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ARTICLE TYPE

Unusual IR ring mode splittings for pyridinium species in $H_3PW_{12}O_{40}$ heteropolyacid: involvement of the δNH internal mode.

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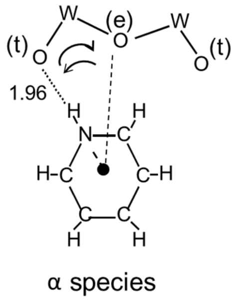
This study aimed at investigating the well-known infrared band splitting affecting the ν8b and ν19b modes of pyridinium species formed by pyridine absorption in tungsten heteropolyacid $H_3PW_{12}O_{40}$, first reported 30 years ago but the origin of which has not yet been satisfactorily explained. To this aim, IR spectra of isotopically substituted pyridinium species *h*$_5$-PyH$^+$, *h*$_5$-PyD$^+$, *d*$_5$-PyH$^+$ and *d*$_5$-PyD$^+$ were analysed and compared in the 1700-1300 cm^{-1} range. DFT calculations were used to assign the IR bands of the 4 isotopomers in this range. The results clearly showed that the splitting specifically affects pyridinium modes presenting a marked δNH character, namely the asymmetric ν8b and ν19b modes of h$_5$-PyH$^+$ and *d*$_5$-PyH$^+$ species. The Davydov nature of the splittings was eliminated upon using mixtures of isotopic pyridinium species. They are explained by an interaction between the δNH internal mode with the in-plane pyridinium ring frustrated rotation in two potential wells, associated to a tunneling effect.

1. Introduction

12-tungstophosphoric acid $H_3PW_{12}O_{40}$ (abbreviated as HPW), and more generally heteropoly acids, have been the subject of a large number of publications.[1] The considerable interest of these compounds as solid catalysts was stimulated by their redox properties and by their strong acidities[2] leading to industrial applications.[3] On the other hand, pyridine is currently used as an IR molecular probe to characterize catalyst acidities, in particular the Brönsted one, the pyridinium cation (PyH^+) being so formed. Thus infrared (IR) study of pyridine absorption in HPW was initiated several decades ago.[4]

The main IR spectroscopic fingerprint for PyH^+ is its ν19b band at around 1540 cm^{-1}. Its wavenumber was found to be unsensitive to the nature of the counter-anion;[5] then its unusual important splitting for $(PyH^+)_3[PW_{12}O_{40}]$,[6-10] as well as that of the ν8b band, were somewhat intriguing. To explain these splittings the presence of bis-pyridinium species (PyH^+...Py)[6,7] or sites effects[8] was proposed. First, associating thermogravimetric analysis with IR spectroscopy we showed that the band splittings concern PyH^+ species and not bis-pyridinium ones.[9] Secondly, associating X ray diffractometry (XRD) with IR spectroscopy and using single crystal samples we excluded that the band splittings were due to site effects but very possibly due to a quantum tunneling effect involving a frustrated rotation of the pyridinium ring in two potential wells.[10]

As previously reported,[10] the Keggin anion $[PW_{12}O_{40}]^{3-}$ is commonly described as a tetrahedral assembly of four W_3O_{13} sets, themselves constituted of three WO_6 octahedra having common edges. The edge-sharing oxygen atoms are labelled O_e, while W_3O_{13} moieties are joined through common corner oxygen atoms labelled O_c. Apex oxygen atoms, the terminal ones, are labelled O_t. The tetrahedral PO_4 moiety occupies the central position. The whole anion is roughly spherical with 1 nm diameter.



Scheme 1 : α species site for $(PyH)_3{}^+[PW_{12}O_{40}]$. Interatomic distances are expressed in Å.

The XRD-IR experiments were performed on CH_3CN-solvated $(PyH^+)_3[PW_{12}O_{40}].2CH_3CN$ **(1)** and CH_3CN-desolvated $(PyH^+)_3[PW_{12}O_{40}]$ **(2)** single-crystals.[10] It was shown that for these two compounds the three PyH^+ species are H-bonded to each Keggin unit $[PW_{12}O_{40}]^{3-}$. Among these three PyH^+ species, two are crystallographically equivalent and are denoted α species, the remaining species being denoted β species. The ν19b and ν8b pyridinium band splittings are only observed for α species. For the XRD best fitted structure of the CH_3CN-solvated compound **1**, the (N)H atom of α species was found to be linearly H-bonded to the W-O_e-W Keggin oxygen atom but the pyridinium ring possibly rotates towards the vicinal W=O_t oxygen atom.[10] Such a frustrated rotation would explain the band splittings by a tunneling effect in a double well potential. For the CH_3CN-

