagner, J. P.; McDonald, D. C.; Duncan, M. A., *Angewandte Chemie-International Edition* **2018**, 57, 5081-5085.