

A Theoretical Study of Properties and Reactions Involving Arsenic and Selenium Compounds Present in Coal Combustion Flue Gases

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Species of arsenic and selenium thought to be present in coal combustion flue gases were studied using density functional theory and a broad range of ab initio methods. At each level of theory, the calculated geometries and vibrational frequencies of each species as well as the reaction enthalpies of anticipated reactions were compared with experimental data where available. Comparisons between each calculation are given along with a discussion of the better performance of some theoretical calculations for a given species/reaction.

Introduction

After the enforcement of stricter mercury emission controls, other trace metals are being examined to determine the feasibility of tightening environmental regulations on them as well. Currently, the focus of these studies has been upon arsenic and selenium, the environmental effects of which are well known.^{1,2} Given that one of the most prolific sources of arsenic and selenium pollution is from coal combustion flue gases, efforts have been made to devise effective means of removal.^{3–5} Because these methods are highly dependent upon the form in which the trace metals occur, investigations into their speciation are extremely important.^{6–8}

Unfortunately, there is scant data available on many of the arsenic and selenium compounds found in the combustion flue gases, and so a kinetic study is more appropriately performed using computational chemistry methods. Before a determination of speciation can be undertaken, however, the computational levels of theory must be compared with any available data so as to discern the best theoretical model for moving forward. To that end, the current work presents an extensive ab initio study of several arsenic- and selenium-containing compounds typically found in coal furnace flue gases. A comparison is made between the theoretically calculated geometries and vibrational frequencies of each compound and any available experimental data. Additionally, the reaction enthalpies for a collection of reactions involving these species are found from theoretical Gaussian total energies and compared to the experimental reaction enthalpies found using the enthalpies of formation of each compound.

The enthalpies of formation of simple arsenic and selenium compounds have been examined in numerous studies such as Shaulov⁹ (AsCl, AsCl₂, AsCl₃), Pankratov¹⁰ (As, AsO, AsCl, AsCl₃), Oppermann¹¹ (SeO₂), and Barin¹² (Se, SeO, SeH₂, SeCl₂). Limited theoretical work has also been carried out to determine the total energies of a few of these species.¹³ While no direct comparison between formation enthalpy and total energy can be made, the energy differences resulting from a reaction may be directly compared to one another. To this end, the accuracy of computational levels of theory in predicting the

enthalpies of selected reactions can be evaluated against the available experimental data.

Experimental geometries have been determined for many of the species mentioned. Researchers have employed a number of techniques including microwave spectroscopy (SeO, SeO₂),¹⁴ electron diffraction, and a combination of these (AsCl₃)¹⁴ to predict structural properties of these compounds. Experimental methods have yielded typical bond length values of 2.165 Å for arsenic chlorides, 2.13–2.18 Å for selenium chlorides, 1.61–1.64 Å for selenium oxides, and 1.46 Å for selenium hydride. Because of the presence of unbonded electron pairs in both arsenic and selenium, the triatomic species (H₂Se, SeO₂, etc.) all possess a bent geometry. The bond angles present in triatomic selenium species have been found to range from 90.6 to 113.8°. Additionally, the common species arsenic trichloride (AsCl₃) is a nonplanar molecule having a geometry similar to that of ammonia. Each Cl–As–Cl bond angle has been calculated experimentally to a value of 98.6° with a dihedral angle of 108.9°.

Because of the extremely brief lifespan of several of these compounds, spectroscopic data is particularly limited. There are, however, several sources which provide the vibrational spectroscopy data for AsCl,¹⁵ AsCl₃ and SeH₂,¹⁶ AsO and SeO,¹⁴ SeO₂,¹⁷ and SeCl₂.¹⁸ Even for the species for which there is experimental data, the mode of vibration that each value represents is unspecified.

By validation of which levels of theory are the most accurate with respect to experimental values, the best theoretical models can be used in future research. In particular, this work is intended to be the first step in the determination of the kinetic parameters of possible gas phase reactions involving arsenic and selenium in the flue gas of coal-fired power plants. In this regard, this work will serve as both a basis of comparison for experimentally determined properties and as the foundation of an in-depth kinetic study.

