MOLECULAR PHYSICS e2262621
https://doi.org/10.1080/00268976.2023.2262621

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Fundamental vibrational frequencies of pnictogen (*Pn*) containing linear triatomic anions: OC*Pn*$^-$ and SC*Pn*$^-$ where *Pn* = N, P, As and Sb

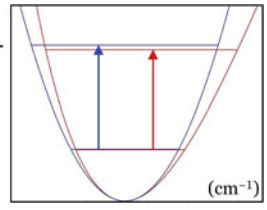
Kayleigh R. Barlow and Gregory S. Tschumper

Department of Chemistry and Biochemistry, University of Mississippi, University, MS, USA

ABSTRACT

The fundamental vibrational frequencies of the isolated OCAs$^-$ and SCAs$^-$ ions, as well as their heavier antimony analogues, are reported for the first time. A thorough analysis of basis set convergence of the bond lengths and harmonic vibrational frequencies, as well as the examination of anharmonic corrections, is conducted using the MP2 and CCSD(T) *ab initio* methods with robust basis sets for the OC*Pn*$^-$ and SC*Pn*$^-$ anions moving down the pnictogen series from *Pn* = N to Sb. Second-order vibrational perturbation theory (VPT2) and vibrational configuration interaction (VCI) theory are used to compute the fundamental vibrational frequencies of each triatomic anion approaching the MP2 and CCSD(T) complete basis set (CBS) limits. While fundamental vibrational frequencies have been reported for OCN$^-$ and SCN$^-$ in the gas phase, only experimental vibrational frequencies of the salts for the heavier pnictogen analogues (P and As) have been reported. Experimental Raman vibrational frequencies for OCAs$^-$ and SCAs$^-$ salts were found to be coincidentally in good agreement with the CCSD(T) VCI frequencies near the CBS limit, differing by at most 13 cm^{-1} from the former and 9 cm^{-1} from the latter. These modest differences are likely due to the presence of counter-ions and other environmental effects in the solid state, and the overall agreement between the salts and gas-phase frequencies is quite similar to that observed for the OCP$^-$ and SCP$^-$ ions.

	OCAs$^-$	SCAs$^-$	OCSb$^-$	SCSb$^-$
ω_1	617	478	494	406
ω_2	445	328	392	293
ω_3	1798	1281	1800	1222
ν_1	608	469	486	399
ν_2	442	327	389	292
ν_3	1768	1261	1772	1203



ARTICLE HISTORY
Received 25 July 2023
Accepted 19 September 2023

KEYWORDS
Pnictogen-containing anions; cyanate analogues; anharmonic fundamental vibrational frequencies; second-order vibrational perturbation theory (VPT2); vibrational configuration interaction (VCI) theory

1. Introduction

Interest in the OCN$^-$ and SCN$^-$ pseudohalides along with their phosphorous analogues (OCP$^-$ and SCP$^-$) has increased over the past decade due to their success as ambidentate ligands and role as important synthetic precursors [1–23]. By comparison, significantly less is known about their heavier pnictogen analogues (i.e., arsenic and antimony). The 2-arsaethynolate and 2-arsaethynthiolate anions (OCAs$^-$ and SCAs$^-$) were recently successfully synthesised in 2016 [24] and 2018 [25], respectively, following the strategies used for OCP$^-$ and SCP$^-$ [10,11,26,27]. While their antimony counterparts (OCSb$^-$ and SCSb$^-$) have remained elusive to date, theoretical computations conducted in 2014 concluded that OCSb$^-$ should be synthetically accessible [28].

The vibrational stretching frequencies associated with the antisymmetric modes (ν_3) for both the OCN$^-$ and SCN$^-$ isolated ions has been recorded experimentally using velocity modulation diode laser spectroscopy to obtain high-resolution gas-phase values of 2124 cm^{-1} and 2066 cm^{-1}, respectively [29,30]. The remaining modes, the symmetric stretch (ν_1) and the doubly degenerate bend (ν_2), for the isolated anions have only been

CONTACT Gregory S. Tschumper tschumpr@olemiss.edu Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677–1848, USA
†Current address: Department of Chemistry and Biochemistry, University of Alabama, Tuscaloosa, AL 35487–0336, USA

Supplemental data for this article can be accessed here. https://doi.org/10.1080/00268976.2023.2262621

determined [31–33] via rigorous theoretical techniques which have been proven to provide reliable fundamental frequencies for a large number molecular species [34–44], including many contributions from Lee and co-workers [45–59]. Following computational protocols that mirror those performed for the nitrogen-containing anions, the fundamental vibrational frequencies of OCP^- and SCP^- were recently computed close to the CCSD(T) complete basis set (CBS) limit [60]. The solid-state Raman frequencies were reported for both stretching modes of the heavier phosphorous analogues as salts [24,25] and were in surprisingly good agreement (differing by $\leq 10\,cm^{-1}$) with the fundamental frequencies computed for the isolated anions. In the same study [25], the stretching frequencies for the $OCAs^-$ and $SCAs^-$ ions were obtained from solid-state Raman spectroscopy of their ionic salts. The symmetric stretches (ν_1) were assigned as $618\,cm^{-1}$ for $OCAs^-$ and $474\,cm^{-1}$ for $SCAs^-$ as well as $1755\,cm^{-1}$ and $1270\,cm^{-1}$ which were assigned to antisymmetric stretches (ν_3) of $OCAs^-$ and $SCAs^-$. Additionally, ν_3 was experimentally determined to be $1756.4\,cm^{-1}$ for $OCAs^-$ via matrix isolation Fourier-transform infrared (FTIR) spectroscopy and was attributed to the CO stretching frequency [61].

This study extends prior computations of the fundamental vibrational frequencies for the isolated $OCPn^-$ and $SCPn^-$ anions (Pn = N and P) and moves down the pnictogen series to their heavier arsenic and antimony analogues [31–33,60]. The nitrogen- and phosphorous-containing anions are revisited in order to examine the pnictogen series as a whole at the same levels of theory. A thorough analysis of basis set convergence of the bond lengths, harmonic vibrational frequencies and anharmonic corrections will be examined using both the MP2 and CCSD(T) *ab initio* methods as well as the second-order vibrational perturbation theory (VPT2) and vibrational configuration interaction (VCI) theory anharmonic methods with large correlation consistent basis sets.