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desolvated compound **2**, the best fitted XRD structure indicates that α species are linearly H-bonded to the W=O_t oxygen atom (Scheme 1). But, for compound **2**, an orientational disorder of the Keggin units prevents XRD measurements of the interatomic distances to be precise enough to evidence any pyridinium ring frustrated rotation.[10] However, as IR band splittings are similar for compounds **1** and **2**, it can be assumed that such a tunneling effect also takes place for α species in compound **2**.

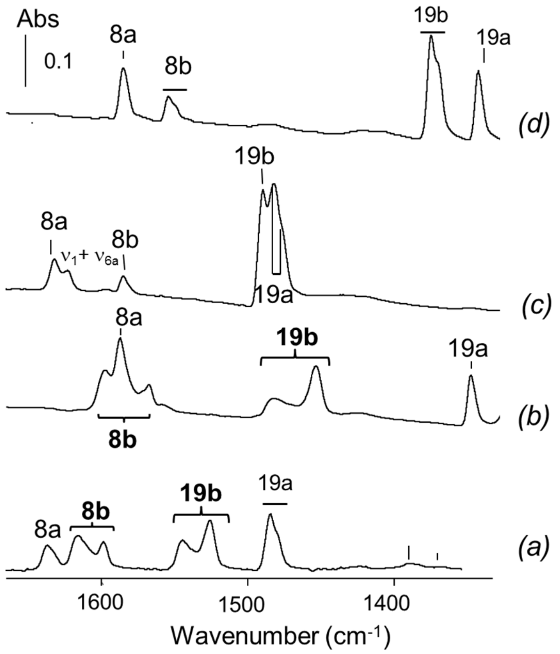

Fig.1 Spectral region of pyridinium ring stretching , "δNH" and δCH modes scanned at 100 K for H/D isotopically substituted species: h_5-PyH$^+$ (a), d_5-PyH$^+$ (b) h_5-PyD$^+$ (c) and d_5-PyD$^+$ (d).

The main purpose of this paper is (i) to assess the presumed δNH internal coordinate role in the hypothetical tunnelling effect and (ii) to examine the possibility of a classical Davydov splitting. To this aim, IR measurements have been carried out on four isotopomers of pyridinium species : h_5-PyH$^+$, h_5-PyD$^+$, d_5-PyH$^+$ and d_5-PyD$^+$; their infrared spectra have been interpreted with the help of DFT calculations.

Experimental details

Infrared spectroscopy

HPW was dispersed in deionised water and spread on a silicon plate. The sample was placed in a homemade quartz cell equipped with KBr windows. The infrared cell was connected to a vacuum line for evacuation and calcination steps. After heating deposited HPW at 373 K under vacuum for 1 hour, the sample was exposed at the same temperature to pyridine vapour (h_5-pyridine or d_5-pyridine) (1 Torr at equilibrium pressure). The so-formed stoichiometric salt was cooled at room temperature or at 100 K under vacuum.

The spectra of pyridinium cations h_5-PyD$^+$ and d_5-PyD$^+$ were obtained by H/D exchange with D_2O of the corresponding species formed on HPW. The H/D exchange procedure consists to the introduction of D_2O vapor into the infrared cell (10 Torr) at 373 K for 30 minutes and followed by outgassing at the same temperature for 30 min. This procedure was repeated three times. After water isotopic exchanges, samples were finally dried *in situ* under vacuum at 373 K during 60 min. The isotopic purity of the deuterated PyD$^+$ forms is higher than 0.8.

Table 1 Calculated wavenumbers for pyridinium ring stretching modes in H/D isotopically substituted species h_5-PyH$^+$, d_5-PyH$^+$, h_5-PyD$^+$ and d_5-PyD$^+$ (scaling factor: 0.982).

Mode (symmetry)[a]	h_5-PyH$^+$	d_5-PyH$^+$	h_5-PyD$^+$	d_5-PyD$^+$
ν8a (A_1)	1638	1588	1634	1584
ν8b (B_2)	1610	1583	1587	1554
ν19b (B_2)	1540	1465	1494	1378
ν19a (A_1)	1488	1334	1483	1329

[a] Symmetries are indicated for the C_{2v} point group.