Computational Methodology

Calculations were carried out using the Gaussian 03 suite of programs.¹⁹ Basis sets incorporating relativistic effects for the inner electrons were employed through the use of small core relativistic effective core potentials (RECP) for arsenic and selenium. The first basis set was LANL2DZ, which uses an

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TABLE 1: Reaction Enthalpies and Experimental Deviations of Selenium Reactions

exp ^a	Se + O ₂ → SeO + O		Se + O ₂ → SeO ₂		SeO + O ₂ → SeO ₂ + O		Se + H ₂ → SeH ₂	
	18.20		−82.05		18.85		−49.25	
B3LYP/LANL2DZ	17.36	0.85	−28.37	53.68	47.42	28.57	−35.93	13.32
QCISD/6-311++G(3df,3pd)	14.20	4.00	−73.17	8.88	19.59	0.74	−47.99	1.26
QCISD(T)/6-311++G(3df,3pd)	14.10	4.10	−82.31 ^b	0.26	17.64	1.22	−49.95 ^e	0.70
CCSD/6-311++G(3df,3pd)	14.56	3.64	−70.84 ^b	11.21	20.80	1.94	−47.95 ^e	1.30
CCSD(T)/6-311++G(3df,3pd)	14.38	3.82	−81.12 ^b	0.93	18.17	0.69	−49.93 ^e	0.68
QCISD/ECP28MWB	9.61	8.60	−75.39	6.66	21.96	3.11	−9.94	10.69
QCISD(T)/ECP28MWB	11.64	6.57	−83.71 ^c	1.66	18.69	0.16	−61.18	11.93
CCSD/ECP28MWB	9.71	8.49	−73.81 ^c	8.24	22.68	3.82	−59.79	10.54
CCSD(T)/ECP28MWB	11.70	6.50	−82.87 ^c	0.82	19.09	0.24	−61.11	11.86
QCISD/RCEP28VDZ	17.50	0.70	−63.34	18.71	26.12	7.26	−56.51	7.26
QCISD(T)/RCEP28VDZ	19.48	1.28	−71.87 ^d	10.18	22.69	3.83	−57.74	8.49
CCSD/RCEP28VDZ	17.64	0.57	−61.63 ^d	20.42	26.93	8.08	−56.35	7.10
CCSD(T)/RCEP28VDZ	19.55	1.34	−70.98 ^d	11.07	23.14	4.29	−57.67	8.42

^a Experimental data for Se species from refs 9–13; data for other species taken from NIST.²² ^b SPE of SeO₂ calculated at the designated level of theory using optimized geometry from QCISD/6-311++G(3df,3pd). ^c SPE of SeO₂ calculated at designated level of theory using optimized geometry from QCISD/ECP28MWB. ^d SPE of SeO₂ calculated at designated level of theory using optimized geometry from QCISD/RCEP28VDZ. ^e SPE of SeH₂ calculated at designated level of theory using optimized geometry from QCISD/6-311++G(3df,3pd).

