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STUDY OF VIBRATIONAL SPECTRA AND THEIR ASSIGNMENTS
FOR PHENYLPHOSPHONIC AND PHENYLTHIOPHOSPHONIC ACID
AND COMPARISON TO EXPERIMENTS

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The structures and conformational stabilities of phenylphosphonic and phenylthiophosphonic acids are investigated using calculations mostly at the DFT/6-311G** level and *ab initio* ones at the MP2/6-311G** level (no frequency calculations in the latter case), because we know from our previous results that the addition of diffuse functions to a valence triple zeta basis with polarization functions might lead to an unbalanced basis set. Further, the experience tells that for large energy differences between conformers, DFT works very well. From the calculations the molecules are predicted to exist in a conformational equilibrium consisting of two non (near)-planar conformers that are identical by symmetry. Interestingly, in the internal rotation potential functions the planar conformer appears to be a stable minimum (also optimization converges to planar), however the vibrational frequencies were computed and the planar conformer exhibited an imaginary one, indicating that it is a maximum with respect to one of the internal coordinates. Only optimization without any restrictions and starting from a non (near)-planar structure converged to a real minimum with a non (near)-planar geometry. In the minimum structure, vibrational infrared and Raman spectra are calculated and those for phenylphosphonic acid are compared to experimental ones, showing satisfactory agreement. The rather low intensity of the OH bands in the experimental infrared spectrum (as compared to normal organic acids) indicates rather weak hydrogen bonding with at most dimers present. Normal coordinate calculations are carried out and potential energy distributions are calculated for the molecules in the non (near)-planar conformations providing a complete assignment of the vibrational modes to atomic motions in the molecules. From the rather low rotational barriers we conclude, in agreement with the results from the literature (for other P=O compounds) based on localized orbitals, that conjugation effects are absent — or at least negligible — as compared to electrostatic and steric ones.

Keywords: DFT and MP2 calculations, normal coordinate analyses, vibrational spectra and assignments, phenylphosphonic acid, phenylthiophosphonic acid.

INTRODUCTION

In the past few years, the conformational structures of many conjugated vinyl compounds with the general formula $R_2C=CRXO$, where X could be fluorine or chlorine and R could be hydrogen or a methyl group, were reported [1—12]. The planar *cis*- and *trans*-conformers in these molecules are in general stabilized by conjugation effects rather than the non (near)-planar *gauche* ones, which leads to a much higher rotational barrier than in the corresponding saturated molecules. For 2-methyl-2-butenoyl fluoride and chloride the *trans*-form was found to be lower in energy than *cis*, while for 3-methyl-2-butenoyl fluoride and chloride the *cis*-conformers were found to be more stable than the *trans*-ones [12, 13]. Some years ago we performed a study of the conformational stability of vinyl sulfonyl chloride, $H_2C=CHSO_2Cl$, and fluoride [14] because of their chemical importance and structural interest [15]. The molecules were predicted to exist predominantly in the non (near)-planar *gauche* conformations with the

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vinyl C=C group being nearly eclipsed to one of the sulfonyl S=O groups again as a result of significant conjugation between the C=C bond and one of the S=O bonds [14].