2. Computational details

Fully optimised geometries and harmonic vibrational frequencies were computed for the $OCPn^-$ and $SCPn^-$ series with the MP2 method [62] utilising the analytic gradients and Hessians available in `Gaussian16` [63]. Geometry optimizations and harmonic vibrational frequency computations were also carried out with the CCSD(T) method [64–66] employing the analytic gradients available in `CFOUR` [67,68] and `Molpro2022` [69–71]. The defaults for displacements and step sizes were adopted in both software packages to evaluate the Hessians numerically from finite differences of gradients, and the two procedures always gave frequencies that differed by less than $1\,cm^{-1}$ across all of the ions for tests performed with the double- and triple-ζ basis sets employed in this study.

A series of correlation consistent basis sets augmented with diffuse functions on all atoms was used for the MP2 and CCSD(T) computations that is simply abbreviated aXZ, where X denotes the cardinal number of the basis set and ranges from D to 5. The aug-cc-pVXZ basis sets [72–74] were used ~~was used~~ for C, N and O. Although the effects of the additional set of tight d-functions were previously found to be negligible for OCP^- and SCP^- [60], the aug-cc-pV($X+d$)Z basis sets [75] were used in this study for P and S. For the two largest atomic centers, As and Sb, the aug-cc-pwCVXZ-PP basis sets were used in conjuctions with small-core relativistic pseudopotentials [76–78] to replace the 10 inner core electrons ($1s^2 2s^2 2p^6$) for As and 28 inner core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) for Sb. Spherical harmonic components of the basis functions (i.e. 5d, 7f, etc.) were used in all computations rather than their Cartesian counterparts.

Only the valence electrons were correlated in the MP2 and CCSD(T) computations for C, N, O, P and S, which corresponds to freezing the 1s orbitals for C, O and the 1s, 2s, 2p orbitals for S, P. For As and Sb, however, the subvalence $(n-1)d$ orbitals cannot be neglected. Consequently they were included in the MP2 and CCSD(T) computations along with the valence orbitals (ns and np), leaving the $(n-1)s$ and $(n-1)p$ orbitals frozen. Results obtained by correlating only the valence electrons with the aug-cc-pVXZ and aug-cc-pVXZ-PP basis sets are provided in the Supplemental Material for comparison. For the optimised structures, the maximum residual component of the Cartesian gradient did not exceed 3×10^{-7} hartree bohr^{-1}, and the following convergence thresholds (in a.u.) were met or exceeded for the electronic structure computations: 10^{-10} for the Hartree-Fock density, 10^{-8} for the coupled cluster amplitudes, 10^{-8} for lambda equations.

Fundamental vibrational frequencies were computed using second-order vibrational perturbation theory (VPT2) [79–81] and vibrational configuration interaction (VCI) theory [82,83]. The VPT2 fundamental frequencies were computed with both `CFOUR` and `Molpro2022`. In `CFOUR`, the necessary force constants were computed from finite differences of analytic gradients using the defaults for displacements and step sizes. In contrast, the VPT2 and VCI anharmonic frequency computations performed in `Molpro2022` utilised analytical representations of the potential energy surfaces constructed with the `SURF` and `POLY` programs [84–87], and the default settings were adopted for all procedures

Table 1. CCSD(T)/a5Z equilibrium bond lengths (in **bold**) for each triatomic anion preceded by the deviations from those values with the smaller basis sets, with all data in Å.

	Bond	2-ζ	3-ζ	4-ζ	5-ζ
OCN^-	r(CO)	+0.017	+0.005	+0.001	**1.229**[a]
	r(CN)	+0.020	+0.004	+0.001	**1.193**[a]
SCN^-	r(CS)	+0.021	+0.006	+0.002	**1.667**
	r(CN)	+0.020	+0.004	+0.001	**1.178**
OCP^-	r(CO)	+0.017	+0.005	+0.001	**1.202**[b]
	r(CP)	+0.022	+0.006	+0.001	**1.625**[b]
SCP^-	r(CS)	+0.022	+0.005	+0.002	**1.632**[b]
	r(CP)	+0.020	+0.006	+0.001	**1.600**[b]
$OCAs^-$	r(CO)	+0.018	+0.005	+0.001	**1.196**
	r(CAs)	+0.018	+0.005	+0.001	**1.743**
$SCAs^-$	r(CS)	+0.022	+0.006	+0.002	**1.626**
	r(CAs)	+0.017	+0.005	+0.001	**1.711**
$OCSb^-$	r(CO)	+0.018	+0.005	+0.001	**1.186**
	r(CSb)	+0.020	+0.006	+0.001	**1.970**
$SCSb^-$	r(CS)	+0.022	+0.006	+0.002	**1.614**
	r(CSb)	+0.022	+0.006	+0.002	**1.928**

[a]From [33].[b]From [60].

Table 2. MP2/a5Z equilibrium bond lengths (in **bold**) for each triatomic anion preceded by the deviations from those values with the smaller basis sets, with all data in Å.

	Bond	2-ζ	3-ζ	4-ζ	5-ζ
OCN^-	r(CO)	+0.015	+0.004	+0.001	**1.229**
	r(CN)	+0.019	+0.004	+0.001	**1.200**
SCN^-	r(CS)	+0.018	+0.005	+0.001	**1.652**
	r(CN)	+0.019	+0.004	+0.001	**1.189**
OCP^-	r(CO)	+0.016	+0.004	+0.001	**1.209**
	r(CP)	+0.020	+0.005	+0.001	**1.620**
SCP^-	r(CS)	+0.019	+0.004	+0.001	**1.623**
	r(CP)	+0.018	+0.005	+0.001	**1.606**
$OCAs^-$	r(CO)	+0.016	+0.004	+0.001	**1.206**
	r(CAs)	+0.016	+0.004	+0.001	**1.726**
$SCAs^-$	r(CS)	+0.019	+0.005	+0.001	**1.621**
	r(CAs)	+0.015	+0.004	+0.001	**1.710**
$OCSb^-$	r(CO)	+0.016	+0.004	+0.001	**1.200**
	r(CSb)	+0.019	+0.005	+0.001	**1.934**
$SCSb^-$	r(CS)	+0.019	+0.005	+0.001	**1.618**
	r(CSb)	+0.019	+0.005	+0.001	**1.912**

associated with these anharmonic vibrational frequency analyses. (Note that the `XSURF` program was not used to facilitate direct comparison with prior results reported for OCP^- and SCP^- [60] that were computed with `Molpro2018`.)

