ROTATIONAL SPECTRA OF p-, m-, AND o-CYANOPHENOL AND INTERNAL ROTATION OF p-CYANOPHENOL

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Rotational spectra of *p*-, *m*-, and o-cyanophenol have been measured in the range of 10.5 - 21 GHz and fit using Watson's A-reduction Hamiltonian coupled with nuclear quadrupole coupling interaction terms for the ^{14}N nuclei. Ab initio calculations at the MP2/6-311++G** level predict the *cis* conformers of *m*- and o-cyanophenol to be more stable due to the intramolecular hydrogen bonding interaction between the hydroxyl hydrogen and the cyano nitrogen. We recorded 14 a- and b-type rotational transitions for *cis m*-cyanophenol and 16 a- and b-type rotational transitions for *trans m*-cyanophenol. The rotational constants are $A = 3408.9200(2)$ MHz, $B = 1205.8269(2)$ MHz, and $C = 890.6672(1)$ MHz and $A = 3403.1196(3)$ MHz, $B = 1208.4903(2)$ MHz, and $C = 891.7241(2)$ MHz for the *cis* and *trans* species respectivly. We recorded 25 a- and b-type rotational transitions for *cis* o-cyanophenol; the rotational constants are $A = 3053.758(2)$ MHz, $B = 1511.2760(3)$ MHz, and $C = 1010.7989(2)$ MHz. The *trans* conformer of o-cyanophenol was not observed. Rotational transitions of the *p*-cyanophenol monomer are split due to the symmetric internal rotation of the hydroxyl group with respect to the aromatic ring. We recorded 25 a- and b-type rotational transitions for *p*-cyanophenol; the b-type transitions are split by 40 MHz. The rotational constants are $A = 5612.96(2)$ MHz, $B = 990.4283(6)$ MHz, and $C = 841.9364(6)$ MHz and the ground state spitting ΔE is 20.1608(6) MHz.