The IR spectra (4 cm^{-1} resolution) were recorded with a Thermonicolet spectrometer equipped with a DTGS detector and a KBr beamsplitter. Spectra were recorded at room temperature or at 100 K. HPW (analysis grade) was purchase from Merck. h_5- and d_5- pyridine (Aldrich, 99 + % grade) were dried on molecular sieves prior to use.

DFT calculations

DFT calculations of pyridinium harmonic vibrational modes were carried out with the Gamess package[11] using the B3LYP functional[12] and 6-31+G** basis set.[13] Vibrational frequencies were computed by finite differences and scaled by a constant factor of 0.982 in order to fit the experimental frequencies of h_5-PyH$^+$. The frequencies of deuterated species were obtained using the same force field and scaling factor while changing the atomic masses.

Results

Figure 1a shows the spectrum of the pyridinium h_5-PyH$^+$ species recorded at 100 K obtained after pyridine absorption at 373 K followed by an evacuation at the same temperature. In such conditions, the spectrum is similar to that previously reported for the pyridinium salt $(PyH^+)_3[PW_{12}O_{40}]$.[10] Figures 1 also shows the spectrum obtained for the d_5-PyH$^+$ (1b).

Table 1 reports the computed harmonic frequencies of the ν8a, ν8b, ν19a and ν19b modes derived from DFT calculations for the h_5-PyH$^+$ species and for the various H/D isotopically substituted pyridinium species. The computed frequencies are in good agreement with previously reported experimental values for normal and deuterated pyridinium salts.[5,14]

As previously reported, in the 1700-1300 cm^{-1} frequency range, h_5-PyH$^+$ species display ν8b and ν19b modes clearly split (1618 / 1600 cm^{-1} and 1546 / 1527 cm^{-1} , respectively). In d_5-PyH$^+$ the ν8a and ν8b bands are both expected near 1580-1590 cm^{-1} [5] and computed at 1588 and 1583 cm^{-1}, respectively (Table 1). In the $(d_5\text{-PyH}^+)_3[PW_{12}O_{40}]$ salt, three bands are observed at 1589 cm^{-1} (ν8a) and 1600, 1570 cm^{-1} (ν8b). Two bands at 1483 and 1454 cm^{-1} are also observed in the expected range for the ν19b mode (5). Finally the ν19a band appears at 1347 cm^{-1} as a single sharp band. We report in Table 2 the wavenumbers relative to these two compounds, spectra being recorded at 100 K.

The analysis of the spectra of the h_5/d_5-PyD$^+$ species was more

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complex due to the presence of isotopic impurities h_5/d_5-PyH$^+$

Table 2 Wavenumbers (cm^{-1}) for pyridinium stretching ring modes for h_5-PyH$^+$ and d_5-PyH$^+$ observed for spectra recorded at 100 K. Values in brackets indicate the doublet components observed at room temperature.

Assignments[a]	h_5-PyH$^+$		d_5-PyH$^+$	
	α species	β species	α species	β species
ν8a (A_1)	1639		1589	1589
ν8b (B_2)	1618 (1614) (1602) 1600	1611	1600 (1594) (1575) 1570	unresolved
ν19b (B_2)	1546 (1542) (1530) 1527	1539	1483 (1473) (1459) 1454	1472
ν19a (A_1)	1487	1480	1347	1347

[a] Symmetries are indicated for the C_{2v} point group.

arising from an incomplete exchange of the parent HPW. The spectra reported in Figure 1c and 1d were obtained by subtraction of the bands due to these isotopic impurities. The spectrum of d_5-PyD$^+$ shows single ν8a (1584 cm^{-1}) and ν19a (1342 cm^{-1}) bands, while the ν8b at 1554 cm^{-1} and ν19b at 1374 cm^{-1} present weak shoulders at slightly lower wavenumber (1549 and 1370 cm^{-1}, respectively). Finally, the spectrum of h_5-PyD$^+$ is more complex because of the overlap of the ν19a (1483 cm^{-1}) and ν19b bands (1491 cm^{-1}) on the one hand and the presence of a combination band (ν1+ν6a) close to the ν8a band (1634 cm^{-1}) on the other hand. However the ν8b mode appears as a single band at 1587 cm^{-1}.