TABLE 2: Reaction Enthalpies and Experimental Deviations of Arsenic Reactions

exp ^a	As + O ₂ → AsO + O		As + HCl → AsCl + H		AsCl + HCl → AsCl ₂ + H		As + Cl ₂ → AsCl ₂	
	0.98		29.87		31.17		−87.30	
B3LYP/LANL2DZ	8.23	7.25	31.65	1.78	33.81	2.65	−77.26	10.04
QCISD/6-311++G(3df,3pd)	7.43	6.44	36.61	6.74	34.05 ^d	2.88	−81.24 ^d	6.06
QCISD(T)/6-311++G(3df,3pd)	6.75 ^b	5.77	34.87 ^c	5.00	32.20 ^{c,d}	1.03	−83.72 ^d	3.58
CCSD/6-311++G(3df,3pd)	9.10 ^b	8.12	36.86 ^c	6.99	34.17 ^{c,d}	3.01	−80.95 ^d	6.35
CCSD(T)/6-311++G(3df,3pd)	7.37 ^b	6.38	35.03 ^c	5.17	32.28 ^{c,d}	1.11	−83.53 ^c	3.77
QCISD/ECP28MWB	5.05	4.06	38.06	8.20	36.40	5.23	−77.43	9.87
QCISD(T)/ECP28MWB	5.33	4.34	37.09	7.22	34.94 ^f	3.77	−78.76 ^f	8.55
CCSD/ECP28MWB	6.00	5.02	38.17	8.30	36.47 ^f	5.30	−77.35 ^f	9.95
CCSD(T)/ECP28MWB	5.67	4.69	37.15	7.29	34.99 ^f	3.81	−78.70 ^f	8.60
QCISD/RCEP28VDZ	11.31	10.33	39.94	10.08	38.99 ^e	7.82	−72.96 ^e	14.34
QCISD(T)/RCEP28VDZ	11.43	10.45	38.95	9.09	37.52 ^e	6.35	−74.32 ^e	12.98
CCSD/RCEP28VDZ	12.25	11.26	40.04	10.18	39.06 ^e	7.89	−72.88 ^e	14.42
CCSD(T)/RCEP28VDZ	11.75	10.77	39.02	9.15	37.56 ^e	6.40	−74.26 ^e	13.04

^a Experimental data for As species from refs 9–13; data for other species taken from NIST.²² ^b SPE of AsO calculated at designated level of theory using optimized geometry from QCISD/6-311++G(3df,3pd). ^c SPE of AsCl calculated at designated level of theory using optimized geometry from QCISD/6-311++G(3df,3pd). ^d SPE of AsCl₂ calculated at designated level of theory using optimized geometry from MP2/6-311++G(3df,3pd). ^e SPE of AsCl₂ calculated at designated level of theory using optimized geometry from MP2/RCEP28VDZ. ^f SPE of AsCl₂ calculated at designated level of theory using optimized geometry from QCISD/ECP28MWB.

all-electron description for atoms of the first row elements, and an RECP of inner electrons, combined with double- ζ quality functions for the valence electrons of heavier atoms of elements such as arsenic and selenium. The second basis set employs the relativistic ECP28MWB pseudopotential of the Stuttgart group²⁰ for both arsenic and selenium, with the respective energy-optimized (4s2p)/[3s2p] and (4s5p)/[2s3p] Gaussian-type orbital (GTO) valence bases optimized using multiconfiguration Dirac–Fock (MCDf) calculations. The third basis set employs a relativistic compact effective potential, RCEP28VDZ of the Stevens et al. group,²¹ which replaces 28 of arsenic’s and 28 of selenium’s atomic core electrons, derived from numerical Dirac–Fock wave functions using an optimizing process based upon the energy-overlap functional. Energy-optimized (5s5p)/[2s2p] Gaussian-type double- ζ quality sp and triple- ζ quality d functions were used, with the triple- ζ d functions essential for describing the orbital shape changes that exist with d occupancy. To compare the theoretical predictions from the pseudopotentials to those of a complete basis set, calculations were performed using the 6-311++G(3pd,3df) for the smaller arsenic and selenium containing compounds. This extended Pople basis set, which includes both diffuse and polarization functions, was used for hydrogen, oxygen, and chlorine as well.

Results and Discussion

In the interest of brevity, only the higher order levels of theory were included in the tables; data from lower levels of theory has been incorporated into the text.

I. Reaction Enthalpy Predictions. Tables 1 and 2 present the reaction enthalpy data for a selection of gas-phase reactions involving arsenic and selenium. Each table includes both the total energy change calculated for each reaction and the deviation of that value from the experimentally determined reaction enthalpy at numerous levels of theory. Upon examination of each table, a number of comparisons can be made between the data within each as well as several cross-table comparisons. Table 1 shows the results of the theoretical calculations for reactions involving selenium. Note that in several instances, the single point energy calculation performed at the designated level of theory utilized the optimized geometry of a less computationally expensive level. By use of DFT B3LYP/LANL2DZ, the enthalpy predictions were very inconsistent throughout each reaction, sometimes falling within 1 kcal/mol of the experimental value and other times being off by as much as 50 kcal/mol; however, the use of the complete 6-311++G(3df,3pd) basis set with each QCI and CC method failed incredibly well, falling within 5 kcal/mol of the experimental value in almost every instance.