3. Results and discussion

3.1. Equilibrium geometries

Figure 1 shows the $OCPn^-$ and $SCPn^-$ ions examined in this study with their CCSD(T) optimised bond lengths computed near the complete basis set (CBS) limit as reported in the rightmost column of Table 1. Similar to prior work for the $OCPn^-$ series where Pn = N through Bi was studied up to the CCSD(T)/cc-pVQZ level of theory [28], the CO bond lengths computed here decrease monotonically with CCSD(T) CBS distances beginning at 1.229 Å and shortening to 1.186 Å as the size of the pnictogen atom increases from nitrogen down to antimony. At the same time, the CPn bond lengths increase from 1.193 Å for CN to 1.970 Å for CSb. These same trends are observed for the $SCPn^-$ series with slightly larger decreases in the carbon-chalcogen bond lengths and somewhat smaller decreases in the carbon-pnictogen bond lengths through the progression from N to Sb.

Table 1 illustrates the basis set convergence of the bond lengths for each triatomic species as they approach the CBS limit. For all of the anions, a triple-ζ basis set provides bond lengths that are slightly larger (by 0.004 to 0.006 Å) than the corresponding a5Z values whereas the aQZ bond lengths differ by no more than 0.002 Å from the a5Z data.

MP2 also appears to provide tightly converged bond lengths with the aTZ, aQZ and a5Z basis sets, as seen in Table 2. The best estimates of the MP2 CBS equilibrium bond lengths (in bold) typically differ by approximately ±0.01 Å from the corresponding CCSD(T)/a5Z values in Table 1, with the largest difference occurring for CSb bond of $OCSb^-$ for which MP2 predicts a bond length 0.036 Å shorter than CCSD(T).

The bond lengths from the valence-only MP2 and CCSD(T) optimizations with the aug-cc-pVXZ and aug-cc-pVXZ-PP basis sets are reported in the Supplemental Material. For $X = 5$ and 6, the CO, CN, CP and CS bonds lengths lie within 0.001 Å of the a5Z results in Tables 1 and 2. In contrast, the r(CAs) and r(CSb) values in the Supplemental Material are too large by roughly 0.02 to 0.03 Å which reflects the importance of including the outer-core $(n-1)d$ electrons in the post-Hartree-Fock correlation procedures for this property.

3.2. Harmonic vibrational frequencies

Assignment of the harmonic vibrational frequencies (ω_i) of the linear triatomic species in this work follows the protocol used by Herzberg [88], where the pseudo-symmetric and pseudo-antisymmetric stretches are denoted as ω_1 and ω_3, while ω_2 is assigned to the doubly degenerate bend. Well-converged CCSD(T) harmonic vibrational frequencies are reported in bold in rightmost column of Table 3 while deviations from these values are reported in the columns to the left for each smaller basis set (similar to the tables for the bond lengths). For a given vibration, the frequencies consistently increase as the size of the basis set increases. The large deviations associated with the double-ζ basis sets rapidly decrease in magnitude to just a few wavenumbers when quadruple-ζ basis sets are employed. For the aQZ basis set, all of the CCSD(T) harmonic vibrational frequencies are with 4 cm^{-1} of the a5Z values (Table 3).

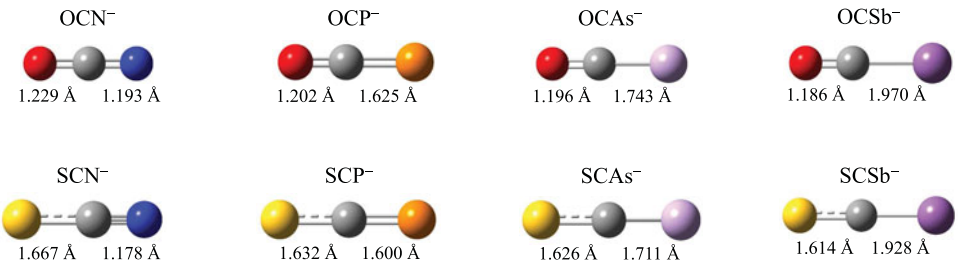


Figure 1. CCSD(T) optimised structures and corresponding bond lengths obtained with the 5-ζ basis sets.

Table 3. CCSD(T)/a5Z harmonic vibrational frequencies (in **bold**) for each triatomic anion preceded by the deviations from those values with the smaller basis sets, with all data in cm^{-1}.

	Mode	2-ζ	3-ζ	4-ζ	5-ζ
OCN^-	ω_1	−36	−9	−2	**1228**[a]
	ω_2	−25	−8	−3	**625**[a]
	ω_3	−48	−14	−4	**2166**[a]
SCN^-	ω_1	−15	−8	−2	**729**
	ω_2	−15	−3	−2	**460**
	ω_3	−39	−15	−3	**2095**
OCP^-	ω_1	−24	−9	−2	**806**[b]
	ω_2	−21	−5	−1	**496**[b]
	ω_3	−49	−13	−3	**1821**[b]
SCP^-	ω_1	−14	−6	−2	**600**[b]
	ω_2	−22	−4	−1	**363**[b]
	ω_3	−29	−11	−3	**1386**[b]
$OCAs^-$	ω_1	−18	−7	−2	**617**
	ω_2	−15	−3	−1	**445**
	ω_3	−53	−13	−3	**1798**
$SCAs^-$	ω_1	−12	−6	−2	**478**
	ω_2	−20	−4	−2	**328**
	ω_3	−29	−10	−3	**1281**
$OCSb^-$	ω_1	−17	−6	−2	**494**
	ω_2	−11	−1	−1	**392**
	ω_3	−56	−15	−3	**1800**
$SCSb^-$	ω_1	−13	−6	−2	**406**
	ω_2	−18	−4	−1	**293**
	ω_3	−29	−11	−4	**1222**

[a]From [33].[b]From [60].

Table 4. MP2/a5Z harmonic vibrational frequencies (in **bold**) for each triatomic anion preceded by the deviations from those values with the smaller basis sets, with all data in cm^{-1}.