To extend our study of conjugated vinyl molecules to the case of an aromatic phenyl substituent at the phosphorus atom, in the present work, we investigate the conformational behavior and structural stability of phenylphosphonic acid, $\text{H}_5\text{C}_6\text{—P(OH)}_2\text{O}$ and phenylthiophosphonic acid, $\text{H}_5\text{C}_6\text{—P(OH)}_2\text{S}$. We carried out DFT and *ab initio* MP2 optimizations [16] of the energies for the stable conformers of the molecules. The data indicate that here the planar form is a saddle point, while a non (near)-planar structure is the only stable conformer in each case (due to the symmetry of the phenyl ring). From our results we can conclude that conjugation effects are almost absent in the compounds, and their stabilities are mainly determined by electrostatic and steric effects because of the bulky phenyl groups. Additionally, vibrational frequencies were calculated at the DFT level and a complete assignment was made for all the normal modes by employing normal coordinate calculations following [17]. We also used the vibrational data to plot the vibrational IR (infrared) and Raman spectra of the molecules. The results for phenylphosphonic and phenylthiophosphonic acids are presented in this work, and in the case of phosphonic acid, they are compared to the experimental spectra. Thus, for one of our systems we can make comparisons to experiment and give assignments of the observed modes, while for the second one, phenylthiophosphonic acid, we present a theoretical prediction of the vibrational spectra and the assignment of the spectral lines. The Raman intensities were calculated as given in the literature [18, 19]. Our interest in organophosphorus compounds actually arose because of the tremendous importance of such compounds in chemistry [20—25]. Importantly, these phosphorus compounds have become very interesting also for the chemical industry as, e.g., starting materials for drug synthesis, polymer additives, flame retardants, and metal extractants [26]. For our calculations we used the valence triple zeta basis set with polarization functions on all atoms, i.e. 6-311G**. Our previous calculations [27, 28] have suggested that this basis set is superior to the larger 6-311+G** or 6-311++G** basis sets that include diffuse functions and seem to be not very well balanced, leading to linear dependencies. Thus, using such basis sets would be no more reliable than the throw of a dice. Also calculations with the other, especially smaller, basis sets or those of comparable quality could hardly yield information about the quality of results. However, it is already a good indication for the correctness of our results that MP2 and DFT with the same basis set do not lead to major differences in the results.

Due to the importance of the compounds in the chemical industry and to the fact that detailed experimental structure determinations are not available in the literature, our calculations are of considerable importance. Reliable calculated spectra can be used as a tool to detect residual reactants in reaction mixtures by inspecting their spectra, which is especially important in drug synthesis. Further, detailed assignments of vibrational lines based on reliable PED calculations would help to find out which details of a structure are attacked in a chemical reaction by the observation of changes in the vibrational spectra after a reaction, again very important in drug synthesis.

DFT AND *AB INITIO* CALCULATIONS

The Gaussian98 program [16] running on an IBM RS/6000 43P model 260 workstation was used to carry out the LCAO—MO—SCF calculations at DFT and MP2/6-311G** levels. The atoms in the phenyl ring are numbered in the same way as we did previously in phenyl cyanamide [29]; those in the substituent as $\text{P}_7\text{X}_{13}(\text{O}_{14}\text{H}_{16})(\text{O}_{15}\text{H}_{17})$, X=O or S. The molecules were optimized by minimizing the energy with respect to all the geometrical parameters. This optimization (both with DFT and MP2) directly converged to a planar form as extremum. However, a calculation of the vibrational frequencies on this structure showed an imaginary one, indicating that the optimization had converged to a maximum along one of the internal coordinates. By relaxing all symmetry constraints and starting the optimization away from the planar geometry with a non (near)-planar one, a true minimum was obtained for which all frequencies turned out to be real and positive. The perpendicular and planar structures are maxima, the latter one being with a very low barrier of only 0.60 kcal/mol in phosphonic acid and 0.13 kcal/mol in thiophosphonic acid. Some calculated structural parameters, rotational barriers, and dipole moments of the two molecules are listed in Table 1.

Table 1

Calculated structural data, barriers for the rotation between the two non-planar minima through the planar maximum, and dipole moments for non-planar phenylphosphonic acid (PO) and phenylthiophosphonic acid (PS), obtained with the DFT/B3LYP method and a 6-311G** basis set

