Vibrational Spectra of Cyclopentadienylphosphine: Infrared and Theoretical Studies from DFT Anharmonic Potentials

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Received: June 1, 2007; In Final Form: July 25, 2007

Both experimental and theoretical infrared investigations of cyclopentadienylphosphine (CpP) are reported. The infrared spectra (3500−500 cm^{-1}) in the gas phase have been recorded at 0.5 cm^{-1} resolution. Infrared absorptions bands of the two lowest stable conformers were observed and assigned. Average integrated intensities of isolated and overlapping vibrational bands were also determined experimentally. The vibrational frequencies of the CpP system and its P-dideuterated isotopologue have been calculated by means of density functional theory. The Becke exchange functional and Lee−Yang−Parr correlation functional method with a combination of the two basis sets, namely 6-31+G(d,p) and the correlation-consistent triple-ζ cc-pVTZ set of Dunning, were used. Hybrid B3LYP/B3LYP//cc-pVTZ/6-31+G(d,p) anharmonic frequencies of the fundamental, overtone, and combination transitions were calculated in the 3500−200 cm^{-1} area with the use of a variational approach, implemented in the P_Anhar_v1.1 code, to assign the experimental data for each conformer.

Introduction

Numerous experimental studies and theoretical calculations have been reported on cyclopentadienyl derivatives bearing a heterosubstituent.[1−8] The presence of a σ bond between the silicon, germanium, tin, mercury, phosphorus, or arsenic atom and the cyclopentadienyl ring means such compounds are subject to fluxional behavior caused by migration of the substituent onto the different positions of the cyclopentadienyl ring. This rearrangement, easily observed by NMR spectroscopy for numerous derivatives, leads to signals at chemical shifts dependent on the temperature and the nature of the substituents. Several theoretical works have been published in the last 30 years, mainly on the study of conformational characteristics[9−15] and on the facial selectivity in Diels−Alder addition reactions.[11]

The preparation of the simplest phosphorus derivative, i.e., cyclopentadienylphosphine (CpP), which is the subject of this work, was first reported in 2001.[12] The characterization of this kinetically unstable compound was performed by NMR, photoelectron, and mass spectrometry. More recently, the microwave spectrum was recorded[14] to characterize the two conformers corresponding to the two minima on the potential energy hypersurface of CpP, determined from high-level quantum chemical calculations. Some vibrational data[15] are also available, but they are not sufficient to characterize these two main conformers.

We have undertaken the first complete vibrational analysis of the two stable conformers through a joint analysis method which couples spectroscopic FTIR measurements and DFT-(B3LYP) anharmonic calculations, with the aim of contributing increased knowledge of the properties of this system. However, solving this problem numerically is not trivial. It is well-known that to accurately describe vibrational spectra of molecules up to 8−10 atoms requires a process based on many perturbative[16] and variational[17−20] processes. If one wants to overcome this critical size, it is necessary to find a compromise, either in the potential surface acquisition or in the method of solving Schrödinger's equation. This last point is critical, especially when data on combination bands, overtones, and hot bands, which are accurately described only in practice by a variational approach, is needed. In the present (CpP) case, lots of these bands exist and some assignments remain complex. Thus, to solve this issue, we have developed a variational treatment, which covers the 200−3500 cm^{-1} area through 21 spectral windows.[18] As this is a 13-atom system, we have also been able to test how robust our parallel approach[18−20] is and gauge technical limits linked to the use of a variational algorithm.

In this paper, the experimental spectra and anharmonic calculations of the complete vibrational assignments of cyclopentadienylphosphine $C_5H_5PH_2$ and one of its isotopologues $C_5H_5PD_2$ are discussed.

Experimental Section

Preparation of the Sample. Cyclopentadienylphosphine was prepared as previously reported by reduction of the corresponding cyclopentadienyldichlorophosphine with lithium aluminum hydride.[12,14] A few hundred milligrams were prepared and stored at 77 K before analysis by infrared spectroscopy.

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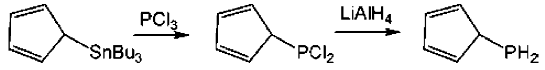
10.1021/jp074244i CCC: $37.00



Spectroscopic Measurement and Intensity Measurements. The sample was vaporized in the gas cell coupled to a White optical system.[21] A multireflection optical system was adjusted to obtain a total optical path of 10.6 m, and the spectra were measured on a 120 HR Bruker Fourier transform interferometer equipped with a KBr beam splitter, a Globar source, and a liquid-nitrogen-cooled MCT detector. The spectra (average 100 scans; Figure 1) were collected at ambient temperature and at a resolution of 0.5 cm^{-1}.

For the measurement of the integrated intensities, more precautions were taken. We used a small gas cell (simple-pass 10 cm cell) to reduce the adsorption of cyclopentadienylphosphine onto the cell walls. CpP presumably agglomerates or polymerizes in the gas phase; therefore, the cell was cooled to −20 °C to prevent this effect. Consequently, the uncertainty in the pressure was limited to about 6%. The spectra have been taken for different values (1−10 mbar) of the pressure of CpP by averaging 10 scans for each spectrum at a resolution of 2 cm^{-1}.

We determined absolute intensities for identified vibrational bands by plotting their integrated absorbance, A_ν, as a function of the partial pressure. One can easily derive the value of the absolute band intensity, S_ν, from the slope of the corresponding straight line:

$$A_\nu = \int \log\left(\frac{I_0}{I}\right) \mathrm{d}\nu \quad A_\nu = S_\nu l\,\mathrm{P}$$

where l is the optical path length and P the partial pressure in the gas cell.

