Comparative ab Initio Study of Molecular Structures and Relative Stabilities of Germanone, Germathione, Germaselenone, and Their Structural Isomers

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The relative stabilities of the $H_2Ge{=}X$, *trans*-HGeXH, and *cis*-HGeXH (X = O, S, Se) species and the transition states for $H_2Ge{=}Se \leftrightarrow$ *trans*-HGeSeH and *trans*-HGeSeH ↔ *cis*-HGeSeH isomerizations were investigated using post-Hartree−Fock ab initio methods. Geometry optimization and frequency calculations were performed at the HF, MP2, DFT, and QCISD(T) levels using TZP(2d,2p), TZP(2df,2pd), and TZP++(2df,2pd) basis sets. In the cases of oxygen and sulfur, the isomers $H_2Ge{=}O$ and $H_2Ge{=}S$ represent the structures with the highest energy, and the global minima corresponds to the *trans*-HGeSH and *cis*-HGeOH forms, respectively. In a more detailed study of the potential energy surface of the Ge[H_2Se] system, we have found that the *trans*-HGeSeH structure is a global minimum separated at the QCISDT/TZP(2df,2pd) level by only 0.5 and 2.0 kcal/mol from $H_2Ge{=}Se$ and *cis*-HGSeH, respectively. In all cases the electron correlation energy plays a dominant role, and reliable assignment of the relative stability of these energetically close-lying isomers was possible using only higher levels of ab initio theory.

Introduction

The chemical bond is a highly complex phenomenon that eludes all attempts at a simple description.[1] In the last 15 years, the chemistry of heavier main-group elements advanced in unexpected ways. We point out here the isolation and characterization of compounds with "genuine" (both covalent s- and p-bond present) double bonds involving elements such as Si and Ge. Silanone ($H_2Si{=}O$) was first detected by Eaborn et al.,[2] and the existence of germanone ($H_2Ge{=}O$) was proved in the studies of photochemical reactions of germane and ozone in solid argon.[3] Using the technique of isotopic substitution and filtered photolysis, Withnall and Andrews identified, besides germanone, hydroxygermylene (HGeOH) and reported a complete assignment of the infrared spectra of both molecules.

Parallel to the progress in experimental research, quantum chemistry has also directed its interest to the molecules involving heavier main-group elements. The structure and bonding of Ge-, S-, P-, and Se-containing molecules have been studied in recent years using a higher correlated level of ab initio techniques up to the CCSD(T) methods.[4−8]

For the title compounds, the earlier ab initio studies of the $H_2Ge{=}O$ potential energy surface (PES) at the SCF level[9,10] and on the MP2/3-21G* correlated level[11] have revealed that hydroxygermylene is the global minimum, and *trans*-HGeOH has been found to be slightly more stable than *cis*-HGeOH. The later conclusion was obtained only after taking the electron-correlation energy into account. Similar results[12,13] have been revealed also in the ab initio study of germathione ($H_2Ge{=}S$). As in the case of germanone, the global minimum is *trans*-HGeSH, and germathione lies energetically higher than *cis*-HGeSH. It is interesting to note that as has been shown in recent extensive theoretical studies[14] of H_2XO molecules (for X = C, Si, Ge, Sn, Pb), only $H_2C{=}O$ is the global minima on the PES; all other studied species prefer to exist as divalent HXOH *cis*- and *trans*-isomers that are close in energy.

Although in many cases selenium compounds closely resemble their sulfur analogues, some significant differences occur.[15] As has been shown in our recent papers many experimentally observed properties of selenium-containing molecules are accurately predicted by ab initio theoretical studies.[16−19] The possibility of replacement of experimental studies of these systems by high-level ab initio calculations is in addition important from the point of view concerning safety when working with the extremely high toxicity of selenium compounds.[20,21] High-level ab initio results could also be used to test the reliability of DFT theory, an inexpensive alternative to classical post-Hartree−Fock calculations in prediction of properties of the systems with a few (e.g., Ge and Se) heavy elements. The DFT approach is not as computer-demanding as other advanced correlation methods since the need for computational resources is formally scaled as N,^{3} where N is the number of basis functions. Such speedup of calculations is equally important for large biomolecules as well as for systems involving heavy atoms.