Parametr	PO (X = O)	Experiment [30] ^a	PS (X = S)
Bond lengths (Å)			
P ₇ =X ₁₃	1.480	1.455 (P=O)	1.945
C ₁ —P ₇	1.800	1.817 (C—P)	1.808
P ₇ —O ₁₄		1.631	1.634
P ₇ —O ₁₅		1.614	1.622
Bond angles (deg.)			
P ₇ C ₁ C ₂	118.16	118.2 (PCC)	120.12
X ₁₃ P ₇ C ₁	115.26	119.5 (O=PC)	117.74
O ₁₄ P ₇ C ₁	106.87		104.76
O ₁₅ P ₇ C ₁	101.72		100.75
X ₁₃ P ₇ O ₁₄	113.26		113.63
X ₁₃ P ₇ O ₁₅	117.63	116.8 (O=PCl)	116.77
O ₁₄ P ₇ O ₁₅	100.33	101.6 (ClPCl)	100.95
H ₁₆ O ₁₄ P ₇	110.89		110.99
H ₁₇ O ₁₅ P ₇	112.76		112.14
Dihedral angles (deg.)			
X ₁₃ P ₇ C ₁ C ₂	5.25		12.34
O ₁₄ P ₇ C ₁ X ₁₃	126.83		127.36
O ₁₅ P ₇ C ₁ X ₁₃	-128.43		-128.16
H ₁₆ O ₁₄ P ₇ X ₁₃	27.63		18.97
H ₁₇ O ₁₅ P ₇ X ₁₃	52.39		41.76
Rotational barriers (kcal/mol)			
Through the planar state	0.60	0.13	
Through the perpendicular state	2.10	0.87	
Dipole moments (D)			
	2.35	2.66	

^a Experimental data [30] are for dichloro vinyl phosphine oxide.

We could find the experimental geometrical data only for vinylchlorophosphine oxide [30—32], but not for the acids or phenyl derivatives. Some of these experimental data for the oxide are included in Table 1 for comparison. Obviously, apart from the O=PC and O—PCl angles, they are rather well reproduced by our calculations indicating their accuracy, and also the deviations in the former two are not that large. Further, CC and CH bond lengths as well as CCC and HCC bond angles within the phenyl ring are reproduced according to expectations and in agreement with the corresponding quantities in other systems containing phenyl rings. From the calculations the barrier to rotation through the perpendicular transition state is 2.10 kcal/mol in the normal acid, but only 0.87 kcal/mol in thioacid (Table 1). The total and relative energies are listed in Table 2.

The extremely small rotational barrier over the planar transition state is probably hard to detect experimentally at all and is so small because it involves only a slight rotation of the P(OH)₂X (X = O or S)

Table 2

Total, E_t (Hartrees), and relative, E_r (kcal/mol), energies as calculated using the MP2 (where available) and DFT (6-311G** basis set) methods for the minima (non-planar, np) and transition states (planar, p, and perpendicular at 90° XPCC torsional angle, pp) for phenylphosphonic (PO) and phenylthiophosphonic (PS) acids

System	state	MP2		DFT	
		E_t (H)	E_r (kcal/mol)	E_t (H)	E_r (kcal/mol)
PO	np ^a	-798.3524348	0.00	-800.1065514	0.00
	p ^b	-798.3513973	0.65	-800.1055894	0.60
	pp ^c	not located	—	-800.1032001	2.10
PS	np ^a	-1120.9209828	0.00	-1123.0661919	0.00
	p ^b	-1120.9207203	0.16	-1123.0659806	0.13
	pp ^c	not located	—	-1123.0648100	0.87

^a Since the two equivalent minima are not perpendicular but near planar, there must be another maximum between the two np minima, but we did not locate it for MP2.

^b In the corresponding frequency calculation always one imaginary frequency, i.e. a maximum appears.

^c Taken from the scans, i.e. the XPOH torsional angles were kept fixed at 0°.

group. The reason for the non (near)-planar energy minimum must be too close a contact between the strongly negative X atoms and also negatively polarized carbon atoms in the ring. Probably there is also some steric hindrance between the X atom and hydrogen atoms bound to the ring. Note that the agreements between *ab initio* MP2 and non-*ab initio* DFT calculations in the same basis set are a good indication that our results should be rather accurate, and thus additional calculations with the other basis sets, as mentioned in the Introduction, would provide not much further information.