For all the bands studied we observed a linear relationship, with the straight line obtained passing through point (0, 0). This indicates that Beer's law is followed, as shown in Figure 2a,b. In addition, the standard deviation from linearity gives a quantitative estimate of the uncertainty on the S_ν value. We have adopted this approach for all of the measured bands. In the case where several vibrational bands overlap, only the sum of their integrated absorbance has been estimated, because they cannot be calculated separately for each component. Both the measured intensities and their associated uncertainties (S_ν values), summarized in Table 1, are expressed in atm^{-1} cm^{-2} and were determined at 253 K. Calculated intensities of the conformers A and B of CpP, obtained at both B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ levels of theory, are relatively equivalent and seem to be insensitive to the choice of basis set. We have also estimated an average molar fraction of 40% and 60% of conformers A and B, respectively, by assuming Boltzmann-type distribution and using the relative free energies (Table 2). Under these conditions, we compared the observed and measured intensities of the isolated bands with those obtained by our calculation. Unfortunately, at this level of analysis, we cannot conclude the quantitative precision of the calculated values. However, from a qualitative point of view, the calculated intensities at the harmonic level remain very useful for the estimation of the variation in the force constants between the various modes of vibration of the molecule, thus contributing to their assignment.

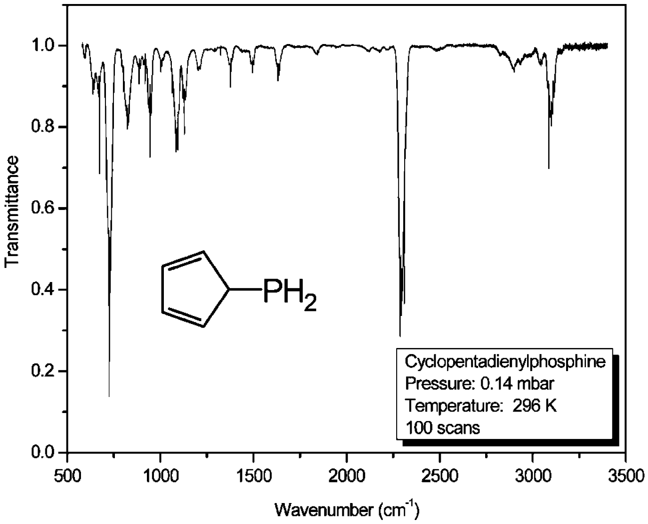


Figure 1. Infrared gas-phase spectrum of cyclopentadienylphosphine in the 500−3500 cm^{-1} range.

Computational Details. *1. Quartic Force Field (QFF).* Anharmonic treatment is necessary but complex. It is well-known that several anharmonic force fields of small molecular systems were calculated with methods that were recognized as providing good vibrational predictions, with wavenumbers varying by less than 10 cm^{-1} from the experimental data. Among those methods, MRCI (multireference configuration interaction) and CCSD(T) (coupled cluster singles and doubles including a perturbative estimation of connected triples) were generally used for the study of tri- and tetraatomic systems and were known to provide very good spectroscopic predictions when the basis sets used are of triple-ζ quality or higher. When the size of the system increases, the anharmonic force field can be calculated by a Møller−Plesset perturbative method or by the popular DFT (density functional theory) method. These last two methods have shown their ability to correctly compute, at lower cost, the anharmonic constants in the study of organic systems. These observations make it reasonable to expect that a combined method of determining the hybrid force fields (HFF) could be adapted for the process of treating large-scale molecular systems. At present the HFF, structural parameters, and harmonic constants are calculated by using a reference method whereas the cubic and quartic force constants expressed in the basis of the normal reference modes are determined by a DFT/6-31+G(d,p) approach.[22−24] These conditions are used in the present case to complement the pure B3LYP/double-ζ approach. The notation used in this article is method1/method2//basis1/basis2; i.e., the harmonic part is evaluated at the method1/basis1 level of calculation and the anharmonic part by using the method2/basis2 level of calculation.

Calculations were carried out with the use of both Dunning correlation consistent pVTZ Cartesian[25] and 6-31+G(d,p) basis sets. For geometry determination, DFT calculations were undertaken for comparison with the experimental data. The Becke[26] three-parameter exchange functional (B3) in combination with the Lee Yang and Parr[27] (LYP) correlation functional was used to describe the cyclopentadienylphosphine, $C_5H_5PH_2$, and one of its isotopologues, $C_5H_5PD_2$. Geometry optimization, energies, and analytical first derivatives were obtained using the GAUSSIAN 03 suite of programs.[28]

2. Vibrational Resolution. Because of numerous interactions between vibrational states and the uncertainties on weak overtones and combination bands revealed by the IR spectra, the vibrational problem should strictly be solved from a complete variational approach. Nevertheless, in its current format, this method is limited to small systems (up to 5 atoms), whatever hardware is used. To reach larger dimensions, one has to consider the selection of multiple spectral windows and the use of a parallel code.[18−20]

