

# Vibrational spectroscopic studies and *ab initio* calculations of phenyl phosphate disodium salt

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The Fourier-transform infrared and Fourier-transform Raman spectra of phenyl phosphate disodium salt were recorded and analyzed. The surface-enhanced Raman scattering (SERS) spectrum was recorded in a silver colloid. The vibrational wavenumbers of the compound were computed using the Hartree–Fock/6-31G\* basis and compared with the experimental values. The molecule is adsorbed on the silver surface with the benzene ring in a tilted orientation. The presence of the phenyl ring and the phosphate group vibrations in the SERS spectrum reveal the interactions between the phenyl ring and the phosphate group with the silver surface. The first hyperpolarizability is calculated, and the calculated molecular geometry is compared with those of similar reported structures. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

**Keywords:** FT-IR spectra; FT-Raman spectra; SERS; phenyl phosphate disodium salt; Hartree–Fock *ab initio* calculations

## Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy is a well-established and highly effective technique for observing Raman scattering from species present at trace concentrations.<sup>[1,2]</sup> It is a useful tool in surface chemistry because of its high sensitivity and potential in providing useful information regarding metal–adsorbate interactions.<sup>[3,4]</sup> Organic phosphates which form macro elements in living organisms are considered as model systems for explaining biological processes and enzyme-catalyzed reactions, and they also have industrial application as extractants in a number of solvent extraction processes.<sup>[5–7]</sup> Organic phosphates are constituents of cell walls, nucleotides and adenosine triphosphates (ATPs).<sup>[6,8]</sup> Phosphate groups are present in proteins, nucleic acid and other biomolecular systems and appear to fulfill the different roles in molecular biology and the living world.<sup>[9,10]</sup> Phenyl phosphate has been used as the acid phosphatase substrate for about 50 years.<sup>[11]</sup> Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties.<sup>[12]</sup> Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing.<sup>[13,14]</sup> Phenyl substituents can increase molecular hyperpolarizability, a result that has been described as surprising.<sup>[15,16]</sup> Many organic molecules containing conjugated  $\pi$  electrons and characterized by large values of molecular first hyperpolarizabilities have been analyzed by means of vibrational spectroscopy.<sup>[17]</sup> Nonlinear optical properties of the phosphate groups have been reported by Liu *et al.*,<sup>[18]</sup> Raj *et al.*<sup>[19]</sup> and Sumej and Beena.<sup>[20]</sup> In the present study, the IR, Raman and SERS spectra along with the theoretical calculations of the vibrational wavenumbers of phenyl phosphate disodium salt are reported.

## Experimental

Phenyl phosphate disodium salt was procured from Sigma-Aldrich, USA. The Fourier-transform infrared (FT-IR) spectrum (Fig. 1) was recorded on a DR/Jasco FT/IR-6300 spectrometer in KBr pellets. The spectral resolution was  $4\text{ cm}^{-1}$ . The FT-Raman spectra (Figs 2 and 3) were obtained on a Bruker RFS 100/S (Germany) spectrometer. For excitation of the spectrum, the emission of a Nd : YAG laser was used, with excitation wavelength 1064 nm and maximum power 150 mW measured on solid sample. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was  $2\text{ cm}^{-1}$ . The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate by sodium citrate, using the Lee–Meisel method.<sup>[21]</sup> Five milliliters of  $2 \times 10^{-4}\text{ M}$  aqueous solution of title compound was added to an equal volume of silver colloid.

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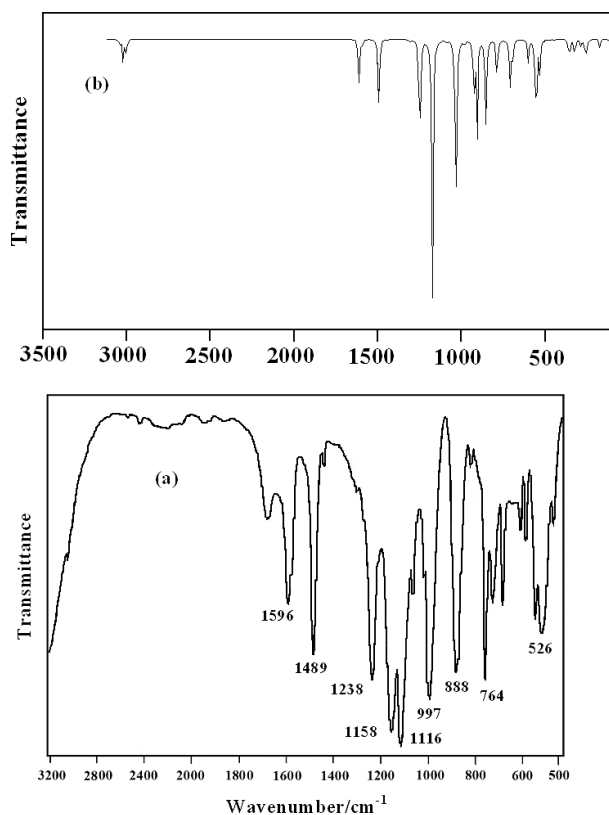
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**Figure 1.** FT-IR spectrum of phenyl phosphate disodium salt: (a) experimental; (b) theoretical.

