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A new experimental and theoretical investigation on the structures of aminoethyl phosphonic acid in aqueous medium based on the vibrational spectra and DFT calculations

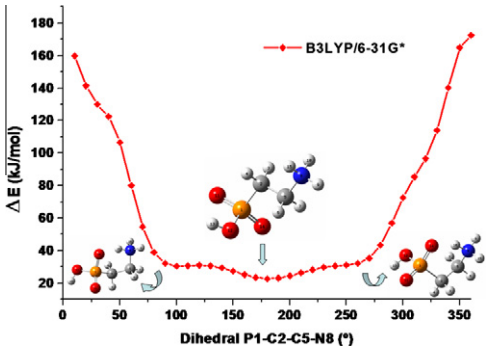
María L. Roldán [a], Ana E. Ledesma [b], Ana B. Raschi [c], María V. Castillo [c], Elida Romano [c], Silvia A. Brandán [c,*]

[a] Department of Scientific Research, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, NY 10028, USA
[b] Centro de Investigaciones y Transferencia de Santiago del Estero (CITSE-CONICET), Universidad Nacional de Santiago del Estero, RN 9, km 1125, 4206 Santiago del Estero, Argentina
[c] Cátedra de Química General, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 471, 4000 San Miguel de Tucumán, Tucumán, Argentina

HIGHLIGHTS

- The zwitterions of the aminoethylphosphonic acid were studied by DFT calculation.
- A new complete assignment of the observed spectral features is proposed.
- The solvent effects for the aminoethylphosphonic acid were analyzed using PCM model.
- The topological properties for the zwitterions in aqueous solution were studied.
- The charge-transfers for the zwitterions in aqueous solution were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A new study on the structural and vibrational properties of the aminoethylphosphonic acid was performed in aqueous solution phase by using the self-consistent reaction field (SCRF) method. We have studied and characterized it by infrared and Raman spectroscopies in solid and aqueous solution phases. The Density Functional Theory (DFT) method with Pople's basis set show that three stable zwitterions for the title molecule have been theoretically determined in aqueous solution and that probably they are present in it medium. Here, the solvent effects were studied by means of the self-consistent reaction field (SCRF) method with the polarized continuum model (PCM). The harmonic vibrational frequencies for the optimized geometries of the three zwitterions were calculated at the B3LYP/6-31G* level of the theory. A complete assignment of the IR and Raman spectra of the compound in aqueous solution was performed combining the DFT calculations with Pulay's Scaled Quantum Mechanics Force Field (SQMFF) methodology in order to fit the theoretical frequency values to the experimental ones. Moreover, Natural Bond Orbital (NBO) and topological properties calculations were performed to analyze the energies and geometrical parameters of its three zwitterions in aqueous medium as well as the magnitude of the intramolecular interactions. The bond orders, atomic charges, solvation energies, dipole moments, molecular electrostatic potentials and force constants parameters calculated for zwitterions in aqueous solution, may be used to gain chemical and vibrational insights into related compounds.

1. Introduction

The organophosphonate compounds are of great chemical and biochemical interest because they have a stable C—P bond highly

* Corresponding author. Tel.: +54 381 4247752; fax: +54 381 4248169.
E-mail address: sbrandan@fbqf.unt.edu.ar (S.A. Brandán).

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resistant to chemical hydrolysis, thermal decomposition, and photolysis and, also due to the presence of the phosphate group in their structures they are important macronutrients involved in essential biological processes, such as, the generation of metabolic energy, regulation of cellular signaling pathways, formation of membrane phospholipids, and the structure of nucleic acids [1–18]. On the other hand, the phosphate groups act also as a hydration sensor in lipid bilayers [2,19]. Additionally, the inert nature of C—P bond has effect on the environment when the phosphonates compound, used as a toxic herbicide is accumulating in numerous ecosystems [1,8]. In particular, the aminoethylphosphonic acid (AEP) from their discovery [3–5] is very studied from different points of view [5–16,18]. So, apart from the chemical interest of AEP, the structural and vibrational studies are of mainly biochemical importance because the α-aminophosphonates compounds have structure analogues to the α-amino acids and for this reason; they can act as inhibitors of enzymes involved in the metabolism of proteins and aminoacids [6]. Also, AEP has found application in nanotechnology as biofunctionalization agent of iron-oxide nanoparticles for cancer-specific targeting thanks to the formation of strong M—O—P bounds that, unlike other functionalization agents such as silanes, produces monolayers which are highly desirable for preserving the magnetic properties of the nanoparticles [16].

Nowadays, the crystal and molecular zwitterionic structure of AEP in solid phase is well known [9,11] but the structure and properties in aqueous solution, so far, still remain unsolved. The infrared spectrum of AEP in solid phase and the Raman spectra of solid samples obtained from evaporating aqueous solutions at pH 0.5, 4.5 and 13 of the compound were published by Ohno et al. [15]. They have recorded and assigned those spectra in the 1600–100 cm^{-1} region but the corresponding assignments of the stretching modes related to the NH_3, CH_2 and OH groups in the 4000–2000 cm^{-1} region were not reported. Additionally, in that work the structural and vibrational analysis of the different zwitterions of AEP in aqueous solution [15] neither the infrared nor Raman spectra of AEP in aqueous solution were published. To the best of our knowledge, there are no theoretical studies concerning geometries and vibrational spectra for the zwitterions of AEP in aqueous solution in the 4000–100 cm^{-1} region. To identify the zwitterionic species of AEP in all systems by means of vibrational spectroscopy, a complete characterization of those species as well in solid phase as in aqueous solution is very useful. In this context, the aim of this paper is to study, from structural and spectroscopic point of view, the theoretical structures of the more stable zwitterionic forms of AEP in aqueous solution in order to know the structural and vibrational properties of AEP in aqueous medium and, this way, to know the change around of the phosphates groups when AEP is dissolved in water. This study constitutes an important first step toward a detailed understanding of the biological properties of an organophosphonate compound in aqueous medium [20,21]. For that purpose, we optimized the theoretical structures of the zwitterions in aqueous solutions by using the DFT methods and taking into account the solvent effect by means of the SCRF method with the PCM model [22,23]. Afterwards, a complete assignment of all observed bands in the IR and Raman spectra in solid state and in aqueous solution were performed by using an approximate normal coordinate analysis combining DFT calculations with the Pulay's SQMFF methodology [24]. Moreover, to analyze the energies and geometrical parameters of the stable zwitterions of AEP in aqueous solution and the magnitude of the intramolecular interactions, Natural Bond Orbital (NBO) [25,26] and atoms and molecules theory AIM [27,28] calculations were performed. Furthermore, the possible charge-transfer and the intermolecular bond path were analyzed. In addition, two dimeric forms of AEP were also studied in accordance with the experimental structure determined by means of X-ray diffraction data [9]. Here, the theoretical properties of the studied species are shown and discussed. Good agreement between theoretical and experimental harmonic vibration frequencies was found.