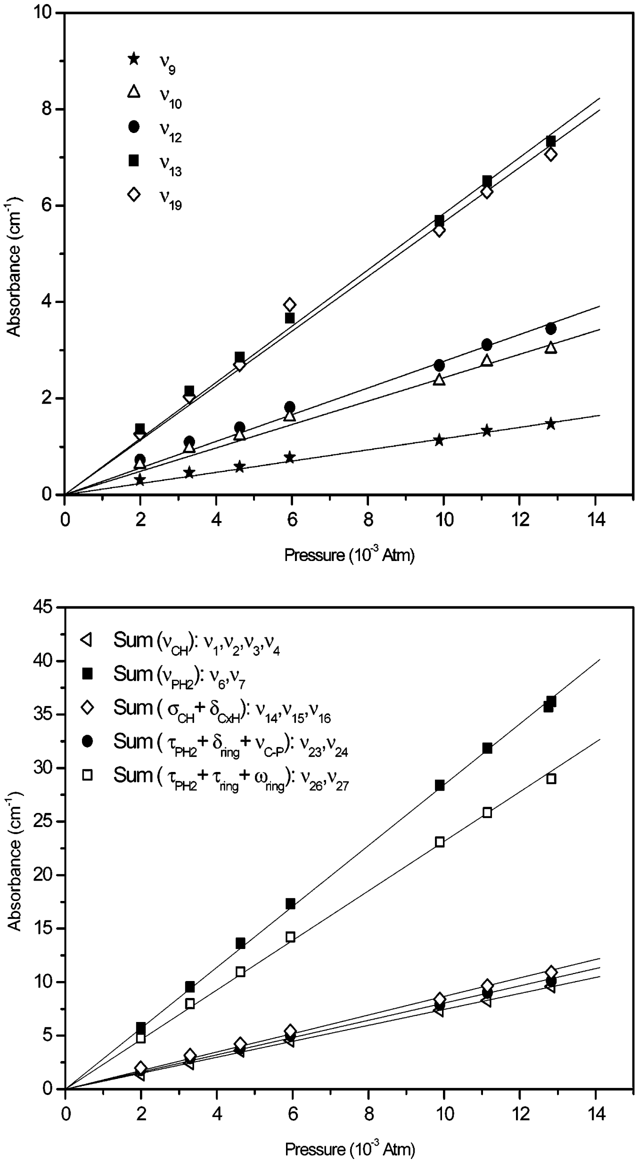


Figure 2. (a) Variation of the integrated absorbance of isolated bands as a function of the pressure of cyclopentadienylphosphine. (b) Variation of the integrated absorbance of the overlapping vibration modes of the cyclopentadienylphosphine according to the pressure.

The present development is named VMWCI (variational multiwindows configuration of interaction). This algorithm[18] builds the vibrational Hamiltonian over several spectral areas, each called a "window". The goal here is to describe a reduced number of vibrational states in a window, in the same way as if the whole spectrum were considered. Consequently, neither truncation of the CI process nor loss of information occurs. The method is described below.

The vibrational solutions are as near of the exact solutions as the (N) vibrational configurations $\{|\nu_1,\nu_2,...,\nu_{n\nu\mathrm{ib}}\rangle_i,\ 1 \leq i \leq N\}$ basis useful for the resolution of the anharmonic vibrational Schrödinger equation tends toward infinity. As this basis is always finite and limited to $N_\mathrm{g} < N$, the problem lies in the choice of configuration space to diagonalize. This choice (N_g) has an influence on the precision of the variational method and on the speed of convergence. Consequently, the best N_s-dimensional space belonging to symmetry Ω is generally built iteratively.[18−20] If one starts at order $\gamma = 0$, from an initial space selected by the user (which includes one or more studied vibrational states), $S_0 = \{|\nu_1,\nu_2,...,\nu_{n\nu\mathrm{ib}}\rangle_i^{\gamma=0},\ 1 \leq i \leq N_0\}^\Omega$. The configuration space S_1, in direct interaction with S_0, is obtained at order $\gamma = 1$ by applying an operator $\hat{T}$ to S_0, generating vibrational excitations

$$\hat{T}S_0 = S_1$$

where $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$, $\hat{T}_x$ generating single, double, triple, or quadruple excitations for $x = 1-4$, respectively. Further applications of $\hat{T}$ lead to the definition of indirect configuration spaces $\gamma > 1$: $\hat{T}S_\gamma = S_\gamma + 1$. Note that the way $\hat{T}$ acts on a given S_γ space means that the one interacting with it through the different terms of the vibrational force field, i.e., $\{k_{sss},k_{ssss}\}$, $\{k_{sss'},k_{ss's'},k_{sss's'},k_{ssss'}\}$, $\{k_{ss's''},k_{ss's's''}\}$, and $\{k_{ss's''s'''}\}$ for $\hat{T}_1,\hat{T}_2,\hat{T}_3$, and $\hat{T}_4$, respectively, must be generated for each configuration of S_γ , where s defines a normal vibration mode.

This topic was considered several years ago but abandoned because of variational collapse and numerous approximations.[29−31] The use of modern computational developments such as parallel algorithms now make these treatments possible. Coupling our multiwindows algorithm with a parallel SPMD (single program multiple data) approach allows us (P(arallel)_VMWCI[18]) to overcome these limitations for medium size molecular systems. In particular, for each CI matrix, the use of both MPI (message passing interface) and increased computational effort on loop optimization enables the equal distribution of tasks among processes with respect to their corresponding CPU power and workload.[19]

Once each matrix of the vibrational Hamiltonian is built, the second step deals with its diagonalization. In our approach, a classic Block−Davidson algorithm is used.[32] It is not realistic to reprise all the work in the framework of filter diagonalization, and there is significant activity in this field discussed elsewhere.[33,34] In this work, there are no major issues associated with extracting and following eigenvalues of a vibrational state as density of state is not large and we are focused in the lower part of the spectrum (3500−200 cm^{-1}).

TABLE 1: Absolute Intensity of the Strongest Isolated Vibrational Bands and the Estimated Sum Intensities for the Overlapping Vibrational Bands[a]

isolated and overlapping vibrn bands	nature of the bonds	absolute intens (cm^{-2} atm^{-1})
CH stretching bands (ν_1, ν_2, ν_3, ν_4)	overlapping	85.7 ± 3.1
PH_2 sym and asym stretching bands (ν_6, ν_7)	overlapping	327.1 ± 9.2
C═C ring stretching out-of-phase ν_9	isolated	13.4 ± 1.1
ν_{CC} ring stretching out-of-phase + σ_{CH} scissoring ν_{10}	isolated	27.9 ± 2.2
ν_{CC} ring stretching in-phase + δ_{C_x}H bending ν_{12}	isolated	31.8 ± 2.6
ρ_{CH} ring rocking ν_{13}	isolated	67.0 ± 2.1
σ_{CH} ring scissoring + δ_{CxH} bending (ν_{14}, ν_{15}, ν_{16})	overlapping	99.6 ± 3.4
τ_{CH} ring twisting ν_{19}	isolated	65.0 ± 3.9
τ_{PH_2} twisting + ring deformation in-plane + ν_{P-C} stretching (ν_{23}, ν_{24})	overlapping	92.6 ± 2.9
τ_{CH} ring twisting + ω_{CH} ring wagging + τ_{PH_2} twisting (ν_{26}, ν_{27})	overlapping	266.3 ± 5.9

[a] Abbreviations used: ν = stretching; δ = in-plane bending; σ = scissoring; τ = twisting; γ = out-of-plane bending; ω = wagging; ρ = rocking.

