

**Carbon-Donated Hydrogen Bonding:
Electrostatics, Frequency Shifts, Directionality and Bifurcation.**

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Structure, energies, electrostatics, and vibrational modes were calculated *ab initio* for dimethyl sulfoxide (DMSO) and its 1:1 hydrogen bonded complex with chloride ion at the MP2/6-311+G** level. The interaction energy is -71kJ/mole. On average, the C-H stretching frequencies decreased by 35 cm⁻¹, while their intensities increased by a factor of 19. Methyl torsion frequencies increased by 50-80 cm⁻¹. We review the past and present understanding of hydrogen bonding, and apply these perspectives to analyze properties of the complex. The stretching shifts conform to the established spectral criteria for hydrogen bonding. The bifurcated geometry of the complex and its electrostatic character are fully consistent with trends observed in classically defined hydrogen bonds. All of the established definitions and criteria for identifying hydrogen bonding have been challenged. By any of the most well-established criteria, the DMSO-chloride ion complex is hydrogen bonded. We propose a generally applicable working definition of hydrogen bonding to clarify and unify understanding of this interaction.