Proton Transfer under High Pressure.

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Our study is devoted to a better understanding of the complex relations between the proton transfer dynamics along a hydrogen bond in the quantum regime, and the chemical nature of donor and acceptor, the distance between the two proton sites, and the shape of the potential function. This distance depends on the pressure.

In AH•••B hydrogen bonds, the proton transfer is governed by a double minimum potential. In symmetric AH•••A systems, the two wells can be equivalent: two tautomeric forms exist and proton tunneling may occur. For shorter hydrogen bonds, the distance and the barrier height between the two minima decrease. The potential may become a single minimum potential and the symmetric structure can be considered as the "intermediate state" for proton transfer.

This dynamics can be observed by infrared and Raman spectroscopy. Very high pressures can be obtained with diamond anvil cell.



The mono-anion of maleic acid in potassium hydrogen maléate, KH(OOC–CH=CH–COO) is a typical example of a symmetric intramolecular hydrogen bond. This bond is strong (2.437 Å), with the proton located at the center. At ambient pressure, the potential function is symmetrical with a central minimum between two secondary minima at higher energy.

The main results are the following ones. Below 29 GPa, three pressure ranges (\sim 3.9, \sim 6.4 and >1.8 GPa) related to irreversible spectral discontinuities can be distinguished. At \sim 4 GPa, the splitting of the CH stretching mode suggests a distortion of the "ring" of the molecule,

leading to a disymetrization of the molecule. At ~6.4 GPa, the simultaneous appearance and disappearance of some intramolecular modes indicate a phase transition, with opening of the "ring".