TABLE 3: Reaction Enthalpy Predictions for Selenium Reactions Lacking Experimental Data

exp ^a	Se + HCl → SeCl + H	SeCl + HCl → SeCl ₂ + H
	B	b
B3LYP/LANL2DZ	45.42	49.06
QCISD/6-311++G(3df,3pd)	45.79	46.43
QCISD(T)/6-311++G(3df,3pd)	43.47	44.33 ^d
CCSD/6-311++G(3df,3pd)	46.05	46.41 ^d
CCSD(T)/6-311++G(3df,3pd)	43.64 ^c	44.32 ^d
QCISD/ECP28MWB	55.33	55.79
QCISD(T)/ECP28MWB	54.21	54.47 ^e
CCSD/ECP28MWB	55.51	55.85 ^e
CCSD(T)/ECP28MWB	54.32	54.48 ^e
QCISD/RCEP28VDZ	57.14	56.99
QCISD(T)/RCEP28VDZ	56.06	55.68 ^f
CCSD/RCEP28VDZ	57.31	57.05
CCSD(T)/RCEP28VDZ	56.16	55.69 ^f

^a Experimental data for Se species from refs 9–13; data for other species taken from NIST.²² ^b No experimental heat of formation data for SeCl found. ^c SPE of SeCl calculated at designated level of theory using optimized geometry from QCISD(T)/6-311++G(3df,3pd). ^d SPE of SeCl₂ calculated at designated level of theory using optimized geometry from QCISD/6-311++G(3df,3pd). ^e SPE of SeCl₂ calculated at designated level of theory using optimized geometry from QCISD/ECP28MWB. ^f SPE of SeCl₂ calculated at designated level of theory using optimized geometry from QCISD/ECP28MWB.

TABLE 4: Reaction Enthalpy Predictions for Arsenic Reactions Lacking Higher-Order Computation

exp ^a	AsCl ₂ + HCl → AsCl ₃ + H		AsCl ₂ + Cl ₂ → AsCl ₃ + Cl	
	25.17		−20.01	
B3LYP/LANL2DZ	36.27	11.10	−19.70	0.31
HF/SDD	34.94	9.78	−28.59	8.58
QCISD/SDD	30.86	5.70	−19.52	0.49
QCISD(T)/SDD	29.78	4.61	−19.58	0.43
CCSD/SDD	30.94	5.78	−19.52	0.49
CCSD(T)/SDD	29.84	4.67	−19.53	0.48
HF/6-311++G(3df,3pd)	30.20	5.03	−25.27	5.26

^a Experimental data for As species from refs 9–13; data for other species taken from NIST.²²

TABLE 5: Calculated and Experimental Bond Lengths (Angstroms) and Bond Angles (Degrees) of Selenium Compounds

species	bond angle (deg)/ bond length (Å)	level of theory									
		exp	B3LYP/ LANL2DZ	QCISD/ 6-311++G- (3df,3pd)	QCISD(T)/ 6-311++G- (3df,3pd)	QCISD/ ECP28MWB	QCISD(T)/ ECP28MWB	CCSD/ ECP28MWB	CCSD(T)/ ECP28MWB	QCISD/ RCEP28VDZ	CCSD/ RCEP28VDZ
SeO	r(SeO)	1.6393 ^a	1.7480	1.6362	1.6484	1.6423	1.6492	1.6392	1.6477	1.6756	1.6718
SeO ₂	r(SeO)	1.6076 ^a	1.7164	1.6009		1.6023				1.6173	
	−OSeO	113.83 ^a	110.97	114.28		113.21				110.94	
SeH ₂	r(SeH)	1.46 ^b	1.4981	1.4650		1.4237	1.4288	1.4236	1.4228	1.4256	1.4255
	−HSeH	90.6 ^b	92.17	91.50		90.81	90.74	90.82	90.74	90.41	90.43
SeCl	r(SeCl)	2.13 ^c	2.3263	2.1355	2.1410	2.1733	2.1788	2.1726	2.1780	2.1875	2.1868
SeCl ₂	r(SeCl)	2.157 ^c	2.3442	2.1551		2.1922				2.2038	2.2036
	−ClSeCl	99.6 ^c	102.17	100.36		99.93				99.97	99.93

^a Reference 14. ^b Reference 23. ^c Reference 24.

