An Ab Initio Study of Atmospheric Selenium and Arsenic Reactions

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Abstract

In order to better understand selenium and arsenic's role in atmospheric reactions, along with its speciation, thermodynamic equilibrium data is essential as a first step to determining how that speciation occurs. Molecular modeling using ab initio methods was used to calculate thermodynamic properties and equilibrium constants for a series of potential important reactions between arsenic, selenium, and various atmospheric gases at standard temperature and pressure. The best calculation methods and accompanying patterns were analyzed. These best methods can be later implemented to determine kinetic properties of the reactions.

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Introduction

In today's world, the need for coal energy is constantly increasing as new technologies are discovered and foreign countries such as China experience their own industrial revolution. This recent increase in energy consumption has made China the number one consumer of coal, accounting for 25% of the entire world's coal use.[1] An increased energy demand brings a plethora of environmental concerns including depletion of natural resources and pollution of our waterways and atmosphere. Acid rain, harmful airborne pollutants, and possible climate shifts are all threats to the well-being of not only the human race, but all life on the planet. Despite increasingly strict air quality standards and innovations in coal-burning flue gas pollution control, pollutants naturally found in coal such as arsenic and selenium continue to enter the atmosphere.[2]

Throughout the world, the use of coal accounts for almost 25% of all fuel sources in terms of energy consumption.[3] While there is a movement to reduce coal consumption in replace of cleaner-burning natural gas in developed countries including the United States, the use of coal in many industrially-developing countries such as China and India is expected to increase, due to the countries' need for an abundant and reliable power source.[4] With an increased worldwide consumption of coal comes an increase in anthropogenic sources of atmospheric species of arsenic and selenium.

In developing areas of the world, such as India and China, populations are steadily growing. With this increase in population, coupled with and increasingly technologically demanding global economy comes and increased demand for reliable energy. For example, the growth of coal combustion as an energy source in China is so rapid, the country is producing the equivalent of two 500 MW power plants every day.[39] This amount of energy is roughly comparable to the entire United Kingdom power grid on a year-to-year basis. Additionally, dwindling oil supplies in the United States, India, and China mean that abundant fuel sources are needed to accommodate the enormous energy demands of these respective countries. Since coal is highly prevalent in all of these areas, the growth of its use as a long-term energy source is almost guaranteed. In the United

States alone, over five hundred, 500 MW coal-fired power plants are in operation with an average age of 35 years.[39] Since the average coal-fired power plant has an average life expectancy of around 50 years, now is a critical time to ensure that future power plants are as efficient and as effective as can be in removing pollutants such as CO_2 and trace elements including arsenic and selenium.

In most cases, concentrations of arsenic and selenium in the atmosphere are not high enough to directly cause bodily harm in humans. However, it is known that many species of these elements are highly water-soluble or are particulate-bound, leading to the potential to precipitate either directly or in aerosol form leading to accumulation in bodies of water and/or soil.[5] The potential poisoning from these species is not only a concern in humans but livestock and fish as well. It has been known for years that certain plants known as *Astragalus* absorb a large quantity of water-soluble forms of Se.[6] Livestock grazing on *Astragalus* have been diagnosed with selenosis, exhibiting symptoms of "blind staggers".[17] Additionally, species of selenium have been proven to bioaccumilate to nearly fatal levels in fish that are exposed to contaminated waterways.[18] While there have been fewer studies regarding the health impacts of atmospheric arsenic compounds, water soluble species can precipitate into drinking water supplies to levels that can be hazardous to the human body.[6]

Since relatively little is known regarding the different species of arsenic and selenium present in the atmosphere, a logical starting point in determining the reaction pathways and stabilities of various species is a study of reaction kinetics under atmospheric conditions. Due to the lack of information regarding these reactions, a kinetic study using computational chemistry is necessary. The goal of the current study is to compute thermodynamic data which will eventually lead to kinetic predictions. Kinetic data for these potential reactions will be determined using ab initio chemistry while applying a suitable level of theory for each reaction. Calculated reaction enthalpies will be compared to combined theoretical enthalpies of reactions for each reactant and product, and vibrational frequencies and geometries will also be compared to theoretical values whenever possible. This research is intended to be a first step for future research in determining kinetic parameters in arsenic and selenium reactions in the atmosphere.