In order to investigate the possibility of band doubling through a dynamical vibrational interaction between equivalent pyridinium ions in the same crystal unit cell (Davydov coupling), an equimolecular mixture of h_5-Py and d_5-Py was absorbed in HPW. The spectrum, recorded at room temperature (Fig.2, spectrum d) is identical to the half-sum (spectrum c) of the spectra a and b resulting from the absorptions of h_5-Py and d_5-Py in separated HPW samples. Then, none of the observed band splittings can be assigned to intermolecular coupling involving vibrations. This conclusion is supported by the spectra of h_5-PyH$^+$ diluted in h_5-PyD$^+$ or d_5-PyH$^+$ in diluted d_5-PyD$^+$(isotopic impurities, Figure 3) which are identical to the spectra of pure h_5-PyH$^+$ and d_5-PyD$^+$, respectively.

Discussion

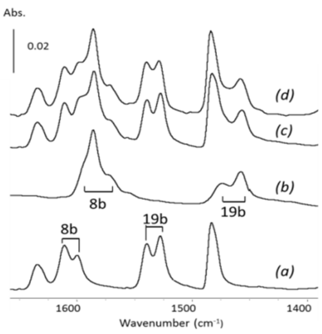

Fig.2: Spectra of H/D substituted pyridinium salts of HPW: (a) h_5-PyH$^+$, (b) d_5-PyH$^+$, (c) half-sum of spectra a and b, (d). equimolecular mixture of h_5-PyH$^+$ and d_5-PyH$^+$species.

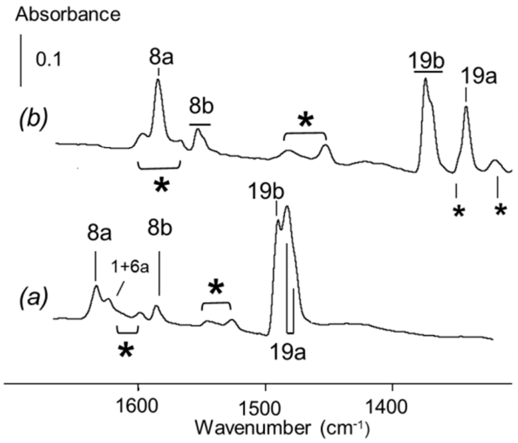

Fig.3: Spectra recorded at room temperature of h_5-PyH$^+$ diluted in h_5-PyD$^+$ (a) or d_5-PyH$^+$ in diluted d_5-PyD$^+$ (b) Relatively weak bands labelled with an asterisk are due to H$^+$ homologous impurities (see spectra a and b in Fig.1).

The present paper is devoted to the study of the split of pyridinium ring bands in HPW salts.[4-10] Two types of band doublings can be distinguished according to their magnitude, large splittings (Δν >10 cm^{-1}) and weaker band doublings, the latter being characterized by the appearance of low wavenumber shoulders to the main bands. In a previous work,[10] we have shown that the weak band doubling arises from static effects: (PyH$^+$)$_3$[PW$_{12}$O$_{40}$] presents two crystallographically distinct PyH$^+$ species H-bonded to each Keggin unit [PW$_{12}$O$_{40}$]$^{3-}$, denoted α and β species, weak lower wavenumbers corresponding to the β species.

In the following, we only consider the large splittings specific to α species. Results reported Table 2 evidence a temperature dependence of these splittings; the lower the temperature, the larger the band splitting. For instance the ν8b splitting of d_5-PyH$^+$ increases from 19 cm^{-1} to 30 cm^{-1} upon decreasing temperature.

The spectra obtained for the isotopomeric species show that the large splittings clearly occur for the ν8b and ν19b modes of the h_5-PyH$^+$ and d_5-PyH$^+$ species, but not on h_5/d_5-PyD$^+$ species. Among the possible origins of such a band splitting, a dynamical vibrational coupling (Davydov coupling) can be definitively excluded as shown by the absence of effects of the isotopic dilution of isotopomer species (equimolar mixtures of h_5-PyH$^+$ and d_5-PyH$^+$ (Fig.2) or isotopic impurities, Fig.3). The large splitting being only observed for PyH$^+$ isotopomers, this suggests that it involves N-H internal modes. Like pyridine, the pyridinium cations belongs to the C_{2v} point group and presents in the 1300-1700 cm^{-1} range non-degenerate vibrational modes distributed into two symmetry species: A_1 (in-plane vibrations, symmetric with respect to the C_2 axis) and B_2 (in-plane, antisymmetric). Table 3 shows the potential energy distribution of the ring vibration modes of the four isotopic species in the 1700-1300 cm^{-1} range. It evidences that the pyridinium ring symmetrical (A_1) modes of h_5-PyH$^+$ mostly involve ring stretching vibrations (C-C and C-N) and C-H bending vibrations,

