Vibrational and structural analysis of (hydroxypyridin-3-yl-methyl)phosphonic acid

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Abstract

In this work the vibrational analysis of (hydroxypyridin-3-yl-methyl)phosphonic acid (**MC5**) is presented using both experimental and theoretical methods. FT-IR spectra of the solid state **MC5** precipitated at certain pH values in which consecutive deprotonations of this ligand occurs were recorded. Thus, we were able to measure IR spectra of cationic, two anionic and zwitterion forms of **MC5**. Additionally, the geometry optimization and vibrational frequencies were performed at the B3PW91 level with the 6-31G** basis set for each species. As was shown, FT-IR spectra could be fairly good reproduced by a theoretical method applied here. Additionally, charge distributions and aromaticity index were calculated for discussed **MC5** forms by using generalized atomic polar tensor and harmonic oscillator model of aromaticity, respectively.
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Keywords: (Hydroxypyridin-3-yl-methyl)phosphonic acid; FT-IR; Quantum-chemical calculation; Density functional theory; Generalized atomic polar tensor; Harmonic oscillator model of aromaticity

1. Introduction

Phosphonopyridines and their derivatives have been studies for decades due to their potential biological importance [1–7]. However, vibrational spectra of (hydroxypyridin-3-yl-methyl)phosphonic acid, abbreviated **MC5** in this work, have not been presented thus far. Four pH dependent species of **MC5** were expected in aqueous solution with pK_a values

calculated previously [6,9]. Their structures are presented in Fig. 1. There are two labile protons in the 2.0–12.0 pH range. One more deprotonation is postulated at pH below 2.0 [6]. This is supported by the NMR measurements and quantum-chemical calculations of **MC5** in D_2O solution [8,9]. However, until now, neither their FT-IR spectra nor density functional theory (DFT) calculations have been reported to give full description of its molecular structure.

Previous potentiometric studies on **MC5** indicated three pK_a constants resulting from consecutive deprotonations of the ligand (Figs. 1 and 2) [6,9]. The first pK_{a1} corresponded to dissociation of a proton

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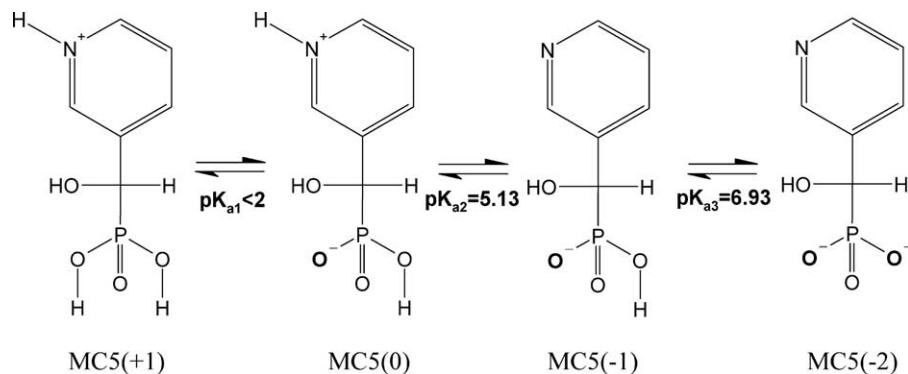
Fig. 1. (Hydroxypyridin-3-yl-methyl)phosphonic acid (**MC5**) species in aqueous solution.

from the phosphonic group and it occurred well below 2.0 [1,4,6]. The structure of the **MC5** zwitterion with deprotonated phosphonate group and protonated pyridine nitrogen is confirmed by crystallographic data of phosphonopyridine derivatives [10,11]. The next two protonation constants, namely $pK_{a2} = 5.13$ and $pK_{a3} = 6.93$, corresponded to two protons leaving the pyridine nitrogen and the phosphonic group, respectively.

In the present work FT-IR spectra and theoretical calculations were performed for all possible **MC5** forms presented in Fig. 1. Their structures (geometrical parameters), aromaticity (index HOMA—harmonic oscillator model of aromaticity) and charge distribution by using generalized atomic polar tensors (GAPT) are discussed. A vibrational assignment is based on DFT calculations combined with normal coordinate analysis and potential energy distribution (PED).

2. Experimental

2.1. Compound

The compound abbreviated as **MC5** was synthesized as described earlier [12,13] in its zwitter-anionic form. The cationic form of solid state **MC5** was obtained by slow and controlled evaporation of **MC5** solution in concentrated HCl at pH below 1.0. Both anions were prepared by titration of **MC5** aqueous solutions with simple base to the values of 6.6 (monoanion) and 8.0 (dianion) followed by solvent evaporation (cation-**MC5**(-1), cation-**MC5**(-2), respectively).

2.2. Spectral measurements

FT-IR spectra of **MC5** were run in KBr discs by using standard procedures of sample preparation for these measurements. One twenty eight scans were accommodated for all samples. Resolution was set at 2 cm^{-1}. FT-IR spectra were measured on a BRUKER spectrometer model EQUINOX55 with GLOBAR excitation source and TGS detector. The accuracy of the frequency readings for all presented spectra was $\pm 1 \text{ cm}^{-1}$.

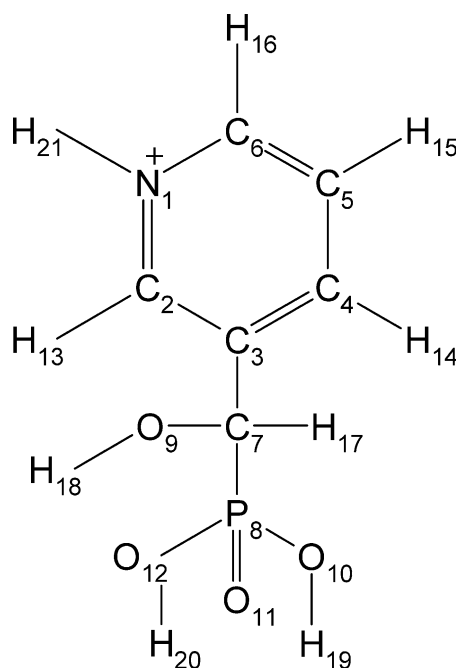Fig. 2. The atom numbering of **MC5**.