	Mode	2-ζ	3-ζ	4-ζ	5-ζ
OCN^-	ω_1	−28	−7	−2	**1217**
	ω_2	−20	−6	−2	**617**
	ω_3	−37	−11	−3	**2149**
SCN^-	ω_1	−10	−6	−2	**757**
	ω_2	−13	−2	−2	**461**
	ω_3	−34	−13	−3	**2002**
OCP^-	ω_1	−19	−7	−2	**816**
	ω_2	−19	−3	−1	**494**
	ω_3	−32	−8	−2	**1848**
SCP^-	ω_1	−9	−5	−1	**604**
	ω_2	−20	−3	−1	**363**
	ω_3	−20	−7	−3	**1418**
$OCAs^-$	ω_1	−15	−5	−1	**646**
	ω_2	−14	−2	−1	**449**
	ω_3	−34	−8	−2	**1802**
$SCAs^-$	ω_1	−8	−4	−1	**481**
	ω_2	−18	−2	−2	**329**
	ω_3	−20	−7	−3	**1337**
$OCSb^-$	ω_1	−14	−5	−1	**544**
	ω_2	−11	+0	−1	**403**
	ω_3	−36	−8	−2	**1753**
$SCSb^-$	ω_1	−9	−4	−1	**418**
	ω_2	−17	−2	−1	**296**
	ω_3	−21	−7	−3	**1293**

Moving down group 15 of the periodic table from *Pn* = N to Sb, the CCSD(T)/a5Z harmonic vibrational frequencies in Table 3 tend to decrease for all 3 modes as atomic mass increases for both the oxygen- and sulphur-containing anions. The sole exception to this trend occurs for $OCAs^-$ and $OCSb^-$ for which ω_3 has nearly identical values (1798 cm^{-1} and 1800 cm^{-1}, respectively).

Compared to CCSD(T), the MP2 harmonic vibrational frequencies in Table 4 exhibit similar rapid convergence to the CBS limit as the 4-ζ frequencies are within 4 cm^{-1} of 5-ζ values. However, comparing the harmonic vibrational frequencies obtained with largest a5Z basis sets for both CCSD(T) and MP2 (bold values in Tables 3 and 4) across the entire series of triatomic anions, the differences were larger than 50 cm^{-1} in several cases and grew as large as 93 cm^{-1} for ω_3 of SCN^-. As a result, only the CCSD(T) harmonic frequencies are used to determine our best estimates of the fundamental frequencies.

The harmonic vibrational frequencies from the valence-only MP2 and CCSD(T) optimizations with the aug-cc-pV*X*Z and aug-cc-pV*X*Z-PP basis sets are reported in the Supplemental Material. For $X = 5$ and 6, the deviations between the data in the Supplemental Material and the corresonding a5Z values in Tables 3 and 4 did not exceed 4 cm^{-1} except for $OCSb^-$ and $SCSb^-$. The largest difference was only 12 cm^{-1} for ω_1 of $OCSb^-$.

3.3. Anharmonic vibrational frequencies

MP2 anharmonic corrections for each mode (δ_i) were obtained using the VPT2 and VCI anharmonic methods with up to pentuple-ζ basis sets for all anions whereas the same CCSD(T) anharmonic analyses were only carried out with the double-, triple- and quadruple-ζ basis sets. The last column of Table 5 lists the VCI CCSD(T)/aQZ

Table 5. CCSD(T)/aQZ VCI anharmonic corrections (in **bold**) for the fundamental vibrational frequencies for each triatomic anion preceded by the deviations from those values at the other levels of theory, with all data in cm^{-1}.

		MP2								CCSD(T)					
		VPT2 correction				VCI correction				VPT2 correction			VCI correction		
	Mode	2-ζ	3-ζ	4-ζ	5-ζ	2-ζ	3-ζ	4-ζ	5-ζ	2-ζ	3-ζ	4-ζ	2-ζ	3-ζ	4-ζ
OCN^-	δ_1	−5[a]	−2[a]	−2[a]	−0[a]	−3	−0	+0	+1	−5[a]	−2[a]	−2[a]	−3	−1	**−48**
	δ_2	+0	+1	+1	+1	+3	+1	+1	+1	−1	+0	+0	−1	+0	**−5**
	δ_3	+5	+4	+4	+4	+5	+5	+4	+4	−1	+0	+1	−1	+0	**−44**
SCN^-	δ_1	−2	−1	−1	−1	−1	−1	−1	−1	−1	+0	+0	−1	+0	**−12**
	δ_2	+0	+0	+0	+0	+0	+1	+1	+0	−1	+0	+0	−1	+0	**−4**
	δ_3	−3	−3	−3	−3	−2	−2	−2	−2	+0	+0	+0	+0	+0	**−30**
OCP^-	δ_1	+0	+1	+0	+1	+1	+1	+1	+1	−1	+0	+0	+0	+0	**−14**
	δ_2	+1	+1	+0	+1	+1	+1	+1	+1	+0	+0	+0	+0	+0	**−4**
	δ_3	+0	+0	−1	−1	+1	+1	+1	+1	−3	−2	−3	−1	+0	**−27**
SCP^-	δ_1	−3	+0	−1	+0	−1	+1	+0	+0	−3	−1	−1	−2	+0	**−12**
	δ_2	+2	+0	+0	+1	+3	+1	+1	+1	+1	+0	+0	+2	+0	**−2**
	δ_3	+2	+1	+1	+2	+2	+2	+2	+2	−1	−1	+0	+0	+0	**−21**
$OCAs^-$	δ_1	+0	+0	+0	+0	+0	+1	+0	+0	+0	+0	+0	+0	+0	**−9**
	δ_2	+1	+1	+1	+0	+1	+1	+1	+1	+0	−1	+0	+0	+0	**−3**
	δ_3	+3	+3	+2	+3	+4	+3	+3	+3	+0	+0	+0	+0	+0	**−29**
$SCAs^-$	δ_1	−1	+1	+1	+1	+0	+1	+1	+1	−2	+0	+0	−1	+0	**−9**
	δ_2	+3	+1	+1	+1	+3	+1	+1	+1	+2	+1	+0	+1	+0	**−2**
	δ_3	+2	+2	+2	+2	+2	+2	+2	+2	+0	+0	+0	+0	+0	**−20**
$OCSb^-$	δ_1	−1	+0	−1	−1	−1	+0	+0	−1	−1	+0	+0	+0	+0	**−7**
	δ_2	+0	+0	+0	+0	+0	+0	+0	+0	−1	−1	+0	+0	−1	**−3**
	δ_3	+4	+3	+3	+3	+4	+4	+4	+4	+0	+0	+0	+0	+0	**−28**
$SCSb^-$	δ_1	+0	+1	+0	+0	+0	+1	+1	+1	−1	+0	+0	−1	+0	**−7**
	δ_2	+3	+1	+1	+1	+3	+1	+1	+1	+1	+0	+0	+1	+0	**−1**
	δ_3	+2	+1	+1	+1	+1	+1	+2	+2	−1	+0	+0	+0	+0	**−19**

[a] After correcting for a known Fermi resonance between ν_1 and $2\nu_2$. (See [31] and [33].)

anharmonic corrections obtained for the three fundamental vibrational frequencies of each anion in bold and is preceded by the deviations of the δ_i values computed at all other levels of theory.