2. Experimental methods

A pure MP Biomedicals commercial sample of aminoethylphosphonic acid (AEP) as a crystalline solid was used. The IR spectrum of the solid substance in KBr pellets was recorded in the wavenumbers range from 4000 to 400 cm^{-1}, while the spectrum of a saturated aqueous solution of the sample between AgCl windows was recorded from 4000 to 400 cm^{-1} and then the corresponding bands due to the solvent were subtracted. Both studies were performed with a FTIR GX1 Perkin Elmer spectrometer, equipped with a Globar source and DGTS detector. The Raman spectrum of the solid substance was measured in a glass capillary between 4000 and 100 cm^{-1} while the liquid sample with a saturated solution of AEP in water was conducted with a 10 mm path length glass cuvette. FTIR GX1 Perkin Elmer spectrometer, equipped with Raman accessory was used for all measurements. Raman has a Nd–YAG* laser (9395 cm^{-1}) and an InGaAs detector. All spectra were recorded with a resolution of 1 cm^{-1} and 200 scans.

3. Computational details

The potential energy curves associated with rotation around the C2—C5 bond, described by the P1—C2—C5—N8 dihedral angle for the β-form of AEP is observed in Fig. S1 (Supporting material) at the B3LYP/6-31G* level of theory [29,30]. The DFT calculations show the presence of three stable zwitterions with geometries C_1, named zw-1, zw-α and zw-β zwitterions, respectively. The zw-1 and zw-α zwitterions have *gauche* conformations with P1—C2—C5—N8 dihedral angles of −60 and 60°, respectively while the zw-β zwitterion has a *trans* conformation and a P1—C2—C5—N8 dihedral angle of 180° in accordance with the experimental value [9]. The structures and labeling of the atoms for all zwitterions of AEP in aqueous solution can be seen in Fig. 1. The theoretical structures of the three zwitterions in aqueous solution were computed by using the SCRF method and the solvent effects were simulated considering the cavity of series of spheres using the PCM model, as implemented in the Gaussian 09 program [31]. The solvation energy values were computed by using the solvation model (SMD) which accomplished by performing gas phase and taking the difference in the resulting energies [32]. The NBO calculations were performed by using the NBO 3.1 [26] program, as implemented in the Gaussian 09 package while the electronic charge density topological analysis was performed by using the AIM methodology, by the AIM200 program package [28]. The harmonic wavenumbers and the valence force field expressed in Cartesian coordinates for the zwitterions in aqueous solution were calculated at the same levels of approximation. In both cases, the resulting force fields were transformed to "natural" internal coordinates by using the MOLVIB program [33]. The natural internal coordinates for the zwitterionic species of AEP have been defined as those reported for molecules with similar groups [34–36] and are listed in Table S1 (Supporting material). Following the SQMFF procedure [24], the harmonic force field for the three AEP zwitterions were evaluated at B3LYP/6-31G* level. The potential energy distribution components (PEDs) higher than or equal to 10% are subsequently calculated with the resulting SQM. The molecular volumes for the zwitterions were calculated by using the MOLDRAW program [37]. The nature of all the vibration modes corresponding to the dimers 1 and 2 of AEP (*Figs.* S2 and S3, respectively) in aqueous solution at B3LYP/6-31G* level was carried out

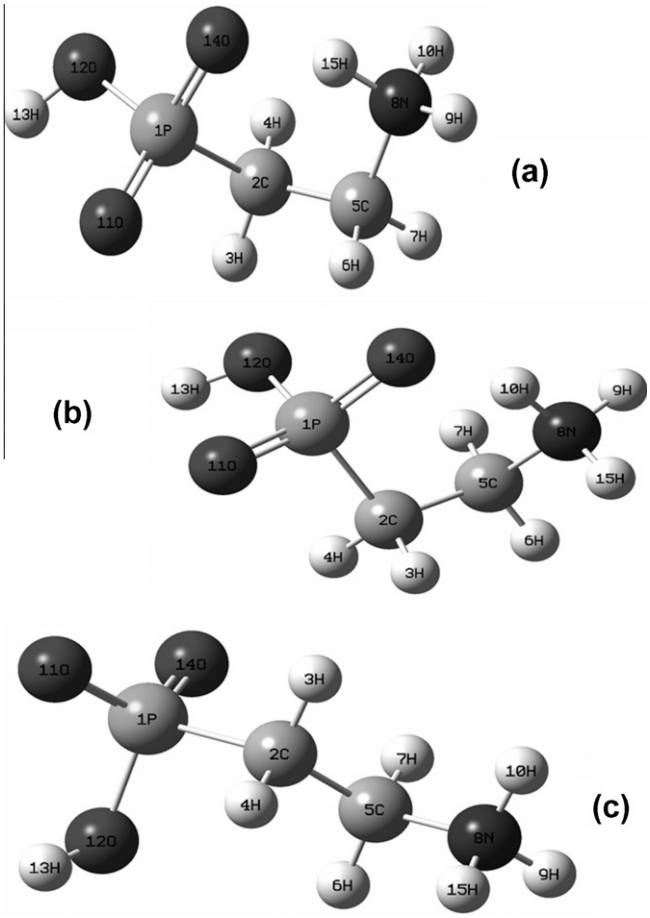

Fig. 1. Theoretical structures and atoms numbering for the stable zwitterions of the aminoethylphosphonic acid: (a) zwitterion-1 form, (b) zwitterion-α form, and (c) zwitterion-β form.