Energetics, including enthalpies and entropies of formation, of simple arsenic and selenium compounds have been determined in numerous studies by Lide[7](As and H_2Se) and Barin[8] (AsO, SeO, SeO_2). Additionally, enthalpies and entropies of formation for many species commonly found in the earth's atmosphere have been studied by Chase[9] (OH, HO_2, H, O, O_2, H_2, H_2O, N, NO, NO_2, NO_3, O_3, SO, SO_2) and Cox, et al[10] (H, O, O_2, H_2 H_2O, N, SO_2). Also, work has been carried out to determine kinetic properties of several reactions involving arsenic and selenium compounds[11,12] using experimental techniques such as Vis-UV absorption and laser induced fluorescence.

Experimental geometries for many species related to this study have been determined in previous studies. Researchers have implemented a variety of techniques to determine bond lengths and bond angles, including microwave spectroscopy (SeO, SeO_2, and other species containing oxygen), ultraviolet spectroscopy (H_2) and IR spectroscopy (H_2O)[13]. This study is concerned exclusively with atomic, diatomic, and triatomic molecules. Smaller diatomic molecules such as H_2 and OH exhibit bond lengths in the range of 0.75 to 1.27 Å, while larger species containing selenium and sulfur range from 1.43 to 1.61 Å. Triatomic molecules in this study have all been found experimentally to possess a bent structure.

Spectroscopic data was obtained primarily from Herzberg's work on diatomics[14] and polyatomics.[15] The experimental data for the SeO_2 vibrational frequencies was found using references from Herzberg[16, 17], as was for HO_2.[35]

Background

Selenium

The presence of selenium in Earth's atmosphere can be contributed to a variety of sources. Many of these sources are naturally from soil, plants, and fresh and salt waters. This naturally occurring process can be attributed to bacteria and fungus, forming dimethylselenide.[20] Selenium is naturally found in coal; therefore a considerable source of atmospheric selenium derives from coal-fired combustion, where an average of 25 μg/m^3 of vapor-phase selenium exists in exiting flue gas.[21] It is believed that species of selenium released into the atmosphere by coal-burning processes are mostly SeO_2. However, in the presence of SO_2, the SeO_2 can be reduced to elemental Se, and at higher temperatures, H_2Se has been found to be prevalent.[2]

While there is scarce information regarding concentrations of selenium in the atmosphere, it is known that typical concentrations are .3 to 5.7 ng/m^3 in urban areas, and .03 to 1.6 ng/m^3 in rural areas.[22] This stands as evidence that the contribution of selenium in the atmosphere due to human-related activities such as coal combustion is much greater than the aforementioned natural sources. Additionally, the concentration of atmospheric selenium can depend highly on wind direction. A 2004 study conducted by researchers in Portugal discovered that while summertime concentrations of selenium in the troposphere varied from .5 to 1 ng/m^3, changes in the wind current in the winter months caused an increase of over 1000 times the summer months.[23]

Selenium is a required nutrient for humans, with 55 μg for women and 70 μg for men being the recommended daily allowance.[24] Excessive amounts of selenium can be detrimental to human health, though. Chronic toxicity has been linked to psychological, gastrointestinal, and pulmonic affects, though it has been found that symptoms subside after exposure levels decreased to recommended levels.[25] Human intake of selenium is primarily from food, which absorbs the selenium from the soil, followed by water and air.[24] There has been at least one documented case of selenium intoxication due to release from coal combustion, occurring in China in the early 1960s.[26]

Arsenic

Similar to selenium, arsenic is a trace element that is naturally found in the earth's crust. While many natural sources such as wind erosion, volcanic activity, sea spray and forest fires attribute to arsenic contamination in the atmosphere, studies have shown that up to 75% of arsenic emissions can be attributed to anthropogenic sources.[28] It is estimated that 90% of coal in regions in the United States contain arsenic, making coal combustion one of the highest sources for arsenic contamination in the atmosphere.[27] Speciation from this process is most commonly found as As_2O_3, however in the presence of SO_2, H_2O_2 and O_3 can be oxidized or reduced under atmospheric conditions.[27]

Like many other industrial air pollutants, arsenic contamination in the troposphere is generally more concentrated in urban areas. In an area of Canada in close proximity to copper smelting plants, concentrations of arsenic in the air reached as high as 6.5 $\mu g/m^3$, while rural concentrations peaked at 0.002 $\mu g/m^3$.[28] While there is no regulation in the United States for atmospheric arsenic concentration, China's Air Quality Permission Standard has established a guideline of 3 $\mu g/m^3$.[29]

According to a 1979 study, it was assumed that arsenic has a tropospheric residence time of about 9 days.[27] This relatively short residence time can be attributed to arsenic's solubility with water. It is not uncommon for arsenic concentrations in rainfall to reach .00005 mg/L in industrialized areas, leading to the concern of arsenic accumulation in drinking water sources.[28] Due to the short residence time of arsenic and its solubility with water, there has been very little concern to its role in stratospheric chemistry.

