Fundamental vibrational frequencies of isolated 2-phosphaethynolate and 2-phosphaethynthiolate anions: OCP^- and SCP^-

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ABSTRACT

Both second-order vibrational perturbation theory (VPT2) and vibrational configuration interaction (VCI) theory have been employed to compute the fundamental vibrational frequencies of the isolated 2-phosphaethynolate and 2-phosphaethynthiolate anions (OCP^- and SCP^-) near the CCSD(T) complete basis set (CBS) limit. Our best estimates of the fundamental frequency associated with the doubly degenerate bending mode of these linear triatomic ions (ν_2) are 492 cm^{-1} for OCP^- and 362 cm^{-1} for SCP^-. Due to strong coupling, the stretching motions of SCP^- are best described as pseudo-symmetric (ν_1) and pseudo-antisymmetric (ν_3) stretches that we estimate to be 588 cm^{-1} and 1367 cm^{-1}, respectively. For OCP^-, our best predictions are 792 cm^{-1} for ν_1 and 1795 cm^{-1} for ν_3, with the latter having predominantly CO stretching character. In the absence of experimental gas-phase vibrational spectra for these species, these computed anharmonic frequencies provide important reference values to help quantify spectroscopic perturbations induced by environmental effects such as those from solvents or counter-ions.

KEYWORDS
2-phosphaethynolate anion (OCP^-);
2-phosphaethynthiolate anion (SCP^-);
anharmonic fundamental vibrational frequencies;
second-order vibrational perturbation theory (VPT2);
vibrational configuration interaction (VCI) theory

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1. Introduction

The cyanate and thiocyanate anions (OCN^- and SCN^-) are well known pseudohalides that are widely utilized in organic synthesis, in inorganic coordination chemistry and even in room temperature ionic liquids (RTILs) [1–15]. In contrast, the chemistry of their valence isoelectronic (or isovalent) analogues in which the N atom is replaced by P has been far less thoroughly explored. The rational synthesis and characterization of the 2-phosphaethynolate ion (OCP^-) was reported in 1992 [16], and that of 2-phosphaethynthiolate (SCP^-) followed shortly thereafter in 1994 [17]. However, the full potential of the former was not realized until different synthetic strategies for OCP^- were developed nearly two decades later [18–21]. As noted in a recent review [22], over the past decade the 2-phosphaethynolate anion has gone '*from a chemical curiosity to a viable reagent for the synthesis of novel phosphorus-containing molecules and compounds, and is now used by numerous research groups world-wide.*' Like their N counterparts (OCN^- and SCN^-), both OCP^- and SCP^- are ambident nucleophiles and ambidendate ligands that can bind via either the chalcogen or pnictogen atom, although coordination through O is less common [22–25].

Of these 4 isovalent species, high-resolution gas-phase infrared (IR) data is available for both OCN^- and SCN^- from velocity modulation diode laser spectroscopy experiments [26, 27]. In this work, the vibrational modes for these linear triatomic anions are numbered according to the convention used by Herzberg [28]. For SCN^-, the vibrational mode associated with ν_3 at 2066 cm^{-1} is dominated by the CN stretch [26]. In contrast, there is significant coupling of the CO and CN stretches in OCN^-, and the ν_3 vibration at 2124 cm^{-1} [27] is perhaps more appropriately described as a pseudo-antisymmetric stretch. The bending (ν_2) and other stretching (ν_1) vibrations were not reported in the gas phase, presumably due to their low IR intensities. However, all three vibrational modes of OCN^- and SCN^- have been observed in solid-state IR spectra using various alkali halide matrices [29, 30].