TABLE 2: Calculated Free Energies Including Zero Point Energy (*G*, ua) and Relative Free Energies (Δ*G*, kJ mol^{-1}) Obtained at Both B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ Levels of Theory[a]

	G (ua)			
	conformer A	conformer B	Δ*G* (kJ mol^{-1})	% A:% B
B3LYP/6-31+G(d,p)	−535.964 287	−535.964 772	1.3	37:63
B3LYP/cc-pVTZ	−536.050 593	−536.050 796	0.52	45:55

[a] Molar fractions in % of each conformer are estimated by assuming Boltzmann type distribution and using the relative free energies.

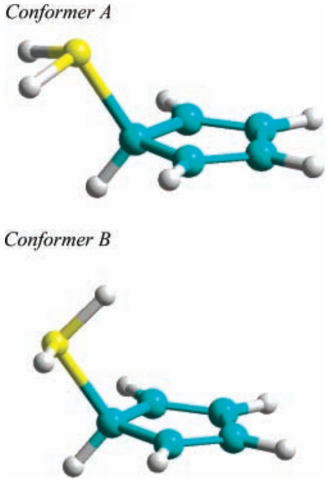


Figure 3. Two A and B stable conformers of cyclopentadienylphosphine. The PH_2 group is rotated approximately 120° between the two forms.

Finally, in the present case, variational anharmonic treatments were carried out with the P_Anhar_v1.1 Parallel software.[20] $\gamma = 2$ for 21 windows, including the two or three energetically closer fundamental vibrational states (3500−200 cm^{-1}), distributed on a spectral range including the experimentally studied one, were used on a 10-processor system to carry out the anharmonic calculations reported in this study. About 50 000 functions/matrix were diagonalized to give the required eigenvalues and eigenvectors in the energy range analyzed. Results are reported in Tables 3−6.

Results

B3LYP/cc-pVTZ and B3LYP/6-31+G(d,p) calculations both confirm the existence of two stable conformers[14] of cyclopentadienylphosphine which correspond to different orientations of the phosphino group as shown in Figure 3. All calculations indicate that conformer B (C_1) is more stable than conformer A (C_s), possibly stabilized by an internal hydrogen-bond interaction between a C═C double bond of the ring and the hydrogen atoms of the phosphino group ($d_{H-C}(B) = 2.960$ and 2.903 Å vs $d_{H-C}(A) = 3.115$ Å). The energy gap (including zero point energy corrections) between the two conformers is found to be 1.3 and 0.5 kJ mol^{-1} at both the B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ levels of theory, respectively (see Table 2).

Harmonic and anharmonic vibrational frequencies of cyclopentadienylphosphine have been systematically calculated at each level of theory. Infrared intensities (I_{IR}) of CpP for both A and B isomers were also calculated.

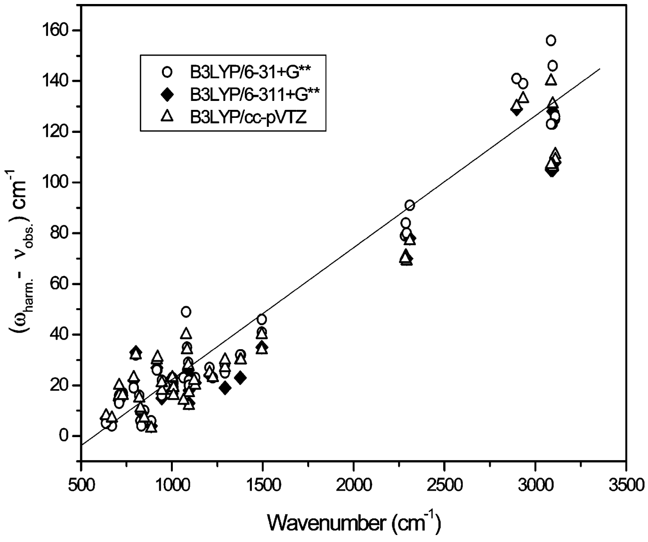


Figure 4. Obtained frequency deviation from the experimental value at B3LYP harmonic calculations with 6-31+G(d,p), 6-311+G(d,p), and cc-pVTZ basis sets.

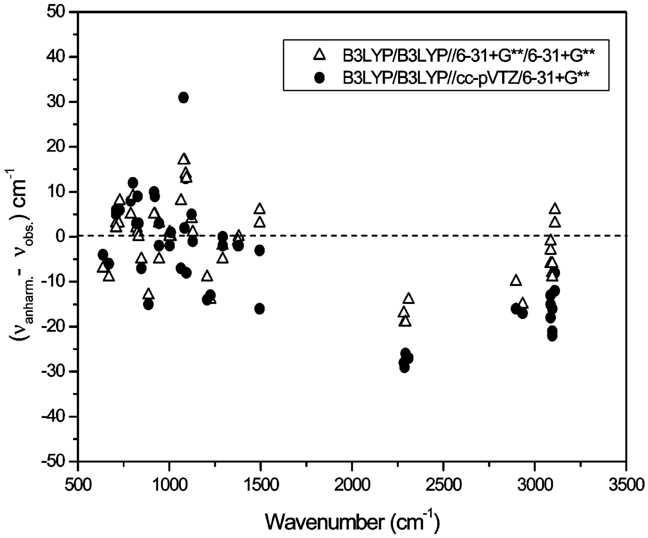


Figure 5. Obtained frequency deviation from the experimental value at B3LYP anharmonic calculations with 6-31+G(d,p)//6-31+G(d,p), 6-311+G(d,p)//6-311+G(d,p) cc-pVTZ//6-31+G(d,p), and cc-pVTZ//6-311+G(d,p) basis sets.

