Spectroscopy of 4(5)-Methylimidazole and its Hydrates in He Droplets

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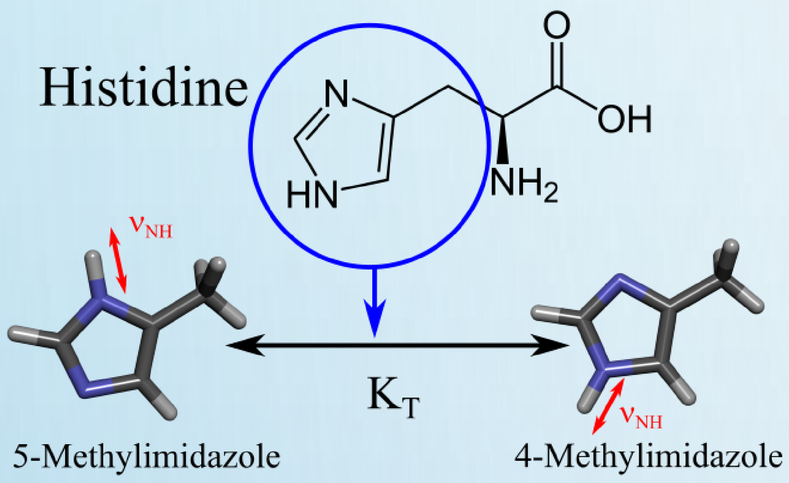
1. Purpose

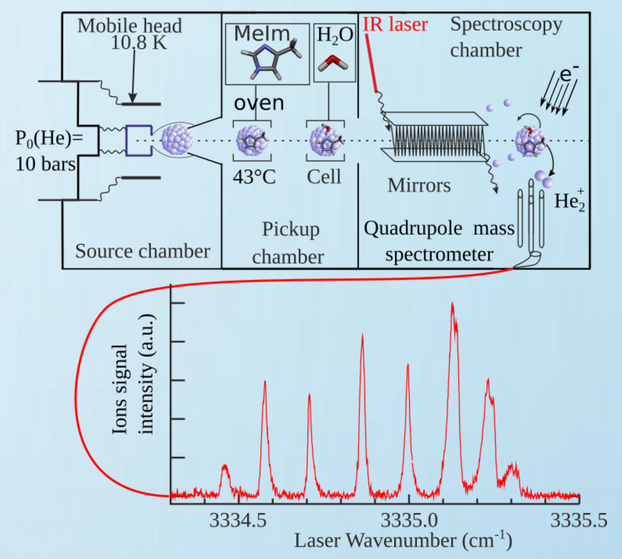
Histidine, one of two amino acids with tautomeric equilibrium, is both a proton acceptor and a proton donor. It plays therefore an essential role in biological processes where proton transfer is involved (e.g. regulation of blood pH). Studies have shown that the tautomeric equilibrium of this molecule is modified by the environment[1], making its intrinsic properties difficult to obtain experimentally. However, knowledge of these properties is important for a full understanding of the behaviour of this molecule when surrounded. The above-mentioned characteristics are carried by the imidazole ring that constitutes the side chain of histidine. Hence, the 4(5)-methylimidazole (MeIm) may appear as an adequate model to study these properties specifically. Experimentally, we characterized the tautomers of MeIm and its hydrates by infrared spectroscopy. Using DFT-D calculations, we unambiguously assigned the two Melm tautomers by NH stretching and the tautomeric constant was determined. Similarly, MeIm-water complexes were formed and partially characterized by the NH stretching of MeIm and the symmetric and asymmetric OH stretching of water.



