RECONCILING EXPERIMENT AND THEORY: THE INTERESTING AND UNUSUAL CASE OF THE HOOO RADICAL

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The $HO_3$ radical, which can be considered a weakly bound OH–$O_2$ complex that consists of two important open-shell species, has been the subject of many theoretical studies. The first high-resolution spectroscopic work was carried out several years ago through rotational analysis[a], work which firmly established the existence of the *cis* isomer, and an initial determination of its molecular structure. More recently, high-level coupled-cluster quantum chemical calculations[b] have revealed large discrepancies between the theoretical and experimental structures for this important atmospheric radical. To better understand the origin of this disagreement, extensive isotopic spectroscopy of HOOO has been performed using Fourier Transform microwave spectroscopy and microwave-millimeter double resonance techniques. The results of these experiments will be presented along with new calculations of the rotation-vibrational coupling constants.

[a] K. Suma, Y. Sumiyoshi, and Y. Endo, *Science* **308**, 1885, (2005)
[b] M. E. Varner, M. E. Harding, J. Gauss, and J. F. Stanton *Chemical Physics* **346**, 53, (2008)