

## ROTAMERS OF METHANEDIOL: COMPOSITE AB INITIO PREDICTIONS OF FUNDAMENTAL FREQUENCIES AND ROVIBRATIONAL CONSTANTS

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The class of geminal diols comprises molecules known to be intermediates in atmospheric ozonolysis and the aerosol cycle. Owing to their thermodynamic propensity to decompose into water and an aldehyde/ketone, geminal diols have proved difficult to isolate and characterize. Recently, experimental evidence was published for the existence of methanediol, the simplest member of this class, in ices of methanol and oxygen following electron bombardment.<sup>a</sup> To aid in future spectroscopic investigations of methanediol in the gas phase, we report fundamental frequencies and rovibrational constants for the two rotamers of methanediol using *ab initio* composite methods along with vibrational perturbation theory. Sensitivity of the predictions to the level of theory and the treatment of anharmonic resonances are carefully assessed. The OH stretching harmonic frequencies of both rotamers are particularly sensitive to the level of theory. The CH stretches of the  $C_s$  rotamer are sensitive to the treatment of anharmonic resonances with VPT2-based effective Hamiltonian models. Equilibrium bond distances and harmonic frequencies are converged to within 0.0001 Å and 1 cm<sup>-1</sup>, respectively. The effect of tunneling on the rotational constants is investigated with a 2D variational calculation, based on a relaxed hydroxyl torsional potential energy surface. Tunneling is found to be negligible in the lower energy  $C_2$  rotamer but should modify the rotational constants of the  $C_s$  rotamer on the order of MHz, giving rise to rotational line splittings of the same order. The rovibrational constants of the  $C_s$  rotamer are dominated by torsional effects, and here we see evidence for the breakdown of vibrational perturbation theory.

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<sup>a</sup>Zhu, C.; Kleimeier, N. F.; Turner, A. M.; Singh, S. K.; Fortenberry, R. C.; Kaiser, R. I. *Proc. Natl. Acad. Sci. U. S. A.* 2022, 119, e2111938119.