## Computational Details

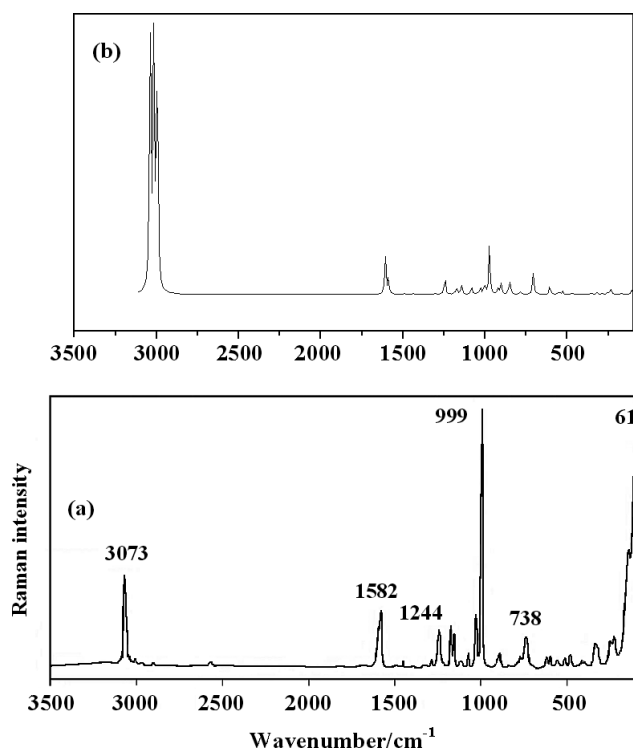
The vibrational wavenumbers were calculated using the Gaussian'03 software package on a personal computer.<sup>[22]</sup> The geometry of phenyl phosphate disodium salt was fully optimized without imposing external symmetry constraints using the 6-31G\* basis set at the Hartree-Fock level of theory. Since normally errors within this type of calculation are systematic, it is common practice to use empirical correction factors.<sup>[23]</sup> In this study, a unique scale factor of 0.8929 was employed for the final wavenumbers.<sup>[23]</sup> Parameters corresponding to optimized geometry of phenyl phosphate disodium salt (Fig. 4) are given in Table S1 (Supporting Information).

The calculated vibrational spectrum had no imaginary wavenumbers, which helped us to confirm that the structure of the title compound deduced following optimization corresponded to energy minimum. The assignment of the calculated wavenumbers was aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.

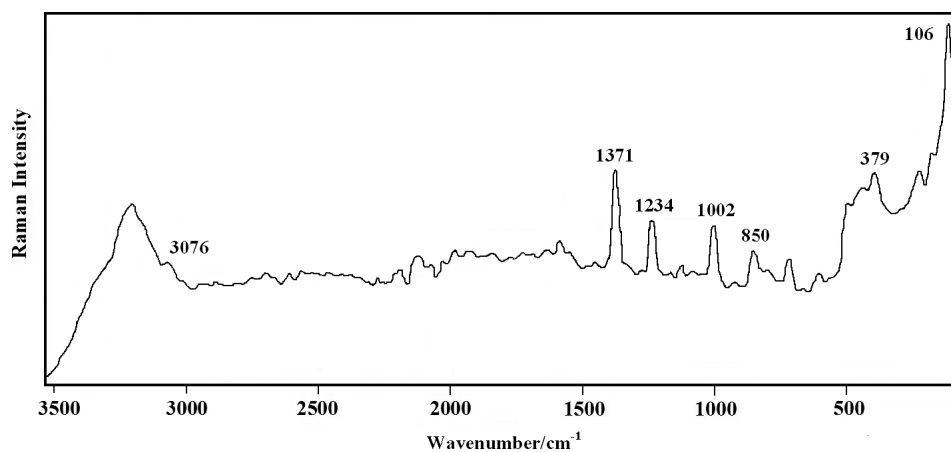
## Results and Discussion

### IR and Raman spectra

The observed IR and Raman bands with their relative intensities, calculated (scaled) wavenumbers and assignments are given in Table 1. From the study of mid-infrared spectroscopy