Although vibrational progressions in the negative ion photoelectron spectra of OCP^- and SCP^- have been assigned to the analogous stretching frequencies of the corresponding neutral radicals ($OCP^\bullet$ and $SCP^\bullet$) [31], no gas-phase vibrational spectra have been reported for the anions. However, the stretching frequencies for these ions have been obtained from solid-state Raman spectroscopy of their $[Na(18\text{-crown-}6)(THF)_2]^+$ salts with the pseudo-symmetric stretches (ν_1) assigned at 802 cm^{-1} for OCP^- and 595 cm^{-1} for SCP^- and the pseudo-antisymmetric stretches (ν_3) assigned at 1780 cm^{-1} for OCP^- and 1374 cm^{-1} for SCP^- [32]. These values are consistent with harmonic vibrational frequencies computed for the anions with DFT and *ab initio* methods [31–34]. Interestingly, the IR spectra of other ionic salts of OCP^- yield similar frequency assignments for the pseudo-antisymmetric stretch (ν_3 ranging from 1730 to 1780 cm^{-1}) but much larger values for the pseudo-symmetric stretch (ν_1 ranging from 1243 to 1282 cm^{-1}). For example, see Table 1 from the review by Goicoechea and Grützmacher and references therein [22].

The present study aims to shed some light on the vibrational spectra of OCP^- and SCP^- ions by computing their anharmonic fundamental frequencies using rigorous computational protocols that mirror those shown to accurately reproduced experimental gas-phase data for their isovalent nitrogen analogues (OCN^- and SCN^-) [35–37]. With SCN^- for example, both variational and perturbative anharmonic analyses using potential energy surfaces generated from CCSD(T) computations with aug-cc-pVQZ correlation consistent basis sets give results [35] that lie within 6 cm^{-1} of the gas-phase CN stretching frequency (ν_3) from velocity modulation diode laser spectroscopy

[26]. When similar theoretical analyses are applied to OCN^- [36, 37], the same good agreement is obtained with the experimental gas-phase fundamental value for ν_3 [27]. It is also possible to reliably characterize IR hot bands if the harmonic components are computed with larger aug-cc-pV5Z basis sets. Based on these encouraging results for OCN^- and SCN^-, the current investigation uses both second-order vibrational perturbation theory (VPT2) and vibrational configuration interaction (VCI) theory in conjunction with CCSD(T) computations employing large correlation consistent basis sets augmented with diffuse functions to characterize the fundamental vibrational frequencies of OCP^- and SCP^-.

2. Computational details

Full geometry optimizations and harmonic vibrational frequency computations were performed on OCP^- and SCP^- in `CFOUR` [38] using the analytic gradients and Hessians available for the CCSD(T) coupled-cluster method that includes single, double and a perturbative estimate of connected triple substitutions [39–41]. These computations were performed with a family of correlation consistent polarized valence basis sets augmented with diffuse functions (aug-cc-pVXZ where X=T, Q, 5, 6 and abbreviated here as aXZ) [42–44]. The effects of an extra set of tight d-functions on the P and S atoms on the optimized structures and harmonic vibrational frequencies were assessed with the aug-cc-pV($X + d$)Z basis sets (abbreviated a($X + d$)Z in this work for X = T–5) [45].

Both second order vibrational perturbation theory (VPT2) [46–50] and vibrational configuration interaction (VCI) theory [51, 52] were used to compute the fundamental vibrational frequencies of the anions with the CCSD(T) method and the aXZ basis sets up through $X = 5$. The implementation of VPT2 in `CFOUR` computed the necessary force constants from finite differences of analytic second derivatives [53–55] which required computing CCSD(T)/aXZ Hessians at 6 displaced geometries. The VCI analyses were performed with `Molpro` (Version 2018.1) [56, 57] using CCSD(T)/aXZ computations at 271 grid points for OCP^- and 251 for SCP^- to generate analytical representations of the potential energy surfaces [58–61].

The frozen-core approximation was applied in all computations corresponding to 2 core electrons for the C and O atoms along with 10 core electrons for the S and P atoms. Only the pure angular momentum components of the basis functions (5d, 7f, 9g, etc.) were utilized rather than their Cartesian counterparts (6d, 10f, 15g, etc.).