2.3. Calculations

The geometry optimization and vibrational frequencies of four **MC5** species were performed by using quantum-chemical calculations. Additionally, GAPT [14] and the aromaticity index HOMA [15,16] were calculated.

All calculations were carried out at DFT level using the B3PW91 [17,18] exchange-correlation functional implemented in GAUSSIAN '98 program [19]. The B3PW91 is a hybrid method consisting of Becke's [18] three-parameter function as a linear combination of: (1) local density approximation, (2) Becke's gradient correlation [20] and (3) Hartree–Fock exchange energy based on Kohn–Sham orbitals [21] and non-local Perdew–Wang 91 [22] gradient-corrected correlation functional. All calculation were performed with the 6-31G** basis set. Polarization functions were added for better description of polar bonds of hydroxylate and phosphonate groups in molecules.

Program GAR2PED [23,24] was used to calculate GAPT and PED of normal modes in terms of natural internal coordinates [24,25]. Visualization and checking of calculated data was done by using ANIMOL [26] and MOLDEN [27] programs.

All calculations were performed assuming C_1 point group symmetry for four species of **MC5**. Thus, obtained frequencies were multiplied by an empirical factor of 0.9573 [28] to correct incomplete incorporation of electron correlation.

3. Results and discussion

3.1. Structural study

The comparison of calculated bond lengths and angles for all discussed **MC5** forms is included in Table 1. The atom numbering of MC5 is presented in Fig 2. As expected, consecutive **MC5** proton dissociation influences the structure of the ligand obtained in a solid state at different pH. Deprotonation of the pyridine nitrogen causes lengthening of both N_1–C_2 and N_1–C_6 bonds and concomitant shortening of adjacent bonds, i.e. C_2–C_3 and C_5–C_6. On the other hand, both protons that dissociate from the phosphonic group do not have significant impact on

Table 1
Calculated length bonds (Å) and angles (°) of **MC5** species

Bonds and angles	MC5(+1)	MC5(0)	MC5(−1)	MC5(−2)
N_1–C_2	1.345	1.343	1.336	1.335
N_1–C_6	1.349	1.355	1.339	1.344
N_1–H_{21}	1.016	1.013	–	–
C_2–C_3	1.390	1.399	1.404	1.414
C_2–H_{13}	1.086	1.083	1.089	1.091
C_3–C_4	1.399	1.394	1.394	1.406
C_3–C_7	1.510	1.497	1.499	1.467
C_4–C_5	1.396	1.399	1.393	1.391
C_4–H_{14}	1.085	1.086	1.085	1.086
C_5–C_6	1.380	1.376	1.391	1.394
C_5–H_{15}	1.084	1.084	1.088	1.091
C_6–H_{16}	1.083	1.082	1.091	1.094
C_7–O_9	1.849	1.902	1.883	2.007
C_7–P_8	1.398	1.404	1.420	1.415
C_7–H_{17}	1.104	1.099	1.103	1.104
P_8–O_{10}	1.613	1.644	1.708	1.565
P_8=O_{11}	1.484	1.506	1.501	1.530
P_8–O_{12}	1.599	1.511	1.505	1.525
O_9–H_{18}	0.966	0.986	0.972	1.022
O_{10}–H_{19}	0.969	0.966	0.967	–
O_{11}–H_{20}	0.968	–	–	–
C_2–N_1–C_6	123.805	124.043	117.165	117.125
C_2–N_1–H_{21}	117.764	117.479	–	–
C_6–N_1–H_{21}	118.429	118.430	–	–
N_1–C_2–C_3	119.427	119.498	124.391	125.595
N_1–C_2–H_{13}	117.611	117.952	116.761	116.417
C_3–C_2–H_{13}	122.918	122.410	118.837	117.984
C_2–C_3–C_4	118.244	117.619	117.198	115.447
C_2–C_3–C_7	120.625	120.240	120.898	122.153
C_4–C_3–C_7	121.131	121.918	121.904	122.395
C_3–C_4–C_5	120.411	121.041	119.120	119.838
C_3–C_4–H_{14}	118.604	117.183	118.676	117.270
C_5–C_4–H_{14}	120.985	121.764	122.204	122.885
C_4–C_5–C_6	119.358	119.329	118.723	119.245
C_4–C_5–H_{15}	121.142	121.244	120.993	120.852
C_6–C_5–H_{15}	119.499	119.422	120.284	119.902
N_1–C_6–C_5	118.753	118.465	123.392	122.729
N_1–C_6–H_{16}	116.977	116.880	116.133	116.425
C_5–C_6–H_{16}	124.270	124.653	120.475	120.846
C_3–C_7–P_8	110.155	108.404	112.061	114.634
C_3–C_7–O_9	108.391	111.600	110.377	112.781
C_3–C_7–H_{17}	107.820	109.599	108.128	109.356
P_8–C_7–O_9	114.165	108.373	111.212	105.237
P_8–C_7–H_{17}	103.947	108.066	104.608	102.404
O_9–C_7–H_{17}	112.160	110.701	110.263	111.974
C_7–P_8–O_{10}	103.201	102.077	94.263	92.993
C_7–P_8=O_{11}	111.886	107.203	106.569	103.229
C_7–P_8–O_{12}	100.871	101.206	112.090	107.520
O_{10}–P_8=O_{11}	115.694	108.643	110.709	115.880
O_{10}–P_8–O_{12}	103.780	109.317	104.405	114.955
O_{11}=P_8–O_{12}	119.267	125.654	124.607	117.776
C_7–O_9–H_{18}	109.320	102.238	102.473	96.666
P_8–O_{10}–H_{19}	112.207	107.386	101.784	–
P_8–O_{12}–H_{20}	114.755	–	–	–

pyridine bonds because this group is not directly attached to the ring. At the same time, fairly dramatic shortening of P_8–O_{12} and P_8–O_{10} bonds is observed due to the dissociation of protons. These observations are in perfect agreement with structural isomer of **MC5** reported earlier [7].