**Figure 2.** FT-Raman spectrum of phenyl phosphate disodium salt: (a) experimental; (b) theoretical.



**Figure 3.** SERS spectrum of phenyl phosphate disodium salt.

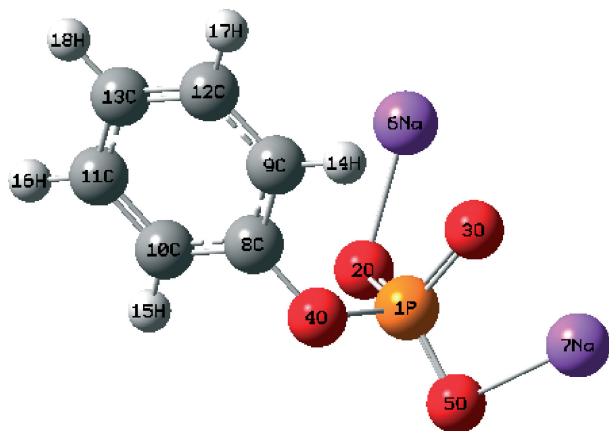


Figure 4. Optimized geometry.

of phosphate mineral pyromorphite, Reddy *et al.*<sup>[24]</sup> reported the vibrations of  $\nu_a\text{PO}_4$  modes at 1017 and 961  $\text{cm}^{-1}$ . The asymmetric stretching wavenumbers of  $\text{PO}_4$  are assigned between 1095 and 1031  $\text{cm}^{-1}$  in the IR spectrum for phosphate complexes.<sup>[25]</sup> These modes are also reported<sup>[10,26]</sup> to appear at 1030 and 970  $\text{cm}^{-1}$  for the pyromorphite mineral and at 1171 and 1102  $\text{cm}^{-1}$  for the creatine phosphate. In the phosphate mineral turquoise,<sup>[27]</sup> the asymmetric stretching modes of  $\text{PO}_4$  are observed between 1184 and 1106  $\text{cm}^{-1}$  (Raman) and between 1195 and 1109  $\text{cm}^{-1}$  (IR). The  $\nu_a\text{PO}_4$  stretching modes are reported in a range 1125–983  $\text{cm}^{-1}$  for uranyl phosphate minerals experimentally.<sup>[28,29]</sup> Chivers *et al.*<sup>[30]</sup> assigned the wavenumbers of the stretching modes of  $\nu_a\text{PO}_4$  for tris(trimethyltin) orthophosphate at 1115  $\text{cm}^{-1}$  as a strong band and for tris(trimethyltin) orthophosphate dioxane at 1113  $\text{cm}^{-1}$ . The  $\nu_a\text{PO}_4$  stretching modes of phosphate mineral kintoreite are reported at 1075 and 1052  $\text{cm}^{-1}$  in the Raman spectrum.<sup>[31]</sup> Frost<sup>[32]</sup> assigned the  $\nu_a\text{PO}_4$  vibrations of the phosphate oxyanions of natural phosphate hopeite, zinc parahopeite, in the range 1150–995  $\text{cm}^{-1}$  (Raman), and for pseudo-malachite, libethenite and cornetite between 1096 and 1000  $\text{cm}^{-1}$  (vibrational) and between 1137 and 995  $\text{cm}^{-1}$  (IR), respectively. According to Baran and Lii,<sup>[33]</sup> the reported values of asymmetric stretching modes of  $\text{PO}_4$  of oxovanadium complexes are at 1076 and 1084  $\text{cm}^{-1}$  in the IR and Raman spectra and assigned the asymmetric stretching modes as a triply degenerate stretching vibration. The phosphate group asymmetric stretching modes were reported at 1150  $\text{cm}^{-1}$  for the metal–adenosine-5-triphosphate complex experimentally.<sup>[8]</sup> Patanayak *et al.*<sup>[34]</sup> assigned the  $\text{PO}_4$  asymmetric stretching modes as a strong band in the range 1150–1000  $\text{cm}^{-1}$  for hydroxyapatite ceramics from IR analysis. For the title compound, the bands observed at 1158 and 1026  $\text{cm}^{-1}$  (IR) and at 1158 and 1030  $\text{cm}^{-1}$  (Raman) are assigned to the asymmetric stretching modes  $\nu_a\text{PO}_4$ . From HF calculations, these modes are at 1170 and 1029  $\text{cm}^{-1}$ , respectively. Etcheverry and Williams<sup>[10]</sup> reported the IR spectrum of creatine phosphate and assigned the symmetric stretching  $\nu_s\text{PO}_4$  modes at 984  $\text{cm}^{-1}$ . From the IR and Raman spectra of the phosphate mineral pyromorphite,<sup>[24,35]</sup> the  $\nu_s\text{PO}_4$  vibration bands were found at 894 and 925  $\text{cm}^{-1}$ . According to Martens and Frost,<sup>[25]</sup> the symmetric stretching vibrational modes of  $\text{PO}_4$  appear in the range 996–917  $\text{cm}^{-1}$ . Farmer<sup>[26]</sup> and Bartholomai and Klee<sup>[36]</sup> reported these modes at 894  $\text{cm}^{-1}$  and at 923, 919  $\text{cm}^{-1}$ , respectively, for the mineral pyromorphite. Bands at 1008 and 992  $\text{cm}^{-1}$  (IR) are assigned to the  $\text{PO}_4$  symmetric stretching vibrations for the phos-