Up to now there are no published experimental or theoretical studies of germanoselenone. The aim of this study is therefore to investigate theoretically the PES of Ge[H_2X] (X = O, S, and Se) species at the reliable QCISD(T) levels of theory in order to contribute to a better understanding of their structural isomerism in this series of molecules. In particular, the predicted molecular parameters and harmonic vibrational frequencies could aid experimental study of unknown Ge[H_2Se] species.

Computational Methods

Calculations were performed using ab initio LCAO-MO methods.[22] For H, O, and S, standard split-valence triple-ζ basis

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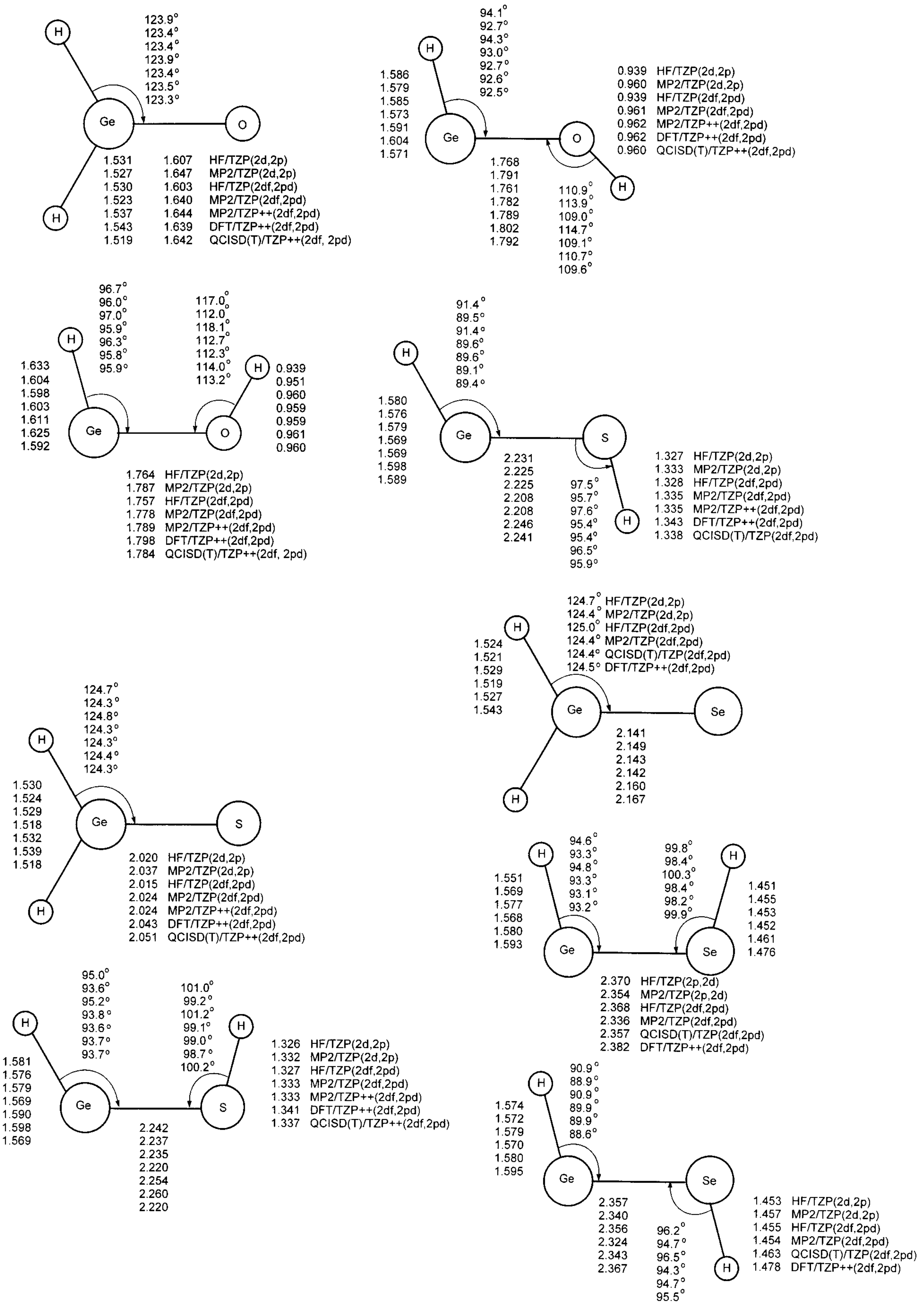

