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Molecular Structure of the $GeH_2\cdots OH_2$ Complex

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Hartree−Fock and post-Hartree−Fock (density functional DFT, many-body perturbation theory MP2 and MP4(SDTQ), and coupled-cluster CCSD, and CCSD[T]) quantum-mechanical methods were applied to establish molecular structures and interaction energies of the $GeH_2\cdots OH_2$ complex. Molecular geometries of nonplanar and planar conformers were optimized at the Hartree−Fock, DFT, and MP2 levels of theory using triple-ζ-quality (TZP) augmented by sets of polarization functions (TZP(2d,2p) and TZP(2df,2pd)) basis sets. The optimized nonplanar structures correspond to minimum-energy species at all applied levels of theory. Calculated interaction energies (corrected for the basis set superposition error, CP) are relatively large and amount to −9.43 kcal/mol (MP4(CP)(SDTQ)/TZP(2df,2pd)//MP2/TZP(2df,2pd)), −9.77 kcal/mol (DFT(CP)/TZP(2df,2pd)//DFT/TZP(2df,2pd)), −8.16 kcal/mol (CCSD(CP)/TZP(2df,2pd)//MP2/TZP(2df,2pd)), and −8.90 kcal/mol at the CCSD[T](CP)/TZP(2df,2pd) levels. The optimized planar molecular structure of the studied complex (MP2/TZP(2df,2pd) level) corresponds to the transition-state form (one imaginary, 66i cm^{-1} harmonic vibrational frequency). A repulsive (2.07 kcal/mol) but minimum-energy planar structure of $GeH_2\cdots OH_2$ is predicted at the DFT/TZP(2df,2pd) level of approximation. However, single-point calculations at the planar DFT-optimized geometry reveal this complex to be slightly nonbounded (0.01 kcal/mol, CCSD-(CP)) or very weakly bounded (−0.17 kcal/mol, CCSD[T](CP)).

1. Introduction

The matrix-isolation technique has been successfully applied to obtain a variety of new species and intermediates that contribute significantly to understanding principles of chemistry as well as atmospheric sciences as well. For example, an analysis of the recorded IR spectra of products from the photolytic reactions of silane/ozone and germane/ozone mixtures in low-temperature argon matrices revealed silicon- and germanium-containing analogs of well-known organic molecules such as methanol, formaldehyde, and formic and carbonic acids.[1,2] Also, molecular complexes, (*e.g.,* $HCl\cdots HClCO$, $HBr\cdots HBrCO$, $CO\cdots(HCl)_2$, and $CO\cdots(HBr)_2$[3] and phosgene complexes with F_2, Cl_2, and Br_2[4,5]) the intermediates and products of UV irradiation of halomethane/ozone mixtures have been detected. However, the IR investigations do not furnish detailed information on structure and energetics of these systems. For example, Whitnall and Andrews identified hydroxygermylene (HGeOH), germanone (H_2GeO), and the $GeH_2\cdots OH_2$ complex among products of matrix GeH_4/O_3 photolysis.[2] So performed a theoretical studies on molecular structure and relative stabilities of the isomeric HGeOH/H_2GeO[6a] and HGeSH/H_2GeS[6b] species. More recently, Kapp *et al.* investigated structures and bonding in HXOH/H_2XO (X = C, Si, Ge, Sn, and Pb) series by *ab initio* correlated methods.[7]

In the present paper, we present a quantum-mechanical study of the molecular structure and stability of the $GeH_2\cdots OH_2$ complex.

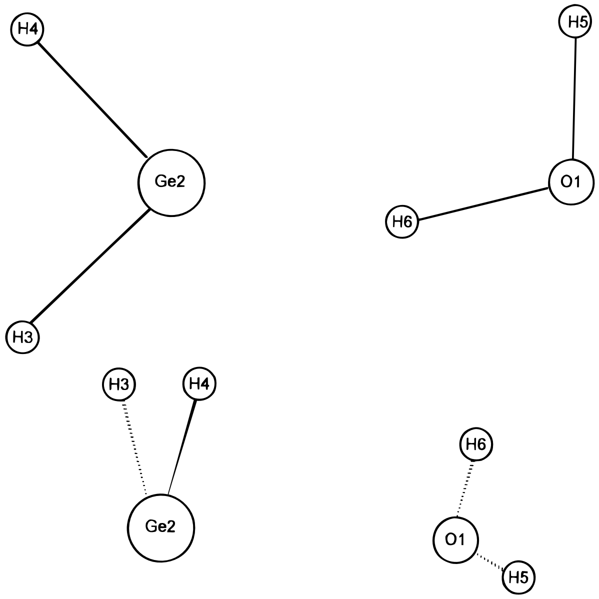

Figure 1. Molecular arrangement of the planar (top) and nonplanar (bottom) $GeH_2\cdots OH_2$ complex.