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Table 3 Potential energy distribution (PED) associated to a tunneling effect of pyridinium ring stretching modes in H/D isotopically substituted species h_5-PyH$^+$, d_5-PyH$^+$, h_5-PyD$^+$ and d_5-PyD$^+$

Species		Vibration mode (cm^{-1})		PED (%) [a]	δNH(D) character (%)
h_5-PyH$^+$	ν8a	1638	A_1	νR (69) + δCH (30)	0
	ν8b	1610	B_2	νR (61) + δNH (27) + δCH (12)	27
	ν19b	1541	B_2	δCH (44) + νR (33) + δNH (22)	22
	ν19a	1486	A_1	δCH (75) + νR (22)	0
		1378	B_2	δCH (76) + δNH (14) + νR (10)	14
		1343	B_2	νR (55) + δCH (34) + δNH (11)	11
h_5-PyD$^+$	ν8a	1634	A_1	νR (62) + δCH (29)	0
	ν8b	1588	B_2	νR (69) + δCH (23)	3
	ν19b	1494	B_2	δCH (52) + νR (35)	8
	ν19a	1483	A_1	δCH (73) + νR (25)	0
		1363	B_2	δCH (98)	0
		1323	B_2	νR (87)	4
d_5-PyH$^+$	ν8a	1589	A_1	νR (76) + δCD (14)	0
	ν8b	1583	B_2	νR (57) + δNH (30)	30
	ν19b	1465	B_2	νR (47) + δNH (39) +δCD (15)	39
	ν19a	1334	A_1	νR (61) + δCD (33)	0
		1333	B_2	νR (79) + δCD (13)	5
d_5-PyD$^+$	ν8a	1585	A_1	νR (76) + δCD (14)	0
	ν8b	1554	B_2	νR (80) + δCD (10)	4
	ν19b	1378	B_2	νR (57) + δCD (25) + δND (10)	10
	ν19a	1328	A_1	νR (53) + δCD (41)	0
		1314	B_2	νR (87)	7

[a] Potential energy distribution (%) of normal modes. Internal modes with contributions lower than 10% are not reported. νR : ring stretching internal modes (CN and CC); δCH(D): C-H(D) bending modes ; δNH(D): N-H(D) bending modes.

while the antisymmetric modes (B_2) ν8b and ν19b, computed at 1610 and 1541 cm^{-1} respectively, also involve a significant contribution of the N-H bending internal mode calculated at 1418 cm^{-1} in the harmonic approximation.[15] The pyridinium ring modes of h_5-PyH$^+$ computed at 1378 and 1343 cm^{-1} belong to the same asymmetric B_2 species and also present a contribution of the bending N-H mode (Table 3). Hence, the internal δNH mode is distributed among all the vibrational modes of B_2 symmetry in the 1300-1700 cm^{-1} range. Note that the band computed at 1378 cm^{-1} has a low intensity and appears as a doublet at 1388, 1368 cm^{-1} in the experimental spectra and more clearly seen for the single crystal.[10] That computed at 1343 cm^{-1} is rather broad for this salt and appears split in $(PyH)_3[PW_{12}O_{40}]\cdot 2CH_3CN$.[10]

Examination of vibration modes of d_5-PyH$^+$ species clearly confirms that only B_2 modes with a large δNH contribution (ν8b, ν19b) give rise to large splittings in the experimental spectra (Figure 1b). In the case of PyD$^+$ species, no B_2 mode presents significant δND contributions (higher than 10%) in the 1300-1700 cm^{-1} range, and no large splitting of these modes is observed experimentally (Spectra 1c and 1d). Table 4 highlights a relationship between the extent of the splittings and the δNH character of the corresponding modes.

Hence, our results clearly show that the pyridinium δNH internal coordinate is specifically implied in the perturbation leading to the large splittings observed in PyH$^+$ formed by pyridine adsorption on HPW.