by means of the *GaussView* program [38]. The total energy for the dimeric species by using the 6-31G* basis set was corrected for Basis Set Superposition Error (BSSE) by the standard Boys–Bernardi counterpoise method [39].

4. Results and discussion

4.1. Geometry

A comparison of the total energies and the corresponding dipole moment values for all the stable zwitterionic structures of AEP in aqueous solution by using the B3LYP/6-31G* method is given in Table S2. The results show that the energies of the zw-1 and zw-α zwitterions are significantly lower than the corresponding to zw-β, and that the differences of potential energy between zw-1 and zw-α in reference to zw-β, are respectively, 34.88 and 31.73 kJ/mol, respectively. On the other hand, the high value of the dipole moment for zw-β could partially explain its stability in aqueous solution, as was observed in other molecules [40–44]. In this study, the zw-1, zw-α and zw-β zwitterions of AEP were analyzed in accordance with the experimental *trans* structure reported for the zw-β zwitterion [9]. Table 1 show a comparison of the calculated geometrical parameters for those zwitterions by using both methods with the corresponding experimental values obtained [9] by means of the root-mean-square deviation (RMSD) values. The results revels a good agreement with the experimental bond lengths for the zw-1 and zw-β zwitterions while the best

Table 1
Comparison of calculated geometrical parameters for the stable zwitterionic forms of the aminoethylphosphonic acid.

Parameter	PCM/B3LYP/6-31G*[a]			Exp[b]
	Zwitterion-1 (gauche)	Zwitterion-α (gauche)	Zwitterion-β (trans)	
Bond lengths (Å)				
P1—O11	1.506	1.504	1.516	1.500
P1—O12	1.653	1.657	1.661	1.560
P1—O14	1.534	1.532	1.516	1.510
C2—P1	1.851	1.849	1.839	1.800
C2—C5	1.531	1.530	1.518	1.510
C5—N8	1.509	1.508	1.508	1.480
O12—H13	0.971	0.971	0.973	0.830
N8—H9	1.022	1.022	1.026	0.900
N8—H10	1.023	1.080	1.026	0.900
RMSD	0.028	0.032	0.028	
Bond angles (°)				
C2—C5—N8	109.7	109.8	110.8	111.9
P1—C2—C5	111.8	113.1	112.8	112.0
C2—P1—O12	102.4	102.5	102.4	105.4
O11—P1—O14	120.3	120.9	120.2	115.6
O12—P1—O14	106.1	104.9	105.3	107.7
H9—N8—H10	107.6	111.0	107.8	111.0
P1—O12—H13	109.1	109.8	110.3	114.0
C5—N8—H9	112.2	112.2	111.2	108.0
C5—N8—H10	111.5	105.5	111.0	108.0
RMSD	1.13	1.06	1.00	
Dihedral angle (°)				
P1—C2—C5—N8	−59.3	57.9	−179.8	180.0

[a] This work.
[b] From Ref. [9].

Table 2
Molecular volume for the stable zwitterionic forms of the aminoethylphosphonic acid by the B3LYP/6-31G* method.

Zwitterions	Molar volume (Å^3)		$\Delta V = V_{AS} - V_G$ (Å3)[a]
	Gas	PCM//SMD	
Zwitterion-1 (*gauche*)	119.5	119.0	0.5
Zwitterion-α (*gauche*)	118.2	118.6	0.4
Zwitterion-β (*trans*)	126.7	119.7	−7.0

[a] See text.

results for the bond angles are observed for the zw-β zwitterion. It is important to note that the N—H and P—O distances values for all the zwitterions by using PCM model are always larger in solution, compared to the solid phase, due to the solvation. The C2—C5 distance of the zw-β zwitterion is practically not affected by hydration. For zw-β, the value of the P1—C2—C5—N8 dihedral angle in aqueous medium is of about 180°, as that observed in solid phase while for the zw-1 and zw-α zwitterions those dihedral angles have values of around 60°. Hence, the charge separation is larger in zw-β than for the other ones and, for this reason; the dipole moment value in zw-β is higher. The differences between the experimental and theoretical results could be attributed to the fact that in solid phase the crystal packing forces are important while in aqueous solution the hydrogen bonding forces prevail, as was also observed in others zwitterions in aqueous solution [34,35]. The calculated molecular volume for the zwitterions, by using the MOLDRAW program [37] for the B3LYP/6-31G* method is observed in Table 2. Zwitterions are species highly hydrated in aqueous solution and consequently; the corresponding volume undergoes an increase or a decrease in this medium, in relation to the values in the gas phase. The volume variations, expressed as a difference between the volume in gas phase and in aqueous solutions by using the PCM/SMD model, show a higher variation (−7.0 Å^3) for the zw-β zwitterion, in agreement with the high uncorrected solvation energy, as can be seen in Table S3.