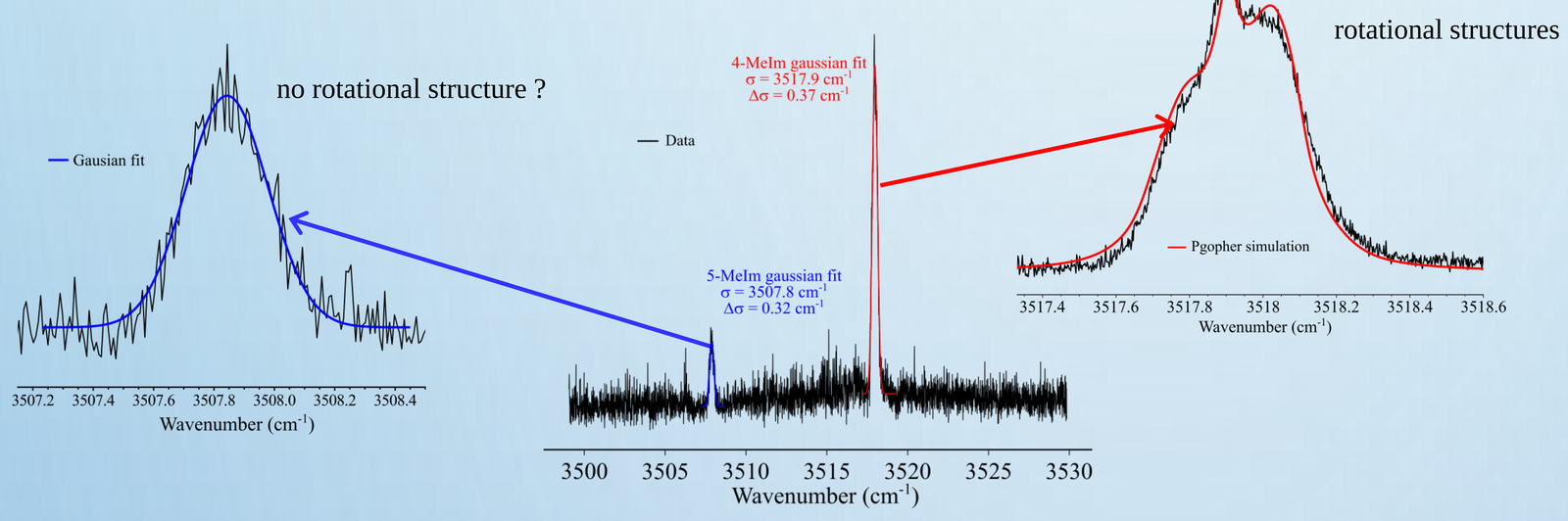
Helium nanodroplet

- **Very cold (0.37 K** [2]**)** : efficient cooling of the molecule
  → Molecule in its ground state (v=0 and a few J populated)
- **Superfluidity** [3] : weak interactions
- Optically transparent below 20 eV
- Possibility to form **unusual complexes** (→ nanoreactor)
- Small binding energy between one helium atom and the droplet : 5 cm^{-1} (→ bolometer)

HENDI method[4]

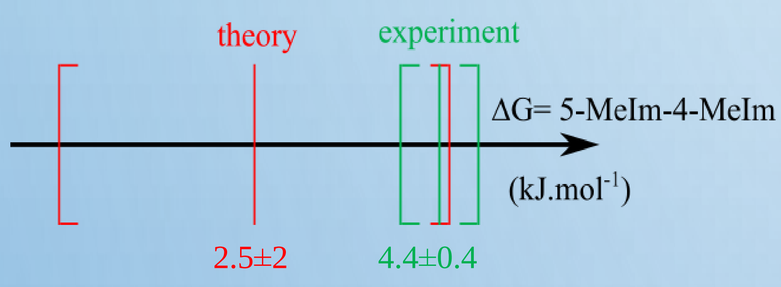


Isolated MeIm



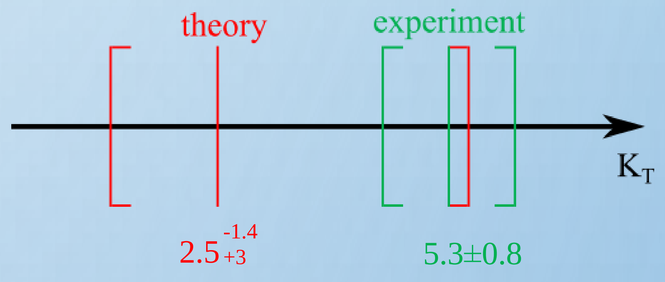
Spectroscopic constants (cm^{-1})	Theory (DFT-D, RI-B97-D3(BJabc)/def2-TZVPPD)	In Droplet (simulation)
5-MeIm NH vibration	3510 (scaled harmonic)	3507,8
4-MeIm NH vibration	3517.1 (scaled harmonic)	3517,9
A	0,3	0,034
B	0,11	0,018
C	0,085	0,015
$\Delta_J, \Delta_{JK}, \Delta_K, \delta_K, \delta_J$	0	10^{-5}