Torsional potential function. The potential function scan for the internal rotation about the C—P single bond was obtained by allowing the CCPX dihedral angle to vary by 15° increments. Full geometry optimizations at each of the fixed CCPX dihedral angles (φ) were carried out at the DFT and MP2/6-311G** levels of calculations. However, it turned out that especially at the lower values of the CCPX angle, more or less undamped oscillations in the HOPX angles showed up, making the computation times for these values of the CCPX angle larger than the time limit for the calculations. In order to be able to perform the calculations, we had to fix the HOPX angles in the *syn* position relative to the P=X bond (0°) and to optimize only the other internal coordinates for each CCPX angle. This torsional potential function was then represented as a Fourier cosine series in the dihedral angle (φ), where the potential coefficients up to the sixth order are considered adequate to describe the potential function (as shown by the root mean square deviations, rms, of the least square fitting, which were of the order of 1 cal/mol). The results of the energy optimizations were used to calculate the six coefficients by least-squares fitting. However, the potential curves calculated with fixed HOPX angles suggest a minimum in the planar geometry and therefore we do not list the calculated potential coefficients or show the functions. Due to the symmetry of the phenyl ring the potentials are symmetric with respect to the perpendicular (pp) transition state (TS, $\varphi = 90^\circ$). The differences between DFT and MP2 calculations are unimportant (compare Table 2). The minimum and its equivalent counterpart near 180° CCPX angle would correspond to a near-*cis* and near-*trans* conformers in an asymmetric vinyl system, however, due to the symmetry of the phenyl ring they are equivalent. As expected, the rotational barriers for thiophosphonic acid are much lower than those for phosphonic acid because an S atom, being less electronegative than an O atom, leads to a much smaller charge separation in the PS bond as compared to the PO bond.

The fact that we have no planar minima indicate that the conjugation between the ring and PX bonds are negligible. First of all, we would expect that because any such conjugation would reduce the aromatic character of the phenyl ring and would thus be avoided. Our detailed previous study on vinyl dichlorophosphine oxide and sulfide [33] has shown that the conjugation effects due to P=O and C=C bonds are,

if present at all, negligible, as it is the case in our acids. Furthermore, Laguna et al. [34] have stated that the PO bond is best viewed as a highly polarized triple bond not able to conjugation. Thus, we do not expect the conjugation to play a major role in the stability of the acid conformers.

VIBRATIONAL FREQUENCIES, NORMAL COORDINATE ANALYSES, AND DISCUSSION OF THE SPECTRA

Our molecules in their non (near)-planar conformations have C_1 symmetry and the vibrational modes span the 45 irreducible representations and should be polarized in the Raman spectra of the liquids. Normal coordinate analyses were carried out for the stable non (near)-planar conformers of the molecules in order to provide a complete assignment of the fundamental vibrational frequencies. A computer program was written by one of us (WF, see [35] for details) for this purpose following Wilson's method [17] to compute the potential energy distribution (PED) for each normal mode among the symmetry coordinates of the molecules in their stable conformation. A complete assignment of the fundamentals was proposed. The data of the vibrational assignments for the most intense features in the spectra are given in Table 3. Internal and symmetry coordinates can easily be derived from those given in [29] for phenyl cyanamide.

The normal modes in our phenyl substituted rings are mostly not very pure symmetry coordinates, but mix several of them together. The antisymmetric torsion is a pure vibration in both acids with very small wave numbers (33 cm^{-1} and 17 cm^{-1}). These small wavenumbers are a further indication for the absence of conjugation, which would imply larger ones, if present. Further, they explain the difficulties in the optimizations. Relatively intense bands in the IR are calculated around 200 cm^{-1} and contain mainly POH symmetric and antisymmetric wags, both in the phosphonic and thiophosphonic molecules. The most intense Raman line is the antisymmetric torsion in both molecules, and it is so high that the others can be seen mostly in an enlarged inset (see below). Another rather intense feature is calculated around 400 cm^{-1} again in both molecules, containing PO_2 twist and wag.