4.2. Solvation energy

The uncorrected solvation energy (ΔG_u), calculated as relative energy (ΔE) and defined as the difference between the total energies in aqueous solutions and the values in gas phase for the three zwitterions using the 6-31G* basis set, are presented in Table S3. The uncorrected (ΔG_u) and corrected (ΔG_c) solvation energies together to the total non-electrostatic terms (ΔG_{ne}) due to the cavitation, dispersion and repulsion energies calculated by means the PCM model for all the studied species are given in Table 3. The ΔG_{ne} values in aqueous phase were obtained using the PCM/SMD model [32]. The ΔG_c values for the three zwitterions of AEP with the two basis sets used increase significantly from zw-1 to zw-β, as seen in Table 3. Thus, the higher ΔG_c value is obtained for the zw-β, due to its larger charge separation, higher value of dipole moment (Table S2) and higher variation of volume in solution (Table 2). These results clearly evidence a higher hydration in aqueous solution for zw-β.

4.3. Molecular electrostatic potential, atomic charges, bond orders

The molecular electrostatic potential values for those zwitterions in aqueous solution by using the B3LYP/6-31G* method are given in Table S4. The most negatives values of molecular electrostatic potential [45–51] were observed for the P atoms and the less negatives for the H atoms belonging to the NH_3^+ groups for all species in aqueous solution. Note that the energetically lower stability for the zw-β zwitterion is justified by the higher molecular electrostatic potential values of the phosphate group that make less stable the molecule. On the other hand, the analysis of the atomic charges derived from the ESPs (MK) [48] using the B3LYP/6-31G* method, for the three zwitterions are very different from the natural atomic charges, as can be seen in Table S5. We observed that the natural and MK charges values for the O and N atoms are most negative in all zwitterions, while the most positive values are observed for the P and H atoms. Moreover, the different charge values observed on those atoms suggest an unlike formation of H bonds and, thus a different hydration in solution for the three zwitterions is expected. The analysis of the bond orders expressed by Wiberg's indexes for the three AEP zwitterions (Table S6) show that the bond order values for the O and H atoms belonging to the phosphate and NH_3^+ groups, respectively in the zw-β have smaller values than the other ones due to a higher solvation. These results clearly indicate that the hydration in the phosphate and NH_3^+ groups are different in the three zwitterions and, obviously, the variations in the observed properties are due to the presence of hydrogen bonding that involves those groups.

4.4. NBO analysis

The second order perturbation energies $E^{(2)}$ (donor → acceptor) that comprise the most important delocalizations for the three zwitterions of AEP are given in Table S7. These results show principally the following: (i) for the three zwitterions, the principal contributions of the stabilization energies are calculated for the $\Delta ET_{LP\to\sigma*}$ charge transfers corresponding to the lone pairs of the O atoms belonging to the phosphate groups, (ii) the contributions of the stabilization energies for the $\Delta ET_{\sigma\to\sigma*}$ charge transfers are higher for the zw-α and zw-β zwitterions, (iii) the contributions of the stabilization energies for the $\Delta ET_{\sigma*\to\sigma*}$ charge transfers are higher for the zw-1 and zw-α zwitterions, and, (iv) the calculated total stabilization energy favors the zw-1 and zw-α zwitterions indicating its probable presence in aqueous solution.

Table 3
Calculated Solvation energies (ΔG) for the stable zwitterions of the aminoethylphosphonic acid.

PCM/B3LYP/6-31G*			
Species	ΔG (kJ/mol)		
	ΔG_u[#]	ΔG_{ne}	ΔG_c
Zwitterion-1 (*gauche*)	−101.77	24.70	−77.07
Zwitterion-α (*gauche*)	−104.40	24.53	−79.87
Zwitterion-β (*trans*)	−268.59	26.33	−242.26

$\Delta G_c = \Delta G_{\text{uncorrected}}$.
[#] $\Delta G_{\text{Total non-electrostatic}}$.

4.5. AIM analysis

The charge electron density, (ρ) and the Laplacian of the electron density, $^2\rho(r)$ for the calculated bond critical Point (BCP) and ring critical points (RCPs) from the topological property analysis for the zw-1 and zw-α zwitterions of AEP are shown in Table S8. The results for both forms in aqueous solution using both basis sets show one BCP and one RCP. The BCPs have the typical properties of the closed–shell interaction and therefore, the values of $\rho(r)$ are relatively low, the relationship $|\lambda_1|/\lambda_3$ are <1 and $^2\rho(r)$ are positive indicating that the interaction is dominated by the charge contraction away from the interatomic surface toward each nucleus. A very important result is that neither BCP nor RCP is observed for the zw-β form. In the zw-1 and zw-α zwitterions in aqueous solution the O14···H15 and the O14···H10 BCPs, respectively are observed which have the typical properties of the closed-shell interaction [47–49]. The calculations with the other method show for these species the same BCPs but with lower values of (ρ) and $^2\rho(r)$. This analysis clearly shows that the zw-1 and zw-α zwitterions are more stable in aqueous solution.

4.6. Vibrational analysis

The recorded infrared and Raman spectra for the compound in aqueous solution compared with the corresponding in solid phase can be seen respectively in Figs. 2 and 3. For this analysis and in according to the above results, the three zwitterions in aqueous solution were considered. The three AEP zwitterions have 39 normal vibration modes, all active in the infrared and Raman spectra. The experimental and calculated wavenumbers for the 39 expected normal vibration modes by using 6-31G* basis set together to the corresponding assignment are shown in Table 4. Fig. 4 shows the experimental infrared spectrum of AEP in aqueous solution compared with the corresponding theoretical calculated using B3LYP/

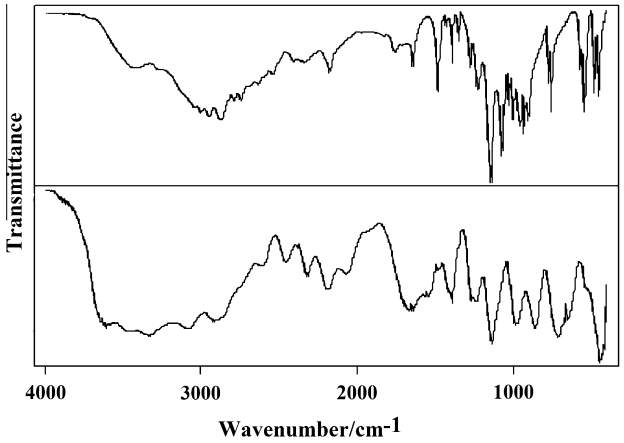

Fig. 2. Experimental Infrared spectra of the aminoethylphosphonic acid compound in the 4000–400 cm^{-1} region: Upper: in solid phase, bottom: in aqueous solution.