As expected, using a harmonic approximation overestimates the observed frequencies, in particular those at high frequency, namely the CH stretching vibrations. Figure 4 clearly indicates that the precision of the harmonic calculations depends on an adequate choice of basis set. Indeed, the use of the B3LYP/6-31+G(d,p) level of theory predicts observed values with a large root-mean-square deviation of 67 cm^{-1} for both rotamers A and B. The extension of the basis set from a valence double-ζ 6-31+G(d,p) to a valence triple-ζ 6-311+G(d,p) has some influence, reducing the root-mean-square deviation to 60 cm^{-1}. As we did not notice a significant difference between calculations obtained at B3LYP/6-311+G(d,p) and B3LYP/cc-pVTZ basis sets, only cc-pVTZ is used in this work.

As shown in Figure 5, all the anharmonic vibration modes are predicted with an absolute difference smaller than 30 cm^{-1} relative to those obtained experimentally. The maximum difference is observed for both PH_2 symmetric and antisymmetric

TABLE 3: Observed and Calculated Vibrational Harmonic, ω, and Anharmonic, ν, Frequencies (cm^{-1}) and Infrared Intensities, I_{IR} (km/mol), of Conformer A of CpP

		$2\zeta^{b}$			$3\zeta^{b}$			
no.	descriptn[a]	ω	ν	I_{IR}	ω	ν	I_{IR}	obsd[c] ν
ν_1	$\nu_{\text{C-H ring}}$	3242	3080	6	3226	3073	6	3086
ν_2	$\nu_{\text{C-H ring}}$	3235	3113	14	3219	3098	12	3110
ν_3	$\nu_{\text{C-H ring}}$	3219	3088	9	3203	3074	8	3096
ν_4	$\nu_{\text{C-H ring}}$	3209	3083	3	3193	3068	3	3086
ν_5	ν_{C_x-H}	3072	2918	2	3066	2916	2	2933
ν_6	$\nu_{\text{as}-PH_2}$	2371	2268	94	2358	2258	76	2287
ν_7	$\nu_{\text{s}-PH_2}$	2362	2266	122	2353	2255	91	2283
ν_8	$\nu_{\text{s-C=C ring}}$	1629	1592	0	1625	1589	1	[-]
ν_9	$\nu_{\text{as-C=C ring}}$	1536	1498	5	1529	1479	4	1495
ν_{10}	$\nu_{\text{as-CC ring}} + \sigma_{\text{ring}}$	1412	1380	4	1410	1378	4	1380
ν_{11}	$\nu_{\text{as-CC ring}} + \rho_{\text{ring}}$	1320	1290	1	1322	1292	1	1292
ν_{12}	$\nu_{\text{s-CC ring}} + \delta_{C_x-H}$	1248	1211	3	1248	1212	4	1225
ν_{13}	$\rho_{\text{C-H}}$	1144	1126	2	1144	1127	1	1122
ν_{14}	$\sigma_{\text{C-H}}$	1119	1101	5	1118	1086	4	1084
ν_{15}	$\sigma_{\text{C-H}}$	1087	1072	16	1078	1057	13	1064
ν_{16}	$\delta_{C_xH\text{ bending}}$	1128	1096	25	1119	1110	26	1079
ν_{17}	γ_{ring}	1030	1009	2	1028	1010	2	1009
ν_{18}	$\delta_{\text{ring}} + \delta_{C_x-H}$	1028	1009	2	1025	1010	1	1009
ν_{19}	τ_{ring}	966	947	10	965	947	6	944
ν_{20}	$\tau_{\text{ring}} + \delta_{PH_2}$	956	933	0	963	940	0	[-]
ν_{21}	σ_{PH_2}	948	927	1	953	931	5	922
ν_{22}	ω_{PH_2}	85	843	8	855	841	7	848
ν_{23}	$\tau_{PH_2} + \delta_{\text{ring}}$	837	823	17	836	824	15	821
ν_{24}	$\nu_{\text{C-P}} + \delta_{\text{ring}}$	833	828	4	838	836	3	827
ν_{25}	τ_{ring}	815	802	1	820	807	0	[-]
ν_{26}	τ_{ring}	746	737	112	745	735	100	729
ν_{27}	$\omega_{\text{ring}} + \tau_{PH_2}$	726	713	2	730	716	2	710
ν_{28}	$\nu_{\text{C-P}}$	674	661	23	677	664	17	670
ν_{29}	γ_{ring}	560	552	0	567	558	0	
ν_{30}	$\nu_{\text{C-P}} + \gamma_{\text{ring}}$	412	402	11	416	406	12	
ν_{31}	$\delta_{\text{C-P}}$	235	210	2	235	209	1	
ν_{32}	$\delta_{\text{C-P}}$	189	176	1	190	176	1	
ν_{33}	ρ_{PH_2}	125	124	1	126	125	1	
	rmsd[d]	67.6	9.1		60.7	13.9		

[a] Abbreviations: ν = stretching; δ = in-plane bending; σ = scissoring; τ = torsion; γ = out-of-plane bending; ω = wagging; ρ = rocking. [b] 2ζ, B3LYP/B3LYP//6-31+G(d,p)/6-31+G(d,p); 3ζ, B3LYP/B3LYP//cc-pVTZ/6-31+G(d,p). [c] Symbol "[-]" indicates frequencies of very weak bands not observed in the spectrum. [d] Root-mean-square deviation (cm^{-1}) obtained at different level of calculation.

stretching modes. The anharmonic approach leads to predicted values both under and over the observed ones depending on the vibration mode and level of theory used. At the same time, the root-mean-square deviation is now reduced 4- or 5-fold. Similar rms values are obtained at both B3LYP/B3LYP//6-31+G(d,p)/6-31+G(d,p) and B3LYP/B3LYP///cc-pVTZ/6-31+G(d,p) levels of calculations, i.e., 8.5 and 9.1 cm^{-1} and 12.1 and 13.9 cm^{-1} for isomers B and A, respectively. Anharmonic results are reported in Tables 3 and 4, where they are compared to our observed fundamental frequencies.

