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***Ab Initio* Calculation of Nuclear Magnetic Resonance Chemical Shift Anisotropy Tensors**

I. Influence of Basis Set on the Calculation of ^{31}P Chemical Shifts

Todd M. Alam

Prepared by

Sandia National Laboratories

Albuquerque, New Mexico 87185 and Livermore, California 94550

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***Ab Initio* Calculation of Nuclear Magnetic Resonance
Chemical Shift Anisotropy Tensors
I. Influence of Basis Set on the Calculation of ³¹P Chemical Shifts**

Todd M. Alam*

Department of Aging and Reliability, Bulk Materials
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-1407

Abstract

The influence of changes in the contracted Gaussian basis set used for *ab initio* calculations of nuclear magnetic resonance (NMR) phosphorous chemical shift anisotropy (CSA) tensors was investigated. The isotropic chemical shift and chemical shift anisotropy were found to converge with increasing complexity of the basis set at the Hartree-Fock (HF) level. The addition of d polarization function on the phosphorous nuclei was found to have a major impact of the calculated chemical shift, but diminished with increasing number of polarization functions. At least 2 d polarization functions are required for accurate calculations of the isotropic phosphorous chemical shift. The introduction of density functional theory (DFT) techniques through the use of hybrid B3LYP methods for the calculation of the phosphorous chemical shift tensor resulted in a poorer estimation of the NMR values, even though DFT techniques result in improved energy and force constant calculations. The convergence of the NMR parameters with increasing basis set complexity was also observed for the DFT calculations, but produced results with consistent large deviations from experiment. The use of a HF 6-311++G(2d,2p) basis set represents a good compromise between accuracy of the simulation and the complexity of the calculation for future *ab initio* calculations of ³¹P NMR parameters in larger complexes.

* Author to whom correspondence should be addressed: tmalam@sandia.gov

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***Ab Initio* Calculation of Nuclear Magnetic Resonance
Chemical Shift Anisotropy Tensors
I. Influence of Basis Set on the Calculation of ³¹P Chemical Shifts**

Introduction

The ability to calculate and correlate material properties directly with molecular structure remains an important objective in material science. The correlation of the chemical shift or magnetic shielding in nuclear magnetic resonance (NMR) spectroscopy with bond angles, bond length, coordination number and neighboring atom interactions has seen a long and rich history for a wide variety of applications. Recently there has been renewed interest in development of these NMR-structural correlations for amorphous materials, including polymers[1], composites and mineral oxide[2,3] and metallic glasses.[4] Due to the difficulty of using standard scattering techniques to probe local and medium range order in these amorphous systems, NMR has become a powerful tool to address specific structural questions.

The prediction of NMR chemical shifts from quantum mechanical methods has undergone major advancements within the last decade, including solutions to the gauge dependence of the chemical shift [5], improvements in the basis sets and the extension to higher levels of theory including density functional techniques.[6,7] Also, advances in computational speed have relaxed many of the restrictions involved in previous investigations of large sized molecular clusters. For the quantum mechanical calculations of NMR chemical shifts different degrees of approximations are utilized in order to make the problem computationally tractable. The choice of basis set used in *ab initio* NMR shielding calculation has been shown to greatly influence the predicted NMR chemical shift results for both proton and carbon nuclei. Initial *ab initio* calculations for the phosphorous nuclei (³¹P) also reveal large basis set effects, and in general heavy nuclei require more complex basis sets than calculations involving first row nuclei. An additional complication for inorganic amorphous materials is that they form three-dimensional networks compared to the typical one dimensional chains for synthetic organic polymers, leading to a larger number of structural variables that can influence the observed NMR chemical shift. It therefore becomes important to separate and distinguish these effects while providing the most accurate predictions possible.

In this report *ab initio* calculations of the ³¹P chemical shift anisotropy (CSA) tensors, at different levels of basis set complexity, for several simple phosphorous containing compounds are presented. This allows an optimal basis set, plus the influence of basis set choice, for future calculations to be addressed.

Theoretical Background

A. Definition of the NMR Shielding Tensor

The NMR chemical shift tensor is given by the second derivative of the electronic energy, E , with respect to the external magnetic field \mathbf{B} and the nuclear magnetic moment m_N

$$\sigma_{ij}^N = \left. \frac{d^2 E}{dm_{Nj} dB_j} \right|_{B, m_N=0} \quad (1)$$

Since the atomic orbitals do not depend on the nuclear magnetic moments m_N the second derivative in Eqn. (1) can be evaluated by a step-wise differentiation,

$$\frac{dE}{dm_{Nj}} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}} \quad (2)$$

where $D_{\mu\nu}$ are the elements of the one-particle density matrix and $h_{\mu\nu}$ are the one-electron portions of the Hamiltonian. Differentiation of Eqn. (2) with respect to the magnetic field gives

$$\sigma_{ij}^N = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}} \quad (3)$$

The evaluation of the shielding tensor σ using Eqn. (3) requires determination of the density matrix and the perturbed density, but not the perturbed density with respect to the magnetic moments.

The chemical shielding tensor is commonly referred to as the chemical shift anisotropy (CSA) tensor due to the possession of second rank properties. The measurement or calculation of the diagonal components (σ_{11} , σ_{22} , σ_{33}) in the principle axis system (PAS) allows the complete description of the CSA tensor. The isotropic or traceless portion of the CSA tensor is given by

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (4)$$

Where the order of the principle components are defined using

$$|\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}| \quad (5)$$

If both the chemical shift and the shielding tensors elements are described in the unitless parts per millions (ppm), they are described by the ratio of the chemical shift frequency ω^{cs} , and the Larmor frequency of the unshielded nucleus ω_0

$$\frac{\omega_{ii}^{\text{cs}}}{\omega_0} \times 10^6 = -\sigma_{ii} = \delta_{ii} \quad (6)$$

If the principal components of the CSA tensor are not available or have not been determined, the tensor can also be described by two distinct parameters. One is referred to as the chemical shift anisotropy ($\Delta\delta$),

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}) \quad (7)$$

and the second the chemical shift anisotropy asymmetry (η)

$$\eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{\text{iso}}} \quad (8)$$

The parameters in Eqn. (4-8) define how the CSA tensor will be described for the remainder of this manuscript.

B. Description of Basis Sets

In this investigation a number of contracted split-valence shell Gaussian basis sets are utilized for the NMR shielding calculations. A basic discussion of the nomenclature and construction of these basis sets is presented allowing a clear understanding of basis set effects. In

general, each molecular orbital is written as a linear combination of atomic orbitals, and can be expressed as

$$\Psi_i(r) = \sum_{\mu} c_{\mu i} \phi_{\mu}(r) \quad (9)$$

where $c_{\mu i}$ are the expansion coefficients, and ϕ_{μ} are the atomic orbitals making up the basis set. These basis functions can further be described using a linear sum of Gaussian wave functions.

$$\phi_{\mu}(r) = \sum_{k=1}^N d_{\mu,k} g_{\mu}(\alpha_{\mu,k}, r) \quad (10)$$

The Gaussian functions are of the form

$$g_{\mu}(\alpha, r) = C \exp(-\alpha_{\mu} r^2) \quad (11)$$

where the exponential α_{μ} and expansion coefficient $d_{\mu,k}$ have been determined from previous optimizations. For a minimal basis set only one ϕ for each atomic orbital is utilized in the full or partially filled valence. For example, a first row nucleus would be described by the atomic orbitals $\phi_{1s}, \phi_{2s}, \phi_{2px}, \phi_{2py}, \phi_{2pz}$. One of the earliest modifications of these Gaussian basis sets was to use two or more functions for the valence shell, while retaining a single function for the inner shell. In these case a first row nucleus would be described by the atomic orbitals

$\phi_{1s}, \phi'_{2s}, \phi''_{2s}, \phi'_{2px}, \phi''_{2px}, \phi'_{2py}, \phi''_{2py}, \phi'_{2pz}, \phi''_{2pz}$. For these split-valence basis sets Eqn. (10) must be expanded to include these additional functions.

$$\phi'_{\mu}(r) = \sum_{k=1}^{N'_2} d'_{\mu,k} g_{\mu}(\alpha'_{\mu,k}, r), \quad (12a)$$

$$\phi''_{\mu}(r) = \sum_{k=1}^{N''_2} d''_{\mu,k} g_{\mu}(\alpha''_{\mu,k}, r), \quad \dots \quad (12b)$$

Basis sets of this type include 4-31G, 5-31G and 6-31G, where 4,5, or 6 Gaussians are used to describe the single function for the inner shells, Eqn. (10), while the valence shell orbital is described by three Gaussians for the inner function $\phi'_{\mu}(r)$ and one Gaussian for the outer function $\phi''_{\mu}(r)$, Eqns. (12a, 12b). Along similar lines the valence shell can be described by three

functions $\phi_{\mu}^{\prime}, \phi_{\mu}^{\prime\prime}, \phi_{\mu}^{\prime\prime\prime}$, such as the basis set 6-311G, which is composed of 6 Gaussian functions for the inner shell and the outer three valence functions being composed of three, one and one Gaussians, respectively.

The next common basis set modification is the addition of polarization functions. This typically involves the addition of d functions to the heavy nuclei of the form

$$(x^2, y^2, z^2, xy, yz, zx) \exp(-\alpha_d r^2) \quad (13)$$

and p polarization functions to hydrogen of the form

$$(x, y, z) \exp(\alpha_p r^2) \quad (14)$$

Basis sets modified in this manner are denoted by the (md,np) nomenclature, where m and n refer to the number of d and p polarization functions. For example, the 6-311G(2d,2p) refers to the 6-311G basis set described above with the additional 2 d and 2 p polarization functions on heavy and hydrogen atoms respectively. Diffuse functions can also be added, and are similar to the form given in Eqn 11.

C. The Gauge Origin Problem

As shown in Eqn. (1) the NMR CSA tensor is given by the interaction of the electrons with the external magnetic field. The Hamiltonian that describes this interaction can be written using a vector potential A

$$\hat{H} = -\frac{e}{mc} A \cdot p + \frac{e^2}{2mc^2} A^2 \quad (15)$$

where p is the momentum. Unfortunately there is no unique choice of the vector potential A for a given static homogenous magnetic field B , giving rise to the question of ‘‘Gauge Invariance’’.