Figure 1. Optimized geometries of all studied minimum-energy species (bond lengths in angstroms and angles in degrees).

sets augmented by two sets of d- (heavy atoms) and p- (hydrogen) (TZP(2d,2p)) and also augmented by f- and d-polarization functions (TZP(2df,2pd) and saturated with s- and p- (O, S) and s-diffuse (H) functions were employed.[23,24] For germanium and selenium the basis sets of Curtiss et al.,[25] compatible in size with split-valence triple-ζ (isotropic part)

TABLE 1: Calculated Harmonic Vibrational Frequencies (Unscaled, in cm^{-1}) and Absolute IR Intensities (in km/mol, in Parentheses) for Selenogermylenes and Germaselenone at the MP2/TZP(2df,2pd) Level

vibration	mode	*cis*	*trans*	vibration	mode	H_2GeSe
$\nu_1(a')$	GeSe str	297 (24)	304 (22)	$\nu_1(a1)$	GeSe str	416 (6)
$\nu_2(a'')$	torsion	501 (9)	573 (0)	$\nu_2(b2)$	rock	537 (10)
$\nu_3(a')$	def	582 (9)	558 (13)	$\nu_3(b1)$	wag	561 (5)
$\nu_4(a')$	def	722 (40)	808 (15)	$\nu_4(a1)$	sciss	917 (104)
$\nu_5(a')$	GeH str	2001 (287)	1998 (284)	$\nu_5(a1)$	GeH_2 s str	2207 (77)
$\nu_6(a')$	SeH str	2512 (3)	2500 (7)	$\nu_6(b2)$	GeH_2 a str	2208 (121)

augmented by two sets of d- (TZP(2d)) and one set of f-polarization (TZP(2df)) and s- and p-diffuse functions, were adopted. Five-component d and seven-component f atomic orbitals were used throughout. The equilibrium geometries were fully optimized with Schlegel's analytical gradient method[27] within the constrained planar C_s point group symmetry of the system at the Hartree−Fock (HF) and the second-order Møller−Plesset (MP2) correlated levels of theory. At the same levels, the harmonic vibrational frequencies were calculated at the optimized geometries. The geometries was further reoptimized at the DFT and QCISD(T) levels. The frozen-core approximation was used throughout; for Se and Ge 1s,2s,2p,3s, and 3p AOs were kept frozen. All calculations were performed using the GAUSSIAN 92/DFT[28a] and GAUSSIAN 94 sets of programs;[28b] for DFT calculations, Becke's [29] three-parameter exchange-correlation gradient corrected functional of Lee, Yang, and Parr[30] (B3LYP)[31] was used. The errors arising from the numerical integration were reduced by the "int=finegrid" option, which corresponds approximately to 7000 grid points/atom.

Results and Discussion

The optimized geometric parameters for minimum-energy structures from various types of calculations predicted in this work are shown in Figure 1. Unfortunately no experimental geometries are available in the literature for these species. Due to this fact, the reliability of the predicted geometries can only be estimated by comparison between different levels of the theory (taking into account the standard errors of each method) or by comparison of experimental data coming from measurements of other compounds bearing similar structural subunits. In our previous study[32] we have compared the theoretical values of the bond lengths of germanium monooxide, monosulfide, and monoselenide (GeX; X = O, S, Se). At the MP2/6-311G(3df) level good agreement was obtained with experimental values.[33−36] Comparing the experimental bond lengths of 1.627, 2.014, and 2.135 Å for GeO, GeS, and GeSe, respectively, with the corresponding lengths of various isomers, one can see that the experimental bond lengths of diatomics are almost the same as the corresponding bond lengths in $H_2Ge{=}X$ isomers. In *trans*- and *cis*-HGeXH isomers, the GeX bond is slightly longer. It is interesting that the HGeX angle is almost the same (∼124°) for all $H_2Ge{=}X$ analogues. Comparing various levels of theory, for example, the O−H bond length in the *cis*-HGeOH isomer in going from HF to MP2 geometry is enlarged by ∼0.012 and ∼0.020 Å using the TZP(2d,2p) and TZP(2df,2pd) bases, respectively. At the highest level used, QCISD(T)/TZP++(2df,2pd), the bond length (0.960 Å) is only slightly enlarged by ∼0.001 Å as compared with the MP2/TZP(2df,2pd) level. In previous calculations,[13] the bond lengths 0.966 and 0.997 Å at HF/3-21G* and MP2/3-21G* levels, respectively, were obtained. Similar results have been obtained for all species studied, and especially data revealed for oxygen- and sulfur-containing species at the QCISD(T)/TZP++(2df,2pd) level and for selenium species at the QCISD(T)/TZP(2df,2pd) level should be reliable and useful for comparison with possible future experimental studies.