The CH stretching ring vibrations ($\nu_1-\nu_4$) are expected around 3090 cm^{-1}. These vibrational modes appear in the spectrum as overlapping absorption bands, with three maxima related to frequencies at 3110, 3096, and 3086 cm^{-1}. Results obtained are all in good agreement with the observed data since the mean-average-deviation is globally less than 0.7%. The ν_5 mode is more sensitive to the level of calculation, being ν_{C_X-H}, where H is in the position α to the PH_2 chemical group. This mode gives a very weak absorption band and is unsurprisingly sensitive to rotamer effects. Corresponding frequencies are assigned to 2930 and 2897 cm^{-1} for isomers A and B, respectively, with an observed gap of 33 cm^{-1} when calculations predict this difference to be 31 and 35 cm^{-1} at both the 6-31+G-(d,p)/6-31+G(d,p) and cc-pVTZ/6-31+G(d,p) levels, respectively.

Both asymmetric and symmetric PH_2 stretching vibrations appear toward 2290 cm^{-1}. All anharmonic calculations underestimate these two vibrations. Whatever the level of calculations employed (Figure 5), frequencies associated with the fullest displacements of the phosphorus atom are systematically less precise (1% in order of magnitude) than the other ones. The stretching ν_{X-H} mode description including a V−A atom (X = P or As) seems to be more problematic. Indeed, whatever the basis set or correlation method employed, this phenomenon is always observed as shown by Bégué et al.[35] in two recent studies on vinylic systems $H_2C{=}CH{-}XH_2$. Nevertheless, the present method allows the assignation of these two intense modes. Isomer B absorbs at higher frequencies, i.e., 2309 and 2293 cm^{-1} ($\Delta\nu = 16$ cm^{-1}), which are predicted at 2295 and 2274 cm^{-1} ($\Delta\nu = 21$ cm^{-1}) at the B3LYP/B3LYP//6-31+G-(d,p)/6-31+G(d,p) level of calculation. Strong interactions with $\nu_{C=C}$ modes are significant in this case. In the same manner, the bands observed at 2287 and 2283 cm^{-1} ($\Delta\nu = 6$ cm^{-1}) are attributed to isomer A and are predicted to absorb at 2268 and 2266 cm^{-1} ($\Delta\nu = 2$ cm^{-1}). At all levels, the observed intensities of these bands are in very good agreement with our calculations and unambiguously permit their assignment.

For the ring $\nu_{C=C}$ frequencies, the out-of-phase stretching vibration is not observed for the two rotamers, in agreement with our calculations which predict quasi-zero intensity for this mode. With respect to the calculations, the weak band observed at 1495 cm^{-1} is attributed to the in-phase stretching C=C vibration for the two conformers. By all methods, this vibration is predicted to have an intensity of less than 0.2% by all methods.

The simple carbon−carbon bond ring stretching modes, notated ν_{10}, ν_{11}, and ν_{12}, have moderate-to-weak intensities. Both ν_{10} and ν_{11} modes, which correspond to the out-of-phase

TABLE 4: Observed and Calculated Vibrational Harmonic, ω, and Anharmonic, ν, Frequencies (cm^{-1}) and Infrared Intensities, I_{IR} (km/mol), of Conformer B of the CpP

		$2\zeta^b$			$3\zeta^b$			
no.	descriptn[a]	ω	ν	I_{IR}	ω	ν	I_{IR}	obsd[c] ν
ν_1	$\nu_{C-H\ ring}$	3242	3087	5	3227	3080	5	3096
ν_2	$\nu_{C-H\ ring}$	3236	3116	12	3221	3102	11	3110
ν_3	$\nu_{C-H\ ring}$	3219	3090	10	3202	3075	9	3096
ν_4	$\nu_{C-H\ ring}$	3209	3085	4	3193	3071	4	3086
ν_5	ν_{C_x-H}	3038	2887	2	3027	2881	2	2897
ν_6	ν_{as-PH_2}	2400	2295	62	2386	2282	50	2309
ν_7	ν_{s-PH_2}	2373	2274	92	2362	2267	71	2293
ν_8	$\nu_{s-C=C\ ring}$	1631	1592	0	1628	1591	1	[-]
ν_9	$\nu_{as-C=C\ ring}$	1541	1501	10	1535	1492	7	1495
ν_{10}	$\nu_{as-CC\ ring} + \sigma_{ring}$	1408	1375	4	1406	1374	4	1376
ν_{11}	$\nu_{as-CC\ ring} + \rho_{ring}$	1317	1287	1	1319	1290	1	1292
ν_{12}	$\nu_{s-CC\ ring} + \delta_{C_x-H}$	1235	1199	5	1233	1194	5	1208
ν_{13}	ρ_{C-H}	1152	1130	10	1149	1128	8	1129
ν_{14}	σ_{C-H}	1119	1104	4	1118	1103	4	1090
ν_{15}	σ_{C-H}	1116	1107	14	1111	1086	13	1094
ν_{16}	δ_{C_xH} bending	1114	1107	14	1106	1086	16	1094
ν_{17}	γ_{ring}	1024	1002	3	1025	1002	3	1002
ν_{18}	$\delta_{ring} + \delta_{C_x-H}$	1025	1003	3	1020	1000	2	1002
ν_{19}	τ_{ring}	960	939	16	962	942	5	944
ν_{20}	$\tau_{ring} + \delta_{PH_2}$	952	929	0	959	938	2	[-]
ν_{21}	σ_{PH_2}	944	923	10	948	928	17	918
ν_{22}	ω_{PH_2}	892	873	8	889	871	7	886
ν_{23}	$\tau_{PH_2} + \delta_{ring}$	833	810	24	833	813	20	801
ν_{24}	$\nu_{C-P} + \delta_{ring}$	836	832	8	842	835	3	832
ν_{25}	τ_{ring}	809	795	3	813	798	6	790
ν_{26}	τ_{ring}	741	727	107	742	730	87	724
ν_{27}	$\omega_{ring} + \tau_{PH_2}$	723	712	6	726	715	7	710
ν_{28}	ν_{C-P}	643	631	9	646	634	7	638
ν_{29}	γ_{ring}	557	548	0	563	555	0	
ν_{30}	$\nu_{C-P} + \gamma_{ring}$	418	417	9	421	416	9	
ν_{31}	δ_{C-P}	226	219	0	227	221	0	
ν_{32}	δ_{C-P}	207	186	3	205	183	2	
ν_{33}	ρ_{PH_2}	135	132	0	136	134	0	
	rmsd[d]	65.8	8.5		58.7	12.1		