A solution to this problem was the introduction of a local gauge origin during the calculation of the NMR shielding tensor. Instead of choosing a single gauge origin to describe the entire molecule (common gauge), different gauge origins (local gauge) are assigned to each of the different Gaussians used during the construction of the wave function. The local gauge origins

can be chosen for either the molecular or atomic orbitals used. Kutzelnigg introduced the IGLO method in which the local gauge was for the molecular orbitals.[5] Problems arise for high level quantum mechanical calculations since local gauge descriptions are meaningful for very localized quantities, requiring the use of “localized molecular orbitals”. A similar difficulty results in the localized orbital/local origin (LORG) method of Hasen and Bouman.[8]

The obvious choice for the local gauge origin is the atomic orbitals, since by definition they are centered at the nucleus. This is the basis of the gauge-including molecular orbital (GIAO) method, and is the gauge for all the calculations presented here. In GIAO the calculations are not performed using a field independent basis function, but instead use basis functions that are explicitly dependent on the magnetic field,

$$\phi_{\mu}(B) = \exp\left(-\frac{i}{2c} B \times [R_{\mu} - R_G] \cdot r\right) \phi_{\mu}(0) \quad (16)$$

where a phase factor is introduced by the gauge transformation from the lab coordinate system R_G to the nuclear position R_{μ} , and $\phi_{\mu}(0)$ is the field free wave function. Thus, the GIAO basis functions already include first order effects of the magnetic field, allowing electron correlations to be introduced using well-defined analytical derivative theory.

D. Density Functional Theory (DFT) Calculations

In Hartree-Fock (HF) theory the evaluation of the exchange energy resulting from the quantum nature of electrons does not include effects of electron correlation. In density functional theory (DFT) an exchange-correlation functional is introduced that includes terms to account for both the exchange energy (E_x) and electron correlation (E_c).

$$E_{\text{exchange-correlation}} = E_x + E_c \quad (17)$$

The method utilized in these calculations depends on the type of functional used for E_x and E_c . It should be noted that HF is simply a limit of DFT theory where $E_c = 0$. We will utilize the hybrid B3LYP functionals, which are a linear combination of Becke’s three parameter method[9] using the LYP correlation functional of Lee, Yang and Parr[10,11], including both local and non-local correlations.

Modeling Details

All NMR chemical shift anisotropy (CSA) tensor calculations were performed using the parallel version of the Gaussian 94 software package.[12] The Gaussian weighting factors (d_{μ}) and exponential factors (α_{μ}) for the STO-3G, 6-31G and the 6-311G basis, along with the d and p polarization exponentials α_d and α_p were the default values and were determined from previous energy minimization investigations. Experimental distances and angles were utilized when available (PH_3 and H_3PO_4). As a comparison the equilibrium structure for PH_3 , H_3PO_4 and $\text{H}_4\text{P}_2\text{O}_7$ were also calculated at B3LYP/6-311++G(2d,2p) level of theory. For the pyrophosphate, $\text{H}_4\text{P}_2\text{O}_7$ a reliable experimental structure was not available, so only a theoretically optimized geometry was used for the NMR CSA tensor calculations. The distances and angles for these various structures are depicted in Fig. 1.

All calculations were performed on a multi-node SGI ONYX parallel processor system using three active nodes (Albuquerque Resource Center, University of New Mexico). Calculation times ranged from 2 minutes CPU time for low level NMR shielding calculations to over 6 days CPU time for DFT level optimization and NMR shielding calculation.

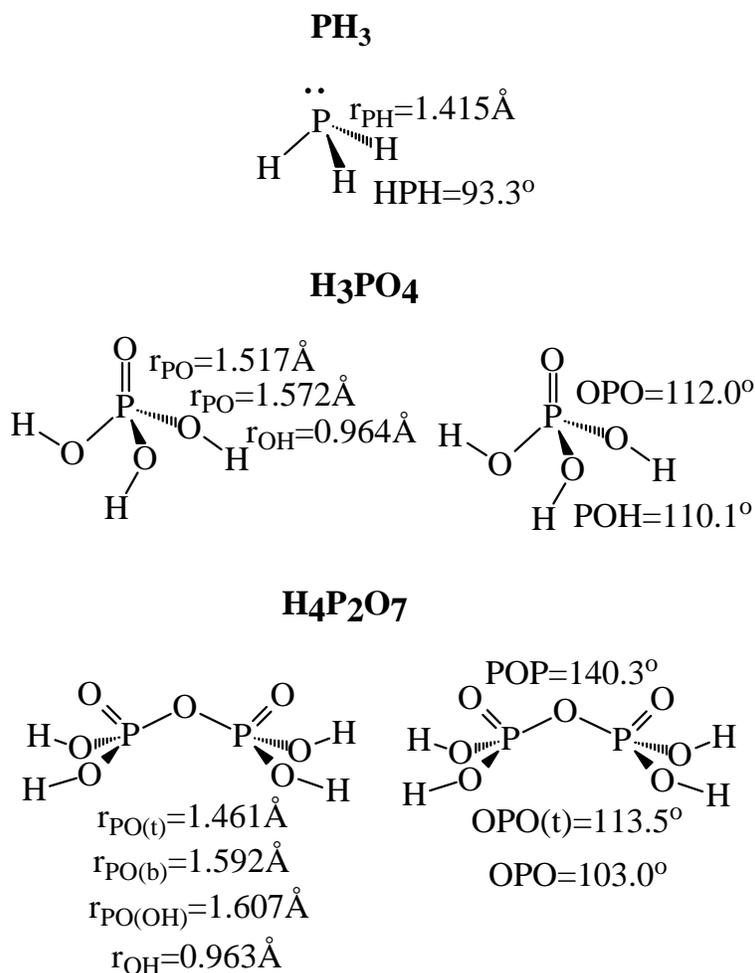


Figure 1: Compound Geometries

Results

The trace or isotropic value plus the principal components of the chemical shift tensor, along with the CSA anisotropy, $\Delta\delta$, and asymmetry parameter, η , obtained using *ab initio* HF and hybrid density functional B3LYP level calculations for PH₃ are given in Tables I and II, respectively. These calculations used the experimentally determined geometry. Structures based on geometry optimization at the B3LYP-6-311++G(2d,2p) level of theory were equivalent to the experimental values. These angles and lengths are depicted in Fig. 1

The isotropic chemical shift and principal components of the chemical shift tensor, along with the CSA anisotropy, $\Delta\delta$, and asymmetry parameter, η , using *ab initio* HF and hybrid density functional B3LYP level calculations for phosphoric acid H₃PO₄ (experimentally determined

geometry) are given in Table III and IV respectively. HF and B3LYP calculations for computationally optimized structures are given in Tables V and VI, respectively. The angles and distances utilized are depicted in Fig. 1. The isotropic chemical shift, referenced to PH_3 ($\delta = -240$ ppm) at the same level of theory is also given in Tables III, IV, V, VI

The isotropic chemical shift, principal components of the chemical shift tensor, along with the CSA anisotropy, $\Delta\delta$, and asymmetry parameter, η , using ab initio HF and hybrid density functional B3LYP level calculations for the computationally optimized structure of the $\text{H}_4\text{P}_2\text{O}_7$ cluster are given in Table VII and VIII, respectively. The angles and distances of the structure utilized are depicted in Fig. 1. The relative isotropic chemical shift referenced to both of the standards PH_3 or H_3PO_4 are given in Tables VII, VIII.

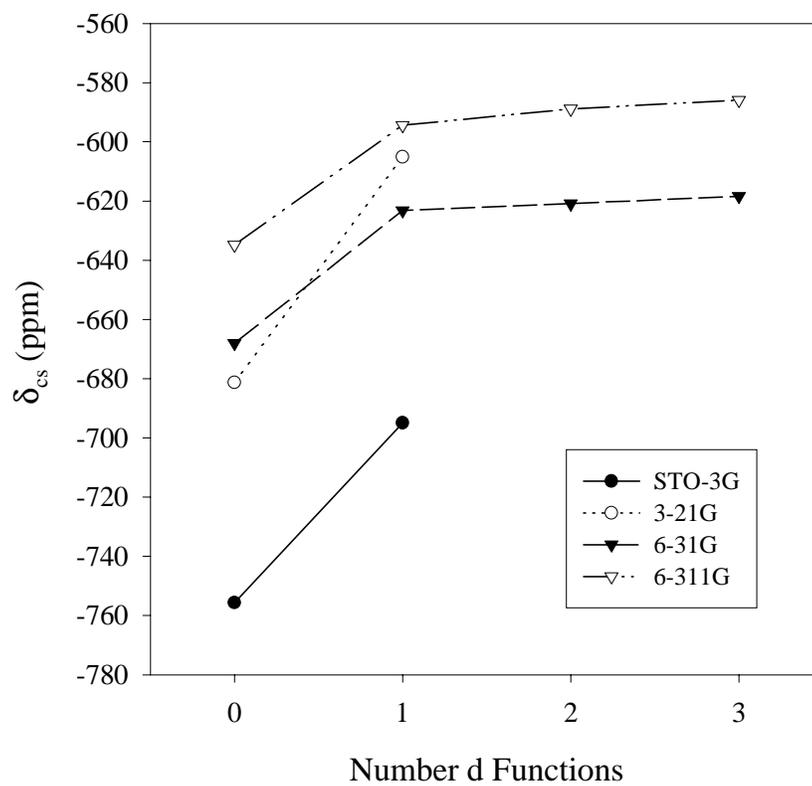
Conclusions

Inspection of Tables I-VIII clearly shows that the choice of basis set influences the calculation of the CSA tensor. The variations will be discussed in two separate sections: 1) the influence of basis set on the trace or isotropic component, and 2) the influence of basis set on the anisotropic nature of the CSA tensor.