The anharmonic corrections for each vibrational mode of each ion are remarkably consistent regardless of the method (CCSD(T) or MP2), basis set (2-ζ through 5-ζ) or anharmonic analysis (VPT2 or VCI) chosen, resulting in deviations of at most 5 cm^{-1}. The CCSD(T) anharmonic corrections with the aTZ and aQZ basis sets fell within ±2 cm^{-1} of each other regardless of whether using the VPT2 and VCI procedures and the deviations only increased to ±3 with the aDZ basis sets. The MP2 method was also able to reliably model the anharmonic corrections to the harmonic vibrational frequencies with similar deviations on average that occasionally grew as large as ±5 cm^{-1}.

The magnitude of the anharmonic corrections decreases as the atomic mass within the molecule increases. For example, the stretching modes of OCN^- have rather large corrections of $\delta_1 = -48\ cm^{-1}$ and $\delta_3 = -44\ cm^{-1}$ from CCSD(T)/aQZ VCI anharmonic analyses that become −12 and −30 cm^{-1}, respectively, when the oxygen atom is replaced with a sulphur atom or −14 cm^{-1} and −27 cm^{-1}, respectively, when the nitrogen atom is substituted with a phosphorous atom. Similar trends are seen for the anharmonic corrections for the stretching modes of all of the other heavier species, with the arsenic and antimony analogues having stretching frequency corrections of −7 to −9 cm^{-1} for δ_1 and −19 to −29 cm^{-1} for δ_3. The anharmonic corrections for the bending vibrations for all of the triatomic species were very small with δ_2 falling between −5 cm^{-1} (for OCN^-) and −1 cm^{-1} (for $SCSb^-$).

Applying the CCSD(T)/aQZ anharmonic corrections from Table 5 to the CCSD(T)/a5Z harmonic vibrational frequencies from Table 3 (each in bold) provides our best estimates of the fundamental vibrational frequencies (ν_i) near the CCSD(T) CBS limit for each triatomic anion. These CCSD(T) composite values are reported in the third column of Table 6 followed by a second set of composite anharmonic frequecnies tabulated in the fourth column that use the MP2 VCI corrections obtained with the pentuple-ζ basis sets in conjunction with the same CCSD(T) harmonic vibrational frequencies. Although the 'CCSD(T)/MP2 estimates' were obtained at a significantly reduced computational cost, they typically fall within 2 cm^{-1} (and always within 4 cm^{-1}) of the CCSD(T) best estimates.

Experimental gas phase and prior theoretical fundamental frequencies of OCN^- and SCN^- are listed in the fifth and seventh columns of Table 6, respectively. Our CCSD(T) best estimates lie within ±2 cm^{-1} of the experimental gas phase pseudo-antisymmetric stretching frequencies (ν_3) of OCN^- and SCN^- [29,30]. Compared to the fundamental frequencies previously computed for

Table 6. Best estimates of the fundamental vibrational frequencies (ν_i in cm^{-1}) for each triatomic anion obtained with the MP2 and CCSD(T) methods alongside available experimental and theoretical frequencies.

		CCSD(T) best	CCSD(T)/MP2	Experiment		Prior
	Mode	estimates[a]	estimates[b]	Gas phase[c]	Solid phase[d]	Theory[e]
OCN^-	ν_1	1180	1181	–	–	1181
	ν_2	620	620	–	–	620
	ν_3	2122	2126	2124	–	2122
SCN^-	ν_1	716	716	–	–	708
	ν_2	456	456	–	–	452
	ν_3	2066	2064	2066	–	2061
OCP^-	ν_1	792	793	–	802	–
	ν_2	492	493	–	–	–
	ν_3	1794	1795	–	1786	–
SCP^-	ν_1	588	588	–	595	–
	ν_2	361	362	–	–	–
	ν_3	1366	1367	–	1370	–
$OCAs^-$	ν_1	608	609	–	618	–
	ν_2	442	443	–	–	–
	ν_3	1768	1771	–	1755	–
$SCAs^-$	ν_1	469	470	–	474	–
	ν_2	327	328	–	–	–
	ν_3	1261	1263	–	1270	–
$OCSb^-$	ν_1	486	486	–	–	–
	ν_2	389	389	–	–	–
	ν_3	1772	1776	–	–	–
$SCSb^-$	ν_1	399	399	–	–	–
	ν_2	292	293	–	–	–
	ν_3	1203	1204	–	–	–

[a]CCSD(T)/a5Z harmonic frequencies with CCSD(T)/aQZ VCI corrections.[b]CCSD(T)/a5Z harmonic frequencies with MP2/a5Z VCI corrections.[c]From [29,30].[d]From [25]. [e]From [31,33]. Full 3D variational calculations at CCSD(T)/a5Z for OCN^- and CCSD(T)/aQZ for SCN^-.

OCN^- and SCN^- [31,33], our CCSD(T) best estimates predict frequencies within ± 1 cm^{-1} for the former anion and within 5 to 8 cm^{-1} for the latter.

While the vibrational frequencies of the heavier analogues have not been reported experimentally in the gas phase, solid-state Raman frequencies (listed in column six of Table 6) were reported for the stretching modes of the phosphorous- and arsenic-containing analogues within their salts [24,25]. In prior work [60], the CCSD(T) fundamental vibrational frequencies computed for the OCP^- and SCP^- anions were found to be in fortuitously good agreement with the solid-state frequencies. That study found the solid-state experimental frequency for ν_1 of OCP^- to be just 10 cm^{-1} larger than the computed anaharmonic value whereas the theoretical values was 8 cm^{-1} larger for ν_3. For SCP^-, the computed fundamental stretching frequencies (ν_1 and ν_3) were merely 7 cm^{-1} and 4 cm^{-1}, respectively, lower in energy than the solid-state Raman values. In the present study, similar agreement is observed for both arsenic-containing ions. Our best estimates of the CCSD(T) fundamental frequencies for both $OCAs^-$ and $SCAs^-$ are within 13 cm^{-1} of the solid-state Raman values.

4. Conclusions

The systematic basis set convergence of the bond lengths and harmonic vibrational frequencies computed for the $OCPn^-$ and $SCPn^-$ ions is illustrated in Tables 1 through 4 for both the CCSD(T) and MP2 methods. A basis set of at least quadruple-ζ quality augmented with diffuse functions can provide bond lengths within 0.002 Å and harmonic vibrational frequencies within 4 cm^{-1} of the a5Z results. MP2 bond lengths and harmonic vibrational frequencies near the CBS limit differ from those at CCSD(T) by as much as 0.036 Å and 91 cm^{-1}, respectively.