[a] Abbreviations: ν = stretching; δ = in-plane bending; σ = scissoring; τ = torsion; γ = out-of-plane bending; ω = wagging; ρ = rocking. [b] 2ζ, B3LYP/B3LYP//6-31+G(d,p)/6-31+G(d,p); 3ζ, B3LYP/B3LYP//cc-pVTZ/6-31+G(d,p). [c] Symbol [-] indicates frequencies of very weak bands not observed in the spectrum. [d] Root-mean-square deviation (cm^{-1}) obtained at different level of calculation.

stretching, are not sensitive to rotamer effects. The two observed bands located at 1380 and 1376 cm^{-1} and calculated at 1380 and 1375 cm^{-1} correspond to the ν_{10} modes of isomers A and B, respectively. For the ν_{11} modes, the same frequency at 1292 cm^{-1} is assigned to both A and B rotamers. Conversely, the two observed ν_{12} in-phase stretching modes are spaced 17 cm^{-1} apart (obsd, 1225 and 1208 cm^{-1}; calcd, 1211 and 1199 cm^{-1}, respectively). For all CC stretching modes, our calculations confirm that the bands associated with the most stable conformer (B) appear at frequencies lower than those associated with conformer A.

The CH rocking ν_{13} mode of both rotamers absorb at 1129 and 1122 cm^{-1} and are very well predicted by our calculations: 1130 and 1126 cm^{-1}. Moreover, the calculated relative intensities ratio of 5 in favor of the B rotamer is in perfect agreement with the observed data.

Despite the use of anharmonic calculations, some experimental assignments are still difficult. For example, in the 1110−1060 cm^{-1} area, which corresponds to the ν_{14}, ν_{15}, and ν_{16} absorption bands, doubts persist because of various overlaps observed in the IR spectra which are sensitive to the conformational effect. Moreover, large discrepancies are found for the calculations of these bands when they are developed with the use of double- and triple-ζ basis sets. A mathematical issue also arises because the modes are strongly coupled, even through quartic force constants.

ν_{17}, ν_{18}, and ν_{19}, namely, the γ_{ring}, δ_{ring}, and τ_{ring}, vibration modes, are found to be in perfect agreement in intensity and frequency with the predicted values at all levels.

In the investigated spectral area between 600 and 900 cm^{-1}, all modes have medium to weak intensities except for the τ_{ring} ν_{26} mode, which absorbs with a very strong band. The band assignments in this region are complicated because of both a strong density of vibrational states and numerous bands overlapping. ν_{22}, ν_{23}, and ν_{28} are sensitive to isomer effects. The ν_{21} (PH_2 scissoring), ν_{22} (PH_2 wagging), ν_{23} (PH_2 twisting), and ν_{24} (C−P stretching) can be affected by deuteration of the PH_2 group of cyclopentadienylphosphine. Calculated harmonic and anharmonic frequencies of the $C_5H_5PD_2$ isotopologue are reported in Table 5 and are used to help with the assignment of bands in this region. These data confirm without any doubt the initial, predicted, assignments.

In the region below 600 cm^{-1}, not covered by our experimental analysis, calculations predict bands centered at (552, 548 cm^{-1}), (417, 402 cm^{-1}), (219, 210 cm^{-1}), (186, 176 cm^{-1}), and (132, 124 cm^{-1}) representing the out-of-plane ring deformation ν_{29}, the C−P stretching ν_{30}, the C−P deformation ν_{31} and ν_{32}, and the PH_2 rocking ν_{33}. Numerous interactions have been identified in this area where there is a strong density of states. All the modes are expected to absorb with very weak intensities except for ν_{30}.

In Table 6 the B3LYP/B3LYP//6-31+G(d,p)/6-31+G(d,p) frequencies of some selected overtone and combination bands in agreement with the experimental investigation are listed. The intensities of these bands are all very low compared to the fundamental absorption bands. It is therefore very difficult to make an unambiguous assignment. All the observed overtone bands, except $2\nu_{15}$, are unambiguously assigned. The 1800−

TABLE 5: B3LYP/6-31+G(d,p) Calculated Vibrational Harmonic, ω, and Anharmonic, ν, Frequencies (cm^{-1}) and Infrared Intensities, I_{IR} (km/mol), of $C_5H_5PD_2$ Isotopologue