A. Basis Set Influence on Isotropic Chemical Shifts Calculations

The absolute theoretical isotropic chemical shifts were negative with respect to a bare nucleus for all the compounds investigated. This corresponds to a shielded nucleus, or lower observation frequency than a bare nucleus, and is what would be expected, since the term chemical shift refers to the shielding of the bare nucleus by electrons from the nucleus of interest as well as neighboring atoms. With increasing complexity of theory there is a steady decrease in the absolute chemical shift, corresponding to a higher observation frequency or a relative deshielding of the nucleus. This deshielding effect is clearly visible in Figures 2,3,4 (below). It is interesting to note that increasing the number of functionals in the split valence, as well as increasing the number of Gaussians in the expansion produces a deshielding effect. The change in isotropic chemical shift observed between basis sets (ie. 6-31G to 6-311G) is approximately 30 to 40 ppm, and is similar for all the compounds investigated. The same order of magnitude variation was observed for both HF and DFT B3LYP calculations. The similarity between HF and DFT variations is also evident in the discussion of correlations (*vide infra*).

HF (PH₃)



B3LYP (PH₃)

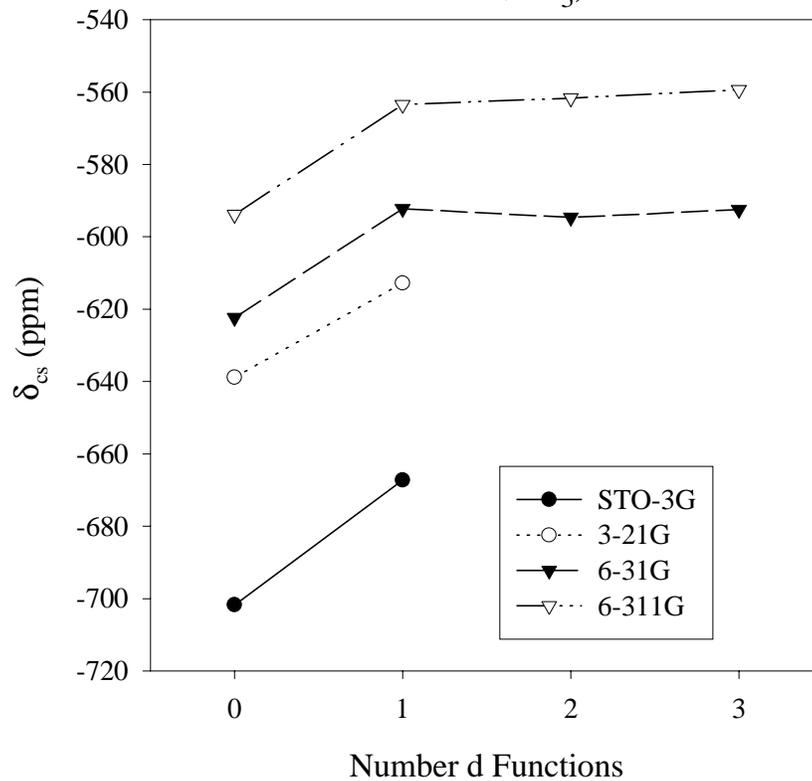


Figure 2: Effect of d Polarization Functions (PH₃)

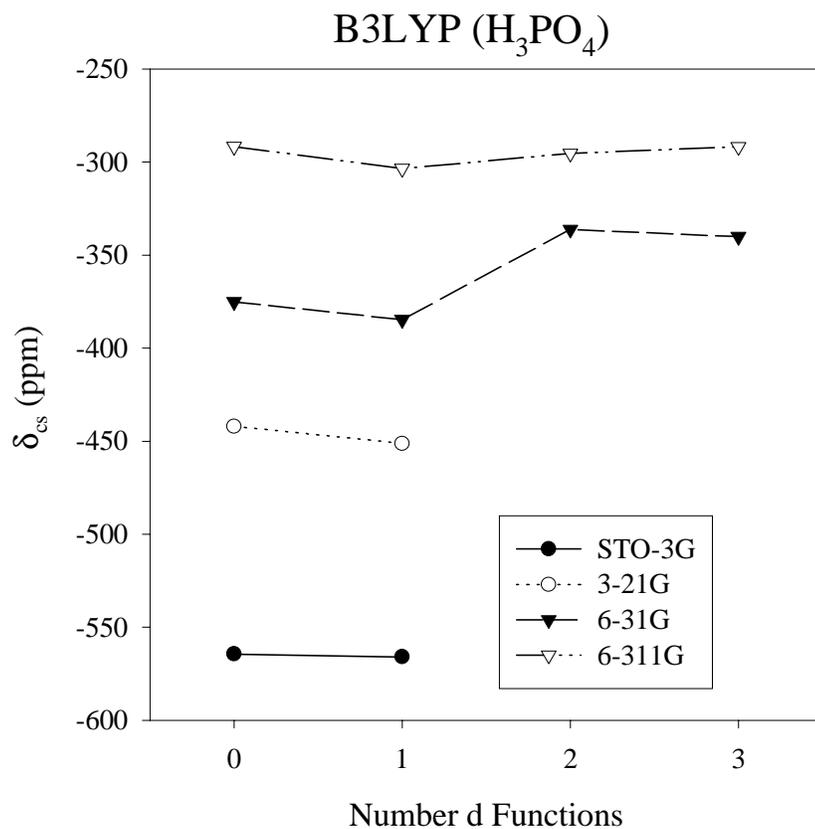
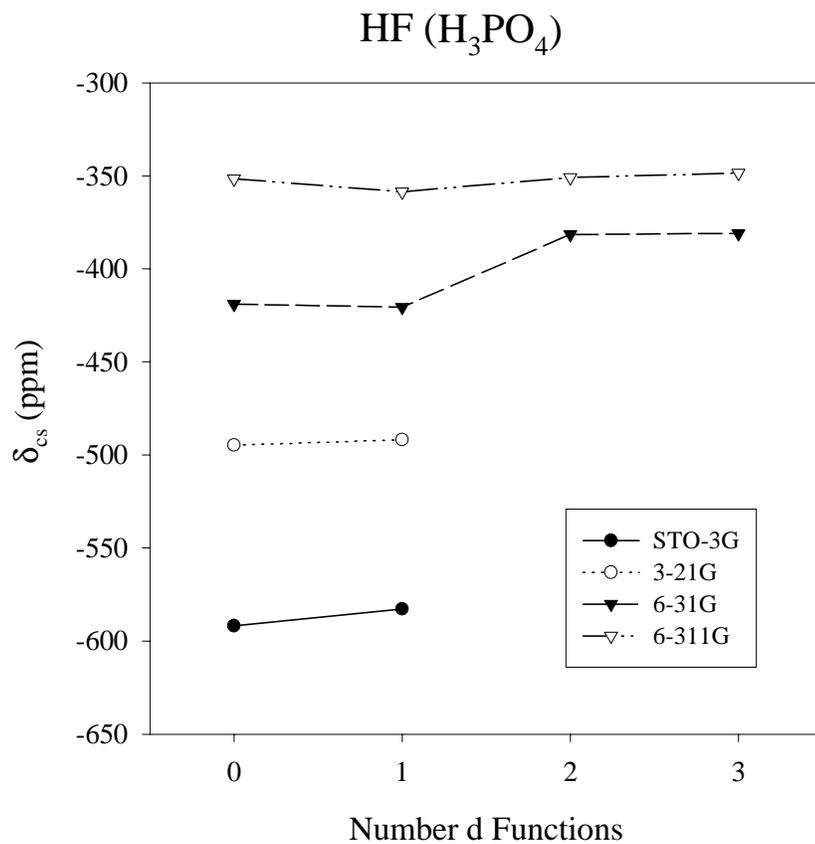


Figure 3: Effect of d Polarization Function (H_3PO_4)

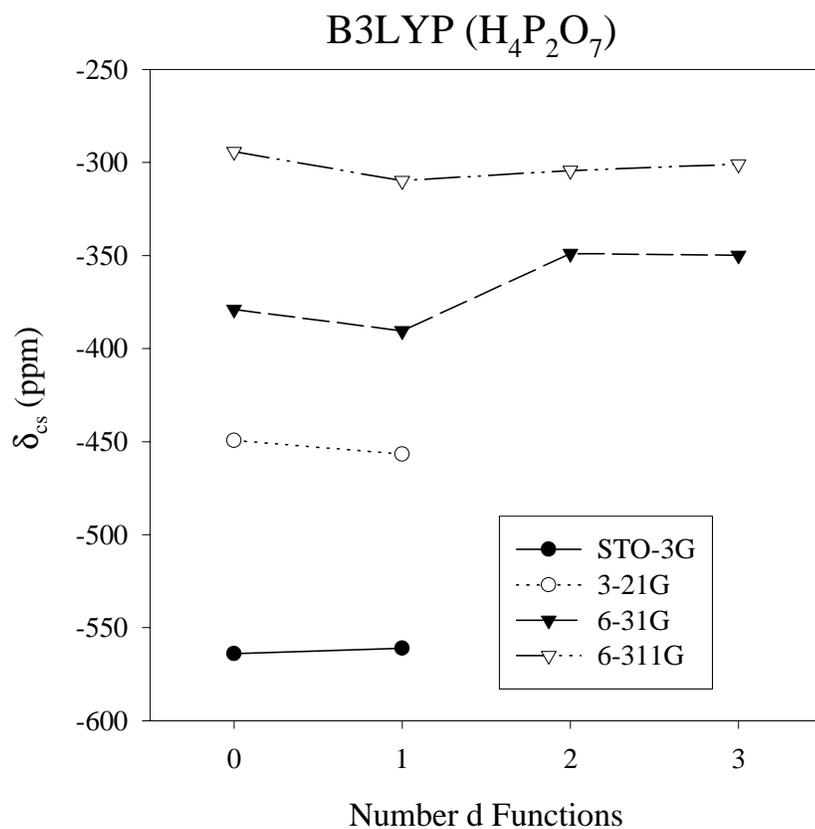
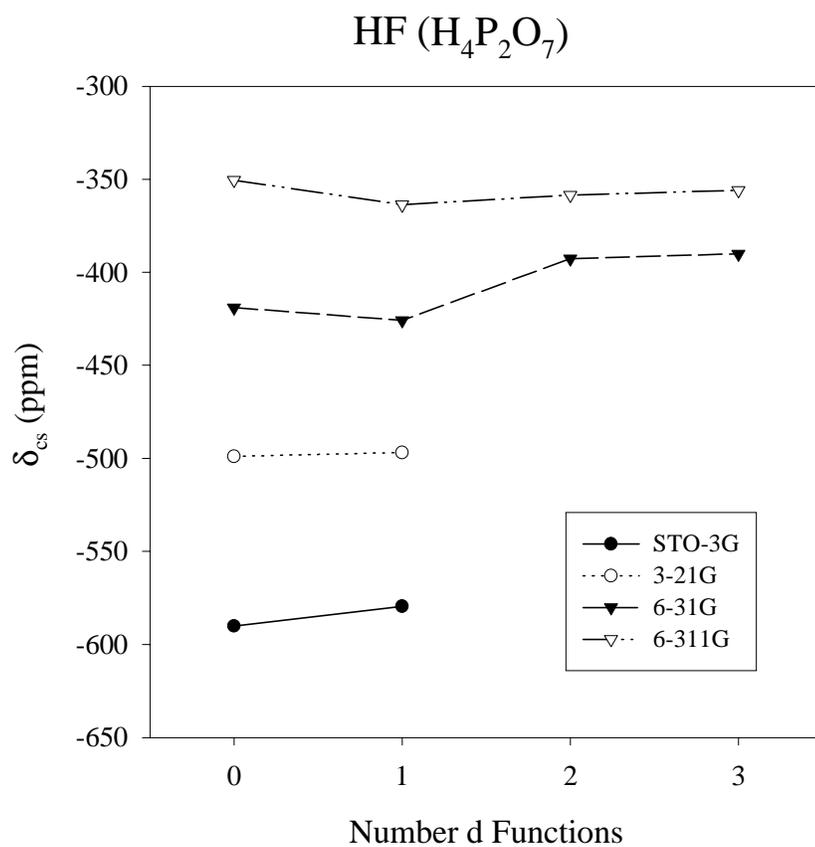