Under normal conditions, the concentration of arsenic in the air is not high enough to cause bodily harm. However, when arsenic precipitates and accumulates in drinking water supplies, ingesting water containing more than .01 mg/L can be hazardous to the body.[17] In the Guizhou Province of China alone, an estimated 3,000 people suffer symptoms of arsenic poisoning, where arsenic seeps into food cooked in coal stoves without proper ventilation.[30] Common symptoms of arsenic poisoning include dermal lesions and liver injury, which could lead to serious conditions such as chronic indigestion, liver cirrhosis, and various skin cancers.[29]

Computational Methodology

Calculations were carried out using the Gaussian 03 suite of programs.[32] Several different basis sets were used for the calculations. An extended Pople basis set, 6-311++G(3df,3pd), including both diffuse and polarization functions was used for all atoms. The second basis set was LANL2DZ, which uses an all-electron description for atoms of the first row elements, and an effective core potential (ECP) for inner electrons combined with double-ς quality functions for the valence electrons for heavier atoms of elements such as arsenic and selenium. The next basis set employs the ECP28MWB pseudopotential of the Stuttgart group.[33] For arsenic, utilized energy-optimized (4s, 2p)/[3s, 2p] gaussian type orbital (GTO) valence bases optimized using multiconfiguration Dirac-Fock (MCDF) calculations, while for selenium utilized (4s, 5p)/[2s, 3p] GTO valence bases. The final bases set employs a relativistic compact effective potential, RCEP28VDZ of the Stevens et al. group[34], 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. For comparison purposes, lower level basis sets were also used but will generally not be discussed in this paper.

Several calculation methods were also used. The standard Hartree-Fock calculation was performed with the lower level and 6-311++G(3df,3pd), basis sets. Density-functional calculations were carried out with the exchange energy functional described by Becke in part three of his series of papers[36] and the correlation functional produced by Lee, Yang, and Parr.[37] Coupled cluster and quadratic configuration interaction calculations including single and double excitations (CCSD and QCISD) along with triple excitations (CCSD(T) and QCISD(T)) were performed with the 6-311++G(3df,3pd), Stuttgart group pseudopotential, and SBKJCVDZ pseudopotential, as well as the lower level basis set. Both the coupled cluster and quadratic configuration interaction methods provide size consistency, which gives accurate geometries, vibrational frequencies, and energies[38] which is appropriate for our analysis.

Results and Discussion

Lower levels of theory including the Hartree Fock approximation and SDD basis set were not included in the following tables in the interest of brevity, but are included in the text.

Enthalpy Predictions

Tables 1 through 3 present the reaction enthalpy data for several gas phase reactions involving arsenic and selenium. All tables include both total energy change calculated for each reaction along with the absolute deviation from experimental values at various levels of theory. Note that the single point energy was calculated using an optimized geometry at the QCISD/6-311++G(3df,3pd) level of theory in several instances In order to minimize the computational expense. It is important to note that experimental values for ΔH_{form} of AsO were listed in NIST[9]as -57.3 while Pankratov and Uchaeva[41] reported a value of +57.3. When comparing both data to our results, it was determined that +57.3 produced a significantly smaller deviation, so this value was used in the analysis.

Table 1: Reaction Enthalpies (kcal/mol) and Absolute Deviation of Arsenic Reactions