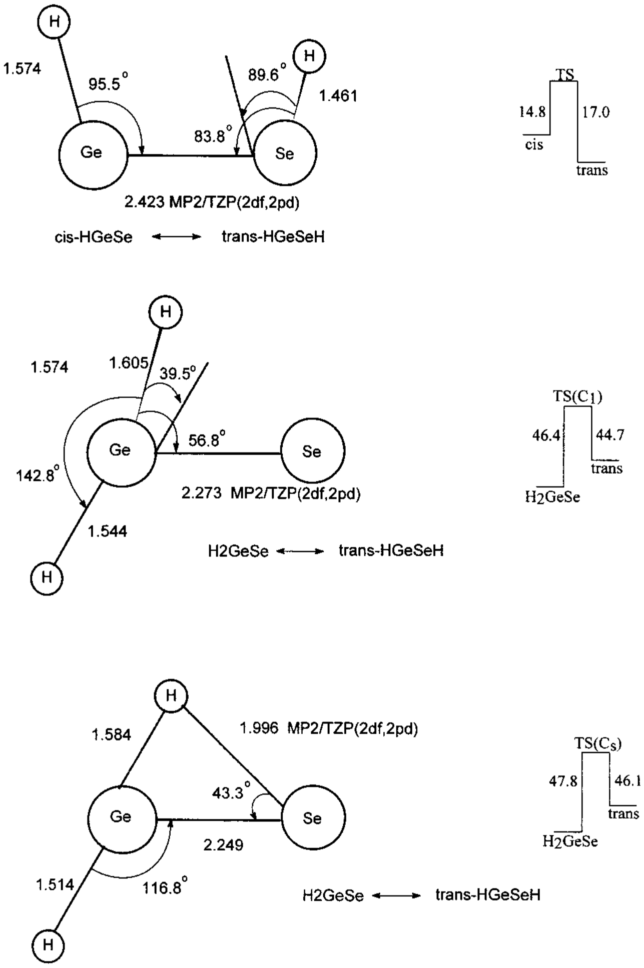

Figure 2. Optimized geometries and energy barriers (kcal/mol) of transition states for germaselenone isomerization (bond lengths in angstroms and angles in degrees).

The previously studied[9−14] molecular parameters and energies of isomerization of Ge[H_2O] and Ge[H_2S] species are in fair agreement with the present reliable QCISD(T) data. Such findings have inspired a more detailed study of selenium-containing compounds. Besides the geometries of the minimum-energy structures, we have calculated also their harmonic vibrational frequencies and intensities; the best values obtained at the MP2/TZP(2df,2pd) level are shown in Table 1. Again, the reliability of these results may be indirectly inferred from our recent prediction of the vibrational harmonic frequencies of the $H_2C{=}Se$ molecule,[37] for which an experimental IR spectrum is available.[38] The calculations, performed at the MP2 correlation level in conjunction with Dunning−Huzinaga valence double-ζ (d,p) basis set for H, C, O and valence triple-ζ (d) basis set for Se, yielded good agreement between experimental and theoretical data.[37]

The main goal of this study was to evaluate the PES of the GeH_2Se molecule. Together with the minimum-energy structures shown in Figure 1, we have located also the transition