		conformer A			conformer B		
no.	descriptn[a]	ω	I_{IR}	ν	ω	I_{IR}	ν
ν_1	$\nu_{C-H\ ring}$	3241	6	3078	3242	5	3085
ν_2	$\nu_{C-H\ ring}$	3235	14	3112	3236	12	3116
ν_3	$\nu_{C-H\ ring}$	3219	9	3088	3219	10	3090
ν_4	$\nu_{C-H\ ring}$	3209	3	3083	3209	4	3085
ν_5	ν_{C_x-H}	3072	2	2922	3037	2	2887
ν_6	ν_{as-PD_2}	1705	49	1652	1725	34	1671
ν_7	ν_{s-PD_2}	1695	66	1646	1703	47	1653
ν_8	$\nu_{s-C=C\ ring}$	1628	0	1590	1630	0	1596
ν_9	$\nu_{as-C=C\ ring}$	1536	5	1498	1541	11	1501
ν_{10}	$\nu_{as-CC\ ring} + \sigma_{ring}$	1412	3	1380	1408	4	1376
ν_{11}	$\nu_{as-CC\ ring} + \rho_{ring}$	1319	0	1289	1316	1	1287
ν_{12}	$\nu_{s-CC\ ring} + \delta_{C_x-H}$	1245	3	1209	1231	5	1195
ν_{13}	ρ_{C-H}	1141	1	1123	1145	4	1126
ν_{14}	σ_{C-H}	1119	5	1100	1117	5	1100
ν_{15}	σ_{C-H}	1078	15	1052	1104	13	1079
ν_{16}	δ_{C_xH} bending	1028	1	1008	1024	4	1004
ν_{17}	γ_{ring}	1021	5	996	1021	5	1000
ν_{18}	$\delta_{ring} + \delta_{C_x-H}$	956	10	938	958	14	936
ν_{19}	τ_{ring}	955	0	932	951	1	931
ν_{20}	$\tau_{ring} + \delta_{PH_2}$	944	7	922	942	13	922
ν_{21}	σ_{PD_2}	833	2	826	836	1	828
ν_{22}	ω_{PD_2}	819	20	809	822	46	816
ν_{23}	$\tau_{PD_2} + \delta_{ring}$	817	4	805	815	5	803
ν_{24}	$\nu_{C-P} + \delta_{ring}$	806	18	789	800	13	786
ν_{25}	τ_{ring}	727	3	714	725	3	714
ν_{26}	τ_{ring}	697	98	681	696	73	684
ν_{27}	$\omega_{ring} + \tau_{PD_2}$	629	5	621	628	16	616
ν_{28}	ν_{C-P}	566	9	562	556	3	549
ν_{29}	γ_{ring}	546	0	540	541	1	534
ν_{30}	$\nu_{C-P} + \gamma_{ring}$	410	10	403	413	8	406
ν_{31}	δ_{C-P}	216	0	211	218	0	217
ν_{32}	δ_{C-P}	145	1	131	158	1	148
ν_{33}	ρ_{PD_2}	123	1	123	127	1	124

[a] Abbreviations used: ν = stretching; δ = in-plane bending; σ = scissoring; τ = twisting; γ = out-of-plane bending; ω = wagging; ρ = rocking.

TABLE 6: Overtone and Combinations Bands of the Conformers A and B of the Cyclopentadienylphosphine Appearing in the Investigated Spectral Region (600−3500 cm^{-1})[a]

	calcd		
obsd	conformer A	conformer B	assignt
1434		1439	$\nu_{26} + \nu_{27}$
1632	1632		$2\nu_{23}$
1637	1650	1640	$\nu_{23} + \nu_{24}$
1642		1652	$\nu_{19} + \nu_{27}$
1646		1659	$\nu_{26} + \nu_{19}$
1641		1669	$\nu_{21} + \nu_{26}$
	1664		$\nu_{22} + \nu_{23}$
		1820	$\nu_{16} + \nu_{27}$
		1821	$\nu_{15} + \nu_{26}$
1833	1830	1829	$\nu_{16} + \nu_{26}$
1840	1837	1838	$\nu_{14} + \nu_{26}$
		1838	$2\nu_{21}$
2114	2116	2105	$\nu_{10} + \nu_{26}$
2121		2136	$\nu_{12} + \nu_{19}$
	2140		$2\nu_{15}$
2174		2174	$3n_{26}$
2215	2233	2226	$\nu_9 + \nu_{26}$
2223		2237	$\nu_{13} + \nu_{15}$ or $\nu_{13} + \nu_{16}$
2488	2484		$2\nu_{24}$
2499		2496	$2\nu_{24}$
3042		3022	$\nu_6 + \nu_{26}$

[a] The assignment are made with respect to theoretical calculations.

2300 cm^{-1} spectral window is particularly interesting as it provides extra information about ν_{14} and ν_{15} and further overall information about ν_{16}, whose assignment remains difficult. In the light of these new calculations, several solutions can be proposed to assign the observed peaks and the corresponding results are given in Table 6. As for the $C_5H_5PD_2$ isotopologue, these assignments are complementary to those performed on the fundamental modes.

Conclusion

Both A and B conformers of the cyclopentadienylphosphine and one of its isotopologues $C_5H_5PD_2$ were experimentally characterized through the analysis of their gas-phase infrared spectra in the mid-infrared region from 3500 to 500 cm^{-1}. The assignments are in agreement with the predictions of anharmonic DFT calculations carried out at both B3LYP/B3LYP//6-31+G-(d,p)/6-31+G(d,p) and B3LYP//cc-pvTZ/6-31+G(d,p) levels of theory. On the basis of these predictions, all the bands observed are unambiguously assigned to fundamental, overtone, and combination bands for the two conformers. Moreover, the accuracy of the calculated spectra opens future prospects to analyze the region below 600 cm^{-1}, not covered here by the experimental analysis. This study also opens the way for studying unsymmetrical systems where fluxional phenomena are present. However, the increase in number of conformers quickly limits what can be achieved by the variational approach. In this study, 10 parallel processors were required to perform the calculations, which is the upper acceptable limit for using whole QFF to deal with larger systems. It is also noticeable that the force field accuracy is linked to the number and quality of calculations used to determine it. Nevertheless, solutions to overcome current limits exist, such as mixed variational methods, mixed QFF (method1/method2//basis1/basis2), fully parallelized developments, and the use of symmetry. Hardware can also be improved by better utilization of memory. Taking into account some of these solutions, we have shown that it is possible to get whole data for the mid-IR, i.e. 200−3500 cm^{-1}, spectral area (10 500 cubic and quartic force constants in this study) at lower cost with satisfactory accuracy of less than 1% (0.46% for both conformers studied here).

Acknowledgment. We thank the "Centre Informatique National de l'Enseignement Supérieur" (CINES) for financial support to this work. J.-C.G. thanks the CNES for financial support. We thank Robert Noble-Eddy and Dr. Sarah Masters for helpul English suggestions.

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