EVIDENCE OF INTERNAL ROTATION IN THE O-H STRETCHING REGION OF THE 1:1 METHANOL-BENZENE COMPLEX IN AN ARGON MATRIX

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Co-depositions of methanol ($\mathrm{CH_3OH}$) and benzene ($\mathrm{C_6H_6}$) in an argon matrix at 20 K result in the formation of a 1:1 methanol-benzene complex ($\mathrm{CH_3OH}$-$\mathrm{C_6H_6}$) as evidenced by the observation of distinct infrared bands attributable to the complex near the O-H, C-H, and C-O stretching fundamental vibrations of $\mathrm{CH_3OH}$ and the hydrogen out-of-plane bending fundamental vibration of $\mathrm{C_6H_6}$. Co-deposition experiments were also performed using isotopically labeled methanol ($\mathrm{CD_3OD}$) and benzene ($\mathrm{C_6D_6}$) and the corresponding deuterated complexes were also observed. Based on ab initio and density functional theory calculations, the structure of the complex is thought to be an H-π complex in which the $\mathrm{CH_3OH}$ is above the $\mathrm{C_6H_6}$ ring with the OH hydrogen atom interacting with the π cloud of the ring. Close inspection of the O-H and O-D stretching peaks of the complexes reveals small, distinct satellite peaks that are approximately 3 – 4 $\mathrm{cm^{-1}}$lower than the primary peak. A series of experiments have been performed to ascertain the nature of the satellite peaks. These consist of co-depositions in which the concentrations of both monomers were varied over a large range (1:200 to 1:1600 S/M ratios), annealing experiments (20 K to 35 K), and lower temperature cycling experiments (20 K to 8 K). Based on the results of these experiments, it is concluded that the satellite peaks are due to rotational structure and not due to matrix site effects, higher aggregation or distinct complex geometries. Given the rigidity of a low temperature argon matrix, it is proposed that the rotational motion responsible for the satellite peaks is internal rotation within the methanol subunit of the complex rather than overall molecular rotation of the complex.