Figure 4: Effect of d Polarization Function ($\text{H}_4\text{P}_2\text{O}_7$)

The influence of polarization functions and diffuse functions on the NMR calculations can also be seen from inspection of Tables I-VIII. The inclusion of the first diffuse function has the largest impact, decreasing the observed chemical shift approximately 1 to 7 ppm. The introduction of the second diffuse function has a smaller effect, decreasing the calculated chemical shift approximately 0.2 to 0.7 ppm. The impact of the diffuse function becomes smaller with increasing number of d polarization functions utilized in the basis set. These observations suggest that 2 diffuse functions be utilized in the basis set of choice when possible. The introduction of the p polarization functions on the hydrogen atoms produces an approximately 0.1 to 1 ppm shift of the isotropic chemical shift, with an approximately 3 ppm variation in PH_3 . This observation reveals that the hydrogen wave functions have only a small impact on the phosphorous chemical shift, even in cases where the hydrogens are directly bonded. The variations in chemical shift due to diffuse and p polarization functions are both smaller in comparison to the variations encountered with introduction of d polarization functions on the phosphorous and oxygen nuclei. Fig. 2 shows the variation of the chemical shift of PH_3 with number of d polarization functions for both the HF and B3LYP calculations. Very large changes are noted with the addition of the first d function for all basis sets investigated. For H_3PO_4 (Fig. 3) and $\text{H}_4\text{P}_2\text{O}_7$ (Fig. 4) a large variation is observed with the addition of two d polarization functions. No more than a single d polarization function is allowed for the STO-3G and the 3-21G basis set, precluding them for future investigations. For both HF and B3LYP methods the isotropic chemical shifts were found to converge for a given basis set once one or two d polarization functions have been included. *These observations suggest that basis sets with at least two d polarization functions and two diffuse functions are required to obtain convergence of the observed chemical shifts. Similar conclusions have been previously reported.*[13]

We have observed an approximately linear relationship between the isotropic chemical shifts calculated using HF and B3LYP methods as shown in Fig. 5. These relationships can be used to compare future results obtained from either method. These linear correlations also reveal that the DFT B3LYP simply produces a scaling factor.

Of the compounds investigated, the absolute isotropic chemical shift of only PH_3 is known. In experimental NMR investigations, chemical shifts are typically referenced to some standard, to produce a relative chemical shift scale. Experimentally, in both solution and solid state ^{31}P NMR, phosphoric acid is the external primary reference ($\delta_{\text{iso}} = 0.0$ ppm). The lack of an absolute chemical shift value for this compound, plus the possible influence of hydrogen bonding makes this a poor choice for referencing of *ab initio* calculations. The accepted standard for

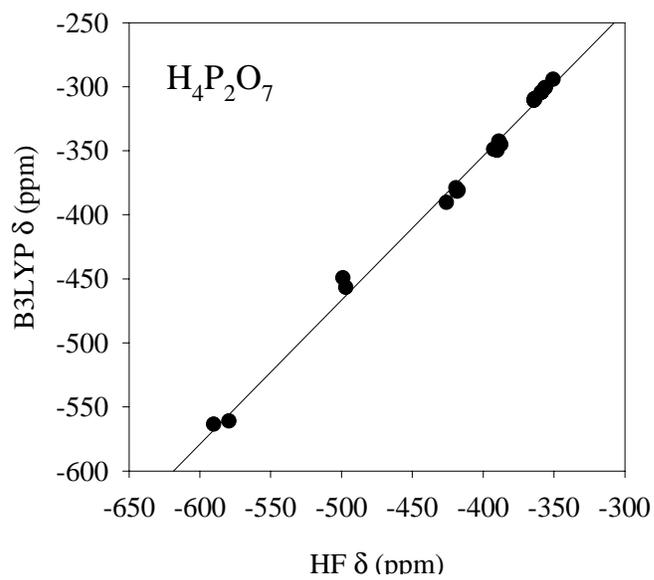
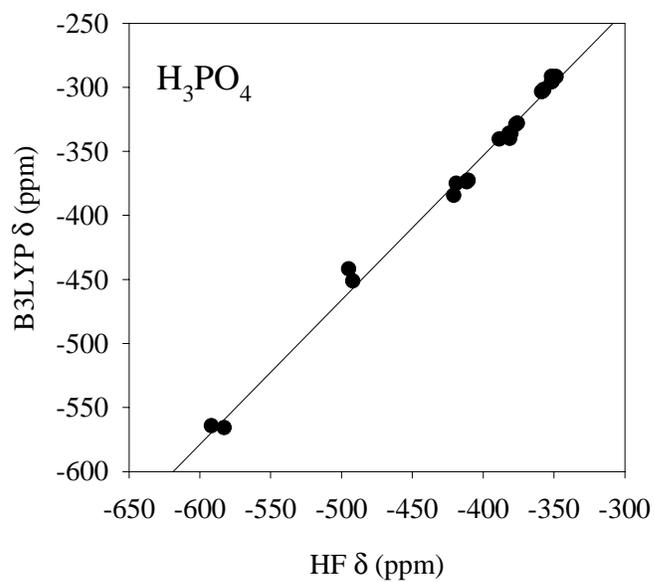
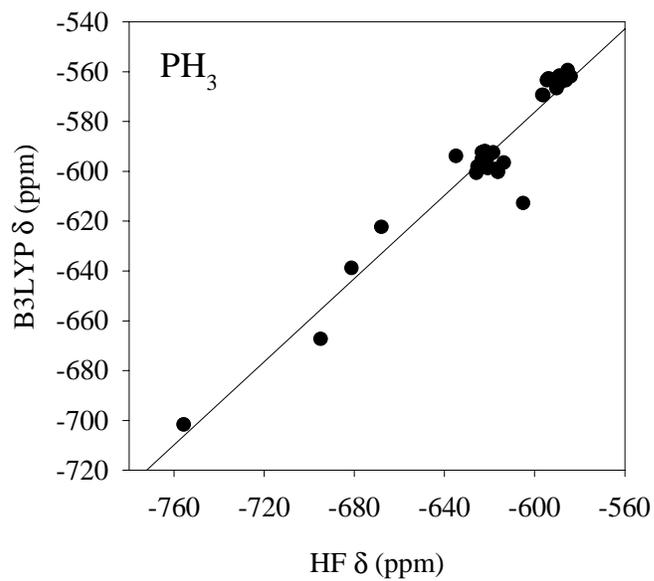


Figure 5: Isotropic Chemical Shift Correlation

referencing of computational results is PH_3 , for which an absolute chemical shift is known ($\delta = -594$ ppm).

Inspection of Table I show that at the HF level the 6-311G basis set results agree with observed experimental values, if polarization functions are employed. Using the B3LYP method the 6-31G basis set, with polarization functions, produces values nearest experimental, while increasing the complexity of the basis set to 6-311G *under-estimates* the chemical shift by approximately 30 ppm, if any polarization functions are employed. For H_3PO_4 (Tables III-VI) a similar trend is observed, with the HF method and the 6-311G basis set producing results consistent with the relative experimental chemical shift if polarization functions are employed, while the use of the B3LYP method *over-estimated* the relative chemical shift by approximately 30 ppm. This is assuming that the relative H_3PO_4 chemical shift (with respect to PH_3) is $\delta = 0.0$ ppm.

The difference between the experimental geometry and the computationally optimized geometry produces a difference in the isotropic chemical shift of approximately 5 ppm. This result again highlights one of the difficulties of using H_3PO_4 as a computation standard. Changes in chemical shift due to variations in local structure (bond lengths and angles) as well as the impact of hydrogen bonding will be detailed in a subsequent report.

For the pyrophosphate $\text{H}_4\text{P}_2\text{O}_7$ cluster the HF method and the 6-311G basis set, the calculated chemical shifts are consistent with experimental values, while the B3LYP method *over-estimates* the chemical shift by approximately 30 ppm. It is interesting to note that using the H_3PO_4 (experimental geometry) as the primary reference produces very similar isotropic chemical shifts for both the HF and B3LYP method. Whether this is fortuitous or represents the mutual cancellation of a basis bias due to referencing to a structurally related compound remains to be determined. From these investigations it appears that HF calculations produce results that are more consistent with experimentally determined values, than results obtained using the DFT B3LYP method.