	$As + HO_2 \rightarrow AsO + HO$		$As + SO_2 \rightarrow AsO + SO$		$As + H_2O \rightarrow AsO + H_2$		$As + NO \rightarrow AsO + N$	
Experimental	-49.79		13.84		-0.82		32.55	
B3LYP / LANL2DZ	-31.92	17.87	-45.52	59.36	8.26	9.07	28.90	3.65
CCSD / 6-311++G(3df,3pd)	-42.05	7.73	18.39	4.56	14.00	14.82	38.08	5.53
QCISD / 6-311++G(3df,3pd)	-43.16	6.63	17.04	3.21	11.80	12.62	37.17	4.63
CCSD(T) / 6-311++G(3df,3pd)	-45.59	4.20	16.76	2.93	8.13	8.94	37.00	4.45
QCISD(T) / 6-311++G(3df,3pd)	-46.11	3.68	16.24	2.41	7.26	8.07	37.06	4.51
CCSD / Stuttgart RLC ECP	-45.16	4.63	15.29	1.45	10.90	11.72	34.97	2.42
QCISD / Stuttgart RLC ECP	-45.54	4.25	14.66	0.83	9.42	10.23	34.79	2.24
CCSD(T) / Stuttgart RLC ECP	-47.28	2.51	15.07	1.23	6.43	7.25	35.31	2.76
QCISD(T) / Stuttgart RLC ECP	-47.54	2.25	14.81	0.98	5.83	6.65	35.63	3.08
CCSD / SBKJCVDZ ECP	-38.91	10.88	21.54	7.70	17.15	17.96	41.22	8.67
QCISD / SBKJCVDZ ECP	-39.28	10.51	20.93	7.09	15.68	16.50	41.06	8.51
CCSD(T) / SBKJCVDZ ECP	-41.20	8.59	21.15	7.31	12.52	13.33	41.39	8.84
QCISD(T) / SBKJCVDZ ECP	-41.43	8.36	20.92	7.09	11.94	12.75	41.73	9.19

Table 2: Reaction Enthalpies (kcal/mol) and Absolute Deviation of Selenium Reactions (1 of 2)

	$Se + HO_2 \rightarrow SeO + OH$		$Se + SO_2 \rightarrow SeO + SO$		$SeO + HO_2 \rightarrow SeO_2 + OH$	
Experimental	-30.56		33.06		-32.28	
B3LYP / LANL2DZ	-22.79	7.77	-36.40	69.46	7.27	39.55
CCSD / 6-311++G(3df,3pd)	-36.60	6.04	23.85	9.22	-30.36	1.92
QCISD / 6-311++G(3df,3pd)	-36.38	5.82	23.82	9.24	-30.99	1.29
CCSD(T) / 6-311++G(3df,3pd)	-38.57	8.01	23.78	9.29	-34.78	2.50
QCISD(T) / 6-311++G(3df,3pd)	-38.76	8.20	23.59	9.47	-35.23	2.95
CCSD / Stuttgart RLC ECP	-41.45	10.89	19.00	14.07	-28.48	3.80
QCISD / Stuttgart RLC ECP	-40.98	10.42	19.23	13.84	-28.62	3.66
CCSD(T) / Stuttgart RLC ECP	-41.25	10.69	21.10	11.97	-33.86	1.58
QCISD(T) / Stuttgart RLC ECP	-41.23	10.67	21.13	11.94	-34.17	1.89
CCSD / SBKJCVDZ ECP	-33.52	2.96	26.93	6.14	-24.23	8.05
QCISD / SBKJCVDZ ECP	-33.08	2.52	27.12	5.94	-24.47	7.81
CCSD(T) / SBKJCVDZ ECP	-33.40	2.84	28.94	4.12	-29.81	2.47
QCISD(T) / SBKJCVDZ ECP	-33.38	2.82	28.97	4.09	-30.18	2.11

Table 3: Reaction Enthalpies (kcal/mol) and Absolute Deviation of Selenium Reactions (2 of 2)

	$SeO + SO_2 \rightarrow SeO_2 + SO$		$SeO + NO \rightarrow SeO_2 + N$		$Se + HO_2 \rightarrow SeO_2 + H$	
Experimental	31.34		50.06		-28.87	
B3LYP / LANL2DZ	-6.33	37.67	68.09	18.03	22.63	51.51
CCSD / 6-311++G(3df,3pd)	30.09	1.25	49.77	0.28	-23.18	5.69
QCISD / 6-311++G(3df,3pd)	29.21	2.13	49.34	0.72	-24.82	4.06
CCSD(T) / 6-311++G(3df,3pd)	27.56	3.78	47.80	2.25	-33.72	4.85
QCISD(T) / 6-311++G(3df,3pd)	27.13	4.22	47.94	2.12	-34.76	5.88
CCSD / Stuttgart RLC ECP	31.97	0.63	51.65	1.60	-26.15	2.72
QCISD / Stuttgart RLC ECP	31.58	0.24	51.71	1.66	-27.04	1.83
CCSD(T) / Stuttgart RLC ECP	28.49	2.85	48.73	1.33	-35.47	6.60
QCISD(T) / Stuttgart RLC ECP	28.18	3.16	49.00	1.06	-36.16	7.29
CCSD / SBKJCVDZ ECP	36.22	4.88	55.90	5.85	-13.97	14.90
QCISD / SBKJCVDZ ECP	35.74	4.39	55.87	5.81	-14.99	13.88
CCSD(T) / SBKJCVDZ ECP	32.54	1.19	52.78	2.72	-23.58	5.29
QCISD(T) / SBKJCVDZ ECP	32.18	0.83	52.99	2.94	-24.32	4.55