In a general manner, band splittings would be explained from molecular considerations such as degeneracy of molecular levels or accidental Fermi resonance. Molecular degeneracy is discarded for pyridinium species since, in its C_{2v} symmetry, vibrations are not degenerate. The ν19b and ν8b vibrational modes are split for both h_5-PyH$^+$ and d_5-PyH$^+$ cations; this does not match with the accidental character of the Fermi resonance phenomenum. Intermolecular couplings between pyridinium species (Davydov splitting) have been considered in the present paper and excluded from mixtures of isotopically substituted pyridinium species. Static interactions between pyridinium species and Keggin anions (site effect) can also be ruled out because the large splittings concern only α pyridinium species which are located at crystallographically equivalent sites.[10]

Table 4: ν8b and ν19b band splittings ($\Delta\nu/cm^{-1}$) at 100 K in relation with the calculated δNH(D) character of these normal modes

Mode	*h*$_5$-PyH^+		*d*$_5$-PyH^+		*h*$_5$-PyD^+		*d*$_5$-PyD^+	
	Δν	% δNH	Δν	% δNH	Δν	% δND	Δν	% δND
ν8b	18	27	30	30	0	3	5	4
ν19b	19	22	31	39	0	8	4	10

Dynamic interactions between α pyridinium species and Keggin anions are now considered. Analysis of the vibration modes suggests that the doublets characterizing α species are due to specific interactions between the δNH bending mode with the Keggin unit. These specific interactions would be hydrogen bondings of the NH group with either a O_t or O_e Keggin atoms. This however does not explain the fact that the average wavenumber of the two components of each doublet is constant, while the extent of the wavenumber differences increases at lower temperatures, hence characterizing a band splitting.

In order to explain such a band splitting, we consider a frustrated in-plane rotation of the pyridinium ring in the two potential wells around a pseudo C_6 axis normal to the ring, that would exchange NH…O_t and NH….O_e directions (scheme 1). Such a rotation was evidenced using XRD in our previous work.[10] The exchange of the NH…O_t and NH….O_e directions would split the δNH energy levels by a tunnelling effect, the tunnelling mode being the frustrated in-plane rotation of the pyridinium ring. Upon progressive pyridine absorption or desorption in $H_3W_{12}O_{40}$ it appears that the band splitting is only very clear when the stoichiometric pyridinium salt is formed and when a good crystallinity of the compound is achieved (see ESI). Then it is inferred that the observed local in-plane pyridinium ring rotation involves a crystal mode. In the literature, rotations of the pyridinium ring around a pseudo-hexagonal C_6 axis normal to it are well recognised in pyridinium salts. Examples involving 60°[16,17] or 30°[18,19] incremental in-plane rotations have been reported. Using combined neutron diffraction and NMR techniques, a potential energy function with two deep wells was established at 300 K for the *d*$_5$-$PyHIO_4$ salt.[20] Most of the studies dealing with the in-plane pyridinium ring rotations were performed using NMR, NQR, neutron diffraction techniques, also calorimetric and dielectric ones, but never with infrared spectroscopy. Note however that in reference 21 relative to the $(PyH^+)_3BiCl_6$ salt, the appearance of multiplets in the pyridinium ring vibration range is reported but unfortunately not discussed by the authors. Further studies are thus necessary to determine in which extent our findings can be generalized to other pyridinium salts.

Conclusion.

In summary, the use of deuterated isotopomers of pyridinium species and DFT calculations allows us to clarify the origin of the unusual splitting of pyridinium ring bands in $(PyH^+)_3[PW_{12}O_{40}]$ first reported by Highfield and Moffat thirty years ago.[8] The present results clearly show that splittings specifically involve ring vibration modes with a significant δNH character. δNH splittings are explained by a tunneling effect in two potential wells due to the frustrated in-plane pyridinium ring rotation in $H_3PW_{12}O_{40}$. This quantum phenomenon was never observed in the infrared spectra of pyridinium salts. Concerning catalytic materials, it could be interesting to determine if such effects are specific to tungsten salts or can be found in other compounds such as pyridinium salts of molybdenum heteropolyacids.