TABLE 6: Calculated and Experimental Bond Lengths (in Å) and Bond Angles (in deg) of Arsenic Compounds

species	bond angle (deg)/ bond length (Å)	level of theory									
		exp	B3LYP/ LANL2DZ	QCISD/ 6-311++G (3df,3pd)	QCISD/ ECP28MWB	QCISD(T)/ ECP28MWB	CCSD/ ECP28MWB	CCSD(T)/ ECP28MWB	QCISD/ RCEP28VDZ	QCISD(T)/ RCEP28VDZ	CCSD/ RCEP28VDZ
AsO	r(AsO)	1.6236 ^a	1.6883	1.6300	1.6260	1.6395	1.6234	1.6396	1.6375	1.6512	1.6319
AsCl	r(AsCl)		2.3208	2.1604	2.2003	2.2055	2.2000	2.2050	2.2124	2.2170	2.2120
AsCl ₂	r(AsCl)		2.3183		2.1979						
	−ClAsCl		101.71		99.84						
AsCl ₃	r(AsCl)	2.165 ^b	2.3186								
	−ClAsCl	98.6 ^b	99.86								
	dihedral	108.3 ^b	101.94								

^a Reference 14. ^b Reference 24.

A similar set of comparisons can be made for the data in Table 2 concerning the reactions involving arsenic. Again, B3LYP/LANL2DZ proves inconsistent deviating from experiment by anywhere from 2 to 10 kcal/mol; however, this deviation is much less than for the selenium reactions. Also, the complete 6-311++G(3df,3pd) basis set performed well but was slightly less accurate than in the previous comparison, most values falling within 7 kcal/mol of the experimental value. A cursory examination of the performance of the RECP's reveals that the ECP28MWB basis set proves to be more accurate than the RCEP28VDZ (utilizing identical methods) in every reaction. It may, in fact, be that the basis functions in the ECP28MWB basis set are simply better at representing the electrons in the arsenic atom than those in the RCEP28VDZ basis set.

Additionally, Tables 3 and 4 present supplementary energetics data. The selenium reactions listed in Table 3 are incomplete due to a lack of experimental data for the heat of formation of SeCl. However, it can be seen that the data is fairly consistent as a whole and more so when comparing the various methods with any one basis set. The arsenic reactions listed in Table 4 are excluded from the others due to a lack of higher level calculations. The size of the AsCl₃ molecule makes the computations very expensive at higher levels of theory, and so reaction enthalpies could only be completed using the less sophisticated techniques. Because the reliability of these lower levels of theory is in question, it was decided to include these data as an addendum rather than incorporate it into the main body of comparison.

II. Geometry Predictions. Tables 5 and 6 show the geometry predictions of the selenium and arsenic species at each level of theory considered. In Table 5, the bond length(s) and bond angle, if applicable, for each selenium compound, are listed at all levels of theory and compared to experimental values with the exception of SeCl for which no experimental geometry could be found. Additionally, some of the larger compounds could not be optimized at the higher levels of theory due to a lack of computational resources. A general comparison of the experimental geometries to the theoretical reveals that the most

consistently accurate is the QCISD/6-311++G(3df,3pd) level of theory which is logical given that each electron is treated explicitly with this extensive Pople basis set. The effective core potential basis sets also performed well, each giving consistent bond length and angle measurements for all levels of theory.