Upon examination of each table, a number of comparisons can be made between the data within each as well as several cross-table comparisons. In Table 1, reactions involving arsenic are presented. Generally speaking, the B3LYP/LANL2DZ level of theory produced the most inaccurate results, varying anywhere from 3.65 kcal/mol to as much as 59.36 kcal/mol. This result was to be expected, as LANL2DZ is a basic density functional theory and is less rigorous a calculation than any other level of theory shown. The lack of d-polarization functions in the LANL2DZ basis set, which is necessary for the central atom, as well as the lack of diffuse functions necessary for all atoms, results in this inaccuracy.[42] Overall, levels of theory involving the Stuttgart RLC ECP basis set yielded the most consistent results when compared to experimentally-derived data. With the exception to the reaction involving H_2O, all enthalpies of reaction fell within 7.09 kcal/mol of the experimental approximations. A cursory examination of the performance of the levels of theory using the ECP reveals that the Stuttgart RLC ECP is more reliable in terms of consistency and minimized deviation from experimental values. More than likely, the Stuttgart RLC ECP is simply more accurate in representing the electrons in an arsenic atom than SBKJCVDZ ECP.

Tables 2 and 3 present reaction enthalpies and absolute deviations for reactions involving selenium. Once again, the B3LYP/LANL2DZ level of theory was the least consistent level of theory, ranging from 7.77 kcal/mol to 69.46 kcal/mol from experimentally-derived values. A definite single most accurate basis set did not for the most part exist, at least to the degree that it did for the arsenic reactions. However, for selenium reactions, 6-311++G(3df,3pd) and SBKJCVDZ ECP appear to be more accurate than the other basis sets in this study. Since the complete Pople basis set was used (6-311++G(3df,3pd)) and this is the most rigorous of all calculations in this study, it is not surprising that a high degree of accuracy is obtained. Meanwhile, the SBKJCVDZ ECP produced similar results to the complete Pople basis set while taking only a portion of the computational demand, due to the electron core potential. In general, the SBKJCVDZ ECP was a more accurate basis set than the Stuttgart RLC ECP in predicting enthalpies for reactions involving selenium.

Geometry Predictions

Tables 4 and 5 presents geometry predictions for the compounds studied along with the experimental values. Experimental geometry values came with few exceptions from NIST, however experimental information was not found for $HO_{2.}$ Effective core potentials were only used for arsenic and selenium compounds as all the other compounds involved atoms which were too small to justify using effective core potentials. As noted earlier, due to computational limitations several species had geometry predictions done only at the QCISD/6-311++G(3df,3pd) level of theory. These are viewed as reasonable approximations of the geometries would be derived from the other levels of theory as calculations at lower levels were within approximately 0.02Ǻ.

Table 4: Calculated and Experimental Bond Lengths (Angstroms) and Bond Angles (Degrees) of Large Species

		Level of Theory													
Species	Bond Length (Å) / Bond Angle (Deg)	exp	B3LYP / LANL2DZ	CCSD / 6-311++G (3df,3pd)	QCISD / 6-311++G (3df,3pd)	CCSD(T) / 6-311++G (3df,3pd)	QCISD(T) / 6-311++G (3df,3pd)	CCSD / Stuttgart RLC ECP	QCISD / Stuttgart RLC ECP	CCSD(T) / Stuttgart RLC ECP	QCISD(T) / Stuttgart RLC ECP	CCSD / SBKJCVDZ ECP	QCISD / SBKJCVDZ ECP	CCSD(T) / SBKJCVDZ ECP	QCISD(T) / SBKJCVDZ ECP
AsO	r(As-O)	1.6236	1.6883	--	1.63	--	--	1.6234	1.626	1.6396	1.6395	1.6319	1.6375	1.6504	1.6512
SeO	r(Se-O)	1.6393	1.748	1.6338	1.6362	1.6463	1.6484	1.6392	1.6423	1.6477	1.6492	1.6718	1.6756	1.6822	1.6837
SeO_2	r(Se-O)	1.6076	1.7164	--	1.6009	--	--	--	1.6023	--	--	--	1.6173	--	--
	r(Se-O)	1.6076	1.7164	--	1.6009	--	--	--	1.6023	--	--	--	1.6173	--	--
	a(O-Se-O)	113.83	110.97	--	114.29	--	--	--	113.21	--	--	--	110.94	--	--

