

Quantum chemical studies and vibrational spectroscopy of hydrogen-bonded molecules in the gas phase

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The study of intermolecular interactions and association is essential to understand the properties of matter in its different physical conditions. Among those interactions, the hydrogen-bond $X-H \cdots Y$ is particularly relevant, since it is one of the most important structural and dynamic elements in molecular association. Vibrational IR and Raman spectroscopy are powerful techniques for looking at intermolecular interactions, since shifts of vibrational bands give information on the local environment of the vibrating group. In addition, quantum-chemical "ab initio" calculations at a sufficiently high level of theory are indispensable to guide and interpret correctly experiments. The vibrational behaviour of the X-H group provides a sensitive and characteristic manifestation of the hydrogen bond. Normally, the frequency of the X-H stretching mode shifts to lower values ("red shift") due to an elongation (weakening) of the X-H bond. There is a growing recent interest in less conventional, weaker hydrogen bonds, mainly of the $CH \cdots O$ or $CH \cdots \pi$ type. They often display a shift of the X-H stretching vibration to higher frequency ("blue shift") which is associated with a contraction of the X-H bond.

H-bonded complexes with $CHCl_3$ or $HCOOH$ are ideal test cases to study the nature of H-bonding. They are capable of forming blue-shifting *and* red-shifting H-bonds, depending on the interaction partner. This allows the study of the distinction between these two types of H-bonding. In our contribution, we introduce ab initio calculations, FTIR and Raman spectroscopy of some blue- and red-shifting compounds in the gas phase which we have recently performed at Sheffield [1, 2, 3, 4]. For this task, we have developed computer code automating BSSE corrections during *ab initio* calculations [1], and we set up a stimulated Raman photoacoustic spectrometer (PARS, [4, 5, 6, 7]) which has been extended to the measurement of corrosive gases and hostile environments using a modification of the optophone detection introduced by Zare and coworkers [6, 7].

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