phate mineral turquoise.<sup>[27]</sup> Frost *et al.*<sup>[28]</sup> reported the symmetric stretching vibrations of  $\text{PO}_4$  at 995 and 980  $\text{cm}^{-1}$  for the uranyl phosphate mineral dewindite in the Raman spectrum. The symmetric stretching vibrations of  $\nu_s\text{PO}_4$  are assigned at 980  $\text{cm}^{-1}$  in the case of some lead phosphate glasses with tungsten ions.<sup>[37]</sup> In the present study, the symmetric stretching vibrations of  $\text{PO}_4$  are observed at 888  $\text{cm}^{-1}$  (IR), at 895  $\text{cm}^{-1}$  (Raman) and at 903  $\text{cm}^{-1}$  theoretically.

The out-of-plane bending vibrations  $\gamma\text{PO}_4$  are reported between 648 and 525  $\text{cm}^{-1}$  for the phosphate complexes,<sup>[25]</sup> at 572 and 542  $\text{cm}^{-1}$  for the phosphate mineral pyromorphite<sup>[26]</sup> and in a range 643–550  $\text{cm}^{-1}$  for the phosphate mineral turquoise from Raman bands.<sup>[27]</sup> According to Frost *et al.*,<sup>[28,31]</sup> the  $\gamma\text{PO}_4$  vibrations are expected in the range 580–493  $\text{cm}^{-1}$ . Chivers *et al.*<sup>[30]</sup> and Geisler *et al.*<sup>[38]</sup> observed the asymmetric bending modes of  $\text{PO}_4$  derivatives at 590  $\text{cm}^{-1}$  and at 604 and 557  $\text{cm}^{-1}$  experimentally. The deformation vibrations of  $\gamma\text{PO}_4$  are reported between 615 and 514  $\text{cm}^{-1}$  for the uranyl phosphate mineral threadgoldite from the Raman spectrum.<sup>[20]</sup> Frost *et al.*<sup>[27,39]</sup> assigned the in-plane bending  $\delta\text{PO}_4$  modes between 492 and 417  $\text{cm}^{-1}$  and between 436 and 375  $\text{cm}^{-1}$  for different phosphate minerals experimentally. The  $\delta\text{PO}_4$  scissoring vibrations are reported in between 477 and 420  $\text{cm}^{-1}$  as strong bands for the phosphate mineral kintoreite<sup>[31]</sup> and in a range 490–399  $\text{cm}^{-1}$  for the uranyl phosphate mineral threadgoldite.<sup>[29]</sup> The in-plane bending  $\delta\text{PO}_4$  vibrations are reported at 423  $\text{cm}^{-1}$  for phosphate complexes in the Raman spectra<sup>[38]</sup> and at 470  $\text{cm}^{-1}$  for tris(trimethyltin) orthophosphate.<sup>[30]</sup> For the title compound, the deformation bands of  $\text{PO}_4$  group are observed at 598, 554 and 526  $\text{cm}^{-1}$  in the IR spectrum and at 598, 557 and 514  $\text{cm}^{-1}$  in the Raman spectrum. The HF calculated values at 596, 555 and 528  $\text{cm}^{-1}$  are in good agreement with experimental values.