Table 5: Calculated and Experimental Bond Lengths (Angstroms) and Bond Angles (Degrees) of Small Species

		Level of Theory					
Species	Bond Length (Å) / Bond Angle (Deg)	exp	B3LYP / LANL2DZ	CCSD / 6-311++G (3df,3pd)	QCISD / 6-311++G (3df,3pd)	CCSD(T) / 6-311++G (3df,3pd)	QCISD(T) / 6-311++G (3df,3pd)
H_2O	r(O-H)	0.9575	0.9769	0.9567	0.957	0.959	0.9594
	r(O-H)	0.9575	0.9769	0.9567	0.957	0.959	0.9594
	a(H-O-H)	104.51	110.04	104.31	104.29	104.15	104.14
HO_2	r(O-H)	--	0.9952	--	0.9685	--	--
	r(O-O)	--	1.3935	--	1.3268	--	--
	a(H-O-O)	--	106.57	--	104.49	--	--
H_2	r(H-H)	0.7414	0.7438	0.7426	0.7426	0.7423	0.7423
NO	r(N-O)	1.1506	1.199	1.1453	1.1505	1.1511	1.1567
OH	r(O-H)	0.9706	1.0015	0.968	0.9683	0.9702	0.9705
SO	r(S-O)	1.4811	1.6321	1.4783	1.4802	1.4889	1.4903
SO_2	r(S-O)	1.4308	1.6106	--	1.4295	--	--
	r(S-O)	1.4308	1.6106	--	1.4295	--	--
	a(O-S-O)	119.33	112.79	--	119.34	--	--

The B3LYP/LANL2DZ level of theory uniformly had the least accurate bond-length predictions, with differences from experimental values ranging from 0.0024 Ǻ for H_2, twice that of the second least accurate calculation, to 0.18 Ǻ for SO_2. This error is consistent with the enthalpy predictions. For the arsenic and selenium oxide species, it was found that the Stuttgart RLC ECP basis set was the most accurate, with errors of only 0.0002 Ǻ or less for both of the single oxides. The error in bond angle of SeO2 was slightly smaller for the Pople basis, but utilizing the Stuttgart RLC ECP basis increased the error by less than 0.2°. Errors for the SBKJCVDZ ECP-based bond length predictions ranged from approximately 0.01-0.04 Ǻ.

For molecules without atoms requiring effective core potentials, the bond lengths were consistently more accurate with quadratic configuration interaction calculations. Between the QCISD and QCISD(T) calculations, all bond lengths between calculated to within 0.002 Ǻ with calculated bond lengths differing from experimental by 0.0001 Ǻ for both NO and OH. Conclusions regarding bond angles for these smaller molecules are not possible as there are only two triatomic molecule for which experimental data was found, and for one of them, specifically SO_2, the only calculation using the 6-311++G(3df,3pd) basis was done using QCISD. It is of note, though, that the difference between calculated angles of coupled cluster and quadratic configuration interactions, utilizing the same excitations, had differences in bond angle of 0.02° or less for H_2O. It therefore seems that small oxygen containing molecules can be consistently modeled using quadratic configuration interaction calculations.

Vibrational Frequency Predictions

Tables 6 and 7 presents the vibrational frequency predictions as well as experimental results. Experimental results were taken from Herzberg.[14,15] For species in which equilibrium bond lengths and angles were not calculated, the equilibrium results from the QCISD calculation with the same basis set were substituted. As stated in the predicted geometries section, calculations involving effective core potentials were limited to species containing either arsenic or selenium.