In contrast, the anharmonic corrections for each vibrational mode are exceptionally consistent regardless of the basis set (aDZ, aTZ, aQZ or a5Z), method (CCSD(T) or MP2) or anharmonic analysis (VPT2 or VCI). Overall, using MP2 anharmonic corrections with CCSD(T) harmonic frequencies yields results that are nearly identical to our best available CCSD(T) fundamental frequencies.

Looking at the entire series, as the atomic radius of the pnictogen atom increases from N to Sb, the expected increase in the carbon-pnictogen bond length was accompanied by a monotonic decrease in the carbon-chalcogen bond length. Despite the contraction in the carbon-chalcogen bonds, the harmonic vibrational frequencies (ω_1, ω_2 and ω_3) tend to systematically decrease for both $OCPn^-$ and $SCPn^-$ as the mass of the pnictogen atom increase from N to P to As to Sb. There was serendipitously good agreement between our best estimates of the fundamental vibrational frequencies near

the CCSD(T) CBS limit and the available solid phase experimental data for the N, P and As containing anions, falling within 13 cm^{-1} of experiment despite the presence of counter-ions and influence of other environmental effects in the solid state. The fundamental vibrational frequencies reported here for the first time for the isolated $OCAs^-$, $SCAs^-$, $OCSb^-$, and $SCSb^-$ ions can be used as reference values in discerning how the presence of a counter-ion, interaction with a solvent or other environmental effects can change the spectroscopic signatures of these anions.

Acknowledgments

This work is dedicated in memory of Dr. Timothy J. Lee, an exceptional theoretical chemist whose contributions left a profound mark on the field. A portion of the work presented here was accomplished thanks to the generous allocation of time on the computational resources available at Mississippi Center for Supercomputing Research (MCSR).

Disclosure statement

Q1 No potential conflict of interest was reported by the author(s).

Funding

This work was supported in part by the National Science Foundation (Division of Chemistry) under Grant CHE-2154403.

ORCID

Kayleigh R. Barlow http://orcid.org/0000-0002-2567-7638
Gregory S. Tschumper http://orcid.org/0000-0002-3933-2200

References

Q2

[1] J. Burmeister, Coordin. Chem. Rev. **1** (1), 205–221 (1966). doi:10.1016/S0010-8545(00)80174-5
[2] A. Norbury, in *Advances in Inorganic Chemistry and Radiochemistry*, edited by H.J. Emeléus and A.G. Sharpe, (Academic Press, Cambridge, 1975), Vol. 17, pp. 231–386.
[3] S. Patai, editor, *Cyanates and Their Thio Derivatives (1977)* (John Wiley & Sons, Ltd., Chichester, 1977).
[4] J. Burmeister, Coordin. Chem. Rev. **105**, 77–133 (1990). doi:10.1016/0010-8545(90)80019-P
[5] J. Pringle, J. Golding, C. Forsyth, G. Deacon, M. Forsyth and D. MacFarlane, J. Mater. Chem. **12**, 3475–3480 (2002). doi:10.1039/b208372h
[6] S. Forsyth, J. Pringle and D. MacFarlane, Aust. J. Chem. **57** (2), 113–119 (2004). doi:10.1071/CH03231
[7] A. Kamal and G. Chouhan, Tetrahedron Lett. **46** (9), 1489–1491 (2005). doi:10.1016/j.tetlet.2005.01.040
[8] T. Tsuda and C. Hussey, in *Modern Aspects of Electrochemistry, No. 45*, edited by R.E. White (Springer New York, New York, NY, 2009), Vol. 45, Chap. 2, pp. 63–174.
[9] J. Janikowski, C. Forsyth, D. MacFarlane and J. Pringle, J. Mater. Chem. **21**, 19219–19225 (2011). doi:10.1039/c1jm14055h
[10] A. Jupp and J. Goicoechea, Angew. Chem. Int. Ed. **52** (38), 10064–10067 (2013). doi:10.1002/anie.201305235
[11] D. Heift, Z. Benko and H. Grützmacher, Dalton Trans. **43**, 831–840 (2014). doi:10.1039/C3DT52359D
[12] V. Chaban, Chem. Phys. Lett. **618**, 89–93 (2015). doi:10.1016/j.cplett.2014.11.008
[13] H. Shekaari, M. Zafarani-Moattar and M. Niknam, J. Mol. Liq. **219**, 975–984 (2016). doi:10.1016/j.molliq.2016.03.061
[14] T. Castanheiro, J. Suffert, M. Donnard and M. Gulea, Chem. Soc. Rev. **45**, 494–505 (2016). doi:10.1039/C5CS00532A
[15] L. Zhang, S. Du, Y. Liu, X. Yuan, J. Huang and S. Guo, CIESC J. **67** (12), 5276 (2016).
[16] M. Jost, L. Finger, J. Sundermeyer and C. von Hänisch, Chem. Commun. **52**, 11646–11648 (2016). doi:10.1039/C6CC06620H
[17] A. Jupp, M. Geeson, J. McGrady and J. Goicoechea, Eur. J. Inorg. Chem. **2016** (5), 639–648 (2016). doi:10.1002/ejic.v2016.5
[18] L. Zhang, S. Du, Q. Song, Y. Liu and S. Guo, Chem. Res. Chin. Univ. **33** (5), 779–784 (2017). doi:10.1007/s40242-017-7100-3
[19] S. Johnson, C. Hutchison, C. Williams, C. Hussey, G. Tschumper and N. Hammer, J. Phys. Chem. C**122** (48), 27673–27680 (2018). doi:10.1021/acs.jpcc.8b07114
[20] J. Goicoechea and H. Grützmacher, Angew. Chem. Int. Ed. **57** (52), 16968–16994 (2018). doi:10.1002/anie.v57.52
[21] L. Weber, Eur. J. Inorg. Chem. **2018** (20-21), 2175–2227 (2018). doi:10.1002/ejic.v2018.20-21
[22] Y. Mei, J. Borger, D. Wu and H. Grützmacher, Dalton Trans. **48**, 4370–4374 (2019). doi:10.1039/C9DT00485H
[23] J.P. Green, J.A.L. Wells and A. Orthaber, Dalton Trans. **48**, 4460–4466 (2019). doi:10.1039/C9DT00574A
[24] A. Hinz and J.M. Goicoechea, Angew. Chem. Int. Ed. **55** (30), 8536–8541 (2016). doi:10.1002/anie.v55.30
[25] F. Tambornino, A. Hinz, R. Köppe and J. Goicoechea, Angew. Chem. Int. Ed. **57** (27), 8230–8234 (2018). doi:10.1002/anie.v57.27
[26] F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. Gal, H. Grützmacher and H. Grützmacher, Angew. Chem. Int. Ed. **50** (36), 8420–8423 (2011). doi:10.1002/anie.v50.36
[27] I. Krummenacher and C. Cummins, Polyhedron **32** (1), 10–13 (2012). doi:10.1016/j.poly.2011.07.016
[28] Y. Lu, H. Wang, Y. Xie, H. Liu and H. Schaefer, Inorg. Chem. **53** (12), 6252–6256 (2014). doi:10.1021/ic500780h
[29] M. Polak, M. Gruebele and R. Saykally, J. Chem. Phys. **87** (6), 3352–3356 (1987). doi:10.1063/1.453030
[30] M. Gruebele, M. Polak and R. Saykally, J. Chem. Phys. **86** (12), 6631–6636 (1987). doi:10.1063/1.452409
[31] Y. Pak, R. Woods and K. Peterson, J. Chem. Phys. **103** (21), 9304–9311 (1995). doi:10.1063/1.469989
[32] Y. Pak, R. Woods and K. Peterson, J. Chem. Phys. **106** (12), 5123–5132 (1997). doi:10.1063/1.473557
[33] C. Léonard, H. Gritli and G. Chambaud, J. Chem. Phys. **133** (12), 124318 (2010). doi:10.1063/1.3483463
[34] J. Neugebauer and B.A. Hess, J. Chem. Phys. **118** (16), 7215–7225 (2003). doi:10.1063/1.1561045
[35] J.C. Howard, J.L. Gray, A.J. Hardwick, L.T. Nguyen and G.S. Tschumper, J. Chem. Theory Comput.**10** (12), 5426–5435 (2014). doi:10.1021/ct500860v