Apart from the antisymmetric torsion, the second highest line in the Raman spectra is the pure ring breathing around 1000 cm^{-1} , which is mixed in the thio derivative with other ring deformations. In phosphonic acid, quite pure normal modes can be found at 408 cm^{-1} (92 % ring deformation), 834 cm^{-1} (79 % PO_2 symmetric stretch), 876 cm^{-1} (82 %, PO_2 antisymmetric stretch), and 1283 cm^{-1} (87 % P=O stretch), most of them with a rather large transmittance. In thiophosphonic acid, quite pure normal modes can be found at 408 cm^{-1} (94 % ring deformation), 1019 cm^{-1} (82 % POH anti-symmetric bend), and 1034 cm^{-1} (79 % POH symmetric bend), some of them with a rather large transmittance. In thiophosphonic acid, the degree of mixing is higher than that in phosphonic acid.

In Fig. 1, we show the calculated infrared (IR) spectrum together with the experimental one, replotted from the website [36] for the stable non (near)-planar conformer of phenylphosphonic acid.

As mentioned above, the largest IR intensities belong clearly to the bands in the skeletal or fingerprint region of the molecule. Note that the spectrum was recorded only above about 400 cm^{-1} . We expect the PO_2 -related vibrations to have some intensity because of the charge separation in the P—O bonds of about $+e$ at P and $-0.5e$ at O. We have to assign the rather intense and closely spaced group of bands around 500 cm^{-1} in the experimental spectrum to those. The corresponding group of lines in the calculated spectrum is not that closely spaced and tends to be slightly lower in frequency. One of the most intense bands both theoretically and experimentally is the P=O stretch in phosphonic and the P=S stretch in thiophosphonic acid, which is a pure normal mode in the former at about 1300 cm^{-1} and a mixed one in the latter at about 850 cm^{-1} . This is again due to the polarization of the P=X group which is about $+e$ for phosphorus and about $-0.58e$ for O in phosphonic acid and about $-0.45e$ for S in thiophosphonic acid, the charge on S being less than that on O. Ring deformations are calculated between 1300 cm^{-1} and 1650 cm^{-1} and are quite intense features also in the experimental spectrum. The most intense and characteristic line of those is, as expected, the one at 1017 cm^{-1} for phenylphosphonic acid, which is 35 % ring breathing.

The two bands, which are the highest in wavenumber, are composed from O—H symmetric and antisymmetric stretch. The bands are a broad feature in the experimental spectrum, which cannot be seen in our replot, because there we assign a line width of 10 cm^{-1} to all the bands. Their relatively low intensity indicates that hydrogen bonding is rather weak in the system, so that mainly the dimer bands contribute to this feature. The reason for this must be the bulky nature of the phenyl ring, which allows at most two molecules to be bound together by a hydrogen bond.

Table 3

Theoretical wavenumbers, k (cm^{-1}), as calculated with the DFT/B3LYP method in a 6-311G** basis set, and the potential energy distribution among the symmetry coordinates, PED (only the largest two are given), calculated with our program for non-planar phenylphosphonic and phenylthiophosphonic acids (features showing the calculated IR intensity $I < 10 \text{ km} \cdot \text{mol}^{-1}$ and Raman activity $A < 5 \text{ \AA}^4 \text{ amu}^{-1}$ are not listed)