Table 6: Calculated and Experimental Vibrational Frequencies (cm^{-1}) of Large Species

		Level of Theory													
Species	Vibrational Mode	exp	B3LYP / LANL2DZ	CCSD / 6-311++G (3df,3pd)	QCISD / 6-311++G (3df,3pd)	CCSD(T) / 6-311++G (3df,3pd)	QCISD(T) / 6-311++G (3df,3pd)	CCSD / Stuttgart RLC ECP	QCISD / Stuttgart RLC ECP	CCSD(T) / Stuttgart RLC ECP	QCISD(T) / Stuttgart RLC ECP	CCSD / SBKJCVDZ ECP	QCISD / SBKJCVDZ ECP	CCSD(T) / SBKJCVDZ ECP	QCISD(T) / SBKJCVDZ ECP
AsO	As-O stretch	967.08	877.92	998.47	978.07	985.62	982.42	1004.36	860.96	959.80	906.43	962.39	887.56	905.69	876.00
SeO	Se-O stretch	907.10	797.44	965.54	958.86	927.66	920.24	918.53	902.64	898.37	891.57	848.38	830.55	831.25	823.94
SeO_2	sym. stretch		301.37	389.02	380.68	364.43	360.13	391.87	385.78	371.97	368.21	398.49	392.14	380.17	376.28
	asym. stretch	910.00	797.39	997.79	988.49	983.86	978.85	949.97	941.23	937.31	932.03	895.91	885.90	882.09	876.05
	scissors	967.00	817.36	1043.29	1031.65	1037.05	1034.73	987.00	975.62	978.03	975.84	982.94	970.43	969.40	967.05

Table 7: Calculated and Experimental Vibrational Frequencies (cm^{-1}) of Small Species

		Level of Theory					
Species	Vibrational Mode	exp	B3LYP / LANL2DZ	CCSD / 6-311++G (3df,3pd)	QCISD / 6-311++G (3df,3pd)	CCSD(T) / 6-311++G (3df,3pd)	QCISD(T) / 6-311++G (3df,3pd)
H_2O	sym. stretch	1594.70	1575.81	1654.23	1652.61	1639.45	1639.09
	asym. stretch	3657.00	3673.57	3895.09	3889.10	3858.63	3852.26
	scissors	3755.70	3865.18	3996.70	3991.07	3962.91	3956.66
HO_2	sym. stretch	1034.20	1066. 33	1160.78	1148.42	1158.36	1150.88
	asym. stretch	2344.50	1364.44	1456.64	1449.42	1425.22	1422.69
	scissors	2357.80	3483.01	3730.21	3726.01	3720.57	3718.85
H_2	H-H stretch	4395.20	4457.97	4402.74	4402.74	4402.84	4402.84
NO	N-O stretch	1904.00	1770.15	1996.40	1821.73	2109.08	1824.29
OH	O-H stretch	3735.21	3494.58	3806.13	3801.21	3774.48	3769.70
SO	S-O stretch	1123.70	955.95	1196.28	1188.42	1151.29	1145.33
SO_2	sym. stretch	517.60	386.72	538.93	531.71	513.95	510.83
	asym. stretch	1151.30	892.57	1217.04	1209.23	1200.65	1196.58
	scissors	1361.70	969.59	1423.14	1415.10	1418.83	1416.71

For molecules involving arsenic and selenium, the most accurate results were found using effective core potentials. For two out of the three molecules, AsO and SeO_2 the best results were found using the SBKJCVDZ ECP basis set. It is important to note that for both of these molecules results using the Stuttgart RLC ECP basis set came within approximately 8 cm^{-1} for AsO, 22 cm^{-1} for SeO_2 asymmetric stretch, and 9 cm^{-1} for SeO_2 scissors, where the best results utilizing the SBKJCVDZ ECP basis set were within approximately 5, 14, and 0.1 cm^{-1} respectively. For SeO, calculations using the Stuttgart RLC ECP basis set were all between approximately 5 and 16 cm^{-1}, whereas the errors utilizing the SBKJCVDZ ECP basis set were between approximately 59 and 84 cm^{-1}. With regards to the best results for SeO_2, the CCSD/ BKJCVDZ ECP level of theory produces the best results for asymmetric stretch while QCISD(T)/SBKJCVDZ ECP produces the best results for the scissors mode. As the error in the CCSD/SBKJCVDZ ECP for the scissors mode is approximately 15 cm^{-1} while the error for QCISD(T)/SBKJCVDZ ECP is approximately 35 cm^{-1}, we suggest using the CCSD/SBKJCVDZ ECP for further calculations involving SeO_2. We conclude that for predicted vibrational frequencies, while the SBKJCVDZ ECP basis set will on occasion produce better results, the Stuttgart RLC ECP basis set consistently produces good results.

For the molecules in Table 7, similar to calculations of the geometries, quadratic configuration interaction calculations were consistently more accurate than coupled cluster calculations. Excluding H_2O and HO_2, the only frequency that had a coupled cluster calculation being the most accurate was the symmetric stretch mode of SO_2. For that calculation, the CCSD(T)/6-311++G(3df,3pd) level of theory predicted value differed from the experimental value by approximately 4 cm^{-1}, while the QCISD(T)/6-311++G(3df,3pd) predicted value differed by approximately 7 cm^{-1}. This would suggest that, as with the geometric predictions, quadratic configuration interaction calculations are most likely to produce good results for oxygen species.