B. Basis Set Influence on Chemical Shift Anisotropy Calculation

The influence of basis set, polarization functions and diffuse functions on the chemical shift anisotropy $\Delta\delta$ are much smaller than variations observed for the isotropic chemical shift. For example, in PH_3 only the primitive STO-3G basis set was unable to produce theoretical anisotropies close to the experimental values. Use of the B3LYP method tended to *over-estimated* the *magnitude* of $\Delta\delta$ by 10 to 30 ppm. For H_3PO_4 the calculated $\Delta\delta$ is approximately -80 ppm

different than observed experimentally. This difference has been attributed to averaging of $\Delta\delta$ due to molecular motion (even at 175K) or due to hydrogen exchange via intermolecular hydrogen bonding. Thermal motion may be a reasonable explanation since at room temperature molecular motion completely averages $\Delta\delta$ to zero, but similar discrepancies in the pyrophosphate $\Delta\delta$ (*vide infra*) suggest a bias in the calculations. Unfortunately this makes comparison between theory and experiment difficult.

A large difference between theoretical and experimental $\Delta\delta$ was observed in the pyrophosphate cluster $\text{H}_4\text{P}_2\text{O}_7$, where the experimental $\Delta\delta$ is approximately 60 ppm smaller than the calculated value using any of the basis sets. Molecular motion may also be responsible for partial averaging of the anisotropy in the pyrophosphate, but for anionic phosphate dimers of the type $(\text{O}_3\text{P}-\text{PO}_3)^{-2} \text{M}^{+2}$, (where motion is not expected) $\Delta\delta$ range between -100 and -120 ppm.[14] The calculated results obtained using the B3LYP method over-estimate $\Delta\delta$ an additional 30 ppm. *The reason for the large discrepancy between theory and experiment remains undetermined.* The possibility that improved electronic correlation functionals for the DFT method needs to be investigated. With the level of theory presently available this large error must be recognized, precluding the calculation of absolute $\Delta\delta$ values. Trends and changes in magnitude could be evaluated using present theory, with the introduction of some scaling factor.

A correlation between the $\Delta\delta$ values obtained using HF and B3LYP methods was also observed. These approximately linear correlations are shown in Figure 6 for PH_3 , H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$.

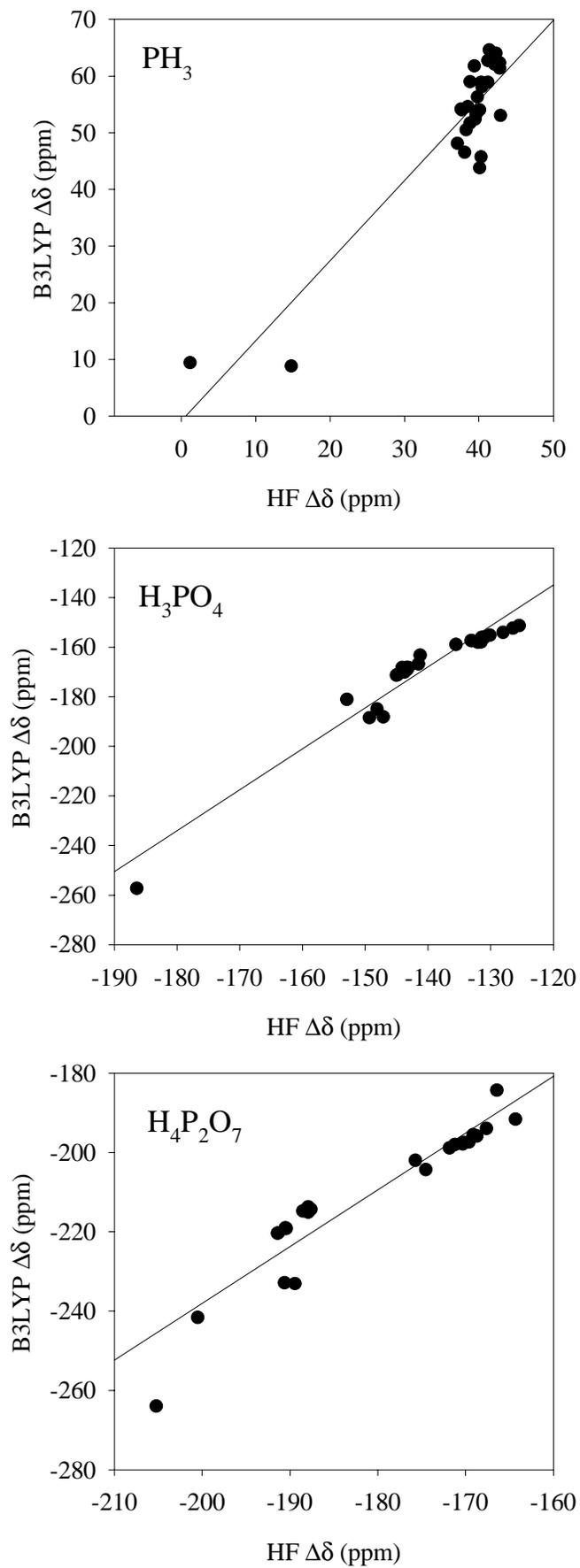


Figure 6: Chemical Shift Anisotropy Correlation

Summary

Ab initio calculations of the isotropic chemical shift and the chemical shift anisotropy were found to converge with increasing complexity of the basis set for both HF and DFT B3LYP methods. The addition of d polarization function on the phosphorous nuclei was found to have a major impact on the calculated chemical shift, with a smaller effect on the anisotropy. The effect was diminished with increasing number of polarization functions. At least 2 d polarization functions are required for accurate calculations of the isotropic phosphorous chemical shift. The introduction of DFT techniques via the hybrid B3LYP method resulted in poorer estimation of the isotropic chemical shift and the chemical shift anisotropy, even though DFT techniques result in improved energy calculations. While the DFT methods produced agreement with the isotropic chemical shift at lower levels of theory, the large fluctuations in the anisotropy with small changes in the number of polarization functions or diffuse functions make them a poor choice for investigations of a variety of simple phosphates. A linear correlation between HF and B3LYP NMR results was observed. These results suggest the HF method and the 6-311++G(2d,2p) basis set represent a good compromise between accuracy of the simulation and the complexity of the calculation for future *ab initio* investigations of larger complexes.

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Table I. Ab initio HF level ^{31}P Chemical Shift Anisotropy Tensor Calculations for PH_3 as a Function of Gaussian Basis Set Using GIAO.^a

Theory/Basis Set	δ_{cs}^b	δ_{33}^c	$\delta_{11} = \delta_{22}^c$	$\Delta\delta^d$	η^e
HF STO-3G	-755.7	-754.9	-756.1	1.2	0.0
HF STO-3G(d)	-694.9	-704.8	-690.0	14.8	0.0
HF 3-21G	-681.3	-655.2	-695.3	40.1	0.0
HF 3-21G(d)	-605.1	-579.7	-617.8	38.1	0.0
HF 6-31G	-668.0	-641.1	-681.4	40.3	0.0
HF 6-31G(d)	-623.2	-598.5	-635.6	37.1	0.0
HF 6-31G(2d)	-620.9	-594.5	-634.1	39.6	0.0
HF 6-31G(3d)	-618.4	-591.9	-631.6	39.8	0.0
HF 6-31+G(d)	-622.0	-596.5	-634.8	38.3	0.0
HF 6-31++G(d)	-623.3	-597.4	-636.2	38.8	0.0
HF 6-31+G(d,p)	-625.2	-598.9	-638.4	39.5	0.0
HF 6-31++G(d,p)	-625.8	-599.0	-639.1	40.1	0.0
HF 6-31++G(2d,p)	-620.7	-593.2	-634.4	41.2	0.0
HF 6-31++G(2d,2p)	-617.4	-588.9	-631.7	42.8	0.0
HF 6-31++G(3d,2p)	-613.7	-585.2	-628.0	42.8	0.0
HF 6-31++G(3df,2p)	-616.2	-588.1	-630.2	42.1	0.0
HF 6-311G	-634.8	-606.3	-649.2	42.9	0.0
HF 6-311G(d)	-594.4	-568.7	-607.2	38.5	0.0
HF 6-311G(2d)	-588.9	-563.0	-601.8	38.8	0.0
HF 6-311G(3d)	-585.3	-559.0	-598.5	39.4	0.0
HF 6-311+G(d)	-593.9	-568.7	-606.4	37.7	0.0
HF 6-311++G(d)	-593.2	-568.2	-605.8	37.6	0.0
HF 6-311+G(d,p)	-596.6	-569.7	-610.1	40.4	0.0
HF 6-311++G(d,p)	-596.2	-569.3	-609.6	40.3	0.0
HF 6-311++G(2d,p)	-588.7	-561.3	-602.5	41.2	0.0
HF 6-311++G(2d,2p)	-590.1	-561.9	-604.2	42.3	0.0
HF 6-311++G(3d,2p)	-586.1	-558.2	-600.0	41.8	0.0
HF 6-311++G(3df,2p)	-584.0	-556.4	-597.8	41.4	0.0
Experimental ^f	-594 ± 10^f			50 ± 15^f	

^a HF - Hartree Fock, GIAO – Gauge Including Atomic Orbitals. ^b Absolute isotropic chemical shift $\delta_{cs} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{cs} = -\sigma_{cs}$ where σ_{cs} is the magnetic shielding in ppm.

^c Principal components of the CSA tensor where $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$.

^d Chemical shift anisotropy defined as, $\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22})$, ^e Chemical shift anisotropy

asymmetry, $\eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{iso}}$. ^f Experimental values from reference [15].