For the title compound, the assignments of the benzene ring vibrations are made by referring the case of benzene derivatives with mono substitution as summarized by Roeges.<sup>[40]</sup> According to Roeges,<sup>[40]</sup> the CH stretching modes for mono-substituted benzene are found in the region 3105–3000  $\text{cm}^{-1}$ . For mono-substituted benzenes, there are five CH stretching modes. According to the selection rule, all five bands are permitted in the IR spectrum.<sup>[41]</sup> Only one IR band of medium intensity and one Raman band of strong intensity are observed at 3041 and 3073  $\text{cm}^{-1}$ , respectively. The calculated values are at 3041, 3036, 3017, 3001 and 2990  $\text{cm}^{-1}$ . The benzene ring possesses six ring-stretching vibrations, of which the four with the highest wavenumbers occurring respectively near 1600, 1580, 1490 and 1440  $\text{cm}^{-1}$  are good group vibrations. In the absence of ring conjugation, the band near 1580  $\text{cm}^{-1}$  is usually weaker than that at 1600  $\text{cm}^{-1}$ . The fifth ring-stretching vibrations  $\nu\text{Ph}$  is active near  $1335 \pm 35$   $\text{cm}^{-1}$  and the intensity is, in general, low or medium high.<sup>[40,41]</sup> The sixth ring-stretching vibration or ring-breathing mode  $\nu\text{Ph}$  appears as a weak band near 1000  $\text{cm}^{-1}$  in mono-substituted benzenes.<sup>[40]</sup> The bands observed at 1596, 1578, 1489, 1453 and 1317  $\text{cm}^{-1}$  in the IR spectrum and at 1594, 1582, 1453 and 1287  $\text{cm}^{-1}$  in the Raman spectrum are assigned as  $\nu\text{Ph}$  ring-stretching modes. As seen from the Table 1, the *ab initio* calculations give these modes at 1608, 1588, 1490, 1441 and 1304  $\text{cm}^{-1}$ . These vibrations are expected in the region<sup>[40]</sup> 1620–1300  $\text{cm}^{-1}$ . For the title compound, the ring-breathing mode is found at 1004  $\text{cm}^{-1}$  theoretically, and very strong bands are observed in the IR and Raman spectra at 997 and 999  $\text{cm}^{-1}$ . There are five in-plane bending CH vibrations for mono-substituted benzene. The bands observed at 1158,

**Table 1.** Calculated vibrational wavenumbers (in  $\text{cm}^{-1}$ , scaled), measured infrared and Raman band positions and assignments for phenyl phosphate disodium salt