Deprotonation of the pyridine nitrogen influences the most dihedral angles in which the nitrogen atom is involved, i.e. N_1–C_2–C_3 and N_1–C_6–C_5 angles. It is worth stressing that the next two dissociations result in decreasing of C_7–O_9–H_{18} angle and bringing the hydroxyl proton closer to the phosphonic group.

3.2. Generalized atomic polar tensors

Table 2 presents the atomic charges of **MC5** dissolved in aqueous solution at different pH calculated by the B3PW91 method with the 6-31G** basis set. In these calculations population analysis based on atomic polar tensor [14]. This commonly used approach has the following advantages: (1) the atomic charges are invariant with respect to rotations and translations of the molecule; (2) partial atomic charges sum up to the total electric charges of the molecule; (3) it reflects the symmetry of the molecule;

Table 2
Generalized atomic polar tensors (GAPT) of **MC5** species

Atom	MC5(+1)	MC5(0)	MC5(−1)	MC5(−2)
N_1	−0.171	−0.154	−0.369	−0.254
C_2	0.093	0.191	0.116	0.015
C_3	0.047	0.084	0.103	0.386
C_4	0.117	0.071	−0.014	−0.170
C_5	−0.074	−0.030	−0.046	0.117
C_6	0.106	0.011	0.123	−0.081
C_7	0.164	−0.063	0.059	−0.359
P_8	1.982	1.908	1.844	1.930
O_9	−0.603	−0.616	−0.662	−0.727
O_{10}	−0.887	−0.887	−0.915	−1.149
O_{11}	−0.848	−0.951	−0.918	−1.034
O_{12}	−0.816	−0.911	−0.895	−0.934
H_{13}	0.172	0.160	0.051	0.005
H_{14}	0.139	0.115	0.066	0.043
H_{15}	0.106	0.067	−0.011	−0.061
H_{16}	0.126	0.090	−0.034	−0.083
H_{17}	−0.019	0.006	−0.081	−0.063
H_{18}	0.339	0.349	0.330	0.420
H_{19}	0.365	0.302	0.251	–
H_{20}	0.365	–	–	–
H_{21}	0.296	0.260	–	–

(4) it has a clear physical meaning; (5) is not dependent upon the choice of a particular basis set [14]. It should be stressed that Mulliken population analysis implemented in GAUSSIAN '98 program does not give correct results especially for species bearing some ionic character. This classical method of the electron distribution analysis yields atomic charges on separate atoms that are strongly influenced by the basis set used in calculations rather than distribution itself. It was one of the reason, why in this work, we decided to use more reliable tool, i.e. the GAPT atomic charges calculated by GAR2PED program.

The pyridine ring shows a negative partial charge on the nitrogen and positive on *ortho*- and *para*-carbon atoms [29]. Analogous charge distribution is seen for the cation and zwitterion of **MC5** (Table 2). However, deprotonation of the pyridine nitrogen (**MC5**(−1)) results in a slight negative charge on C_4 carbon (−0.014). Consecutive proton dissociation from the phosphonic group (**MC5**(−2)) creates negative charges on C_4 (−0.170) and C_6 (−0.081) carbons. Simultaneously, a negative charge on the pyridine nitrogen is getting larger. For all **MC5** forms significant charge changes on phosphorus atom are not observed. They vary from 1.844 (**MC5**(−1)) to 1.982 (**MC5**(+1)) (Table 2). More drastic changes in negative charge are calculate for oxygen atoms of the phosphonic group as a result of the deprotonations (first deprotonation: $\Delta Q_{GAPT}(O_{11}) = 0.103$ and $\Delta Q_{GAPT}(O_{12}) = 0.095$; second deprotonation: $\Delta Q_{GAPT}(O_{10}) = 0.234$ and $\Delta Q_{GAPT}(O_{11}) = 0.116$). It is worth noticing O_9 is less negatively charged than oxygen atoms from the phosphonic group, i.e. O_{10}, O_{11} and O_{12}. This is probably caused by a polarization effect of C–O bond in comparison to P–O bonds.

3.3. Aromaticity

The aromatic character of **MC5** is considered in terms of index HOMA divided into geometric and energetic contributions [15,16]. The energetic term (EN) may be interpreted as, so called, dearomatization that describes a decrease of aromaticity due to a decrease of the resonance energy. The geometric term (GEO) represents the part related to dearomatization caused by the changes of bond length alternation. The EN and GEO terms are not correlated with each other. The index of aromaticity is described by
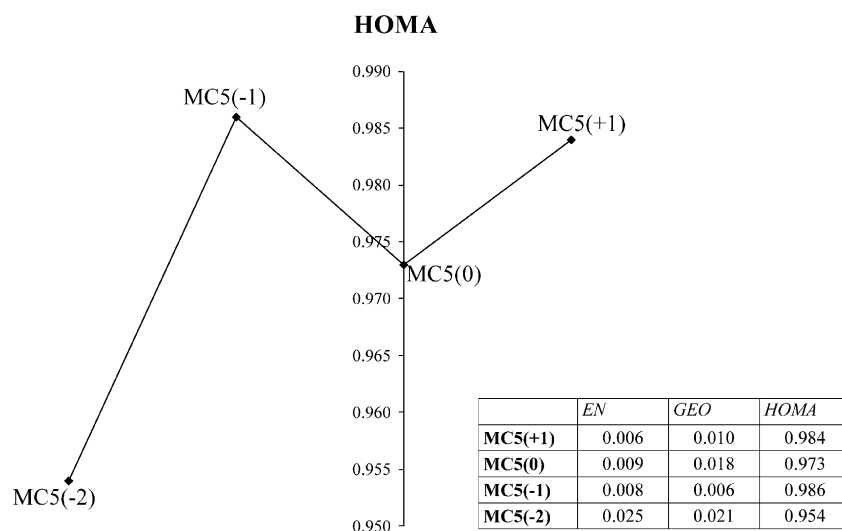
HOMA

Fig. 3. The aromaticity index HOMA for **MC5** species in aqueous solution.