Table II. Ab Initio DFT ³¹P Chemical Shift Anisotropy Tensor Calculations for PH₃ as a Function of Gaussian Basis Set. ^a

Theory/Basis Set	δ_{cs}^b	δ_{33}^c	$\delta_{11} = \delta_{22}^c$	$\Delta\delta^d$	η^e
B3LYP STO-3G	-701.8	-708.2	-698.8	9.4	0.0
B3LYP STO-3G(d)	-667.3	-673.1	-664.3	8.8	0.0
B3LYP 3-21G	-638.9	-609.7	-653.5	43.8	0.0
B3LYP 3-21G(d)	-612.8	-581.8	-628.3	46.5	0.0
B3LYP 6-31G	-622.4	-591.9	-637.6	45.7	0.0
B3LYP 6-31G(d)	-592.3	-560.2	-608.3	48.1	0.0
B3LYP 6-31G(2d)	-594.7	-559.2	-612.4	53.2	0.0
B3LYP 6-31G(3d)	-592.5	-555.0	-611.3	56.3	0.0
B3LYP 6-31+G(d)	-592.0	-558.3	-608.8	50.5	0.0
B3LYP 6-31++G(d)	-595.1	-560.6	-612.3	51.7	0.0
B3LYP 6-31+G(d,p)	-598.1	-563.2	-615.6	52.4	0.0
B3LYP 6-31++G(d,p)	-600.7	-564.7	-618.7	54.0	0.0
B3LYP 6-31++G(2d,p)	-598.8	-559.6	-618.5	58.9	0.0
B3LYP 6-31++G(2d,2p)	-599.1	-558.2	-619.6	61.4	0.0
B3LYP 6-31++G(3d,2p)	-596.6	-555.2	-617.5	62.3	0.0
B3LYP 6-31++G(3df,2p)	-600.3	-558.9	-621.0	62.1	0.0
B3LYP 6-311G	-593.9	-558.6	-611.6	53.0	0.0
B3LYP 6-311G(d)	-563.5	-527.1	-581.7	54.6	0.0
B3LYP 6-311G(2d)	-561.7	-581.4	-522.1	59.0	0.0
B3LYP 6-311G(3d)	-559.4	-518.2	-580.0	61.8	0.0
B3LYP 6-311+G(d)	-562.9	-526.9	-580.9	54.0	0.0
B3LYP 6-311++G(d)	-563.0	-526.9	-581.1	54.2	0.0
B3LYP 6-311+G(d,p)	-569.3	-588.8	-530.7	58.1	0.0
B3LYP 6-311++G(d,p)	-569.5	-589.1	-530.2	58.9	0.0
B3LYP 6-311++G(2d,p)	-564.5	-585.4	-522.7	62.7	0.0
B3LYP 6-311++G(2d,2p)	-566.7	-588.0	-524.0	64.0	0.0
B3LYP 6-311++G(3d,2p)	-563.5	-585.2	-520.2	64.0	0.0
B3LYP 6-311++G(3df,2p)	-561.9	-583.4	-518.8	64.6	0.0
Experimental ^f		-594 ± 10^f		50 ± 15^f	

^a DFT, Density Functional Theory, B3LYP, Becke's Hybrid LYP Correlation Functional [6,9,11], GIAO – Gauge Including Atomic Orbitals. ^b Absolute isotropic chemical shift

$\delta_{cs} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{cs} = -\sigma_{cs}$ where σ_{cs} is the magnetic shielding in ppm. ^c Principal

components of the CSA tensor where $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$. ^d Chemical shift

anisotropy defined as, $\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22})$, ^e Chemical shift anisotropy asymmetry,

$\eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{iso}}$. ^f Experimental values from reference [15].

Table III. Ab initio HF level ^{31}P Chemical Shift Anisotropy Tensor Calculations for H_3PO_4 as a Function of Gaussian Basis Set.^a

Theory/Basis Set	$\delta_{\text{cs}}^{\text{b}}$	$\delta_{\text{iso}}(\text{PH}_3)^{\text{c}}$	δ_{33}^{d}	$\delta_{11} = \delta_{22}^{\text{d}}$	$\Delta\delta^{\text{e}}$	η^{f}
HF STO-3G	-591.8	-76.1	-716.1	-529.7	-186.4	0.0
HF STO-3G(d)	-582.8	-127.9	-684.7	-531.9	-152.9	0.0
HF 3-21G	-494.8	-53.5	-594.3	-445.0	-149.3	0.0
HF 3-21G(d)	-491.8	-126.7	-582.1	-446.6	-135.5	0.0
HF 6-31G	-418.9	9.1	-516.9	-369.9	-147.1	0.0
HF 6-31G(d)	-420.6	-37.4	-507.4	-377.3	-130.1	0.0
HF 6-31G(2d)	-381.5	-0.6	-466.8	-338.8	-128.0	0.0
HF 6-31G(3d)	-381.0	-2.6	-475.1	-33.9	-141.2	0.0
HF 6-31+G(d)	-411.5	-29.5	-499.0	-367.7	-131.4	0.0
HF 6-31++G(d)	-411.4	-28.1	-499.3	-367.4	-132.0	0.0
HF 6-31+G(d,p)	-410.5	-25.3	-497.8	-366.9	-130.9	0.0
HF 6-31++G(d,p)	-410.5	-24.7	-498.2	-366.7	-131.5	0.0
HF 6-31++G(2d,p)	-375.7	5.0	-459.4	-333.9	-125.4	0.0
HF 6-31++G(2d,2p)	-376.7	0.7	-461.0	-334.6	-126.4	0.0
HF 6-31++G(3d,2p)	-380.1	-6.4	-468.7	-335.8	-132.9	0.0
HF 6-31++G(3df,2p)	-388.5	-12.3	-477.3	-344.2	-133.1	0.0
HF 6-311G	-351.6	43.2	-450.3	-302.3	-148.1	0.0
HF 6-311G(d)	-358.6	-4.2	-454.4	-310.7	-143.7	0.0
HF 6-311G(2d)	-350.9	-2.0	-446.5	-303.1	-143.4	0.0
HF 6-311G(3d)	-348.5	-3.2	-444.5	-300.4	-144.1	0.0
HF 6-311+G(d)	-357.0	-3.1	-452.5	-309.2	-143.3	0.0
HF 6-311++G(d)	-357.2	-4.0	-452.8	-309.4	-143.4	0.0
HF 6-311+G(d,p)	-357.9	-1.3	-454.4	-309.6	-144.8	0.0
HF 6-311++G(d,p)	-358.0	-1.9	-454.7	-309.7	-145.0	0.0
HF 6-311++G(2d,p)	-351.6	-2.9	-446.9	-303.9	-143.1	0.0
HF 6-311++G(2d,2p)	-351.5	-1.4	-447.0	-303.9	-143.3	0.0
HF 6-311++G(3d,2p)	-348.6	-2.5	-444.3	-300.8	-143.6	0.0
HF 6-311++G(3df,2p)	-349.4	-5.4	-443.7	-302.2	-141.5	0.0
Experimental		0.9 ^g -0.2 ^h			-65 ^g -61 ^h	

^a HF - Hartree Fock, GIAO – Gauge Including Atomic Orbitals. ^b Isotropic chemical shift with respect to the secondary reference PH_3 ($\delta = -240$ ppm) calculated at the same level of theory.

^c Absolute isotropic chemical shift $\delta_{\text{cs}} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{\text{cs}} = -\sigma_{\text{cs}}$ where σ_{cs} is the magnetic shielding in ppm. ^d Principal components of the CSA tensor where $|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}|$. ^e Chemical shift anisotropy defined as,

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}), \quad \text{f Chemical shift anisotropy asymmetry, } \eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{\text{iso}}}.$$

^g Experimental value from reference[16]. ^h (Personal communication, T. M. Alam).

Table IV. Ab initio DFT ³¹P Chemical Shift Anisotropy Tensor Calculations for H₃PO₄ as a Function of Gaussian Basis Set.^a

Theory/Basis Set	δ_{cs}^b	$\delta_{iso}(PH_3)^c$	δ_{33}^d	$\delta_{11} = \delta_{22}^d$	$\Delta\delta^e$	η^f
B3LYP STO-3G	-564.4	-102.6	-736.0	-478.6	-257.4	0.0
B3LYP STO-3G(d)	-566.0	-138.7	-686.7	-505.6	-181.1	0.0
B3LYP 3-21G	-442.0	-43.1	-567.9	-379.4	-188.5	0.0
B3LYP 3-21G(d)	-451.2	-78.4	-557.3	-398.2	-159.0	0.0
B3LYP 6-31G	-375.1	7.3	-500.5	-312.3	-188.2	0.0
B3LYP 6-31G(d)	-384.7	-32.4	-488.2	-332.9	-155.3	0.0
B3LYP 6-31G(2d)	-336.2	18.5	-439.0	-284.9	-154.1	0.0
B3LYP 6-31G(3d)	-340.1	12.3	-449.0	-285.6	-163.4	0.0
B3LYP 6-31+G(d)	-373.8	-21.8	-478.0	-321.8	-156.2	0.0
B3LYP 6-31++G(d)	-373.8	-18.7	-479.2	-321.0	-158.1	0.0
B3LYP 6-31+G(d,p)	-373.0	-14.9	-477.0	-320.9	-156.0	0.0
B3LYP 6-31++G(d,p)	-372.9	-12.2	-478.3	-320.2	-158.0	0.0
B3LYP 6-31++G(2d,p)	-328.2	30.6	-429.2	-277.8	-151.4	0.0
B3LYP 6-31++G(2d,2p)	-329.0	30.1	-430.6	-278.2	-152.4	0.0
B3LYP 6-31++G(3d,2p)	-336.2	20.4	-441.2	-283.7	-157.5	0.0
B3LYP 6-31++G(3df,2p)	-340.5	19.8	-445.4	-288.0	-157.4	0.0
B3LYP 6-311G	-291.7	62.2	-415.6	-229.7	-185.0	0.0
B3LYP 6-311G(d)	-303.5	20.0	-417.0	-246.8	-170.1	0.0
B3LYP 6-311G(2d)	-295.4	26.3	-407.7	-284.9	-168.3	0.0
B3LYP 6-311G(3d)	-291.8	27.6	-404.0	-285.6	-168.3	0.0
B3LYP 6-311+G(d)	-302.0	20.9	-414.6	-245.6	-169.0	0.0
B3LYP 6-311++G(d)	-302.1	20.9	-414.8	-245.7	-169.2	0.0
B3LYP 6-311+G(d,p)	-303.1	26.2	-417.2	-246.1	-171.2	0.0
B3LYP 6-311++G(d,p)	-303.2	26.3	-417.4	-246.1	-171.4	0.0
B3LYP 6-311++G(2d,p)	-295.8	28.7	-408.0	-239.7	-168.3	0.0
B3LYP 6-311++G(2d,2p)	-295.8	30.9	-408.3	-239.6	-168.6	0.0
B3LYP 6-311++G(3d,2p)	-291.8	31.7	-404.3	-235.6	-168.7	0.0
B3LYP 6-311++G(3df,2p)	-292.3	29.6	-403.5	236.7	-166.8	0.0
Experimental		0.9 ^g -0.2 ^h			-65 ^g -61 ^h	

^a DFT, Density Functional Theory, B3LYP, Becke's Hybrid LYP Correlation Functional [6,9,11], GIAO – Gauge Including Atomic Orbitals. ^b Isotropic chemical shift with respect to the secondary reference PH₃ ($\delta = -240$ ppm) calculated at the same level of theory. ^c Absolute

isotropic chemical shift $\delta_{cs} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{cs} = -\sigma_{cs}$ where σ_{cs} is the magnetic

shielding in ppm. ^d Principal components of the CSA tensor where

$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$. ^e Chemical shift anisotropy defined as,

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}), \quad \eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{iso}}$$

^g Experimental values from reference[16]. ^h (Personal communication, T. M. Alam).