More specifically, an evaluation of each of the higher levels of theory, those utilizing the RECP's or the 6-311++G(3df,3pd) basis set, identifies which method and basis set are the most accurate for a given species. Because of its relatively low number of electrons and simple geometry, the most detailed evaluation is in regard to SeO. The level of theory that most closely approximates the experimental bond length of 1.6393 Å is CCSD/ECP28MWB, which deviates by only 0.0001 Å. Other methods using this basis set are not quite as good but nonetheless achieve an accuracy of within 0.001 Å. Calculations using the 6-311++G(3df,3pd) basis set also produced values within 0.001 Å, while the RCEP28VDZ basis set generated deviations roughly one magnitude greater. In contrast, the most accurate levels of theory for the other diatomic species, SeCl, were primarily those using the 6-311++G(3df,3pd) basis set. CCSD/6-311++G(3df,3pd) produced a deviation of 0.0041 Å (not included in table), the smallest value for this molecule, while the QCISD and QCISD(T) methods deviated from experiment by 0.0055 and 0.0110 Å, respectively. The RECP basis sets were slightly less accurate but were very consistent. Overall, the ECP28MWB basis set performed better than the RCEP28VDZ, deviating by about 0.045 Å on average as opposed to 0.06 Å. Also, as with the 6-311++G(3df,3pd), the addition of the triple excitations increased the deviation.

Specific comparison of the larger, triatomic selenium species is hampered by a lack of results at the higher levels of theory, but a general idea can be gleaned from what has been completed. For SeO₂, the most accurate level of theory regarding bond length is QCISD/ECP28MWB, deviating from experiment by only 0.0053 Å. Calculations with the same method using the 6-311++G(3df,3pd) and RCEP28VDZ basis set achieved an accuracy on the same order of magnitude. In the case of bond angles, both the 6-311++G(3df,3pd) and ECP28MWB basis sets were off by less than a degree while the RCEP28VDZ basis set deviated from experiment by almost 3°. Unfortunately, no data could be collected when utilizing triple excitations or coupled-cluster theory. More data was available for SeH₂ due to its fewer number of electrons. All levels of theory utilizing a RECP basis set fared similarly; bond length deviation was around 0.035 Å and bond angle deviation was 0.2°. The best level of theory, however, was the QCISD/6-311++G(3df,3pd) with a bond length deviation an order of magnitude smaller (0.005 Å) and a comparable bond angle deviation of 0.9°; no other methods could be completed using the 6-311++G(3df,3pd) basis set. Finally, the accuracy of each level of theory in predicting the SeCl₂ geometry is similar to that for SeH₂. The most accurate is QCISD/6-311++G(3df,3pd) with a deviation of 0.0019 Å in bond length and 0.76° in angle, while the RECP calculations are 1 order of magnitude less accurate in determining the bond length and of the same order of magnitude in finding the bond angle.

Table 6 presents similar data for the species of arsenic considered in this study. The lack of data, both experimental and theoretical, makes any definitive conclusions of the entire data set difficult. Additionally, because many higher levels of theory were unavailable for AsCl₂, geometry optimizations were carried out using the MP2 method in combination with both the 6-311++G(3df,3pd) and RCEP28VDZ basis sets generating

bond lengths of 2.1579 and 2.2022 Å and bond angles of 99.74 and 99.81°, respectively.

Specific species observations are also affected by the lack of data. The only arsenic species having both an experimental geometry and a significant number of higher level computations was AsO, for which the most accurate level of theory was found to be CCSD/ECP28MWB having a deviation of only 0.0002 Å. The remaining RECP calculations had deviations ranging from 1 to 2 orders of magnitude greater than this value, while the QCISD/6-311++G(3df,3pd), the only one using this complete basis set to be completed, had a deviation of 0.0064 Å; because other calculations using this basis set were too computationally expensive to run, it is unknown if they would behave in a more consistent manner than the RECP values. While experimental data for the other diatomic species, AsCl, is absent, the theoretical data collected can be evaluated for consistency. The ECP28MWB and RCEP28VDZ basis sets generated consistent bond lengths using each method, the values falling in the 2.20–2.21 Å range for the ECP28MWB basis set and in the 2.21–2.22 Å range for the RCEP28VDZ. QCISD/6-311++G(3df,3pd) generated a bond length of 2.16 Å, the only calculation using the complete basis set to be completed.