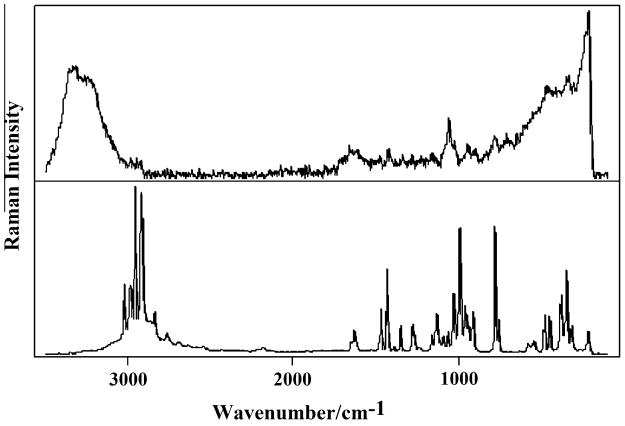

Fig. 3. Experimental Raman spectra of the aminoethylphosphonic acid compound in the 4000–100 cm^{-1} region: Upper: in aqueous solution, bottom: in solid phase.

6-31G* method for the three zwitterions. The vibrational assignment of the experimental bands to the normal AEP vibration modes is based on the comparison with the previous assignment [15], with related molecules [20,21,34,35,44,45] and with the results of the calculations performed here (Tables S9, S10 and S11). The theoretical infrared spectra for the dimers 1 and 2 of AEP using B3LYP functional and 6-31G* basis together to the corresponding experimental in aqueous solution can be seen in Fig. S4. Note that the presence of both dimers justifies the occurrence of bands in the 2500–2000 cm^{-1} region attributed to the H bonds, as is shown in Figs. S2 and S3. The SQM force fields for all the zwitterions of AEP can be obtained at request. The discussion of assignment of the most important groups is presented as follows.

4.6.1. Assignments

4.6.1.1. OH modes. As the 4000–2000 cm^{-1} region is characteristic of the O—H stretching [20,21,34–36,44,45], the broad band in the IR spectrum of the compound in solid phase at 3420 cm^{-1} and that appears as a strong band at 3610 cm^{-1} in solution aqueous, is assigned to the O—H stretching. For the dimer 1, the B3LYP/6-31G* calculations predicted two intense IR bands at 2553 and 2036 cm^{-1}, which are clearly assigned to the N—H···O—P and P—O···H—N bonds while for the dimer 2 the most intense IR bands at 3347, 3192, and 2061 cm^{-1} are assigned respectively to the OH···OP, PO—H and N—H···O—P bonds, as is shown in Fig. S4. Taking into account the assignment of L-tyrosine in aqueous solution [34], the IR band and shoulder respectively at 987 cm^{-1} is assigned to the OH in plane deformation modes for the three zwitterions and the corresponding out-of-plane deformation modes are associated to the Raman bands at 348, 240, and 217 cm^{-1}. For the HPO_4^{2-} ion in aqueous solution, the POH deformation was assigned to the band at 986 cm^{-1} while the corresponding out-of-plane deformation mode was assigned at 234 cm^{-1} [21]. These modes were not previously assigned by Ohno et al. [15].

4.6.1.2. NH_3 modes. For the three zwitterions of AEP, the theoretical assignments of the three expected N—H stretching modes in aqueous solution for the zw-1 and zw-α zwitterions are different than those for zw-β, as observed in Table 4. Thus, for the zw-1 and zw-α zwitterions, the IR bands at 3457 and 3330 cm^{-1} are assigned to the NH_3 antisymmetric and symmetric stretching modes, respectively, while for zw-β, those bands are assigned to the two antisymmetric modes of this group. For zw-1 and zw-α, the remaining antisymmetric modes are calculated at 2373 and 2377 cm^{-1}, respectively, which can be associated with the weak IR band at 2345 cm^{-1}. Note that the strong IR and Raman bands at 3082 and 3240 cm^{-1}, assigned to the symmetric stretching modes of zw-β, support its presence in aqueous solution. These NH_3 stretching modes were not previously assigned by Ohno et al. [15]. According to the calculations, the Raman bands at 1645, 1620, 1475, and 1427 cm^{-1} are clearly assigned to the antisymmetric and symmetric NH_3 deformation modes corresponding to the three zwitterions. In the previous assignment [15] the symmetric NH_3 deformation mode was not assigned in aqueous solution but it was associated with the band observed at 1558 cm^{-1} in the spectrum in solid phase. The two rocking modes for the three zwitterions are assigned to the shoulder and bands in the Raman spectrum observed at 1080, 1061, and 992 cm^{-1}, respectively. Newly, in the previous assignment [15] the rocking mode was not assigned in aqueous solution but instead it was associated with the bands observed at 1134 and 1089 cm^{-1} in the spectrum in solid phase. As predicted by calculation, the corresponding twisting modes for the zw-1 and zw-α zwitterions were assigned to the Raman band at 307 cm^{-1} and for zw-β in aqueous solution this mode is assigned at 237 cm^{-1}, as indicated in Table 4. This mode was not previously assigned by Ohno et al. [15].