	EN	GEO	HOMA
MC5(+1)	0.006	0.010	0.984
MC5(0)	0.009	0.018	0.973
MC5(-1)	0.008	0.006	0.986
MC5(-2)	0.025	0.021	0.954

the equation: HOMA = 1 − EN − GEO [15,16]. Successful applications of index HOMA to pyridine molecule and its derivatives confirm the usefulness of this method [15]. For example, for a neat pyridine HOMA = 0.998 (EN = − 0.009, GEO = 0.011) [15].

In this work we calculated aromaticity of four **MC5** species existing in aqueous solutions at different pH (Fig. 1). Obtained results are presented in Fig. 3 as a graph. Additionally, calculated values of EN and GEO terms are listed in the table and
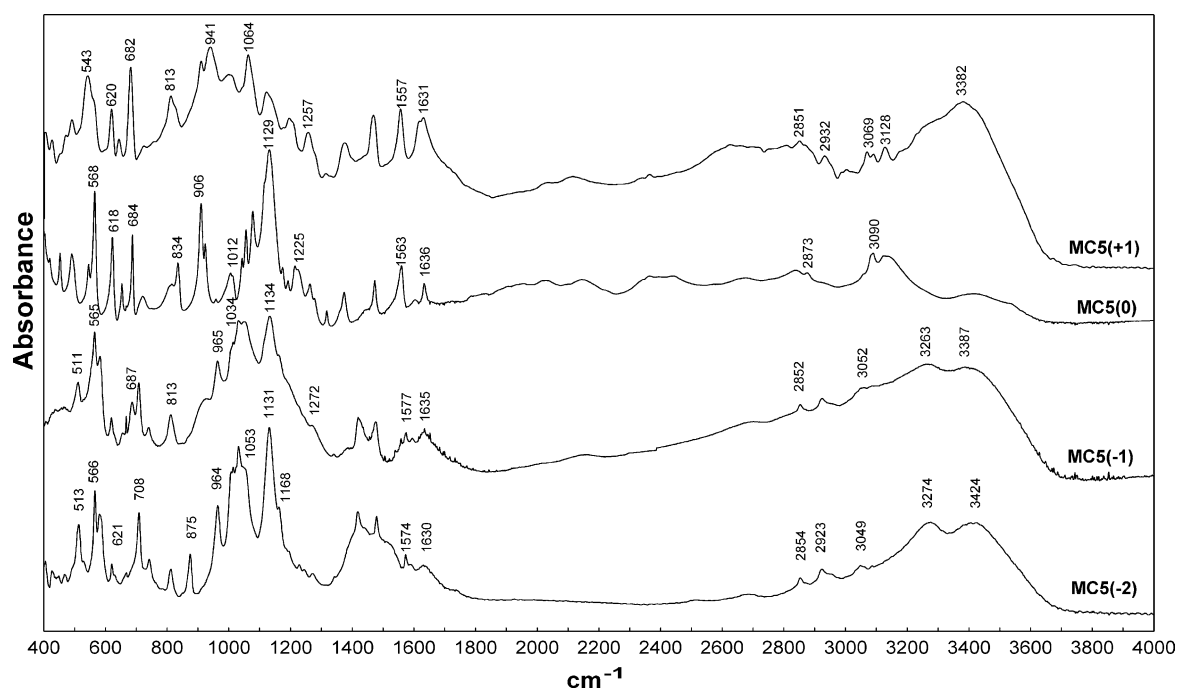
Fig. 4. FT-IR spectra of **MC5** in solid state precipitated from aqueous solution at the pH values: 8.0, **MC5(−2)**; 6.6, **MC5(−1)**; 3.5, **MC5(0)**; <1.0, **MC5(+1)**.

included in the figure. It is not surprising that all investigated ligands show high aromaticity with the index HOMA above 0.95. This value, as expected, is below of that obtained for a neat pyridine molecule. The highest and almost identical values (~ 0.985) are observed for the cation **MC5**(+1) and the monoanion **MC5**(−1). Somehow unexpectedly

the, deprotonation of the phosphonic group decreases the index HOMA. On the other hand, deprotonation of the pyridine nitrogen causes the increase in **MC5** aromaticity. **MC5**(−1) anion is characterized by the lowest EN and GEO terms that may be explained by a small decrease of resonance energy and a slight increase of bond length alternation.

Table 3
Experimental and calculated (B3PW91/6-31G**) frequencies for **MC5**(+1) in cm^{-1}