FREE ENTHALPY @43°C (oven)



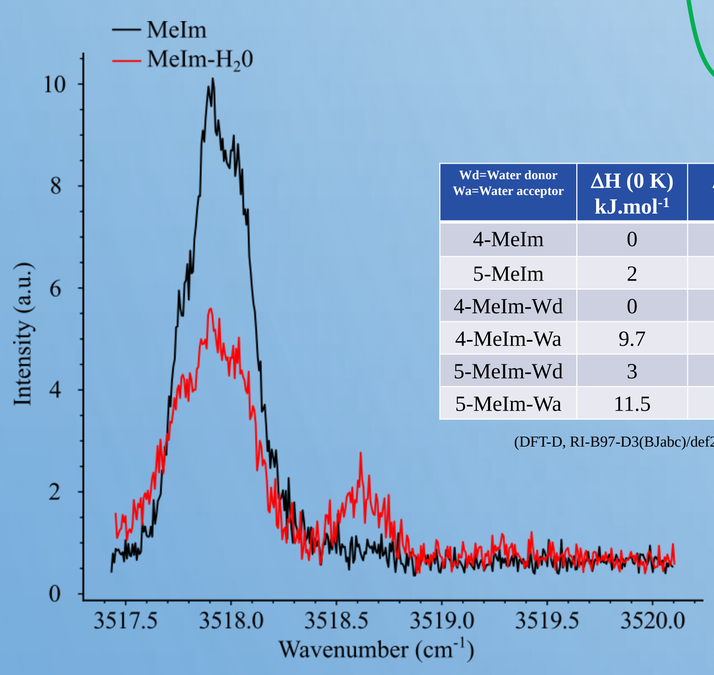
$$K_T = \frac{\textit{4-MeIm/5-MeIm intensity ratio of the NH band}}{\textit{4-MeIm/5-MeIm oscillator strengths ratio}} = e^{\frac{\Delta G}{RT}}$$

TAUTOMERIZATION CONSTANT @43°C (oven)



4(5)-MeIm complexes

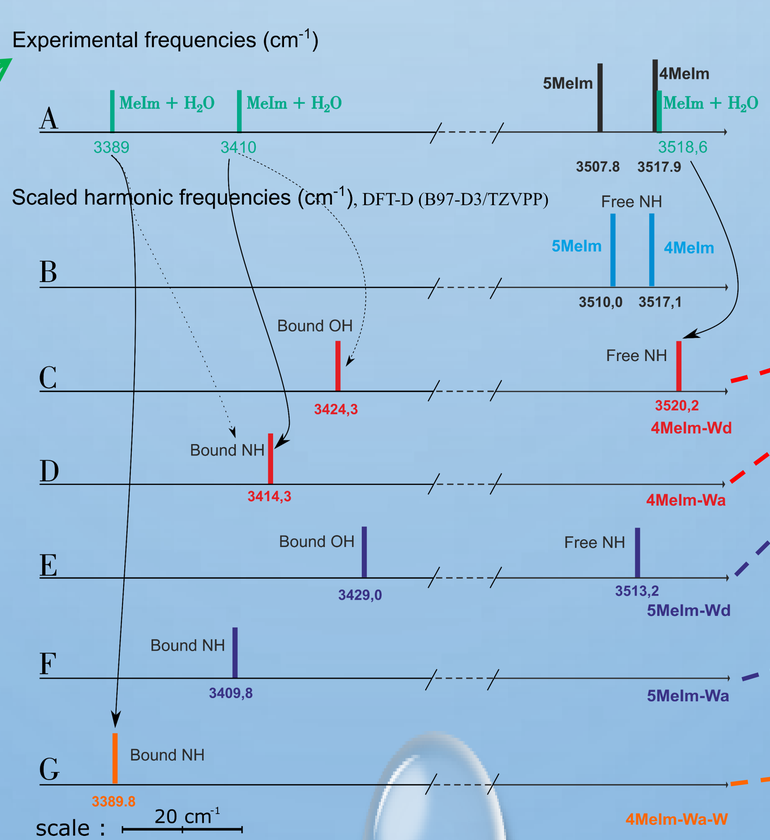
A wide spectral range was scanned.
Only three signals, like the one below, were observed