4.6.1.3. CH_2 modes. Here, the theoretical assignments of the four expected C—H stretching modes in aqueous solution for zw-1 and zw-α are different than those for zw-β, as was also observed in the above groups. The Raman bands between 3034 and 2942 cm^{-1} are assigned to the two stretching modes expected for the three zwitterions, as observed in Table 4. The bands at 2921 and 2876 cm^{-1} are respectively assigned to the C—H symmetric stretching modes of both dimers. These modes were not previously assigned by Ohno et al. [15]. As predicted by the calculation, the Raman and IR bands in the spectra in aqueous solution at 1427 and 1415 cm^{-1} are easily assigned to the corresponding scissoring modes in agreement to compounds containing these groups [34–36,44,45]. The wagging and rocking modes were assigned by Ohno et al. [15], respectively, between the 1396 and 1312 cm^{-1} and 896 and 710 cm^{-1} regions. In this study, the wagging modes are associated with the IR bands in aqueous solution at 1395 and 1271 cm^{-1} while the expected rocking modes are assigned to the shoulder and band of the medium intensity at 1355 and 1238 cm^{-1}, respectively, as observed in Table 4. The twisting modes of these groups in the previous assignment were reported at 1342 and 1243 cm^{-1} [15]. In this work, our SQM calculations for the zw-1, zw-α and zw-β zwitterions predict these modes at 748, 743 and 689 cm^{-1}, respectively. Therefore, they were assigned to the Raman bands at 742 and 707 cm^{-1}, as indicated in Table 4.

4.6.1.4. PO_3 groups. It is important to note in Table 4, that in the previous assignment the tetrahedral PO_3 groups were studied with C_{3v} symmetry [15] while in this case they were studied with a local C_{2v} symmetry. Therefore, significant differences in the corresponding assignments are expected. Here, the two P=O antisymmetric and symmetric stretching modes are in accordance with the previous assignments [15], and taking into account the calculation results, both modes are assigned to bands appearing on the 1200–1000 cm^{-1} region. For this reason, the antisymmetric stretching modes for the three zwitterions are associated with the bands at 1222 and 1162 cm^{-1}, while, the bands at 1026 and 992 cm^{-1} are easily assigned to the symmetric stretching modes. The P—O stretching for the three zwitterions are clearly assigned, in accordance with calculations and previous assignment [15], to the Raman bands in the spectrum in aqueous solution at 774 and 742 cm^{-1}. The corresponding waging, rocking and twisting modes of the phosphate group for the three zwitterions were also assigned as observed in Table 4. These modes were not previously assigned by Ohno et al. [15]. Note that the bands related to the PO_2

Table 4
Observed and calculated wavenumbers (cm^{-1}), potential energy distribution for the zwitterions of the aminoethylphosphonic acid.