Table V. Ab initio HF level ^{31}P Chemical Shift Anisotropy Tensor Calculations for H_3PO_4 (Optimized Geometry) as a Function of Gaussian Basis Set.^a

Theory/Basis Set	δ_{cs}^b	$\delta_{iso}(\text{PH}_3)^c$	δ_{33}^d	$\delta_{11} = \delta_{22}^d$	$\Delta\delta^e$	η^f
HF STO-3G	-586.7	-71.0	-713.6	-523.3	-190.4	0.0
HF STO-3G(d)	-569.6	-114.7	-676.4	-358.4	-160.2	0.0
HF 3-21G	-483.9	-42.6	-600.4	-425.7	-174.7	0.0
HF 3-21G(d)	-390.5	-25.4	-516.0	-327.8	-188.2	0.0
HF 6-31G	-410.9	17.1	-530.2	-351.2	-179.0	0.0
HF 6-31G(d)	-416.2	-33.0	-529.0	-359.8	-169.2	0.0
HF 6-31G(2d)	-382.6	-1.7	-500.0	-324.2	-175.4	0.0
HF 6-31G(3d)	-380.6	-2.2	-506.2	-317.8	-188.4	0.0
HF 6-31+G(d)	-408.1	-26.1	-523.9	-350.2	-173.7	0.0
HF 6-31++G(d)	-408.2	-24.9	-525.1	-349.7	-175.5	0.0
HF 6-31+G(d,p)	-407.0	-21.8	-522.6	-349.2	-173.4	0.0
HF 6-31++G(d,p)	-407.1	-21.3	-523.8	-348.8	-175.0	0.0
HF 6-31++G(2d,p)	-377.0	3.7	-492.7	-319.0	-173.8	0.0
HF 6-31++G(2d,2p)	-377.6	-0.2	-493.6	-319.6	-174.0	0.0
HF 6-31++G(3d,2p)	-377.2	-3.5	-498.5	-316.4	-182.0	0.0
HF 6-31++G(3df,2p)	-385.4	-9.2	-508.2	-324.0	-184.2	0.0
HF 6-311G	-342.0	52.8	-468.9	-278.6	-190.3	0.0
HF 6-311G(d)	-352.4	2.0	-481.4	-287.9	-193.5	0.0
HF 6-311G(2d)	-346.4	2.5	-476.0	-281.6	-194.3	0.0
HF 6-311G(3d)	-343.9	1.4	-474.5	-278.6	-195.9	0.0
HF 6-311+G(d)	-351.0	2.9	-480.1	-286.4	-193.6	0.0
HF 6-311++G(d)	-351.2	2.0	-480.3	-286.6	-193.8	0.0
HF 6-311+G(d,p)	-352.3	4.3	-482.8	-287.0	-195.8	0.0
HF 6-311++G(d,p)	-352.5	3.7	-483.1	-287.1	-196.0	0.0
HF 6-311++G(2d,p)	-347.3	1.4	-477.5	-282.2	-195.3	0.0
HF 6-311++G(2d,2p)	-347.3	2.8	-477.8	-282.1	-195.7	0.0
HF 6-311++G(3d,2p)	-344.0	2.1	-474.5	-278.8	-195.7	0.0
HF 6-311++G(3df,2p)	-344.9	-0.9	-474.4	-280.2	-194.2	0.0
Experimental		0.9 ^g -0.2 ^h			-65 ^g -61 ^h	

^a HF - Hartree Fock, GIAO – Gauge Including Atomic Orbitals. Calculations performed on B3LYP- 6-311++(2d,2p) optimized structure. ^b Isotropic chemical shift with respect to the secondary reference PH_3 ($\delta = -240$ ppm) calculated at the same level of theory. ^c Absolute

isotropic chemical shift $\delta_{cs} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{cs} = -\sigma_{cs}$ where σ_{cs} is the magnetic

shielding in ppm. ^d Principal components of the CSA tensor where

$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$. ^e Chemical shift anisotropy defined as,

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}), \quad \eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{iso}}$$

^g Experimental value from reference[16]. ^h (Personal communication, T. M. Alam).

Table VI. Ab initio B3LYP level ^{31}P Chemical Shift Anisotropy Tensor Calculations for H_3PO_4 , optimized geometry, as a Function of Gaussian Basis Set.^a

Theory/Basis Set	$\delta_{\text{cs}}^{\text{b}}$	$\delta_{\text{iso}}^{\text{c}}$	δ_{33}^{d}	$\delta_{11} = \delta_{22}^{\text{d}}$	$\Delta\delta^{\text{e}}$	η^{f}
B3LYP STO-3G	-556.6	-94.8	-721.0	-474.4	-246.6	0.0
B3LYP STO-3G(d)	-549.4	-122.1	-669.3	-489.4	-180.0	0.0
B3LYP 3-21G	-429.4	-30.5	-566.9	-360.6	-206.3	0.0
B3LYP 3-21G(d)	-435.6	-62.8	-558.1	-374.4	-183.7	0.0
B3LYP 6-31G	-365.1	17.3	-506.7	-294.3	-212.4	0.0
B3LYP 6-31G(d)	-377.6	-25.3	-502.6	-315.1	-187.5	0.0
B3LYP 6-31G(2d)	-335.6	19.1	-467.2	-269.8	-197.4	0.0
B3LYP 6-31G(3d)	-338.0	14.5	-476.1	-269.0	-207.1	0.0
B3LYP 6-31+G(d)	-368.7	-16.7	-497.8	-304.1	-193.6	0.0
B3LYP 6-31++G(d)	-368.8	-13.7	-499.7	-303.3	-196.4	0.0
B3LYP 6-31+G(d,p)	-367.6	-9.5	-496.7	-303.1	-193.7	0.0
B3LYP 6-31++G(d,p)	-367.8	-7.1	-498.7	-302.3	-196.3	0.0
B3LYP 6-31++G(2d,p)	-327.5	31.3	-458.6	-262.0	-196.7	0.0
B3LYP 6-31++G(2d,2p)	-327.8	31.3	-459.3	-262.0	-197.3	0.0
B3LYP 6-31++G(3d,2p)	-332.4	24.2	-467.4	-265.0	-202.4	0.0
B3LYP 6-31++G(3df,2p)	-336.0	24.3	-472.0	-268.0	-204.0	0.0
B3LYP 6-311G	-280.4	73.5	-492.2	-205.9	-223.3	0.0
B3LYP 6-311G(d)	-294.9	28.6	-437.7	-223.6	-214.2	0.0
B3LYP 6-311G(2d)	-286.4	35.3	-431.5	-216.9	-214.6	0.0
B3LYP 6-311G(3d)	-284.9	34.5	-429.0	-217.8	-216.2	0.0
B3LYP 6-311+G(d)	-293.5	29.4	-436.2	-222.1	-214.1	0.0
B3LYP 6-311++G(d)	-293.6	29.4	-436.3	-222.2	-214.1	0.0
B3LYP 6-311+G(d,p)	-295.2	34.1	-439.8	-222.8	-217.0	0.0
B3LYP 6-311++G(d,p)	-295.3	34.2	-440.0	-222.9	-217.2	0.0
B3LYP 6-311++G(2d,p)	-289.2	35.3	-433.2	-217.1	-216.1	0.0
B3LYP 6-311++G(2d,2p)	-289.3	37.4	-433.9	-217.0	-216.8	0.0
B3LYP 6-311++G(3d,2p)	-285.0	38.5	-429.7	-212.6	217.1	0.0
B3LYP 6-311++G(3df,2p)	-285.5	36.4	-429.3	-213.7	-215.6	0.0
Experimental		0.9 ^g -0.2 ^h			-65 ^g -61 ^h	

^a DFT, Density Functional Theory, B3LYP, Becke's Hybrid LYP Correlation Functional [6,9,11], GIAO – Gauge Including Atomic Orbitals. Calculations performed on B3LYP- 6-311++(2d,2p) optimized structure. ^b Isotropic chemical shift with respect to the secondary reference PH_3 ($\delta = -240$ ppm) calculated

at the same level of theory. ^c Absolute isotropic chemical shift $\delta_{\text{cs}} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{\text{cs}} = -\sigma_{\text{cs}}$

where σ_{cs} is the magnetic shielding in ppm. ^d Principal components of the CSA tensor where

$|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}|$. ^e Chemical shift anisotropy defined as,

$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22})$. ^f Chemical shift anisotropy asymmetry, $\eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{\text{iso}}}$. ^g Experimental

values from reference[16]. ^h (Personal communication, T. M. Alam).