The results for species with three or more atoms are even more inconclusive. For instance, for the AsCl₂ molecule, the only higher order level of theory for which there was enough computational resources was QCISD/ECP28MWB; which calculated a bond length of 2.2 Å and an angle of 99.84°. Unfortunately, with no experimental geometry data or additional theoretical calculations, there is no means of comparison except with the less sophisticated levels of theory. To provide a more efficient comparison, additional calculations were performed at the intermediate levels of theory MP2/6-311++G(3df,3pd) and MP2/RCEP28VDZ determining the geometry to be 2.16 Å, 99.82° and 2.20 Å, 99.74°, respectively. The size of the AsCl₃ molecule made any higher-level theoretical calculations too computationally expensive to attempt and so while there are experimental results to compare to, the available levels of theory are of a very simplistic nature. While each level of theory predicted similar values, the most accurate of these appears to be B3LYP/LANL2DZ, which predicted deviations of 0.11 Å in the bond lengths, roughly 0.53–0.55° in the bond angles, and 8.05° in the dihedral angle.

III. Vibrational Frequency Predictions. The vibrational frequencies of the species of interest are given in Tables 7 and 8. Table 7 contains the magnitude of each mode of vibration, as calculated experimentally and predicted computationally, for the selenium compounds list additional computational data. Because experimental frequencies were not available for every compound and many of the higher-order levels of theory could not be completed for some of the larger species, most of the conclusions drawn from the data are dependent upon less sophisticated theoretical computations. Additionally, the lack of the frequency scaling factors for each level of theory means that any comparisons made have to be relative to another at the same level. For instance, the experimental vibrational frequency values for SeH₂ are (in cm⁻¹) 1074, 2260, and 2350. For a low level of theory such as HF/SDD, these values are found to be roughly 1180, 2451, and 2478, while for a higher level of theory such as QCISD(T)/ECP28MWB, these same values are 1155, 2569, and 2599, suggesting that the more rigorous calculation is less accurate. However, it may be that once the frequency scaling factors for these respective theoretical levels are determined and applied, the higher level will more closely mimic the experiment.

TABLE 7: Calculated and Experimental Vibrational Frequencies (in cm^{-1}) of Selenium Compounds

species	vibrational mode description	exp	level of theory								
			B3LYP/LANL2DZ	QCISD/6-311++G-(3d f,3pd)	QCISD(T)/6-311++G-(3d f,3pd)	QCISD/ECP28MWB	QCISD(T)/ECP28MWB	CCSD/ECP28MWB	QCISD/RCEP28VDZ	QCISD(T)/RCEP28VDZ	CCSD/RCEP28VDZ
SeO	Se–O stretch	914.69 ^a	797.44	958.86	920.24	902.64	891.57	918.53	830.55	823.94	848.38
SeO ₂	Sym stretch	910 ^b	797.32	988.49		941.24			886.00		
	asym stretch	967 ^b	817.79	1031.6 5		975.63			970.52		
SeH ₂	scissors		301.37	380.68		385.78			392.14		
	sym. stretch	2260 ^c	2268.4 0	2465.5 3		2566.2 4	2569.1 7	2567.1 5	2529.7 8	2532.5 2	2530.1 5
	asym stretch	2350 ^c	2312.6 6	2474.6 5		2596.4 1	2599.4 6	2597.1 1	2543.0 3	2544.3 9	2543.8 8
	scissors	1074 ^c	1089.8 5	1075.9 9		1162.1 3	1155.3 0	1163.5 9	1153.8 6	1147.6 0	1155.1 8
SeCl	Se–Cl stretch		372.82	446.30	438.81	408.92	403.43	409.94	405.56	399.59	406.56
SeCl ₂	sym stretch	377 ^d	355.57	434.30		402.35			397.88		398.08
	asym stretch	415 ^d	347.97	420.44		388.21			387.05		386.63
	scissors	153 ^d	121.63	165.99		157.10			153.52		153.76

^a Reference 14. ^b Reference 17. ^c Reference 16. ^d Reference 18.