Experimental[b]					Experimental[a]				Zwitterion-1[a]		Zwitterion-α[a]		Zwitterion-β[a]	
Raman Solut pH0.5	Raman Solut pH4.5	Raman Solut pH9	Raman Solut pH13	Assignment	IR solid	Raman Solid	IR Solut	Raman Solut	SQM[c]	Asignment	SQMc	Asignment	SQM[c]	Asignment
					3420m		3610s		3594	νO12—H13	3587	ν(O12—H13)	3567	ν(O12—H13)
							3457s		3387	ν_aNH_3	3386	ν_aNH_3	3365	ν_aNH_3
							3330s	3331vs,br	3317	ν_sNH_3	3316	ν_sNH_3	3351	ν_aNH_3
					3286sh		3082s	3240vs,br					3271	ν_sNH_3
					3044s	3021m		3034w	3031	ν_aCH_2(C5)	3033	ν_aCH_2(C5)	3062	ν_aCH_2(C5)
					3004s	2988m		2983w	2996	ν_aCH_2(C2)	2992	ν_aCH_2(C2)	3004	ν_sCH_2(C5)
						2979m		2961w	2979	ν_sCH_2(C5)	2979	ν_sCH_2(C5)	2980	ν_aCH_2(C2)
					2956s	2955vs	2949sh	2942w	2940	ν_sCH_2(C2)	2939	ν_sCH_2(C2)	2935	ν_sCH_2(C2)
					2926sh	2916s	2919s	2921w						dim
					2887s	2838w	2888sh	2876w						
					2345w	2328vw	2317w		2373	ν_aNH_3	2377	ν_aNH_3		
			1650b,w	δHOH	1643w	1648w	1649s,br	1645w	1603	δa NH_3	1601	δa NH_3	1557	δa NH_3
1628b,w	1629b,w	1630b,w	1600b,w	δa NH_3		1630w	1565m	1620w	1576	δa NH_3	1579	δa NH_3	1548	δa NH_3
			1479w	δCH_2	1483m	1476sh	1482w	1475w	1476	δs NH_3	1477	δs NH_3		
1472w	1470w	1473w	1467w	δCH_2	1467w	1469m			1448	δ CH_2(C5)	1447	δCH_2(C5)	1457	δCH_2(C5)
1424w	1425w	1430w		δCH_2	1432w	1432s		1427w	1425	δCH_2(C2)	1420	δCH_2(C2)	1436	δs NH_3
1412sh,vw	1414sh,w	1420sh,w	1418m	δCH_2			1415m						1419	δCH_2(C2)
1396vw	1388vw	1384vw	1363vw	wagCH_2,δCH_2	1390w	1390w	1395m	1382w	1378	wagCH_2(C5)	1381	wagCH_2(C5)	1393	wagCH_2(C5)
1342w	1339w	1338w		τCH_2	1350w	1351w	1355sh	1342w	1329	ρCH_2(C5)	1330	ρCH_2(C5)	1351	ρCH_2(C5)
			1312w	wagCH_2										
1272w	1271w	1270w	1279w	POH	1277w	1278w1261w	1271m	1275w	1251	wagCH_2(C2)	1259	wagCH_2(C2)	1278	wagCH_2(C2)
1243vw	1242b,vw	1248sh,vw	1234b,vw	τCH_2		1239vw1230vw	1238m		1234	ρCH_2(C2)	1227	ρCH_2(C2)	1246	ρCH_2(C2)
					1227m	1219vw		1222w			1200	$\nu_a(PO_2)$		
1175b,m				$\nu_a(PO_3)$	1156sh	1161w		1162w	1188	$\nu_a(PO_2)$			1175	$\nu_a(PO_2)$
	1153b,vw	1148b,vw		$\nu_a(PO_3)$	1143vs	1132m	1138 s	1140w						
1070sh,w		1078sh,w	1068sh,m	ν(C—N)	1074s	1092w		1080sh	1068	ρ NH_3	1063	ρNH_3	1094	ρNH_3
1058m	1055vs	1058vw	1051m	ν(C—C)	1058w	1064w	1067sh	1061m	1040	ρ NH_3	1043	ρNH_3		
1028m	1025s	1026m		$\nu a(POH)_2$	1031w	1029m		1026w					1035	$\nu_s(PO_2)$
					1002s			992w	1000	$\nu_s(PO_2)$	1004	$\nu_s(PO_2)$	1010	ρNH_3
		975vs	975vvs	$\nu_s(PO_3)$		993s	987m,br	970w	975	POH	974	POH	979	POH
954s	952m			$\nu s(POH)_2$	956s	959m	987m,br						975	ν(C2—C5)
	934sh,w	938sh,m		$\nu_s(PO_3)$	933s	938w	940sh	947w	964	ν(C2—C5)	961	ν(C2—C5)		
896sh,w	907m	905vw		ν(C—C), ρCH_2	905s	912m		900w	864	ν(C5—N8)	864	ν(C5—N8)	892	ν(C5—N8)
					852sh	854vw	864shm,br		840	τCH_2(C5)	847	τCH_2(C5)		
						832vw		786w					838	τCH_2(C5)
	802sh,vw	805w	805sh,vw	ρCH_2										
782s	779s	780s	781s	ν(C—P),$\nu_s(PO_3)$	778m	780s	754sh,br	774w	789	ν(P1—O12)	778	ν(P1—O12)		
745vw	744sh,vw	750sh,vw	750b,vw	ρCH_2	757s	758w		742vw	748	τCH_2(C2)	743	τCH_2(C2)	759	ν(P1—O12)
710m	710m	711m	710w	ν(C—P),ρCH_2			713m,br						714	ν(C2—P1)
					695sh	683vw		707w					689	τCH_2(C2)
					661vw	664vw	660m	651w	663	ν(C2—P1)	657	ν(C2—P1)		
		557w	560bw	δsPO_3	572w	573vw		553sh						
	539w			τPO, δaPO_3	549s	553vw								
528w				δsPO_3		542w	536w,br	521sh	515	wagPO_2	520	δC5C2P1		
	470m	490m	492m	τPO, δaPO_3	484s	480m	479sh	474m					506	δPO_2
455m			455sh,w	δaPO_3	455s	463vw		448m	451	δPO_2				
440sh,m		449w		δaPO_3	448s	448m	443vs,br				437	wag PO_2		
					433sh	432vw							432	wagPO_2
					419vw	423vw	420sh	420m	419	δν8C5C2	424	δPO_2		
					411sh			395m	392	ρPO_2	402	δν8C5C2		
						380m		370m					375	τPO_2
334m	344m	349s	347m	ρPO_3		348m		332m			328	τOH	324	ρPO_2

Table 4 (*continued*)

Experimental[b]				Experimental[a]			Zwitterion-1[a]		Zwitterion-α[a]		Zwitterion-β[a]	
Raman Solut pH0.5	Raman Solut pH4.5	Raman Solut pH9	Raman Solut pH13	Assignment	IR solid	Raman Solid	IR Solut	Raman Solut	SQM[c]	Asignment	SQMc	Asignment	SQM[c]	Asignment
						317w		307m	319	τNH$_3$	312	τNH$_3$	304	δν8C5C2
						297sh		281sh	296	τPO$_2$			294	δC2P1O12
						288vw		278sh	286	δC5C2P1	285	δC2P1O12		
						240vw		237m	244	τOH	245	ρPO$_2$	254	τNH$_3$
						227sh		224s			221	τPO$_2$		
						217w	204	215vs	204	δC2P1O12			187	τOH
						160vw	159	151vw	159	τC2—C5	161	τC2—C5	148	δC5C2P1
						138vw		133vw					88	τC2—C5
						106vw		108vw					84	τw(PO$_2$)
									64	τw(PO$_2$)	68	τw(PO$_2$)		

ν, stretching; δ, scissoring; wag, wagging or out-of plane deformation; ρ, rocking; τ, torsion, twist, twisting; a, antisymmetric; s, symmetric.
[a] This work.
[b] From Ref [15].
[c] From scaled quantum mechanics force field PCM/B3LYP/6-31G*.

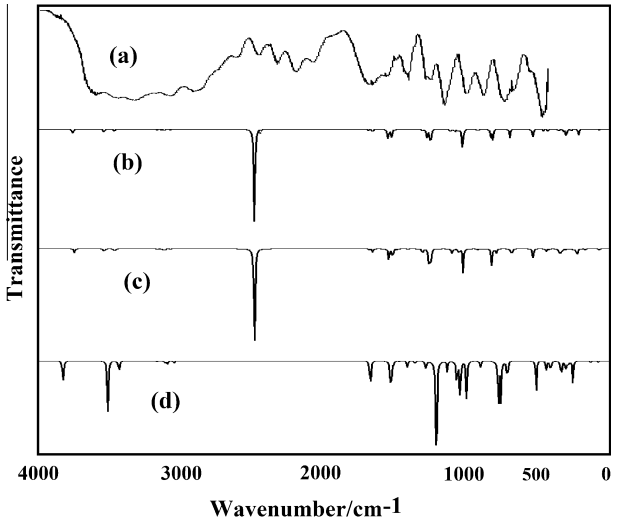

Fig. 4. (a) Experimental infrared spectrum of the aminoethylphosphonic acid compound in aqueous solution compared with the corresponding theoretical calculated using B3LYP functional and 6-31G* basis set for, (b) zwitterion-1, (c) zwitterion-α, and (d) zwitterion-β.