With many of the triatomic molecules, predicted vibrational frequencies from the 6-311++G(3df,3pd) basis have differed from the experimental value in a consistent manner. For SeO_2, H_2O, and HO_2 symmetric stretch mode, the calculated vibrational frequencies from the Pople basis exceed the experimental value by between 3.5% and 10%. The consistency between the different levels of theory as well as the agreement of those levels of theory with other, diatomic species, suggests that there is a scaling factor involved.

Reaction Equilibrium Constants

After enthalpy and entropy of each reaction were calculated for each level of theory, reaction equilibrium constants at 298 K were determined through the following set of equations:

1) $\Delta G = \Delta H - T\Delta S$

2) $K_{eq} = \frac{-\Delta G}{RT}$

Table 6 lists all reactions studied in this research. Also listed are their respective reaction equilibrium constants at 298.15 K, along with the level of theory that most closely matched experimental data in terms of ΔH_{rxn}. It was at this level of theory that K_{eq} was determined.

Table 8: Reaction Equilibrium Constants at 298 K

Reaction	**K_{eq} (298.15 K)**	**Best Level of Theory**
$SeO + HO_2 \rightarrow SeO_2 + HO$	1.15E+21	CCSD/6-311++G(3df,3pd)
$As + HO_2 \rightarrow AsO + HO$	1.36E+35	QCISD(T)/ Stuttgart RLC ECP
$Se + HO_2 \rightarrow SeO_2 + H$	7.22E+24	QCISD/SBKJCVDZ ECP
$Se + HO_2 \rightarrow SeO + OH$	3.55E+18	QCISD/Stuttgart RLC ECP
$SeO + SO \rightarrow Se + SO_2$	1.14E+23	QCISD/Stuttgart RLC ECP
$SeO_2 + SO \rightarrow SeO + SO_2$	1.54E+09	QCISD/Stuttgart RLC ECP
$AsO + SO \rightarrow As + SO_2$	2.22E+19	QCISD(T)/SBKJCVDZ ECP
$SeO + N \rightarrow Se + NO$	5.56E+37	CCSD/6-311++G(3df,3pd)
$SeO_2 + N \rightarrow SeO + NO$	1.96E+25	QCISD/Stuttgart RLC ECP
$AsO + N \rightarrow As + NO$	9.07E+35	QCISD(T)/SBKJCVDZ ECP

It is important to note that in some cases, reactants and products were switched in order to yield a positive K_{eq} to show that all of these reactions are forward reactions under atmospheric conditions. As seen in Table 6, with the exception of HO_2 reactions, arsenic and selenium would be reduced under atmospheric conditions. It is important to note that HO_2 plays a key role in the marine boundary layer, where the crashing of ocean waves against shoreline allows radical compounds to play a key role in atmospheric chemistry.[40] Additionally, N in its elemental form is not abundant in the earth's atmosphere, however it was included in this study as its modeling further proves that under standard atmospheric conditions outside of the marine boundary layer, the reduction of oxidized forms of arsenic and selenium are expected.

Conclusions

In summary, results from these theoretical calculations show that the more computationally rigorous methods of coupled cluster and quadratic configuration interaction produce more accurate results than the Hartree-Fock and density functional theory calculations, as would be expected. The use of effective core potentials was found to substantially reduce computation times while at some times increasing accuracy versus the complete Pople basis set. In particular, it was found that while the SBKJCVDZ ECP produced some of the best results, the consistent accuracy of the Stuttgart RLC ECP, especially in the area of molecule geometries and vibrational frequencies, suggest using both for future calculations. In the future, we hope that the best calculation methods found for these species can be further used to produce potential energy surfaces so that kinetic data for these reactions can be found. With kinetic data, the transport and ultimate fate of the arsenic and selenium species through the environment can be understood and effective mitigation techniques found.

In future studies, it would also be important to examine additional NO_x, SO_x, and carbonaceous gases in addition to the atmospheric gases in this study. These gases could also play an important role in atmospheric arsenic and selenium reactions, as they are prevalent in coal combustion flue gases. Further examinations of reactions involving elemental nitrogen are more than likely not necessary due to its instability under atmospheric conditions.

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