Experimental frequency	Calculated frequency	Assignment based on PED [%]
3069	3127	$\nu(C_6-H_{16})[83] + \nu(C_5-H_{15})[15]$
3007	3115	$\nu(C_4-H_{14})[53] + \nu(C_5-H_{15})[35] + \nu(C_6-H_{16})[11]$
2932	3107	$\nu(C_5-H_{15})[49] + \nu(C_4-H_{14})[45]$
2851	3097	$\nu(C_2-H_{13})[99]$
2867	2865	$\nu(C_7-H_{17})[99]$
1631	1615	$\nu(C_5-C_6)[21] + \nu(N_1-C_2)[17] + \nu(C_2-C_3)[15] + \nu(C_4-C_5)[12] + \delta(C_4-H_{14})[13] + \delta(C_2-H_{13})[12]$
1557	1591	$\nu(N_1-C_6)[23] + \nu(C_3-C_4)[19] + \delta(N_1-H_{21})[15]$
1469	1524	$\delta(N_1-H_{21})[27] + \nu(C_5-C_6)[11] + \nu(C_3-C_4)[10]$
1419	1441	$\delta(C_5-H_{15})[24] + \delta(C_6-H_{16})[21] + \nu(C_4-C_5)[18]$
1375	1349	$\nu(C_2-C_3)[17] + \nu(C_3-C_4)[11] + \nu(C_5-C_6)[11]$
1318	1340	$\delta(O_9-H_{18})[21] + \delta_1(C_7-H_{17})[10] + \nu(C_3-C_7)[10]$
	1312	$\delta(C_4-H_{14})[30] + \delta(C_2-H_{13})[21]$
1280	1262	$\delta(N_1-H_{21})[23] + \nu(N_1-C_2)[17] + \nu(P_8=O_{11})[11] + \delta(C_2-H_{13})[11] + \delta(C_6-H_{16})[11]$
1257	1245	$\nu(P_8=O_{11})[50] + \delta(C_7-H_{17})[12]$
1196	1221	$\delta(C_7-H_{17})[44] + \nu(P_8-O_{11})[17] + \delta(O_9-H_{18})[10]$
1122	1181	$\delta(C_7-H_{17})[46]$
	1163	$\delta(C_5-H_{15})[33] + \delta(C_6-H_{16})[26]$
1064	1152	$\delta(O_9-H_{18})[37] + \delta(C_7-H_{17})[16] + \nu(C_3-C_7)[14]$
1052	1114	$\nu(C_7-O_9)[57]$
1040	1075	$\nu(C_7-O_9)[57] + \delta(C_4-H_{14})[18] + \nu(N_1-C_2)[16] + \nu(C_4-C_5)[13]$
1007	1029	$\nu(N_1-C_6)[36] + \nu(C_5-C_6)[24]$
997	1000	$\delta(ring)[68] + \nu(C_3-C_4)[10]$
	992	$\gamma(C_4-H_{14})[49] + \gamma(C_5-H_{15})[32]$
941	981	$\delta(O_{10}-H_{19})[67] + \nu(P_8-O_{12})[11]$
910	969	$\delta(O_{12}-H_{20})[77]$
	944	$\gamma(C_6-H_{16})[37] + \gamma(C_2-H_{13})[19] + \gamma(N_1-H_{21})[13] + \gamma(C_5-H_{15})[13]$
828	913	$\gamma(C_2-H_{13})[46] + \gamma(C_6-H_{16})[10]$
813	886	$\nu(P_8-O_{11})[50] + \nu(P_8-O_{12})[30] + \nu(P_8-O_{10})[29]$
760	840	$\nu(P_8-O_{10})[27] + \nu(P_8-O_{12})[17] + \nu(C_7-P_8)[14] + \delta(O_{12}-H_{20})[14]$
	824	$\gamma(N_1-H_{21})[39] + \gamma(C_5-H_{15})[28] + \gamma(C_6-H_{16})[13] + \gamma(C_4-H_{14})[10]$
720	805	$\nu(C_3-C_7)[19] + \nu(P_8-O_{10})[13]$
683	769	$\tau(ring)[21] + \gamma(C_6-H_{16})[19] + \gamma(N_1-H_{21})[14] + \gamma(C_3-C_7)[13]$
682	703	$\nu(C_7-P_8)[22] + \delta(C_3-C_7)[12] + \delta(C_7-O_9)[12]$
643	654	$\tau(ring)[62] + \gamma(N_1-H_{21})[18] + \gamma(C_5-H_{15})[11]$
620	624	$\delta(ring)[39] + \delta(C_7-C_3)[22] + \tau(ring)[12]$
543	604	$\delta(ring)[73]$
492	484	$\delta(P_8-O_{12})[13] + \delta(C_3-C_7)[13] + \delta(P_8-O_{10})[11]$
467	477	$\gamma(C_3-C_7)[25] + \delta(C_3-C_7)[26] + \tau(ring)[14] + \delta(P_8-O_{10})[11]$
454	419	$\tau(ring)[30] + \gamma(C_3-C_7)[21] + \delta(P_8=O_{11})[10]$
427	410	$\delta(P_8-O_{12})[30] + \tau(P_8-O_{10})[16]$

3.4. Vibrational study

Experimental FT-IR spectra of solid state **MC5** precipitated from aqueous solutions at the pH values: 8.0, 6.6, 3.5 and below 1.0 are presented in Fig. 4. The calculated B3PW91/6-31G** vibrational frequencies and experimental data together with proposed assignment for all **MC5** species are listed in Tables 3–6.

The assignment together with PEDs of the normal modes is presented only for bands in the range of 3100–400 cm^{-1}. Since these above 3100 cm^{-1} are not important in determination of structure discussed in this work. As seen in Fig. 4 there are significant differences in the spectra but quantum-chemical calculations were based on isolated molecules thus, they did not take into consideration the strong

Table 4
Experimental and calculated (B3PW91/6-31G**) frequencies for **MC5**(0) in cm^{-1}