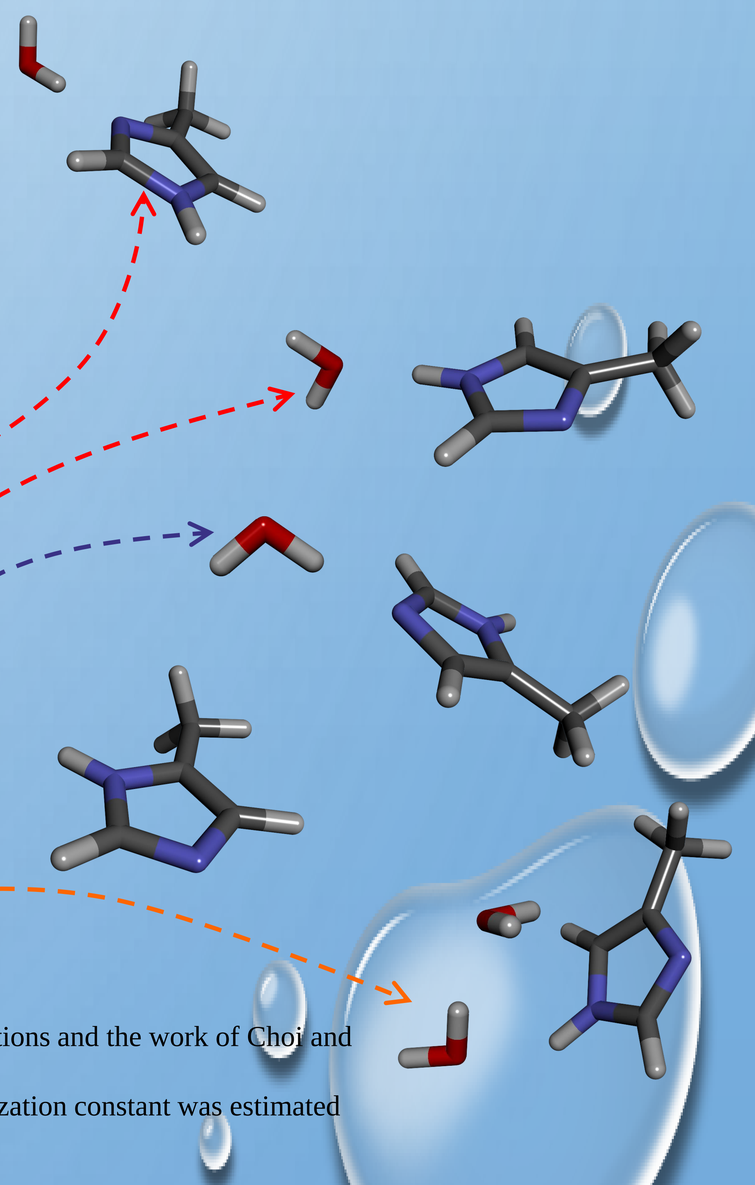


Wd=Water donor Wa=Water acceptor	ΔH (0 K) $kJ.mol^{-1}$	ΔG (298 K) $kJ.mol^{-1}$
4-MeIm	0	0
5-MeIm	2	2.4
4-MeIm-Wd	0	0
4-MeIm-Wa	9.7	8.5
5-MeIm-Wd	3	3.7
5-MeIm-Wa	11.5	9.8

(DFT-D, RI-B97-D3(BJabc)/def2-TZVPPD)

Summary of the position of the different stretching bands found either by DFT-D calculation or experimentally





Conclusion:

Assignment of the observed bands using DFT-D calculations and the work of Choi and Miller[5]
The two tautomers were characterised and the tautomerization constant was estimated
4-MeIm –Wa, Wd and the dehydrate was observed
5-MeIm hydrated not observed

References:

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