k	PED	k	PED
Non-planar phenylphosphonic acid			
33	97% antisymm. torsion	18	100% antisymm. torsion
109	63% β -CH and ring-P def., 12% ring def.	107	53% β -CH and ring-P def., 14% ring def.
192	32% POH antisymm. wag, 26% POH symm. wag	173	47% POH antisymm. wag, 26% ring-P bend
228	30% POH symm. wag, 23% POH antisymm. wag	217	53% PO ₂ twist, 36% POH symm. wag
290	39% ring-P stretch, 21% PO ₂ rock	254	25% ring-P stretch, 25% PO ₂ rock
298	31% POH symm. wag, 31% ring def.	304	34% ring def., 29% PO ₂ wag
361	27% POH antisymm. wag, 26% ring-PX bend	324	38% POH symm. wag, 24% PO ₂ wag
400	34% PO ₂ wag, 29% PO ₂ twist	332	24% ring-P bend, 22% POH antisymm. wag
450	37% PO ₂ scissor, 17% PO ₂ rock	397	33% PO ₂ rock, 19% PO ₂ scissor
505	34% PO ₂ rock, 18% ring def.	454	32% PO ₂ scissor, 15% ring def.
515	32% β -CH and ring-P def., 26% PO ₂ wag	507	43% β -CH and ring-P def., 21% ring def.
632	90% ring def.	630	75% ring def., 11% PX stretch
710	61% ring def., 18% β -CH and ring-P def.	638	45% PX stretch, 17% ring def.
716	48% ring def., 21% ring-P stretch	708	61% ring-def., 19% β -CH and ring-P def.
761	67% γ -CH and δ -CH def. 12% ring def.	737	36% ring def., 25% ring-P stretch
834	79% PO ₂ symm. stretch	763	67% γ -CH and δ -CH def., 12% ring def.
864	50% γ -CH def., 45% β -CH def.	846	64% PO ₂ symm. stretch, 22% PO ₂ antisymm. stretch
876	82% PO ₂ antisymm. stretch	862	35% γ -CH def., 32% β -CH def.
993	45% β -CH def., 36% γ -CH def.	866	55% PO ₂ asymm. stretch, 16% γ -CH def.
1012	50% POH symm. bend, 20% ring def.	1015	37% ring-def., 26% γ -CH and δ -CH def.
1017	35% ring breath., 30% POH symm. bend	1019	82% POH antisymm. bend
1020	62% POH antisymm. bend, 12% ring breath.	1034	79% POH symm. bend
1048	42% ring def., 22% ring def.	1048	40% ring def., 18% ring def.
1101	53% ring def., 20% β -CH bend	1107	53% ring def., 18% β -CH bend
1141	23% ring-P stretch, 20% ring breath.	1134	25% ring-P stretch, 21% ring def.
1184	39% γ -CH bend, 36% δ -CH bend	1185	39% γ -CH bend, 35% δ -CH bend
1206	38% γ -CH bend, 37% β -CH bend	1210	37% β -CH bend, 37% γ -CH bend
1283	87% PX stretch	1323	69% ring def., 16% γ -CH bend
1324	64% ring def., 17% γ -CH bend	1355	62% β -CH bend, 15% ring def.
1353	59% β -CH bend, 19% ring def.	1471	33% ring def., 29% γ -CH bend
1472	32% ring def., 29% γ -CH bend	1516	35% β -CH bend, 33% γ -CH bend
1517	34% γ -CH bend, 32% β -CH bend	1618	68% ring def., 11% δ -CH bend
1619	70% ring def., 11% δ -CH bend	1634	66% ring def., 12% β -CH bend
1637	68% ring def., 13% β -CH bend		
3166	52% δ -CH stretch, 42% γ -CH symm. stretch	3168	53% δ -CH stretch, 41% γ -CH symm. stretch
3177	66% γ -CH antisymm. stretch, 30% β -CH antisymm. stretch	3179	70% γ -CH antisymm. stretch, 29% β -CH antisymm. stretch
3184	48% β -CH symm. stretch, 32% δ -CH stretch	3187	53% β -CH symm. stretch, 32% δ -CH stretch
3193	63% β -CH antisymm. stretch, 26% γ -CH antisymm. stretch	3194	70% β -CH antisymm. stretch, 29% γ -CH antisymm. stretch
3197	42% β -CH symm. stretch, 38% γ -CH symm. stretch	3198	45% γ -CH symm. stretch, 41% β -CH symm. stretch
3823	53% OH antisymm. stretch, 47% OH symm. stretch	3809	53% OH antisymm. stretch, 47% OH symm. stretch
3834	53% OH symm. stretch, 47% OH antisymm. stretch	3830	53% OH symm. stretch, 47% OH antisymm. stretch