[36] Q. Yu and J.M. Bowman, J. Am. Chem. Soc. **139** (32), 10984–10987 (2017). doi:10.1021/jacs.7b05459

[37] S.N. Johnson and G.S. Tschumper, J. Comput. Chem. **39** (14), 839–843 (2018). doi:10.1002/jcc.v39.14

[38] S. Maystrovsky, M. Keçeli and O. Sode, J. Chem. Phys. **150** (14), 144302 (2019). doi:10.1063/1.5089460

[39] Q. Yu and J.M. Bowman, J. Phys. Chem. A **124** (6), 1167–1175 (2020). doi:10.1021/acs.jpca.9b11983

[40] T.M. Sexton, W.Z. Van Benschoten and G.S. Tschumper, Chem. Phys. Lett. **748**, 137382 (2020). doi:10.1016/j.cplett.2020.137382

[41] B.R. Westbrook, E.M. Valencia, S.C. Rushing, G.S. Tschumper and R.C. Fortenberry, J. Chem. Phys.**154** (4), 041104 (2021). doi:10.1063/5.0040050

[42] T. Mathea, T. Petrenko and G. Rauhut, J. Phys. Chem. A **125** (4), 990–998 (2021). doi:10.1021/acs.jpca.0c10429

[43] T.K. Roy, J. Phys. Chem. A **126** (4), 608–622 (2022). doi:10.1021/acs.jpca.1c09989

[44] A. Fayaz, S. Banik and T. Kanchan Roy, Comput. Theor. Chem. **1222**, 114059 (2023). doi:10.1016/j.comptc.2023.114059

[45] X. Huang and T.J. Lee, J. Chem. Phys. **131** (10), 104301 (2009). doi:10.1063/1.3212560

[46] R.C. Fortenberry, X. Huang, J.S. Francisco, T.D. Crawford and T.J. Lee, J. Chem. Phys. **135** (13), 134301 (2011). doi:10.1063/1.3643336

[47] X. Huang, P.R. Taylor and T.J. Lee, J. Phys. Chem. A **115** (19), 5005–5016 (2011). doi:10.1021/jp2019704

[48] R.C. Fortenberry, X. Huang, J.S. Francisco, T.D. Crawford and T.J. Lee, J. Chem. Phys. **135** (21), 214303 (2011). doi:10.1063/1.3663615

[49] R.C. Fortenberry, X. Huang, J.S. Francisco, T.D. Crawford and T.J. Lee, J. Chem. Phys. **136** (23), 234309 (2012). doi:10.1063/1.4729309

[50] R.C. Fortenberry, X. Huang, J.S. Francisco, T.D. Crawford and T.J. Lee, J. Phys. Chem. A **116** (38), 9582–9590 (2012). doi:10.1021/jp3073206

[51] X. Huang, R.C. Fortenberry and T.J. Lee, J. Chem. Phys. **139** (8), 084313 (2013). doi:10.1063/1.4819069

[52] X. Wang, X. Huang, J.M. Bowman and T.J. Lee, J. Chem. Phys. **139** (22), 224302 (2013). doi:10.1063/1.4837177

[53] N. Inostroza, R.C. Fortenberry, X. Huang and T.J. Lee, Astrophys. J. **778** (2), 160 (2013). doi:10.1088/0004-637X/778/2/160

[54] R.C. Fortenberry, X. Huang, T.D. Crawford and T.J. Lee, J. Phys. Chem. A **118** (34), 7034–7043 (2014). doi:10.1021/jp506441g

[55] R.C. Fortenberry, X. Huang, M.C. McCarthy, T.D. Crawford and T.J. Lee, J. Phys. Chem. B **118** (24), 6498–6510 (2014). doi:10.1021/jp412362h

[56] R.C. Fortenberry, X. Huang, T.D. Crawford and T.J. Lee, Astrophys. J. **796** (2), 139 (2014). doi:10.1088/0004-637X/796/2/139

[57] Q. Yu, J.M. Bowman, R.C. Fortenberry, J.S. Mancini, T.J. Lee, T.D. Crawford, W. Klemperer and J.S. Francisco, J. Phys. Chem. A **119** (47), 11623–11631 (2015). doi:10.1021/acs.jpca.5b09682

[58] R.C. Fortenberry and T.J. Lee, in *Annual Reports in Computational Chemistry*, edited by D.A. Dixon (2019), Vol. 15, pp. 173–202.

