

Unusual IR ring mode splittings for pyridinium species in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid: involvement of the δNH internal mode.

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Supplementary information

Infrared spectra of PyH^+ species formed during pyridine absorption in $\text{H}_3\text{W}_{12}\text{O}_{40}$

Firstly gaseous pyridine is absorbed in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ under 1 Torr (Fig.S1, left part A), this pressure is low enough to ensure that the *bis*-pyridinium salt would not be produced.⁹ Secondly, pyridine is desorbed at increasing temperatures (Fig. S1, right part B). From this figure, it is deduced that band splittings are not observed when the quantity of absorbed pyridine is low (spectra a and g). After heating the sample from room temperature (spectrum a) to 373 K (spectrum b), the quantity of absorbed pyridine increases, as evidenced by the growing intensity of the bands, concomitantly the bands split but the components are not resolved. Thus the observance of the splitting of the bands depends upon the quantity of absorbed pyridine. Increasing the time of exposure to pyridine vapour at 373 K increases the absorbed quantity of pyridine and the spectral resolution of the splittings (spectrum c). In such thermal and pressure conditions the stoichiometric pyridinium salt is produced (9). A better spectral resolution of the splittings is achieved upon evacuation (spectrum d) although no more pyridine is absorbed (as it is particularly seen from the constant intensity of the ν_{19a} band). Thus the stoichiometry of the salt is a necessary condition to observe the band splittings but not a sufficient one. We assume that the time of pyridine exposure is another parameter which determines the crystallinity of the sample. In conclusion band splittings are optimally observed for the stoichiometric and well crystallized sample.

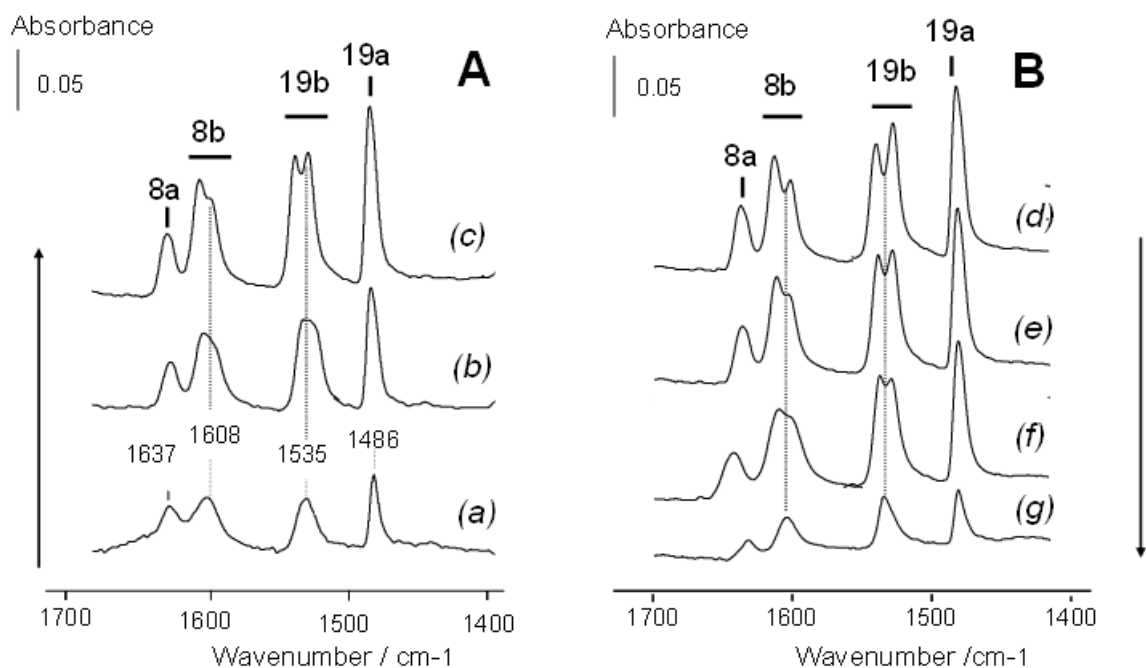


Fig.S1: Pyridine absorption in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (part A) and desorption (part B). Gaseous pyridine absorption was performed under 1 Torr while desorption was under a vacuum. All spectra were scanned at room temperature after the indicated treatment of the samples. Lateral arrows indicate the order for the successive experiments: absorption at room temperature after 5 min exposure (a), spectra after heating at 373 K for 5 min (b) and for 60 min (c); spectra under vacuum, at room temperature (d) and after heating at 373 K (e), 523 K (f), 573 K (g).