

BLUE SHIFTED HYDROGEN BOND IN CH/D₃CN...HCCL₃COMPLEXES

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H-bonded complexes between CHCl₃ and CH/D₃CN have been identified by FTIR spectroscopy in the gas phase at room temperature. With increasing partial pressure of the components, The C-H stretching fundamental shifts to the blue which has been identified as due to C-H...N interaction. The C-H stretching frequency of CHCl₃ with CH₃CN and CD₃CN are shifted by +8.7 and +8.6 cm⁻¹, respectively. By using quantum chemical calculations at the MP2/6-311++G** level, we predict the geometry, electronic structural parameters, binding energy, and spectral shift in the H-bonded complexes. The potential energy scans of the above complexes as a function of C...N distance shows that the H-bonding interaction is predominantly due to contribution of two opposing forces i.e., electrostatic attraction between H and N which leads to the C-H bond elongation with consequent red-shift and the electronic and nuclear repulsion between the C and N which results in C-H bond contraction and blue-shift of the C-H stretching frequency. The net effect of these two opposing forces at the equilibrium complex geometry dictates the nature of the shift although the influence of the surrounding atoms bonded to the atoms that are directly involved in the H-bonding cannot be fully underestimated. The total interaction energy (-14.23 kJ/mol) is characterized by Morokuma energy decomposition analysis where the binding in CH/D₃CN...CHCl₃ is dominated by electrostatic attraction (-25.86 kJ/mol). The attraction, however, is considerably suppressed by exchange repulsion (+19.54 kJ/mol). Other components like polarization (-5.44 kJ/mol) and charge transfer (-5.06 kJ/mol) make significant contribution to the interaction energy.