Table 5
Scaled force constants for the stable zwitterionic forms of aminoethylphosphonic acid.

Force constant	PCM/B3LYP/6-31G*[a]		
	Zwitterion-1	Zwitterion-α	Zwitterion-β
f(νO—H)	7.23	7.20	7.12
f(νN—H)	5.14	5.14	6.16
f(νC—H)	4.91	4.91	4.90
f(νP=O)	7.51	7.59	7.61
f(νP—O)	4.09	4.02	3.81
f(νC—N)	4.09	4.10	3.87
f(νC—P)	3.00	3.03	2.87
f(νC—C)	4.36	4.36	4.26
f(δH—C—H)	0.84	0.84	0.73
f(δH—N—H)	0.60	0.60	0.55
f(δP—O—H)	0.49	0.48	0.49

ν, stretching; δ, angle deformation.
Units in mdyn Å^{-1} for stretching and mdyn Å rad^{-2} for angle deformations.
[a] This work.

group change in aqueous solution in relation to the solid phase as consequence of the hydration due to the H bonds.

4.6.1.5. Skeletal modes. In the three zwitterions of AEP, the description of the skeletal stretching modes appears strongly mixed among them as can be seen in Tables 4, *S9*, S10 and S11. The C—N, C—C and C—P stretching modes are predicted by the calculations in different regions for the three zwitterions of AEP. Hence, the Raman band at 987 cm^{-1} and the shoulder at 964 cm^{-1} are mainly associated with C—C stretching modes while the band in the Raman spectrum in the solid phase at 912 cm^{-1}, is associated with the C—N stretching modes of the three zwitterions. The C—P stretching modes are related to the bands at 713 and 660 cm^{-1}. Finally, the observed modes in the lower wavenumber region (330–100 cm^{-1}) for the three zwitterions of AEP were not characterized by Ohno et al. [15]. In this work, those modes are identified and assigned, as observed in Table 4.

4.7. Force field

The force constants expressed in terms of simple valence internal coordinates were calculated from the corresponding

scaled force fields by using the MOLVIB program [33]. A comparison of the principal force constants for the three zwitterions of AEP calculated in aqueous solution is given in Table 5. Note that the values for zw-1 and zw-α are practically similar between them while slightly change for zw-β. In general, the $f(O—H)$, $f(\nu C—H)$ and $f(\nu N—H)$ values are in agreement with those reported for molecules with similar groups [34–36,44,45]. Here, the $f(O—H)$ force constants have values between 7.12 and 7.49 mdyn Å^{-1}, as the reported for chloro-quinolin-8-yloxy acetic acid compounds [44] and, greater values compared with the two zwitterions most stable of tyrosine in aqueous solution [34]. Obviously, the observed variations between both compounds are justified by the different involved groups, which are the P—OH group in AEP and the C—OH group in tyrosine. Previously [15], the force constants for the NH_3^+—CH_2C and CCH_2PO_3—H^- moieties of AEP were transferred from those for glycyltaurine [52] and aminomethylphosphonic acid [53], respectively. Thus, the C—N, C—C and C—P force constants values were assumed as those for taurine [54], with a value for the C—P stretching force constant of 3.6 mdyn Å^{-1}, in slightly agreement with the values reported here for AEP. Finally, the different force constants of AEP in aqueous solution are attributed to the unlike hydration of the involved groups in each zwitterion. The lower values of the $f(\nu O—H)$ and $f(\nu P—O)$ force constants for the zw-β zwitterion are in accordance with the H bonds formed due to its higher hydration.

5. Conclusions

We have characterized the substance by infrared and Raman spectroscopic techniques in aqueous solution. The theoretical molecular structures of the three zwitterions and the two dimeric forms derived from the aminoethylphosphonic acid were determined in aqueous solution by using the B3LYP/6-31G* method employing the PCM model. The stability of the three zwitterions was justified by means of the bond orders, atomic charges, solvation energies, dipole moments, molecular electrostatic potentials, intramolecular deslocalization energies and AIM analysis. The calculated harmonic vibrational frequencies for the aminoethylphosphonic acid are consistent with the observed infrared and Raman spectra in aqueous solution. The presence of bands attributed to the zwitterions zw-1, zw-α and zw-β and the two dimeric forms of the aminoethylphosphonic acid was detected in the IR and Raman spectra in aqueous solution phase and a complete assignment of the vibrational modes was accomplished. The previously reported assignments [15] were confirmed, corrected and completed in accordance with the present theoretical results. The SQM force fields for all the zwitterions of the aminoethylphosphonic acid were obtained after adjusting the theoretical force constants to minimize the mean deviation between observed and calculated frequencies. Differences in the studied properties for the three zwitterions were found, especially for the zw-β zwitterion, which are justified by the presence of the hydrogen bonding between phosphate and amino groups which appears to have influence on the solvation energies. A higher solvation energy calculated for the zw-β zwitterion revels it presence in aqueous solution and suggest a higher hydration of this zwitterion. The PCM model used in this study highlights the relevance of the solvent effects. The variations observed on the solvation energies are principally related to the hydrogen bonding and the donor–acceptor interactions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.02.032.

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