3. Results and discussion

3.1. Equilibrium bond lengths

Both OCP^- and SCP^- are linear with $C_{\infty v}$ symmetry and a $^1\Sigma^+$ ground electronic state. The CCSD(T) equilibrium bond lengths of both anions are presented in Table 1 from optimizations with the aXZ and a($X+d$)Z basis sets along with some previously reported CCSD(T) values. Prior CCSD(T) optimizations of both anions [31, 33] with conventional or modified aTZ (denoted mod-aTZ) basis sets give CO, CS and CP bond lengths that are very similar to the aTZ results obtained here.

The last row of data in Table 1 lists CCSD(T)/cc-pVQZ equilibrium bond lengths that have been reported for OCP^- (but unfortunately not for SCP^-) [34]. The addition

of diffuse functions to the basis set has a minimal effect on the computed bond lengths (increasing them by no more than 0.002 Å). The tight *d*-functions also have a very small impact on the interatomic distances of these anions. The largest change is seen with the triple-ζ basis sets where the CP and CS bond lengths contract by *ca.* 0.004 Å but the effect quickly vanishes with the larger basis sets. The a5Z and a$(5 + d)$Z bond lengths do not differ by more than 0.001 Å.

All of the CCSD(T) equilibrium bond lengths are well converged with the a5Z and a6Z results never differing by more than 0.001 Å. Our CCSD(T)/a6Z optimized structures indicate that the CP bond length in OCP^- is 0.026 Å longer than in SCP^-. This result is consistent with the CP bond orders of approximately 1.8 and 2.3, respectively, that were determined from natural bond orbital (NBO) analyses and with the greater delocalization of the lone pair orbitals from O than from S into a π^* NBO for the CP bond observed in natural localized molecular orbitals formed from NBOs [33].

Table 1. CCSD(T) equilibrium bond lengths (r(CZ) in Å where Z = O, P, S) computed for OCP^- and SCP^- using various basis sets.

	OCP^-		SCP^-	
Basis	r(CO)	r(CP)	r(CS)	r(CP)
aTZ	1.206	1.635	1.642	1.609
aQZ	1.203	1.629	1.636	1.603
a5Z	1.202	1.626	1.633	1.600
a6Z	1.202	1.625	1.632	1.599
a(T+*d*)Z	1.207	1.631	1.637	1.605
a(Q+*d*)Z	1.203	1.627	1.634	1.601
a(5+*d*)Z	1.202	1.625	1.632	1.600
mod-aTZ[a]	1.204	1.639	1.649	1.610
aTZ[b]	1.206	1.636	1.642	1.608
QZ[c]	1.202	1.627	–	–

[a]From reference 33 using a valence modified basis set.

[b]From reference 31.

[c]From reference 34.

3.2. Harmonic vibrational frequencies

Following the convention of Herzberg [28], the doubly degenerate bend is labeled ω_2 with ω_1 and ω_3 denoting the pseudo-symmetric and pseudo-antisymmetric stretches, respectively, as described in the Introduction. The CCSD(T) harmonic vibrational frequencies computed with the aXZ and a$(X+d)$Z basis sets are collected in Table 2 for OCP^- and SCP^- along with other previously reported CCSD(T) data [33, 34]. As with the bond lengths, harmonic frequencies obtained with a modified aTZ (mod-aTZ) basis set are reasonably consistent with the conventional aTZ results. The differences never exceed 12 cm^{-1} for OCP^- or 32 cm^{-1} for SCP^-. Those deviations are comparable to the effects of adding diffuse functions to the quadruple-ζ basis sets where the cc-pVQZ frequencies for OCP^- are consistently larger than aQZ results by 5 to 19 cm^{-1}. The tight *d*-functions have an almost imperceptible impact on the harmonic vibrational frequencies of these anions. The largest difference is only 3 cm^{-1} for triple-ζ basis sets and that decreases to 1 cm^{-1} or less for a5Z and a$(5 + d)$Z frequencies.