$\nu_{(\text{HF})}(\text{cm}^{-1})$	IR intensity (km/mol)	Raman activity	$\nu_{(\text{IR})}(\text{cm}^{-1})$	$\nu_{(\text{Raman})}(\text{cm}^{-1})$	$\nu_{(\text{SERS})}(\text{cm}^{-1})$	Assignments
3041	4.18	124.05	3041 m	3073 vs	3076 wbr	$\nu\text{CH}$
3036	7.53	79.81	–	–	–	$\nu\text{CH}$
3017	42.41	132.26	–	–	3000 wbr	$\nu\text{CH}$
3001	24.44	96.91	–	–	–	$\nu\text{CH}$
2990	4.61	58.61	–	–	–	$\nu\text{CH}$
1608	85.36	20.95	1596 s	1594 sh	1583 m	$\nu\text{Ph}$
1588	9.89	9.34	1578 m	1582 m	1545 w	$\nu\text{Ph}$
1490	129.74	0.58	1489 vs	–	–	$\nu\text{Ph}$
1441	1.35	0.56	1453 w	1453 vw	1371 vs	$\nu\text{Ph}$
1304	2.93	0.59	1317 w	1287 w	1273 w	$\nu\text{Ph}$
1245	237.52	12.18	1238 vvs	1244 m	1234 s	$\nu\text{C-O}$
1185	1.02	1.50	–	1176 m	–	$\delta\text{CH}$
1170	485.40	2.89	1158 vvs	1158 m	1147 w	$\nu_3\text{PO}_4/\delta\text{CH}$
1145	6.21	5.44	1116 vvs	1115 w	1117 w	$\delta\text{CH}$
1083	4.33	4.75	1074 s	1076 w	1076 w	$\delta\text{CH}$
1049	2.12	0.39	–	–	–	$\delta\text{CH}$
1029	357.15	4.00	1026 m	1030 m	–	$\nu_a\text{PO}_4$
1004	6.71	6.55	997 vvs	999 vvs	1002 s	$\nu\text{Ph}/\text{ring breathing}$
992	1.71	0.35	–	–	–	$\gamma\text{CH}$
979	7.74	3.85	–	–	–	$\gamma\text{CH}$
972	1.71	25.15	–	–	–	$\delta\text{Ph}$
922	111.61	3.87	–	–	925 w	$\gamma\text{CH}$
903	188.44	6.25	888 vvs	895 w	–	$\nu_s\text{PO}_4$
851	188.40	7.54	–	–	850 m	$\gamma\text{CH}$
845	34.28	1.74	833 w	–	–	$\gamma\text{CH}$
783	85.63	1.80	764 vvs	–	778 w	$\gamma\text{CH}$
706	90.33	11.71	734 s	738 w	718 m	$\nu\text{P-O}/\gamma\text{CH}$
691	61.01	0.74	694 s	–	667 w	$\gamma\text{Ph}$
605	1.46	4.57	621 m	619 w	620 w	$\delta\text{Ph}$
596	51.56	1.28	598 m	598 w	–	$\gamma\text{Ph}/\omega\text{PO}_4$
555	101.80	0.80	554 s	557 w	–	$\omega\text{PO}_4/\delta\text{Ph}$
545	79.37	0.81	–	–	–	$\gamma\text{Ph(X)}$
528	63.34	1.63	526 s	514 w	500 m	$\delta\text{PO}_4$
469	2.31	0.90	481 m	482 w	–	$\gamma\text{Ph(X)}$
443	2.12	0.23	–	–	439 m	$\delta\text{PO}_4/\gamma\text{Ph(X)}$
417	0.11	0.05	–	417 w	379 s	$\gamma\text{Ph}$
352	42.87	0.02	–	–	–	$\tau\text{Ph}, \tau\text{PO}_4$
318	34.85	1.09	–	333 m	–	$\tau\text{Ph}$
283	17.87	0.40	–	–	–	$\tau\text{PO}_4$
261	10.44	0.35	–	–	–	$\tau\text{P-O}$
252	32.33	1.06	–	242 m	–	$\tau\text{P-O}$
235	5.09	3.44	–	227 m	212 m	$\tau\text{Ph(X)}$
170	16.02	0.41	–	–	167 m	$\tau\text{Ph}$
105	9.04	2.81	–	136 sh	106 vs	$\tau\text{Ph(X)}$
83	15.96	0.37	–	90 sh	–	$\tau\text{Ph}, \tau\text{PO}_4$
49	25.26	0.44	–	61 vvs	–	$\tau\text{Ph}, \tau\text{PO}_4$

$\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending;  $\omega$ , wagging;  $\tau$ , torsional; X, substituent sensitive; Ph, phenyl; s, strong; w, weak; br, broad; v, very; m, medium; sh, shoulder; subscripts: a, asymmetric; s, symmetric.

1116 and  $1074\text{ cm}^{-1}$  in the IR spectrum and at 1176, 1158, 1115 and  $1076\text{ cm}^{-1}$  in Raman spectrum are assigned as the in-plane bending vibrations of CH modes. HF calculations give these modes at 1185, 1170, 1145, 1083 and  $1049\text{ cm}^{-1}$ . In the case of light substituent, the out-of-plane CH deformations  $\gamma\text{CH}$  of mono-substituted benzene derivative modes are expected in

the range<sup>[40]</sup>  $1000\text{--}730\text{ cm}^{-1}$ . In general, the  $\gamma\text{CH}$  out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. The stronger  $\gamma\text{CH}$  band occurring in the region  $775 \pm 45\text{ cm}^{-1}$  ( $\gamma\text{CH}$  umbrella mode) tends to shift to lower (higher) wavenumbers with increasing electron donating (attracting) power of the substituent,



but seems to be more sensitive to mechanical interaction effects. The lowest wavenumbers for this umbrella mode are found in the spectra of mono-substituted benzene.<sup>[41–44]</sup> The bands at 888, 833, 764 and 734  $\text{cm}^{-1}$  from the IR spectrum and 738  $\text{cm}^{-1}$  from the Raman spectrum are assigned as the out-of-plane CH deformations of the phenyl ring. The bands at 992, 979, 922, 851, 845, 783 and 706  $\text{cm}^{-1}$  are the *ab initio* calculated values for the  $\gamma$ CH deformation modes. From the IR spectrum, the  $\gamma$ CH band at 764  $\text{cm}^{-1}$  and the  $\gamma$ Ph band at 694  $\text{cm}^{-1}$  form a pair of strong bands characteristics of mono-substituted benzene derivatives.<sup>[40,44]</sup>