Experimental frequency	Calculated frequency	Assignment based on PED [%]
3127	3126	$\nu(C_6-H_{16})$[89]
3090	3125	$\nu(C_2-H_{13})$[98]
	3104	$\nu(C_5-H_{15})$[64] + $\nu(C_4-H_{14})$[28] + $\nu(C_6-H_{16})$[11]
3082	3083	$\nu(C_4-H_{14})$[71] + $\nu(C_5-H_{15})$[27]
2873	2922	$\nu(C_7-H_{17})$[99]
1636	1600	$\nu(C_5-C_6)$[31] + $\nu(C_2-C_3)$[16] + $\delta(C_6-H_{16})$[10]
1563	1582	$\delta(N_1-H_{21})$[19] + $\nu(C_3-C_4)$[18] + $\nu(N_1-C_6)$[15] + $\nu(N_1-C_2)$[14] + $\nu(C_4-C_5)$[14]
	1514	$\delta(N_1-H_{21})$[26] + $\delta(C_2-H_{13})$[19] + $\nu(C_2-C_3)$[13] + $\delta(C_4-H_{14})$[11] + $\nu(C_4-C_5)$[10]
1474	1435	$\delta(C_5-H_{15})$[23] + $\delta(C_6-H_{16})$[21] + $\nu(C_4-C_5)$[20]
1378	1399	$\delta(O_9-H_{18})$[77] + $\delta(C_7-H_{17})$[12]
1378	1359	$\nu(C_2-C_3)$[18] + $\nu(C_3-C_4)$[17] + $\nu(C_5-C_6)$[16] + $\nu(N_1-C_2)$[13] + $\nu(N_1-C_6)$[13]
1317	1301	$\delta(C_4-H_{14})$[16] + $\delta(C_2-H_{13})$[16] + $\delta(C_7-H_{17})$[12]
1284	1267	$\delta(C_7-H_{17})$[35]
1261	1253	$\delta(N_1-H_{21})$[31] + $\delta(C_2-H_{13})$[15] + $\delta(C_6-H_{16})$[14] + $\nu(N_1-C_2)$[14]
1225	1225	$\nu(P_8{=}O_{11})$[38] + $\nu(P_8O_{12})$[35]
1190	1182	$\nu(C_3-C_7)$[25] + $\delta(ring)$[12]
1129	1149	$\delta(C_6-H_{16})$[31] + $\delta(C_5-H_{15})$[30] + $\nu(C_5-C_6)$[11] + $\delta(C_4-H_{14})$[10]
1110	1093	$\nu(C_7-O_9)$[48]
1075	1055	$\delta(C_7-H_{17})$[36] + $\nu(C_7-O_9)$[16]
1057	1046	$\delta(C_7-H_{17})$[32]
1040	1028	$\nu(P_8{=}O_{11})$[21] + $\nu(P_8O_{12})$[20] + $\nu(N_1-C_6)$[12]
1012	1021	$\nu(C_6-H_{16})$[21] + $\nu(P_8{=}O_{11})$[15] + $\nu(P_8{=}O_{12})$[11]
1000	996	$\delta(ring)$[56] + $\nu(C_2-C_3)$[10]
	995	$\delta(O_{10}-H_{19})$[84]
958	977	$\gamma(C_4-H_{14})$[52] + $\gamma(C_5-H_{15})$[26]
921	904	$\gamma(C_6-H_{16})$[40] + $\gamma(C_5-H_{15})$[28] + $\gamma(C_4-H_{14})$[15]
906	828	$\gamma(C_2-H_{13})$[30] + $\gamma(N_1-H_{21})$[25] + $\tau(ring)$[12]
834	814	$\nu(C_3-C_7)$[19] + $\gamma(N_1-H_{21})$[11]
810	794	$\nu(P_8-O_{10})$[74]
810	776	$\gamma(C_2-H_{13})$[29] + $\gamma(C_6-H_{16})$[28] + $\gamma(C_5-H_{15})$[22]
721	748	$\tau(ring)$[26] + $\gamma(C_6-H_{16})$[19] + $\gamma(C_3-C_7)$[14] + $\gamma(N_1-H_{21})$[11]
684	695	$\tau(C_7-O_9)$[87]
684	672	$\nu(C_7-P_8)$[26] + $\tau(ring)$[23]
650	639	$\tau(ring)$[50] + $\gamma(N_1-H_{21})$[24] + $\gamma(C_5-H_{15})$[12]
618	621	$\delta(ring)$[38] + $\delta(C_3-C_7)$[16] + $\tau(ring)$[15]
568	601	$\delta(ring)$[72]
538	528	$\delta(P_8{=}O)$[51]
489	474	$\delta(C_7-O_9)$[24] + $\delta(P_8{=}O)$[12] + $\delta(C_3-C_7)$[10]
454	433	$\tau(ring)$[27] + $\delta(C_4-H_{14})$[27] + $\delta(P_8-O_{10})$[12]
416	408	$\delta(P_8{=}O)$[19] + $\delta(P_8-O_{10})$[17] + $\tau(ring)$[15]

intermolecular interactions that in some cause may be important the determination of molecular structure of **MC5** forms.

The spectra presented in the figure show several well documented features associated with the characteristic pyridine ring and phosphonic group vibrations. These modes are clearly assigned in Tables 3–6. The spectra of all **MC5** species show dramatic changes caused by the consecutive deprotonations. For example, the most characteristic

vibrations of pyridine ring are observed at 1631 and 1557 cm^{-1} for **MC5**$(+1)$, 1636 and 1563 cm^{-1} for **MC5**(0), 1633 and 1577 cm^{-1} for **MC5**(-1) and 1630 and 1574 cm^{-1} for **MC5**(-2). It is seen from Tables 3–6 that deprotonation influence strongly mode compositions. Thus, the 1557 and 1563 cm^{-1} vibrations consist of more than 10% of $\delta(N_1-H)$ vibration, while after deprotonation of the pyridine nitrogen this mode disappears as expected. Instead a new band frequency of 1577 cm^{-1} appears. Its

Table 5
Experimental and calculated (B3PW91/6-31G**) frequencies for **MC5**(-1) in cm^{-1}