TABLE 2: Comparison of Relative Energies (kcal/mol) (ZPE Contributions Included) for H_2GeX, *cis*-HGeXH, and *trans*-HGeXH (X = O, S, Se) Calculated at Various Levels

	cis-HGeOH	*trans*-HGeOH	$H_2Ge{=}O$	*cis*-HGeSH	*trans*-HGeSH	$H_2Ge{=}S$
HF/TZP(2d,2p)	−32.0	−33.3	0.0	−5.7	−7.4	0.0
MP2/TZP(2d,2p)	−18.3	−18.1	0.0	−1.0	−3.0	0.0
MP2/3-21G* [a]	−13.0	−13.3	0.0			
MP4/3-21G* [a,b]	−11.4	−10.8	0.0	−0.9	−3.2	0.0
MP4/DZ+P[c]	−26.26	−26.20	0.0			
CCSD(T)/DZ+P[c]	−30.92	−30.74	0.0			
DFT/DZP+P[c]	−31.12	−30.73	0.0			
HF/TZP(2df,2pd)	−33.3	−32.5	0.0	−5.0	−6.6	0.0
MP2/TZP(2df,2pd)	−18.3	−18.1	0.0	−0.2	−2.3	0.0
MP2/TZP++(2df,2pd)	−18.6	−18.8	0.0	−0.4	−2.5	0.0
DFT/TZP++(2df,2pd)	−28.0	−27.3	0.0	−6.6	−8.5	0.0
QCISD(T)/TZP++(2df,2pd)	−21.7	−21.3	0.0	−3.5	−5.2	0.0

	cis-HGeSeH	*trans*-HGeSeH	H_2GeSe
HF/TZP(2d,2p)	−0.2	−2.0	0.0
MP2/TZP(2d,2p)	4.1	2.0	0.0
MP4(SDTQ)[b]/TZP(2d,2p)	1.9	−0.1	0.0
HF/TZP(2df,2pd)	1.2	−1.7	0.0
MP2/TZP(2df,2pd)	3.7	1.6	0.0
MP4(SDTQ)[b]/TZP(2df,2pd)	2.1	0.2	0.0
QCISD(T)/TZP(2df,2pd)	1.5	−0.5	0.0
DFT/TZP++(2df,2pd)	−2.4	−4.6	0.0

[a] Reference 13. [b] MP4(SDTQ) and CCSD(T) single-point calculations using MP2-optimized geometry. [c] Reference 14.

states for *trans*-HGe−SeH $\leftrightarrow$ *cis*-HGe−SeH and $H_2Ge{=}Se$ $\leftrightarrow$ *trans*-HGe−SeH isomerization reactions (Figure 2). It is interesting that $H_2Ge{=}Se$ $\leftrightarrow$ *trans*-HGe−SeH isomerization proceeds via two, planar and nonplanar, transition structures that have been also found in the study of $H_2C{=}S$ $\leftrightarrow$ *trans*-HC−SH[39] and $H_2N{=}N$ $\leftrightarrow$ *trans*-HN−NH[40] isomerizations but not for, for example, the $H_2C{=}O$ $\leftrightarrow$ *trans*-HC−OH[41] reaction. The revealed transition states are also structurally similar to those found previously[11,13] for *trans*-HGe−OH $\leftrightarrow$ *cis*-HGe−OH, $H_2Ge{=}O$ $\leftrightarrow$ *trans*-HGe−OH, *trans*-HGe−SH $\leftrightarrow$ *cis*-HGe−SH, and $H_2Ge{=}S$ $\leftrightarrow$ *trans*-HGe−SH isomerization reactions.

The total energies of all species studied are given in Supporting Information (Table 2b) and the relative energies of the corresponding isomers in Table 2. The predicted relative energies are strongly dependent on the applied computational level. Previous studies[11,13,14] whose results are also included in Table 3 have concluded that the *trans*-HGe−OH isomer at the HF level is more stable than the cis-HGe−OH isomer by ∼0.3−0.6 kcal/mol, depending on the basis set used. In going to the MP2 correlation level, the *cis*-isomer is more stable by ∼0.2 kcal/mol[13] and by ∼0.4 kcal/mol[14] (in this study the relativistic pseudopotentials of Stoll et al. were used[26]) than the *trans*-isomer. Using the larger basis set TZP(2df,2pd) and TZP++(2df,2pd) in our study, we have found that the *cis*-isomer is more stable at the MP2 level by ∼0.2 kcal/mol than the *trans*-isomer, and this difference in their stabilities is ∼0.1 kcal/mol at the QCISD(T) level.

