AN EMPIRICAL APPROACH TO OBTAINING ACCURATE MOLECULAR ROTATIONAL CONSTANTS FOR ISOTOPICALLY-SUBSTITUTED SPECIES FROM *AB INITIO* CALCULATIONS

BRETT A. McGUIRE, P. BRANDON CARROLL, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125*; GEOFFREY A. BLAKE, *Division of Chemistry and Chemical Engineering and Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125*.

Recent advances in microwave spectroscopy, namely the development of broadband, chirped-pulse Fourier-transform microwave spectrometers, allow the acquisition of rotational spectra of isotopically-substituted species in natural abundance. The characterization and assignment of these spectra is of particular interest as it applies to astrochemical observations of such species in the interstellar medium. Here, we demonstrate an empirical method for determining rotational constants to aid in the initial assignment of such spectra using a combination of laboratory data and *ab initio* calculations. The result is an increase in the accuracy of these constants by as much as two orders of magnitude versus those resulting from simple structure optimizations. We have applied this method to a variety of species including diatomic molecules (e.g. HCl), large molecules with internal motion (e.g. CH_3COOH), ions (e.g. HCO^+), clusters (e.g. $H_2O{\cdot}H_2O$), and long carbon chain molecules (e.g. HC_7N). We present the results of these analyses and comment on the applicability of this method to other systems.