### SERS spectrum

SERS is already regarded as a valuable method because of its high sensitivity, which enables the detection and spectroscopic study of even single molecules.<sup>[2]</sup> The vibrational information contained in the SERS spectrum provides the molecular specificity required to characterize the adsorbate–surface interactions, specifically, the orientation of the adsorbed species on the metal surface. The relative intensities from the SERS spectra are expected to differ significantly from those in the normal Raman spectra owing to specific surface selection rules.<sup>[45]</sup> The surface selection rules suggest that, for a molecule adsorbed flat on the silver surface, the out-of-plane bending modes will be more enhanced when compared to its in-plane bending modes, and vice versa when it is adsorbed perpendicular to the surface.<sup>[45,46]</sup> It is further seen that vibrations involving atoms that are close to the silver surface will be enhanced. In the SERS spectrum of the title compound, the aromatic C–H stretching vibrations phenyl ring is observed as weak, broad bands at 3076 and 3000  $\text{cm}^{-1}$ , which suggest that the phenyl ring may be in a position close to the perpendicular to the silver surface possibly in a tilted position.<sup>[47,48]</sup> It has also been documented in the literature that when a benzene ring moiety interacts directly with a metal surface, the ring-breathing mode is red-shifted by 10  $\text{cm}^{-1}$ , with substantial band broadening in the SERS spectrum.<sup>[49]</sup> In the present case, the ring-breathing mode of the phenyl ring is at 1002  $\text{cm}^{-1}$  without any wavenumber shift. Neither a substantial red shift nor significant band broadening was identified in the SERS spectrum of the title compound, implying that the probability of a direct ring  $\pi$ -orbital to metal interaction should be low, in accordance with the tilted position of the ring.

The in-plane bending modes  $\delta$ CH of the aromatic ring are observed at 1147, 1117 and 1076  $\text{cm}^{-1}$  for the phenyl ring as weak bands. The presence of these modes suggests that the benzene ring is tilted with respect to the silver surface.<sup>[45,46]</sup> The benzene ring vibrations observed at 1583, 1545, 1371 and 1273  $\text{cm}^{-1}$  in the SERS spectrum support this fact. Also the out-of-plane  $\gamma$ CH vibrations are present in the SERS spectrum at 925, 850 and 778  $\text{cm}^{-1}$ , which are absent in the normal Raman spectrum. According to the surface selection rules,<sup>[50,51]</sup> the presence of in-plane and out-of-plane vibrational modes in the SERS spectrum of the title compound suggests that there is a certain angle between the phenyl ring and the surface of the silver particle. The  $\text{PO}_4$  vibrations at 1147, 718, 500 and 439  $\text{cm}^{-1}$  and the substituent-sensitive vibrations at 439, 212 and 106  $\text{cm}^{-1}$  in the SERS spectrum suggest that there is an interaction between the  $\text{PO}_4$  group and the metal surface. The presence of these modes revealed the nearness of the  $\text{PO}_4$  moiety to the metal surface. An interaction of the  $\text{PO}_4$  group with the benzene ring is found to affect the  $\nu$ C–O mode as evidenced by the strong band at 1234  $\text{cm}^{-1}$  in the SERS spectrum. Podstawka *et al.*<sup>[52]</sup> assigned the bending deformation