Experimental frequency	Calculated frequency	Assignment based on PED [%]
3090	3094	$\nu(C_4-H_{14})$[96]
3052	3050	$\nu(C_5-H_{15})$[83]
3044	3045	$\nu(C_2-H_{13})$[98]
3007	3008	$\nu(C_6-H_{16})$[93]
2852	2855	$\nu(C_7-H_{17})$[99]
1635	1583	$\nu(C_4-C_5)$[25] + $\nu(N_1-C_2)$[17] + $\nu(C_3-C_4)$[11]
1577	1568	$\nu(C_5-C_6)$[22] + $\nu(C_3-C_4)$[21] + $\nu(N_1-C_6)$[14] + $\nu(C_2-C_3)$[13] + $\delta(C_6-H_{16})$[10]
1477	1457	$\delta(C_5-H_{15})$[22] + $\delta(C_2-H_{13})$[20] + $\nu(N_1-C_2)$[13] + $\nu(C_4-C_5)$[13] + $\delta(C_6-H_{16})$[21]
1419	1398	$\delta(C_6-H_{16})$[29] + $\nu(C_2-C_3)$[16] + $\nu(N_1-C_2)$[14]
1382	1364	$\delta(O_9-H_{18})$[65] + $\delta(C_7-H_{17})$[12]
	1309	$\delta(C_2-H_{13})$[36] + $\delta(C_6-H_{16})$[17] + $\delta(C_4-H_{14})$[15]
1300	1295	$\nu(N_1-C_2)$[22] + $\nu(N_1-C_6)$[18] + $\nu(C_5-C_6)$[10]
1272	1267	$\nu(P_8O_{11})$[39] + $\nu(P_8O_{12})$[36]
	1253	$\delta(C_7-H_{17})$[25] + $\delta(O_9-H_{18})$[12] + $\nu(C_2-C_3)$[11] + $\nu(C_3-C_4)$[10]
1188	1189	$\nu(C_3-C_7)$[27] + δ(ring)[11] + $\delta(C_2-H_{13})$[11]
1167	1171	$\delta(C_6-H_{16})$[22] + $\delta(C_5-H_{15})$[17] + $\nu(N_1-C_6)$[16] + $\nu(N_1-C_2)$[11]
1136	1131	$\delta(C_7-H_{17})$[73]
1061	1090	$\delta(C_4-H_{14})$[27] + $\delta(C_5-H_{15})$[22] + $\nu(C_7-O_9)$[18] + $\nu(C_4-C_5)$[14]
1054	1059	$\nu(P_8O_{11})$[33] + $\nu(P_8O_{12})$[23] + $\nu(C_7-O_9)$[13]
1034	1043	$\nu(C_7-O_9)$[48] + $\nu(P_8O_{11})$[10] + $\nu(P_8O_{12})$[10]
1022	1026	$\nu(C_5-C_6)$[32] + $\nu(N_1-C_6)$[23] + $\delta(C_5-H_{15})$[13]
1006	994	δ(ring)[68] + $\nu(C_3-C_4)$[11]
963	977	$\delta(O_{10}-H_{19})$[79] + $\nu(P_8O_{12})$[16]
	949	$\gamma(C_4-H_{14})$[43] + $\gamma(C_5-H_{15})$[24] + $\gamma(C_2-H_{13})$[17]
911	926	$\gamma(C_2-H_{13})$[52] + $\gamma(C_4-H_{14})$[16] + τ(ring)[10]
	898	$\gamma(C_6-H_{16})$[55] + $\gamma(C_5-H_{15})$[16] + $\gamma(C_4-H_{14})$[11]
812	823	$\nu(C_3-C_7)$[21] + δ(ring)[13] + $\nu(C_3-C_4)$[12] + $\delta(C_7-O_9)$[11]
739	789	τ(ring)[24] + $\gamma(C_6-H_{16})$[21] + $\gamma(C_5-H_{15})$[18] + $\gamma(C_3-C_7)$[11] + $\gamma(C_4-H_{14})$[11]
705	703	$\nu(C_7-P_8)$[17] + $\gamma(C_5-H_{15})$[14] + $\nu(P_8-O_{10})$[13] + τ(ring)[13] + $\delta(C_7-H_{17})$[11]
687	697	τ(ring)[61] + $\gamma(C_5-H_{15})$[14]
	676	$\nu(P_8-O_{10})$[37] + τ(ring)[14] + $\nu(C_7-P_8)$[10]
640	639	δ(ring)[44] + $\delta(C_7-O_9)$[21]
615	601	$\pi(C_7-O_9)$[46] + δ(ring)[26] + $\tau(P_8-O_{10})$[10]
587	596	δ(ring)[54] + $\tau(C_7-O_9)$[24]
563	516	$\delta(P_8{=}O_{12})$[33] + $\delta(P_8-O_{10})$[18]
511	488	$\delta(C_3-C_7)$[18] + $\delta(C_7-O_9)$[12] + τ(ring)[22]
436	423	$\delta(P_8{=}O_{12})$[35] + $\delta(P_8-O_{10})$[21] + $\tau(P_8-O_{10})$[13]
430	422	τ(ring)[33] + $\delta(C_3-C_7)$[21]

mode description differs from that above. It has to be noted that deprotonation of the pyridine nitrogen results in lowering of its calculated negative charge (-0.154 for **MC5**(0) and -0.369 for **MC5**(-1), see Table 2). This causes simultaneous change of charges on *ortho*- and *para*-carbons. Since these changes are not very pronounced thus only slight variation of characteristic vibrations frequencies of the pyridine is observed.

Phosphonic acids in ionic forms, i.e. compounds containing $R-PO_3H_2$, $R-PO_3H^-$ or $R-PO_3^{2-}$ groups, can be characterized based on their P=O stretching, ν(P=O), (P=O), stretching, ν(P=O), P–O(H) stretching, ν(P–O), and P–C stretching, ν(P–C), vibrations. However, in many cases, deformation vibrations may easily obscure bands that are associated with the discussed stretchings listed above. Additionally, in the presence of the strong hydrogen bonds that are often

Table 6
Experimental and calculated (B3PW91/6-31G**) frequencies for **MC5**(-2) in cm^{-1}