[59] M.B. Gardner, B.R. Westbrook, R.C. Fortenberry and T.J. Lee, Spectrochim. Acta A Mol. Biomol. Spectrosc. **248**, 119184 (2021). doi:10.1016/j.saa.2020.119184

[60] K.R. Barlow, S.M. Goodlett, S.N. Arradondo and G.S. Tschumper, Mol. Phys. **119** (21-22), e1967495 (2021). doi:10.1080/00268976.2021.1967495

[61] L. Zhang, J. Dong and M. Zhou, Chem. Phys. Lett. **335** (3), 334–338 (2001). doi:10.1016/S0009-2614(01)00015-X

[62] C. Møller and M. Plesset, Phys. Rev. **46** (7), 618–622 (1934). doi:10.1103/PhysRev.46.618

[63] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman and D.J. Fox, Gaussian 16 Revision C.01 2016, Gaussian Inc. Wallingford CT.

[64] R. Bartlett, Ann. Rev. Phys. Chem. **32** (1), 359–401 (1981). doi:10.1146/physchem.1981.32.issue-1

[65] G. Purvis and R. Bartlett, J. Chem. Phys. **76** (4), 1910–1918 (1982). doi:10.1063/1.443164

[66] K. Raghavachari, G. Trucks, J. Pople and M. Head-Gordon, Chem. Phys. Lett. **157** (6), 479–483 (1989). doi:10.1016/S0009-2614(89)87395-6

[67] J.F. Stanton, J. Gauss, L. Cheng, M.E. Harding, D.A. Matthews and P.G. Szalay, CFOUR version 2.1, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package With contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, S. Blaschke, Y. J. Bomble, S. Burger, O. Christiansen, D. Datta, F. Engel, R. Faber, J. Greiner, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, G.M. KopperW.J. Lauderdale, F. Lipparini, T. Metzroth, L.A. Mück, D.P. O'Neill, T. Nottoli, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A.V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

[68] D. Matthews, L. Cheng, M. Harding, F. Lipparini, S. Stopkowicz, T.C. Jagau, P. Szalay, J. Gauss and J. Stanton, J. Chem. Phys. **152** (21), 214108 (2020). doi:10.1063/5.0004837

[69] H.J. Werner, P.J. Knowles, P. Celani, W. Györffy, A. Hesselmann, D. Kats, G. Knizia, A. Köhn, T. Korona, D. Kreplin, R. Lindh, Q. Ma, F.R. Manby, A. Mitrushenkov, G. Rauhut, M. Schütz, K.R. Shamasundar, T.B. Adler, R.D. Amos,

Q3

S.J. Bennie, A. Bernhardsson, A. Berning, J.A. Black, P.J. Bygrave, R. Cimiraglia, D.L. Cooper, D. Coughtrie, M.J.O. Deegan, A.J. Dobbyn, K. Doll, M. Dornbach, F. Eckert, S. Erfort, E. Goll, C. Hampel, G. Hetzer, J.G. Hill, M. Hodges, T. Hrenar, G. Jansen, C. Köppl, C. Kollmar, S.J.R. Lee, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, B. Mussard, S.J. McNicholas, W. Meyer, T.F. Miller III, M.E. Mura, A. Nicklass, D.P. O'Neill, P. Palmieri, D. Peng, K.A. Peterson, K. Pflüger, R. Pitzer, I. Polyak, M. Reiher, J.O. Richardson, J.B. Robinson, B. Schröder, M. Schwilk, T. Shiozaki, M. Sibaev, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, J. Toulouse, M. Wang, M. Welborn and B. Ziegler, MOLPRO, version 2022.1, a package of ab initio programs Stuttgart, Germany, see https://www.molpro.net.

[70] H.J. Werner, P. Knowles, G. Knizia, F. Manby and M. Schütz, WIREs Comput. Mol. Sci. **2**, 242–253 (2012). doi:10.1002/wcms.82

[71] H.J. Werner, P.J. Knowles, F.R. Manby, J.A. Black, K. Doll, A. Heßelmann, D. Kats, A. Köhn, T. Korona, D.A. Kreplin, Q. Ma, T.F. Miller, I, A. Mitrushchenkov, K.A. Peterson, I. Polyak, G. Rauhut and M. Sibaev, J. Chem. Phys. **152** (14), 144107 (2020). doi:10.1063/5.0005081

[72] T. Dunning, Jr., J. Chem. Phys. **90** (2), 1007–1023 (1989). doi:10.1063/1.456153

[73] R. Kendall, T. Dunning, Jr. and R. Harrison, J. Chem. Phys. **96** (9), 6796–6806 (1992). doi:10.1063/1.462569

[74] D. Woon and T. Dunning, Jr., J. Chem. Phys. **98** (2), 1358–1371 (1993). doi:10.1063/1.464303

[75] T. Dunning, Jr., K. Peterson and A. Wilson, J. Chem. Phys. **114** (21), 9244–9253 (2001). doi:10.1063/1.1367373

[76] B. Metz, H. Stoll and M. Dolg, J. Chem. Phys. **113** (7), 2563–2569 (2000). doi:10.1063/1.1305880

[77] K.A. Peterson, J. Chem. Phys. **119** (21), 11099–11112 (2003). doi:10.1063/1.1622923

[78] K.A. Peterson and K.E. Yousaf, J. Chem. Phys. **133**, 174116 (2010). doi:10.1063/1.3503659

[79] I.M. Mills, in *Molecular Spectroscopy: Modern Research*, edited by K.N. Rao and C.W. Mathews, Chap. 3.2 (Academic Press, New York, NY, 1972), pp. 115–140.

[80] J. Vázquez and J. Stanton, Mol. Phys. **104** (3), 377–388 (2006). doi:10.1080/00268970500290367

[81] R. Ramakrishnan and G. Rauhut, J. Chem. Phys. **142** (15), 154118 (2015). doi:10.1063/1.4918587

[82] M. Neff and G. Rauhut, J. Chem. Phys. **131** (12), 124129 (2009). doi:10.1063/1.3243862

[83] M. Neff, T. Hrenar, D. Oschetzki and G. Rauhut, J. Chem. Phys. **134** (6), 064105 (2011). doi:10.1063/1.3551513

[84] G. Rauhut, J. Chem. Phys. **121** (19), 9313–9322 (2004). doi:10.1063/1.1804174

[85] T. Hrenar, H. Werner and G. Rauhut, J. Chem. Phys. **126** (13), 134108 (2007). doi:10.1063/1.2718951

[86] G. Rauhut and T. Hrenar, Chem. Phys. **346** (1), 160–166 (2008). doi:10.1016/j.chemphys.2008.01.039

[87] B. Ziegler and G. Rauhut, J. Chem. Phys. **144** (11), 114114 (2016). doi:10.1063/1.4943985

[88] G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*, 2nd ed. (Van Nostrand Reinhold, New York, 1966).