Characterization of H–π and CH–O Structures of the 1:1 Methanol–Benzene Complex Using Matrix Isolation Infrared Spectroscopy

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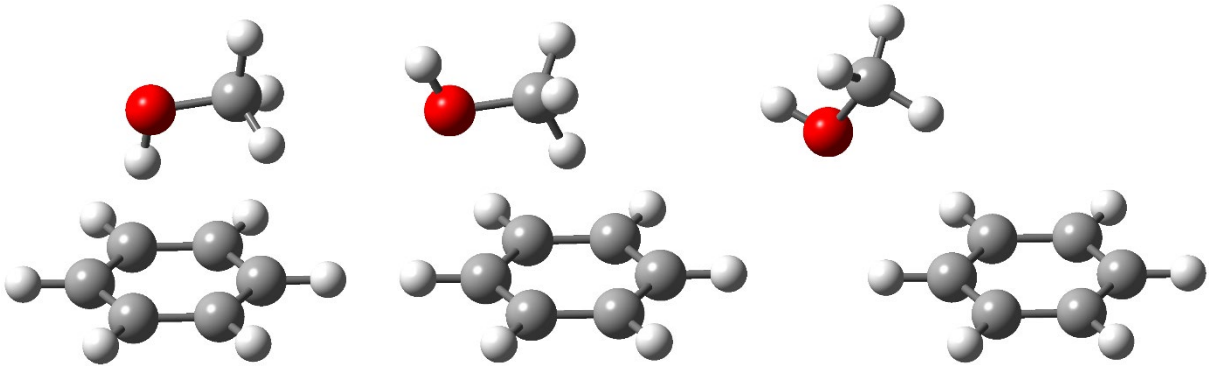
Matrix isolation infrared spectroscopy was used to characterize a 1:1complex of methanol (CH_3OH) and benzene (C_6H_6). Co-deposition experiments with CH_3OH and C_6H_6 were performed at 17 - 20 K using nitrogen and argon as the matrix gases. Several new infrared peaks in the co-deposition spectra were observed near the fundamental absorptions of the CH_3OH and C_6H_6 parent molecules and these new peaks have been attributed to CH_3OH-C_6H_6 complexes. Experiments were also performed with isotopic CD_3OD and C_6D_6 and the corresponding infrared peaks of the isotopologue complexes have also been observed. Theoretical calculations were performed for the CH_3OH-C_6H_6 complex using MP2 and CCSD(T) methods using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Full geometry optimizations followed by vibrational frequency calculations were performed for several initial starting geometries and three stable minima were found for the CH_3OH-C_6H_6 complex. The first has the CH_3OH above the C_6H_6 ring with the OH hydrogen interacting with the π cloud of the ring (H-π complex), the second has the CH_3OH above the C_6H_6 ring with the OH oxygen interacting with one of the C-H bonds of the ring (CH-O 1 complex), and the third has the CH_3OH towards the side of the C_6H_6 ring with the OH oxygen interacting with two of the C-H bonds of the ring (CH-O 2 complex). The H-π complex structure is predicted to be the lower energy structure by approximately 8 kJ/mol compared to the two CH-O structures. Comparing the theoretically predicted infrared spectra for the optimized CH_3OH-C_6H_6 complex structures to the experimentally observed infrared peaks in argon and nitrogen matrices, it is concluded that in the argon matrices only the H-π complex structure is being observed, whereas in the nitrogen matrices the H-π complex and CH-O 1 complex structures are being observed.



H-π complex CH-O 1 complex CH-O 2 complex