

BRIEF SUMMARY OF THE MILLIMETER-WAVE ROTATIONAL SPECTRA OF 2-, 3-, AND 4-CYANOPYRIDINE: THEIR VIBRATIONAL GROUND STATES AND THE CORIOLIS-COUPLED DYADS OF THEIR LOWEST-ENERGY VIBRATIONALLY EXCITED STATES

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The rotational spectra of 2-, 3-, and 4-cyanopyridine ($C_6H_4N_2$) were recorded from 130 – 360 GHz, and an analysis of the ground vibrational state and two lowest-energy excited vibrational states for each isomer was completed. Each ground state was least-squares fit to a partial octic, distorted-rotor Hamiltonian with several thousand distinct transitions assigned ($\sigma_{fit} < 50$ kHz). The B3LYP/6-311+G(2d,p)-predicted quartic and sextic distortion constants are in excellent agreement with their experimentally determined values for all three isomers. Given the large dipole moments of 2-, 3-, and 4-cyanopyridine ($\mu = 5.8$ D, 3.7 D, 2.0 D, respectively) and the astrochemical community's interest in detecting nitriles, the cyanopyridines are an attractive set of aromatic species for detection by radioastronomy. This work provides the fundamental constants needed to support an astronomical search of the cyanopyridine isomers in the interstellar medium. We also examined the two lowest-energy fundamentals of each isomer, which correspond to the in-plane and out-of-plane CN bending modes for all three species. These states are $\sim 150\text{ cm}^{-1}$ higher in energy than the ground state and are separated by less than 30 cm^{-1} , an energy separation small enough that each corresponding pair exhibits Coriolis coupling. The dyads display *a*-type Coriolis coupling for 4-cyanopyridine (C_{2v}) and both *a*- and *b*-type Coriolis coupling in 2- and 3-cyanopyridine (C_s), resulting in both global and local perturbations to the rotational transitions. Each isomer required the inclusion of several coupling terms in the two-state least-squares fit in order to fit all observed rotational transitions, including numerous resonances. Fitting each dyad's spectroscopic parameters allowed for the precise experimental determination of each dyad's energy separation, the Coriolis coupling coefficients, and the deperturbed vibration-rotation interaction constants. Combined with the recently published work on the analogous dyad of benzonitrile, this coupling in the cyanopyridines provides an opportunity to compare the Coriolis interactions of cyano-substituted aromatic molecules in greater detail.