MODELING THE TORSION-STRETCH COUPLING IN THE OH SPECTRUM OF *cis-cis* HOONO USING A THREE DIMENSIONAL POTENTIAL SURFACE

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The lowest energy conformer of HOONO, the *cis-cis* isomer, forms a ring structure with an internal hydrogen bond. Because of this hydrogen bond, the OH stretch frequency and band intensity are dependent on the dihedral angles HOON and OONO. The torsional motions about these angles have comparable frequencies and are coupled. Previous calculations used two dimensional models that explicitly treated the OH stretch and the HOON torsion (rotation of the OH out of the ring plane)[b,c,d], or three dimensional models that also explicitly treat the OOH bond angle[e]. These models were used to compute the 2D or 3D energies, and $\Delta\ \nu_{OH}$ transition intensities. In this work, we extended the previous 2D treatments in order to examine the importance of the remaining OONO torsional mode. The minimum energy path along the two dihedral angles of HOONO was computed at the CCSD(T)/cc-pVTZ level. The three dimensional potential energy surface was then computed as a function of the HOON and OONO dihedral angles, and of the OH bond length. Vibrational levels were obtained by solving the three dimensional Hamiltonian in the vibrationally adiabatic approximation. The potential surface shows coupling of the two torsional angles and the OH stretch. This coupling is harmonic at small torsional angles, and anharmonic at large torsional angles. The effects of the coupling on the torsional energy levels are compared to previous coupling treatments.

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