In the case of sulfur species, the *trans*-isomer is more stable by ∼2 kcal/mol at all levels used, which is also in agreement with previous studies.[13] For both O- and S-containing species, the “formaldehyde”-like isomers $H_2Ge{=}X$ are less stable at the QCISD(T) level by ∼21−22 and ∼3−5 kcal/mol for germanone and germathione, respectively, than their trans- and cis-isomers. When comparing relative stabilities of selenium-containing species at the highest used QCISD(T)/TZP(2df,2pd) level, the *trans*-HGeSeH isomer is more stable by ∼0.5 and ∼2.0 kcal/mol than $H_2Ge{=}Se$ and the *cis*-isomers.

We have also performed optimization of the structural isomers of Ge[H_2X] using the density functional method at the Becke3LYP/TZP++(2df,2pd) level. Interestingly, the relative energies predicted by the DFT and QCISD(T) methods do not vary too much. For oxygen and sulfur species, the *trans*- and *cis*-isomers are slightly lower in energy than their $H_2Ge{=}X$ isomers, but the assignment of relative stability is the same at the QCISD(T) level; even the energy differences between the trans- and cis-isomers are almost the same. For selenium-containing species the predicted relative stabilities are slightly different. The *trans*-isomer was predicted to be energetically the most stable structure in agreement with the QCISD(T) theory; but contrary to the later results at the DFT level, the $H_2Ge{=}Se$ isomer possesses the highest energy.

It should be mentioned that the positions of the global/local minimum species on the PES of H_2GeSe depend significantly on the level of theory used, and the MP4(SDTQ) and MP2 level calculations with the TZP(2df,2pd) basis set predict H_2GeSe to be the global minimum isomer. Therefore, DFT theory predicts the global minimum isomer to be in better agreement with the QCISD(T) evaluation and can be used with caution as a fast alternative to the post-Hartree−Fock calculations for systems with two (and perhaps more) heavy elements.

As has been suggested previously, germanium does not prefer to form a double bond with oxygen[11,14] and with sulfur.[13] Our present results indicate that germanium is also reluctant to form double bonds with selenium which support the tendency of germanium to adopt divalent structures whenever such an alternative exists. The barriers for $H_2Ge{=}X \rightarrow$ *trans*-HGe−XH isomerizations are relatively high (52.8 kcal/mol for X = S,[13] 36.5 kcal/mol for X = O,[11] and as we have found, 46.4 kcal/mol for X = Se); therefore, double-bonded $H_2Ge{=}X$ isomers should be at least kinetically stable and amenable for experimental study.

Conclusions

The following conclusions emerge from this investigation:

1. For germanone and germathione, the ordering of the relative stabilities of isomers obtained previously at the lower levels of theory was confirmed by the highest QCISD(T)/TZP++(2df,2pd) level predictions. However, the relative stabilities depend strongly on the applied basis set and level of theory.

2. For the first time we have studied isomers of germaselenone and predicted their relative stabilities, harmonic vibrational frequencies, and intensities. A detailed analysis of transition states between isomers was also performed and revealed that they are structurally similar to their oxygen and sulfur analogues.

3. For the studied species, optimized minimal energy structures have been reported at the QCISD(T)/TZP(2df,2pd) level (for O and S species with even larger basis set), which may be useful for the possible identification of these molecules using microwave spectroscopy and X-ray diffraction. However, such experimental tasks might be challenging since the relative stabilities of some of the studied isomers are very similar.

4. All structures were optimized also at the B3LYP/TZP++(2df,2pd) level of density functional theory, and for all studied species the energetically lowest isomers are the same as those obtained at the much more computationally demanding QCISD(T) level. This finding is promising from the point of view of the possible further applications of DFT methods to larger compounds containing several heavier atoms.

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Supporting Information Available: Total energies of all species studied (2 pages). Ordering and accessing information is given on any current masthead page.

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