INFRARED SPECTROSCOPIC DEMONSTRATION OF COOPERATIVE STRENGTHENING OF AN INTRAMOLECULAR OH–O HYDROGEN BOND BY A WEAK CH–O COUNTERPART

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Cooperativity is an important attribute of interconnected hydrogen bonds, and the classic examples are the size and shape dependent stability of small water clusters. The effect involving CH–O hydrogen bonds has been theoretically predicted and inferred also by analyzing crystallographic data. However, direct demonstration by infrared spectroscopy, in terms of spectral shifts, is scarce. We report here such effect probing the spectral shifts of various stretching fundamentals associated with an intramolecular OH–O=C linkage of the tautomer of 1,2-cyclohexanedione. Two types of interconnected CH–O bonds, intra- and intermolecular, with the above linkage are generated. In the first case, we have used 3-methyl 1,2-cyclohexane dione and spectral measurements reveal that the cooperative stabilization occurs with displaying a blue-shifting of the CH stretching fundamental of the hydrogen-bonded methyl CH group. For the intermolecular case, a 1:1 complex between 1,2-cyclohexanedione and chloroform has been used, and the complexation results further red-shifting of the OH stretching fundamental and a concomitant blue-shifting of the C=O stretching fundamental. The details of the spectral effects are corroborated by predictions of electronic structure calculations.