bands of  $\text{PO}_4$  in a region between 572 and 561  $\text{cm}^{-1}$  from SERS spectrum for some phosphate complexes. Dorain *et al.*<sup>[53]</sup> reported a strong SERS band at 920  $\text{cm}^{-1}$  corresponding to  $\nu$ s $\text{PO}_4$  in the SERS spectrum and suggested an interaction between phosphate and the metal surface. But in the present study no such interaction is observed. According to Podstawka *et al.*,<sup>[52]</sup> the presence of a band at around 1140  $\text{cm}^{-1}$  in the SERS spectrum of phosphate complexes points to the phosphate group interacting with or being in close proximity to the metal surface. Chen *et al.*<sup>[54]</sup> reported the phosphate stretching bands at around 1110  $\text{cm}^{-1}$  in the SERS investigations of  $\text{PO}_4$  derivatives. Cortes *et al.*<sup>[55]</sup> assigned the asymmetric stretching vibrations of  $\text{PO}_4$  at around 1100  $\text{cm}^{-1}$  in the SERS study. In the present study, the SERS band at 1147  $\text{cm}^{-1}$  of  $\text{PO}_4$  vibrations shows the nearness of phosphate group to the metal surface and supports the above argument.

### Geometrical parameters and first hyperpolarizability

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of the parent molecules. The P–O bond lengths in phosphates are reported in the range 1.642–1.5  $\text{\AA}$ <sup>[56–67]</sup> and the P=O bond length between 1.529 and 1.470  $\text{\AA}$ .<sup>[56,57,60]</sup> For the title compound, the P–O bond length is found to be 1.6552  $\text{\AA}$  and the P=O bond length is in the range 1.5531–1.4957  $\text{\AA}$ , and these values are in agreement with the reported values. For the title compound, the bond angles at  $\text{P}_1$  are  $\text{O}_2\text{--P}_1\text{--O}_4$  ( $106.4^\circ$ ),  $\text{O}_2\text{--P}_1\text{--O}_5$  ( $121.3^\circ$ ),  $\text{O}_2\text{--P}_1\text{--O}_3$  ( $108.7^\circ$ ),  $\text{O}_4\text{--P}_1\text{--O}_3$  ( $104.8^\circ$ ),  $\text{O}_4\text{--P}_1\text{--O}_5$  ( $104.9^\circ$ ) and  $\text{O}_3\text{--P}_1\text{--O}_5$  ( $109.4^\circ$ ). The O–P–O bond angles are reported in the range  $114.9\text{--}102.7^\circ$  for phosphate derivatives.<sup>[58–61,64,67]</sup> All the carbon–carbon bond lengths in the phenyl ring lie in the range 1.390–1.383  $\text{\AA}$  (HF) and C–H bond lengths in the range 1.077–1.073  $\text{\AA}$  (HF). In the present case, the phenyl ring is a regular hexagon with bond lengths somewhere in between the normal values for a single (1.54  $\text{\AA}$ ) and a double (1.33  $\text{\AA}$ ) bond.<sup>[68]</sup>

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research.<sup>[69]</sup> The potential application of the title compound in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using IR and Raman spectroscopy. The ring-stretching bands at 1596, 1578, 1453, 1317 and 997  $\text{cm}^{-1}$  observed in IR have their counterparts in the Raman spectrum at 1594, 1582, 1453, 1287 and 999  $\text{cm}^{-1}$ , respectively, and their relative intensities in IR and Raman spectrum are comparable. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using the density functional theory (DFT) method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.<sup>[70]</sup>

The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion

becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots$$

where  $E_0$  is the energy of the unperturbed molecule;  $F^i$  is the field at the origin; and  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are the components of dipole moment, polarizability, the first hyper polarizabilities and second hyperpolarizabilities, respectively. The calculated first hyperpolarizability of the title compound is  $4.101 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives,<sup>[71]</sup> but experimental evaluation of this data is not readily available. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

In order to investigate the performance and vibrational wavenumbers of the title compound, the root mean-square (RMS) values were evaluated using the following expression:<sup>[72]</sup>

$$\text{RMS} = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{\text{calc}} - v_i^{\text{exp}})^2}$$

The RMS error of the observed Raman and IR bands are found to be 15.61 and 13.21, respectively, for HF method. Small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen-bond vibrations present in the crystal lead to strong perturbation of the infrared wavenumbers and intensities of many other modes. Also, we state that the experimental results pertain to the solid phase, whereas the theoretical calculations to the gaseous phase.

## Conclusion

The FT-IR, FT-Raman and SERS spectra of phenyl phosphate disodium salt were studied. The molecular geometry and wavenumbers were calculated theoretically. The presence of in-plane and out-of-plane modes of the phenyl ring in the SERS spectrum suggests a tilted orientation of the molecule with respect to the silver surface. The presence of phosphate group vibrations in the SERS spectrum shows the interaction between this group and the silver surface.

## Supporting information

Supporting information may be found in the online version of this article.

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