All of the CCSD(T) harmonic frequencies computed in this study are well converged. For a given vibration, the frequencies increase monotonically with the cardinal number of the basis set, and the largest change from aTZ to a6Z is only 14 cm^{-1}. In addition,

the a5Z and a6Z results never differ by more than 2 cm^{-1}.

Table 2. CCSD(T) harmonic vibrational frequencies (ω_i in cm^{-1}) computed for OCP^- and SCP^- using various basis sets.

	OCP^-			SCP^-		
Basis	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
aTZ	795	489	1809	592	356	1373
aQZ	802	493	1819	597	361	1381
a5Z	805	496	1821	600	363	1386
a6Z	806	496	1822	601	364	1387
a(T+*d*)Z	797	491	1809	594	359	1375
a(Q+*d*)Z	804	494	1819	598	362	1383
a(5+*d*)Z	806	496	1821	600	363	1386
mod-aTZ[a]	786	475	1804	580	335	1341
QZ[b]	807	504	1838	–	–	–

[a]From reference 33 using a valence modified basis set.

[b]From reference 34.

3.3. Fundamental vibrational frequencies

The VPT2 and VCI anharmonic corrections (δ_i) for the 3 fundamental vibrational frequencies of both ions obtained with the CCSD(T) method and aXZ basis sets are reported in Table 3. These δ_i values are defined by the difference between the fundamental (ν_i) and harmonic (ω_i) vibrational frequencies, respectively, so that $\nu_i = \omega_i + \delta_i$. The a$(X+d)$Z basis sets were not used for these anharmonic analyses because their harmonic vibrational frequencies were so similar to the values obtained with their smaller aXZ counterparts. Neither OCP^- or SCP^- are affected by the type of Fermi resonance interaction found in OCN^- [36, 37]. Consequently, the VPT2 and VCI results are nearly identical without variational corrections or other *ad hoc* procedures.

The anharmonic corrections for each vibrational mode are remarkably consistent regardless of the basis set (aTZ, aQZ or a5Z) or anharmonic analysis (VPT2 or VCI). For the pseudo-symmetric stretching and bending of OCP^-, for example, $\delta_1 = -14$ cm^{-1} and $\delta_2 = -4$ cm^{-1} for both VPT2 and VCI with all three basis sets. The pseudo-antisymmetric stretch for OCP^- exhibits the largest variation, but δ_3 still only ranges from -27 cm^{-1} to -30 cm^{-1}. Similar trends are seen with the anharmonic corrections for SCP^-. Very small values are obtained for the bending vibration with δ_2 falling between -1 cm^{-1} and -3 cm^{-1}. Again, the pseudo-antisymmetric stretch has the largest correction ($\delta_3 = -20$ or -21 cm^{-1}) while the correction for the pseudo-symmetric stretch has roughly half the magnitude ($\delta_1 = -12$ or -13 cm^{-1}).

Table 3. VPT2 and VCI anharmonic corrections (δ_i in cm^{-1}) for the fundamental vibrational frequencies of OCP^- and SCP^- obtained with the CCSD(T) method and various basis sets.

Anharm	Basis	OCP^-			SCP^-		
Method	Set	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3
VPT2	aTZ	−14	−4	−30	−13	−2	−21
VPT2	aQZ	−14	−4	−30	−13	−1	−21
VPT2	a5Z	−14	−4	−30	−13	−3	−21
VCI	aTZ	−14	−4	−28	−13	−2	−21
VCI	aQZ	−14	−4	−28	−13	−2	−21
VCI	a5Z	−14	−4	−27	−12	−3	−20

These corrections from Table 3 can be combined with the CCSD(T)/a6Z harmonic vibrational frequencies from Table 2 to provide our best estimates for the fundamental vibrational frequencies of OCP^- and SCP^-. Using the VCI corrections obtained with the a5Z basis set yields $\nu_1 = 792$ cm^{-1}, $\nu_2 = 492$ cm^{-1} and $\nu_3 = 1795$ cm^{-1} for OCP^-. The corresponding VCI fundamental frequencies for the SCP^- ion are 588 cm^{-1} for ν_1, 362 cm^{-1} for ν_2 and 1367 cm^{-1} for ν_3. If the VPT2 anharmonic corrections are used instead, all of the resulting fundamentals are within 1 cm^{-1} of the VCI values except for the ν_3 mode of OCP^- which decreases by 3 cm^{-1} to 1792 cm^{-1}.