TABLE 8: Calculated and Experimental Vibrational Frequencies (in cm^{-1}) of Arsenic Compounds

species	vibrational mode description	exp	level of theory						
			B3LYP/LANL2DZ	QCISD/SDD	QCISD(T)/SDD	HF/6-311++G-(3df,3pd)	QCISD/6-311++G-(3df,3pd)	QCISD/ECP28MWB	QCISD/RCEP28VDZ
AsO	As–O stretch	967.08 ^a	877.99	713.27	818.95	1156.90	978.044	861.32	836.58
AsCl	AsCl stretch	424 ^b	363.37	346.66	347.22	432.44	426.24	391.94	386.72
AsCl ₂	sym stretch		361.90	350.42	349.42	443.29		399.97	
	asym stretch		353.91	352.54	350.64	420.49		380.02	
	scissors		127.95	128.75	127.61	179.32		158.66	
AsCl ₃	sym str	370 ^c	357.12	350.24	346.97				
	v4b	154 ^c	122.59	124.39	122.19				
	v4a	159 ^c	122.86	124.38	122.11				
	v3b	410 ^c	349.59	355.36	350.96				
	v3a	404 ^c	349.14	355.35	351.06				
	scissors	193 ^c	154.11	157.37	154.56				

^a Reference 14. ^b Reference 15. ^c Reference 16.

However, a few conclusions may be drawn from the data as calculated. In the compounds for which a number of RECP basis sets completed, namely, SeO, SeCl, and SeH₂, the wavenumbers for each mode of vibration are very consistent, suggesting that these levels of theory are accurately determining these quantities but are off by some common scaling factor. For these species, the “best” level of theory varies not only for each compound but also for each mode of vibration in a single compound. CCSD/ECP28MWB comes closest to the experimental value of the bond stretch in SeO, while both the symmetric and asymmetric stretch in SeH₂ are best approximated by the DFT B3LYP/LANL2DZ and the “scissors” vibration by QCISD/6-311++G(3df,3pd). The same is true of the remaining selenium compounds; the symmetrical stretch in SeO₂ is best represented by HF/SDD while the asymmetric stretch is more accurate using the QCISD/RCEP28VDZ level of theory, and in SeCl₂ the stretching and the “scissors” vibrations most accurate using B3LYP/LANL2DZ and QCISD/RCEP28VDZ, respectively.

The values presented in Table 8, are even less conclusive since there are so few completed calculations using the more complex techniques. It is hoped that the higher-level calculations can be completed in the future and that, once the scaling factors for each level of theory are known, a full comparison of the data to available experimental results can be made.

The RECPs present a vastly different story for the two species completed. The values for AsCl are very consistent much like those for the selenium compounds, however, for AsO the values fall into a broader range, roughly 800–1000 cm^{-1} . This may suggest that the prediction of modes of vibration are affected by the number of unpaired electrons (AsCl has 2 while AsO

has only 1) but without additional calculations at these levels of theory with other arsenic compounds, this cannot be confirmed. The “best” level of theory for each mode of vibration as dictated by the completed calculations are as follows: AsO stretch, CCSD(T)/ECP28MWB; AsCl stretch, QCISD/6-311++G(3df,3pd); AsCl₃ symmetric stretch, B3LYP/LANL2DZ; all others modes of AsCl₃, HF/SDD.

Conclusions

In summary, the calculations fit the general trends one would expect in conducting a computational study: the more sophisticated basis sets and more rigorous mathematical methods produced the greatest degree of accuracy with regard to the available experimental data. The use of the 6-311++G(3df,3pd) basis set in conjunction with the QCI and CC methods produced theoretical values which deviated from experiment by roughly 1–7 kcal/mol, 0.001–0.01 Å and 1–4°, and 2–200 cm^{-1} , in the prediction of reaction enthalpies, species geometries, and vibrational frequencies, respectively. In contrast, the lower levels of theory (those utilizing DFT, the HF method, and/or the SDD basis set) predicted values with deviations of 1–80 kcal/mol, 0.005–0.5 Å and 1–4°, and 2–600 cm^{-1} , while those calculations making use of RECP's predicted deviations of only 1–20 kcal/mol, 0.005–0.05 Å and 1–2°, and 4–300 cm^{-1} . These observations then serve a two-fold purpose; first, the theoretical values, particularly the higher order ones, can provide validation to the experimental values or, perhaps discredit them, and second, the knowledge of what level(s) of theory work best within a particular reaction or reaction scheme will be the starting point for the investigation into the kinetics

and thermodynamics of those reactions involving arsenic and selenium in coal combustion flue gases.

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