Table VII. Ab initio HF level ^{31}P Chemical Shift Anisotropy Tensor Calculations for $\text{H}_4\text{P}_2\text{O}_7$ Cluster (Optimized Geometry) as a Function of Gaussian Basis Set.^a

Theory/Basis Set	δ_{cs}^b	δ_{iso}^c (PH_3)	δ_{iso}^c (H_3PO_4)	δ_{33}^d	δ_{22}^d	δ_{11}^d	$\Delta\delta^e$	η^f
HF STO-3G	-590.2	-74.5	1.6	-727.0	-554.1	-489.4	-205.2	0.47
HF STO-3G(d)	-579.5	-124.6	3.3	-689.0	-531.8	-517.7	-164.3	0.13
HF 3-21G	-498.9	-57.6	-4.1	-626.0	-450.5	-420.2	-190.6	0.24
HF 3-21G(d)	-496.9	-131.8	-5.1	-613.3	-440.5	-437.0	-174.5	0.03
HF 6-31G	-419.0	9.0	-0.1	-545.2	-378.7	-333.0	-189.4	0.36
HF 6-31G(d)	-425.9	-42.7	-5.3	-536.8	-378.3	-362.6	-166.4	0.14
HF 6-31G(2d)	-392.7	-11.8	-11.2	-504.4	-340.8	-332.9	-167.6	0.07
HF 6-31G(3d)	-390.1	-11.7	-9.1	-507.2	-332.1	-331.0	-175.7	0.01
HF 6-31+G(d)	-418.2	-36.2	-6.7	-531.0	-369.9	-359.8	-169.1	0.09
HF 6-31++G(d)	-418.6	-35.3	-7.2	-532.1	-364.1	-359.7	-170.2	0.04
HF 6-31+G(d,p)	-417.6	-32.4	-7.1	-530.0	-362.7	-359.9	-168.7	0.03
HF 6-31++G(d,p)	-418.0	-32.2	-7.5	-531.1	-363.1	-359.9	-169.6	0.03
HF 6-31++G(2d,p)	-388.6	-7.9	-12.9	-502.7	-337.2	-326.0	-171.2	0.10
HF 6-31++G(2d,2p)	-388.7	-11.3	-12.0	-503.3	-336.7	-326.2	-171.8	0.09
HF 6-31++G(3d,2p)	-387.3	-13.6	-7.2	-500.9	-330.7	-330.5	-170.3	0.00
HF 6-31++G(3df,2p)	--	--	--	--	--	--	--	--
HF 6-311G	-350.5	44.3	1.1	-484.2	-308.5	-258.8	-200.5	0.37
HF 6-311G(d)	-363.7	-9.3	-5.1	-490.6	-306.6	-293.8	-190.4	0.10
HF 6-311G(2d)	-358.5	-9.6	-7.6	-484.2	-298.7	-291.7	-188.5	0.06
HF 6-311G(3d)	-355.9	-10.6	-7.4	-481.1	-295.9	-290.6	-187.9	0.04
HF 6-311+G(d)	-363.4	-9.5	-6.4	-490.4	-306.0	-293.7	-190.5	0.10
HF 6-311++G(d)	-363.4	-10.2	-6.2	-490.3	-306.0	-293.8	-190.5	0.10
HF 6-311+G(d,p)	-364.1	-7.5	-6.2	-491.7	-306.9	-293.7	-191.4	0.10
HF 6-311++G(d,p)	-364.1	-7.9	-6.1	-491.7	-306.9	-293.7	-191.3	0.10
HF 6-311++G(2d,p)	-358.9	-10.2	-7.3	-484.2	-300.2	-292.3	-187.9	0.06
HF 6-311++G(2d,2p)	-358.9	-8.8	-7.4	-484.1	-300.0	292.4	-187.9	0.06
HF 6-311++G(3d,2p)	-356.3	-10.2	-7.7	-481.4	-296.5	-291.2	-187.6	0.04
HF 6-311++G(3df,2p)	--	--	--	--	--	--	--	--
Experimental		-12.5 ^g	-12.5 ^g				-111 ^g	

^a HF - Hartree Fock, GIAO – Gauge Including Atomic Orbitals. Calculations performed on B3LYP- 6-311++(2d,2p) optimized structure. ^b Isotropic chemical shift with respect to the secondary reference PH_3 ($\delta = -240$ ppm) or primary reference H_3PO_4 ($\delta = 0.0$ ppm) calculated at

the same level of theory. ^c Absolute isotropic chemical shift $\delta_{cs} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{cs} = -\sigma_{cs}$

where σ_{cs} is the magnetic shielding in ppm. ^d Principal components of the CSA tensor where

$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$. ^e Chemical shift anisotropy defined as,

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}), \quad \eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{iso}}$$

^g (Personal communication, T. M. Alam).

Table VIII. Ab initio B3LYP level ^{31}P Chemical Shift Anisotropy Tensor Calculations for $\text{H}_4\text{P}_2\text{O}_7$ Cluster (Optimized Geometry) as a Function of Gaussian Basis Set.^a

Theory/Basis Set	$\delta_{\text{cs}}^{\text{b}}$	$\delta_{\text{iso}}^{\text{c}}$ (PH_3)	$\delta_{\text{iso}}^{\text{c}}$ (H_3PO_4)	δ_{33}^{d}	δ_{22}^{d}	δ_{11}^{d}	$\Delta\delta^{\text{e}}$	η^{f}
B3LYP STO-3G	-563.6	-101.8	0.8	-739.6	-505.7	-445.5	-264.0	0.34
B3LYP STO-3G(d)	-561.1	-133.8	4.9	-688.9	-506.4	-487.9	-191.7	0.15
B3LYP 3-21G	-449.4	-50.5	-7.4	-604.7	-388.8	-354.7	-232.9	0.22
B3LYP 3-21G(d)	-456.8	-84.0	-5.6	-591.1	-394.8	-384.6	-204.4	0.08
B3LYP 6-31G	-379.0	3.4	-3.9	-534.0	-324.8	-277.9	-233.1	0.30
B3LYP 6-31G(d)	-390.5	-38.2	-5.8	-520.1	-337.8	-313.5	-184.4	0.19
B3LYP 6-31G(2d)	-349.0	5.7	-12.8	-478.3	-290.1	-278.6	-194.0	0.09
B3LYP 6-31G(3d)	-349.9	2.6	-9.8	-484.6	-286.1	-279.0	-202.0	0.05
B3LYP 6-31+G(d)	-381.7	-29.7	-7.9	-512.3	-322.1	-310.7	-195.6	0.09
B3LYP 6-31++G(d)	-381.5	-26.4	-7.7	-513.2	-321.2	-310.2	-197.6	0.08
B3LYP 6-31+G(d,p)	-381.0	-22.9	-8.0	-511.6	-320.8	-310.7	-195.9	0.08
B3LYP 6-31++G(d,p)	-380.9	-20.2	-8.0	-512.5	-319.9	-310.3	-197.4	0.07
B3LYP 6-31++G(2d,p)	-342.8	16.0	-14.6	-474.9	-284.3	-269.3	-198.1	0.11
B3LYP 6-31++G(2d,2p)	-342.8	16.3	-13.8	-475.5	-283.7	-269.4	-198.9	0.11
B3LYP 6-31++G(3d,2p)	-345.2	11.4	-9.0	-477.2	-283.3	-275.2	-197.9	0.06
B3LYP 6-31++G(3df,2p)	--	--	--	--	--	--	--	--
B3LYP 6-311G	-294.2	59.7	-2.5	-455.2	-239.5	-187.8	-241.6	0.32
B3LYP 6-311G(d)	-309.8	13.7	-6.3	-455.9	-246.2	-227.2	-219.2	0.13
B3LYP 6-311G(2d)	-304.4	17.3	-9.0	-447.6	-239.5	-226.0	-214.8	0.09
B3LYP 6-311G(3d)	-300.9	18.5	-9.1	-443.3	-234.6	-224.7	-213.7	0.07
B3LYP 6-311+G(d)	-309.6	13.3	-7.6	-455.8	-246.1	-227.1	-219.2	0.13
B3LYP 6-311++G(d)	-309.6	13.4	-7.5	-455.7	-246.1	-227.0	-219.1	0.13
B3LYP 6-311+G(d,p)	-310.7	18.6	-7.6	-457.6	-247.3	-227.1	-220.4	0.14
B3LYP 6-311++G(d,p)	-310.6	18.9	-7.4	-457.5	-247.3	-227.1	-220.3	0.14
B3LYP 6-311++G(2d,p)	-304.5	20.0	-8.7	-447.9	-239.7	-226.0	-215.0	0.10
B3LYP 6-311++G(2d,2p)	-304.5	22.2	-8.7	-447.9	-239.6	-226.1	-215.1	0.09
B3LYP 6-311++G(3d,2p)	-301.1	22.4	-9.3	-444.0	-234.9	-224.3	-214.4	0.01
B3LYP 6-311++G(3df,2p)	--	--	--	--	--	--	--	--
Experimental		-12.5 ^g	-12.5 ^g				-111 ^g	

^a DFT, Density Functional Theory, B3LYP, Becke's Hybrid LYP Correlation Functional [6,9,11], GIAO – Gauge Including Atomic Orbitals. Calculations performed on B3LYP- 6-311++(2d,2p) optimized structure. ^b Isotropic chemical shift with respect to the secondary reference PH_3 ($\delta = -240$ ppm) or primary reference H_3PO_4 ($\delta = 0.0$ ppm) calculated at the same level of theory. ^c

Absolute isotropic chemical shift $\delta_{\text{cs}} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$, $\delta_{\text{cs}} = -\sigma_{\text{cs}}$ where σ_{cs} is the magnetic shielding in ppm. ^d Principal components of the CSA tensor where

$|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}|$. ^e Chemical shift anisotropy defined as,

$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22})$. ^f Chemical shift anisotropy asymmetry, $\eta = \frac{(\delta_{22} - \delta_{11})}{\delta_{33} - \delta_{\text{iso}}}$. ^g (Personal

communication, T. M. Alam).

Distribution:

2 Prof. Richard K. Brow
University of Missouri-Rolla
Ceramic engineering Department, 222 Menuff Hall
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