4. Conclusions

The CCSD(T) quantum mechanical electronic structure method and large correlation consistent basis sets have been used to compute the harmonic and fundamental vibrational frequencies of the 2-phosphaethynolate and 2-phosphaethynthiolate negative ions. The anharmonic effects in these systems have been assessed with both VPT2 and VCI, and neither anion suffers from Fermi resonance interactions. As such, the anharmonic corrections from the two analyses typically differ by ≤ 1 cm^{-1}. The largest differece between VCI and VPT2 was 3 cm^{-1} for ν_3 of OCP^-.

For SCP^-, the CCSD(T)/a6Z harmonic vibrational frequencies are $\omega_1 = 601$ cm^{-1} $\omega_2 = 364$ cm^{-1} and $\omega_3 = 1387$ cm^{-1}. Our best estimates of the anharmonic corrections (last row of δ_i values from Table 3) only decrease these values by 3 to 20 cm^{-1} to give fundamental vibrational frequencies of 588 cm^{-1} for ν_1, 362 cm^{-1} for ν_2 and 1367 cm^{-1} for ν_3. The computed fundamental stretching frequencies (ν_1 and ν_3) for an isolated 2-phosphaethynthiolate negative ion are in fortuitously good agreement with the solid-state Raman values of 595 cm^{-1} and 1374 cm^{-1} [32].

For OCP^-, the CCSD(T)/a6Z values for ω_1, ω_2 and ω_3 are 806 cm^{-1}, 496 cm^{-1} and 1822 cm^{-1}, respectively. The VCI anharmonic corrections for the bending ($\delta_2 = -4$ cm^{-1}) and pseudo-symmetric stretching ($\delta_1 = -14$ cm^{-1}) are also relatively small and nearly identical to the corresponding values for SCP^- whereas the magnitude of the anharmonic correction for the pseudo-antisymmetric stretch (δ_3) of OCP^- grows to 27 cm^{-1}. As with SCP^-, these harmonic values and anharmonic shifts are combined to estimate the fundamental vibrational frequencies near the CCSD(T) complete basis set (CBS) limit to give the following values for OCP^-: $\nu_1 = 792$ cm^{-1} $\nu_2 = 492$ cm^{-1} and $\nu_3 = 1795$ cm^{-1}. These results for the isolated anion are again surprisingly close to the experimental stretching frequencies (ν_1 and ν_3) reported from solid-state Raman measurements at 802 cm^{-1} and 1780 cm^{-1} [32].

IR measurements of 2-phosphaethynolate salts report pseudo-antisymmetric stretching frequencies (ν_3) that fall between 1730 cm^{-1} and 1780 cm^{-1} [22]. The upper limit of that window matches the Raman value [32]. Collectively those results indicate that the identity of the counter-ion and other effects can readily induce shifts on the order of 50 cm^{-1} in the ν_3 mode of OCP^-. The IR values reported for the pseudo-symmetric stretch (ν_1) span a similar range of 40 cm^{-1}, but with values between 1243 cm^{-1} to 1282 cm^{-1}, they are more than 400 cm^{-1} larger than both the Raman measurement and the anharmonic value computed here. This large difference could suggest that ν_1, which has more pronounced CP stretching character, is exquisitely sensitive to environmental effects. It could also indicate that those features in the IR spectra have been misassigned. As such, the fundamental vibrational frequencies reported in this investigation provide important reference values for OCP^- and SCP^- that can be used to discern how the spectroscopic signatures of these anions change due to the presence

of a counter-ion, interactions with a solvent or other environmental effects. In a subsequent study, for example, we will examine the vibrational perturbations induced by the microhydration of these negative ions.

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