Experimental frequency	Calculated frequency	Assignment based on PED [%]
3274	3079	$\nu(C_4-H_{14})$[98]
3080	3021	$\nu(C_2-H_{13})$[98]
3049	3003	$\nu(C_5-H_{15})$[85] + $\nu(C_6-H_{16})$[12]
2923	2965	$\nu(C_6-H_{16})$[87] + $\nu(C_5-H_{15})$[12]
2853	2840	$\nu(C_7-H_{17})$[97]
1630	1561	$\nu(C_4-C_5)$[24] + $\nu(N_1-C_2)$[17] + $\nu(C_2-C_3)$[10]
1574	1539	$\nu(C_3-C_4)$[25] + $\nu(C_5-C_6)$[18] + $\nu(N_1-C_6)$[15] + $\nu(C_4-C_5)$[14] + $\delta(C_6-H_{16})$[11]
1479	1482	$\delta(O_9-H_{18})$[82] + $\nu(O_9-H_{18})$[10]
1419	1449	$\delta(C_5-H_{15})$[23] + $\delta(C_2-H_{13})$[21] + $\nu(C_4-C_5)$[15]
1343	1386	$\delta(C_6-H_{16})$[22] + $\nu(N_1-C_2)$[16] + $\nu(C_2-C_3)$[14]
	1314	$\delta(C_7-H_{17})$[47] + $\delta(C_2-H_{13})$[15]
	1307	$\nu(N_1-C_2)$[21] + $\nu(N_1-C_6)$[17] + $\nu(C_3-C_4)$[12] + $\nu(C_5-C_6)$[11]
1271	1268	$\delta(C_4-H_{14})$[19] + $\delta(C_2-H_{13})$[15] + $\delta(C_5-H_{15})$[12] + $\nu(C_2-C_3)$[10]
1245	1207	$\nu(C_3-C_7)$[28] + $\delta(C_7-H_{17})$[15] + $\delta(C_2-H_{13})$[11] + $\nu(C_2-C_3)$[10] + $\delta(ring)$[10]
1231	1162	$\delta(C_6-H_{16})$[25] + $\nu(N_1-C_6)$[15] + $\delta(C_5-H_{15})$[11] + $\nu(N_1-C_2)$[10]
1168	1152	$\nu(P_8-O_{12})$[44] + $\nu(P_8-O_{11})$[35]
1131	1079	$\nu(C_7-O_9)$[29] + $\delta(C_4-H_{14})$[17] + $\delta(C_5-H_{15})$[17]
1053	1060	$\nu(P_8-O_{10})$[29] + $\nu(P_8-O_{11})$[27] + $\nu(P_8-O_{12})$[17]
1031	1039	$\nu(C_7-O_9)$[38] + $\delta(C_4-H_{14})$[10]
1015	1015	$\nu(C_5-C_6)$[34] + $\nu(N_1-C_6)$[19] + $\delta(C_5-H_{15})$[10] + $\nu(C_4-C_5)$[10]
964	994	$\delta(ring)$[49] + $\delta(C_7-H_{17})$[11]
966	955	$\delta(C_7-H_{17})$[50]
921	929	$\gamma(C_4-H_{14})$[44] + $\tau(C_7-O_9)$[23] + $\gamma(C_5-H_{15})$[17]
919	916	$\tau(C_7-O_9)$[55] + $\gamma(C_4-H_{14})$[14] + $\gamma(C_2-H_{13})$[12]
	895	$\gamma(C_2-H_{13})$[58] + $\tau(ring)$[11] + $\gamma(C_5-H_{15})$[10]
875	866	$\nu(P_8-O_{10})$[53] + $\nu(P_8-O_{11})$[18] + $\nu(P_8-O_{12})$[16]
830	839	$\gamma(C_6-H_{16})$[37] + $\gamma(C_5-H_{15})$[27] + $\gamma(C_4-H_{14})$[20]
814	810	$\nu(C_3-C_7)$[22] + $\delta(ring)$[12] + $\delta(C_7-O_9)$[12] + $\nu(C_3-C_4)$[11]
742	758	$\gamma(C_6-H_{16})$[44] + $\tau(ring)$[27]
708	693	$\tau(ring)$[68] + $\gamma(C_5-H_{15})$[23]
660	638	$\delta(ring)$[54] + $\delta(C_7-O_9)$[24]
621	608	$\delta(C_7-O_9)$[29] + $\nu(C_7-P_8)$[13] + $\delta(C_3-C_7)$[11]
582	588	$\delta(ring)$[51] + $\nu(C_7-P_8)$[14] + $\delta(C_7-O_9)$[10]
566	540	$\delta(P_8-O)$[77]
513	503	$\delta(C_3-C_7)$[16] + $\delta(P_8-O_{12})$[14] + $\delta(C_7-O_9)$[12]
469	445	$\delta(P_8-O)$[50]
440	434	$\delta(P_8-O)$[74]
409	408	$\tau(ring)$[78]

encountered in these compounds, $\nu(P{=}O)$ and $\nu(P{-}O)$ can be broadened and down-shifted below expected regions.

The successive proton dissociation shifts the phosphonic group vibrations as the result of change of $P{-}O$ bond order. For example, **MC5**$(+1)$ is characterized by the $P{=}O$ and $P{-}O$ stretchings observed at 1257 and 941 cm^{-1}, respectively. The $P{=}O$ mode was observed earlier in the experimental spectra and calculations for **MC5** derivatives (carboxylopyridine phosphonic acids) in the range of 1260–1280 cm^{-1} [7]. The first deprotonation of phosphonic group is followed by delocalization of additional negative charge and thereby loss of a double bond $P_8{=}O_{11}$ nature. As a consequence two $(P_8{=\!=}O_{11})$ and $(P_8{=\!=}O_{12})$ stretchings are seen at 1225, 1040 and 1012 cm^{-1}. On the other hand, the deprotonation of the pyridine ring does not influence significantly $(P{=\!=}O)$ vibrations that appear in mode compositions observed at frequencies of 1272, 1054 and 1034 cm^{-1}. However, **MC5**(-2) dianion can be characterized by the equivalent $P{-}O$ bonds observed at 1168 and 1053 cm^{-1}. Variations in $P{=}O$, $(P{=\!=}O)$ or $P{-}O$ vibrational frequencies follow calculated charge changes on the P_8 and O_{11-13} atoms. The first deprotonation causes a significant lowering of the negative charge on O_{11} and O_{12} (vide supra). Additionally, the $P{=}O$ bond loses its double bond character. These cause a decrease in characteristic frequency (1257 for **MC5**$(+1)$ and 1225 for **MC5**(0)). Consecutive lowering of the negative charge on the O_{10} and O_{11} atoms is observed after the second phosphonic group deprotonation. This forces, lowering of the phosphonic group vibrational frequencies. At the same time, the deprotonation of the pyridine nitrogen does not influence significantly charges on the P_8 and O_{11-13} atoms (see Table 2) as well as vibrational frequency of the phosphonic group.

The $\nu(P{-}C)$ mode that should be seen in the spectrum at around 700 cm^{-1} appears at: 682 **MC5**$(+1)$, 684 **MC5**(0), 687 **MC5**(-1) and 621 cm^{-1} **MC5**(-2).

Quite good agreement between experimental and calculated data indicate that assumed forms of **MC5** (Fig. 1) used in calculation reflect well structures of **MC5** at individual pH range.

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