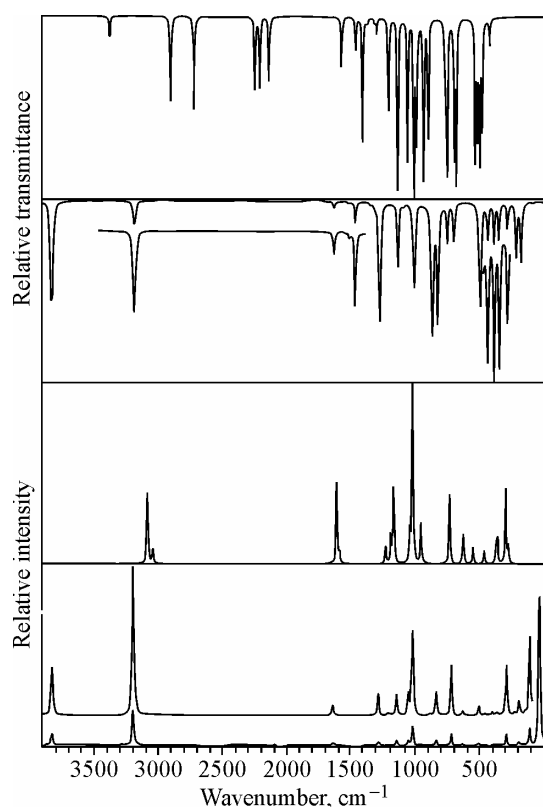


Fig. 1. Experimental (upper one in each pair of panels) and theoretical (lower one in each pair of panels) IR (upper pair of panels) and Raman (lower pair of panels) spectra of near planar phenylphosphonic acid, theoretical spectra calculated with the DFT/B3LYP method in a 6-311G** basis set and the experimental spectra replotted with a uniform line width of 10 cm^{-1} for better comparability with our theoretical spectra

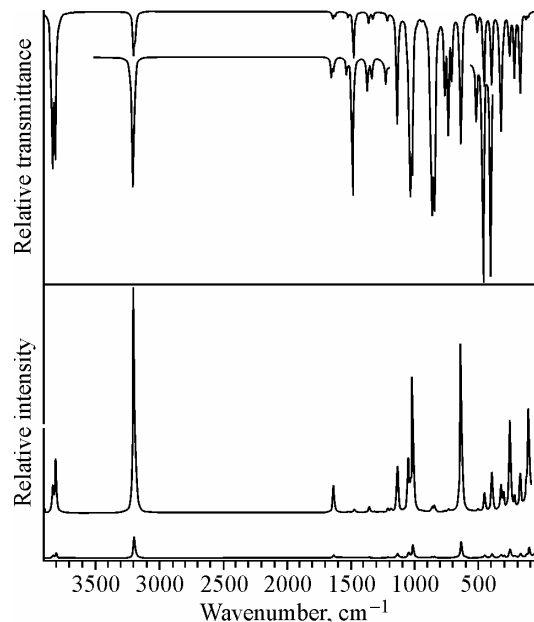


Fig. 2. Infrared (upper) and Raman (lower) spectra of the stable non (near)-planar conformer of phenylthiophosphonic acid, calculated with the DFT/B3LYP method in a 6-311G** basis set

The theoretical and experimental [36] Raman spectra for phosphonic acid are also shown in Fig. 1. In the calculated Raman spectra of the compounds the largest intensity is calculated at the line corresponding to the antisymmetric torsion, being so high in intensity that the other lines can be seen only in the enlarged inset. This effect is not seen in the experimental Raman spectrum of phosphonic acid because there recording starts only above roughly 200 cm^{-1} . As expected, the second highest intensity (highest in experiment) occurs at ring motions (which lead to the largest changes in polarizability) around 1000 cm^{-1} , both theoretically and experimentally at roughly the same wavenumber.

Since theory reproduces the experimental spectra rather well for phosphonic acid, we show in Fig. 2 the theoretical spectra for thiophosphonic acid.

The general appearance of the spectra is very reasonable, as discussed above, and we are in no doubt that Fig. 2 is a reasonable prediction of those spectra. Also we expect the assignments given in Table 3 to be quite correct.

CONCLUSIONS

One of our main conclusions is that the structural properties of phenylphosphonic and phenylthiophosphonic acids are dominated by electrostatic and steric effects rather than conjugation. Vibrational spectra are reproduced rather well by DFT for phosphonic acid, which leads us to the conclusion that our prediction of the vibrational spectra of thiophosphonic acid should be a reasonable one, as well as the assignments.

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