In a practical view concerning the widely use of pyridine as an infrared probe for the measurement of the catalytic materials acidities, our clarification of the nature of the observed splittings would avoid misleading experimental conclusions such as assigning them to two distinct catalytic sites.[8] Moreover, our calculated δNH internal mode distribution over observed normal pyridinium ring modes would be helpful for the interpretation of the perturbation of the corresponding IR bands observed upon adsorbing pyridine on catalytic sites having a high Bronsted acidity.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Infrared spectra of PyH+ species formed during pyridine absorption in $H_3W_{12}O_{40}$]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 *(a)* C. Hill; *J. Mol. Catal. A*, 2007, **262**, 2. *(b)* G. Li, Y. Ding, J. Wang, X. Wang and J. Suo, *J. Mol. Catal. A*, 2007**, 262**, 67.
2 A. Corma, *Chem. Rev.*, 1995, **95**, 559.
3 M. Misono and J.Nojiri, *Appl. Catal.*, 1990, **64**, 1.
4 M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara and Y. Yoneda, *Bull. Chem. Soc. Jpn.,* 1982, **55**, 400.
5 V.P. Glazunov and S.E. Odinokov, *Spectrochim. Acta*, 1982**, 38A**, 399.
6 N. Essayem, A. Holmqvist, G. Sapaly, J.C. Védrine and Y. Ben Tâarit, *Stud.Surf. Sci. Catal.*, 2001,**135**, 340.
7 N. Essayem, C. Lorentz, A. Tuel and Y. Ben Tâarit, *Catal. Comm.*, 2005, **6**, 539.
8 J.G. Highfield and J.B. Moffat, *J. Catal.***,** 1984, **89**, 185.
9 A.Vimont, A. Travert, C. Binet, C. Pichon, P. Mialane, F. Sécheresse and J.C. Lavalley, *J. Catal*., 2006, **241**, 221.
10 C. Pichon, P. Mialane, J. Marrot, C. Binet, A. Vimont, A. Travert and J.C. Lavalley, *Phys. Chem. Chem. Phys.,* 2011, **13**, 322.
11 M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M.Dupuis, J.A. Montgomery, *J. Comput. Chem.,* 1993, **14**, 1347
12 a) A.D. Becke, *J. Chem. Phys*., 1993, **98**, 5648; (b) P.J. Stephens, F.J. Devlin, C.F. Chablowski, M.J. Frisch, *J. Phys. Chem*., 1994, **98**, 11623; (c) R.H. Hertwig, W. Koch, *Chem. Phys. Lett.*; 1997, **268**, 345.
13 (a) R. Ditchfield, W.J. Hehre, J.A. Pople, *J. Chem. Phys.* 1971, **54**, 724; (b) J.D. Dill, J.A. Pople, *J. Chem. Phys.*,1975, **62**, 2921; (c) W.J. Hehre, R. Ditchfield, J.A. Pople, *J. Chem. Phys.* 1972, **56**, 2257; (d) M.M. Francl,W.J. Pietro,W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. De Frees, J.A. Pople, *J. Chem. Phys.,* 1982, **77**, 3654; (e) P.C. Hariharan, J.A. Pople, Theor. Chim. Acta., 1973, **28**, 213.
14 R. Foglizzo and A. Novak, *J. Chim. Phys. Phys.-Chim.Biol.*, 1969, *66,* 1539.
15 M. Castella-Ventura, Y. Akacem and E. Kassab, J. Phys. Chem. C, 2008, **112**, 19045.

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16 H. Maluszynska, P. Czarnecki, S. Lewicki, J. Wasicki and M. Gdaniec, *J. Phys*.: *Condens. Matter*, 2001, **13**,11053.

17 T. Asaji, K. Eda, H. Fujimori, T. Adachi, T. Shibusawa and M. Oguni, *J .Mol. Struct*., 2007, **826** ,24.

18 M. Hanaya, N. Ohta and M. Oguni, *J. Phys. Chem.Solids*, 1993, **54**, 263.

19 T. Asaji, H. Fujimori, H. Ishida, K. Eda, M. Hashimoto and M. Oguni, *J Phys. Chem.Solids*, 2005, **66**, 869.

20 J. Wasicki, A. Pajzderska and Z. Fojud, *J. Phys. Chem*. *C*, 2008, **112**, 7503

21 J. Tarasiewicz, R. Jakubas, G. Bator, J. Zaleski, J. Baran and W. Medycki, *J. Mol. Struct*., 2009, **932**, 6.

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