2. Computational Details

The equilibrium structures of the title system were optimized with the Gaussian92/94 set of programs[8] at the Hartree−Fock (HF), the second-order Møller-Plesset perturbation (MP2), and the density functional theory (DFT) with the exchange potential of Becke and correlated functional of Lee, Yang, and Parr (Becke3LYP option in Gaussian terminology) correlated levels of theory within C_s (planar arrangement, see below) and C_1 point-group symmetry of the complex. Additionally, single-point MP4(SDTQ) and coupled-cluster including single and double excitations (CCSD) and perturbative triple substitutions (CCSD[T]) calculations were performed at the MP2- and DFT-optimized geometries of the complex and its components. Two triple-ζ- quality basis sets augmented by sets of p and/or d (hydrogen atoms) and five-component d and/or seven-component f functions (Ge and O) were employed. The smaller basis set referred to as TZPH(2d,2p), consisted of the standard Pople's split-valence 6-311G with two sets of p-polarization functions for H, two sets of d-polarization functions for O,[9] and the

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TABLE 1: Selected Optimized Geometry Parameters for the $GeH_2 \cdots OH_2$ Complex and Its Components (in Parentheses)[a]

			TZPR (2df,2pd)			
	TZPH (2d,2p) nonplanar		nonplanar		planar	
	HF	MP2	MP2	DFT	MP2	DFT
		Bond Lengths				
O1−Ge2	2.286	2.214	2.214	2.268	3.687	3.720
Ge2−H3	1.582	1.579	1.577	1.607	1.561	1.591
		(1.570)	(1.569)	(1.597)		
Ge2−H4	1.574	1.569	1.567	1.595	1.563	1.590
O1−H5	0.942	0.961	0.962	0.963	0.957	0.964
		(0.957)	(0.957)	(0.961)		
O1−H6	0.942	0.961	0.961	0.963	0.960	0.961
		Bond Angles				
H3−Ge2−H4	94.0	92.6	92.4	91.4	92.9	91.9
		(91.7)	(91.7)	(90.9)		
H5−O1−H6	107.8	105.7	105.5	106.3	102.9	103.8
		(103.3)	(103.1)	(103.9)		
Ge2−H6−O1					176.6	172.3
		Dihedral Angles				
H6−O1−Ge2−H4	63.9	63.3	62.0	56.4		
H5−O1−Ge2−H4	173.6	177.0	175.4	170.5		
H5−O1−Ge2−H3	92.1	84.1	82.6	78.7		
H6−O1−Ge2−H3	−30.3	−29.6	−30.8	−35.4		
angle between GeH_2 and OH_2 plane	40.1	29.3	28.7	27.9		
angle between O1−H6 and GeH_2 plane	27.5	23.0	22.6	22.8		
angle between O1−H5 and GeH_2 plane	17.3	11.6	11.3	10.0		
O distance from GeH_2 plane	2.276	2.203	2.202	2.255		

[a] Distances in Å, angles in degrees.

partially decontracted [433111/43111/4*] Huzinaga's basis supplemented with two d-polarization functions[10] for Ge. A larger basis set was obtained by saturation of the previous basis set with additional d-polarization (H) and f-polarization sets (O). For Ge, the 6-311G-like basis set of Curtiss *et al.*[11] augmented with one set of d- and one set of f-polarization functions was used. This basis set will be refered to as the TZPR(2df,2pd). Spherical five-component d and seven-component f polarization functions were used. Calculated interaction energies were corrected for the basis set superposition error using the full Boys−Bernardi counterpoise (CP) scheme.[12] The interaction energies were partitioned into the SCF (ΔE^{SCF}) and second-(ΔE^{2}), third-(ΔE^{3}), and fourth-order ($\Delta E(SDTQ)^{4}$) intermolecular Møller−Plesset perturbation theory components. ΔE^{SCF} was divided into Heitler−London first-order electrostatic and exchange ($\Delta E^{(1)}$), and mutual induction (deformation), ΔE^{SCF}(def) terms: $\Delta E^{SCF} = \Delta E^{(1)} + \Delta E^{SCF}(def)$ (for example, see: ref 13). Pure cartesian d- (six-component) and f- (10-component) polarization functions were used.[14] Frozen core (1s2s2p3s3p for Ge and 1s for O atomic orbitals) approximation was adopted at the MP2, CCSD, CCSD[T], and MP4 levels of theory.

3. Results and Discussion

Optimized molecular arrangements assuming planar (C_s) and unconstrained C_1 symmetry of the $GeH_2 \cdots OH_2$ system are displayed schematically in Figure 1. As a possible structure for the title complex, Whitnall and Andrews[2] suggested coplanar orientation of the H_2O and GeH_2 subunits with the $Ge \cdots O$ contact. However, depending on the applied level of approximation, the stationary-point structures for the planar $H_2O \cdots GeH_2$ complex correspond to a second-order transition form at the MP2/TZPH(2d,2p) (two imaginary harmonic vibrational frequencies of 147i and 71i cm^{-1}), a first-order transition form at the MP2/TZPR(2df,2pd) (one imaginary frequency of 66i cm^{-1}), and a minimum-energy structure at the DFT/TZPR(2df,2pd) levels of theory. Profoundly nonplanar global-minimum geometries of the complex are predicted at all applied levels of theory. The H_2O and GeH_2 subunits form two nonparallel and twisted planes (Figure 1 and Table 1). The HF/TZPH(2d,2p)- and DFT/TZPR(2df,2pd)-optimized structures of the title complex correspond to more separated GeH_2 and H_2O subunits. The O−Ge intermolecular distance (2.286 Å at the HF/TZPH(2d,2p) and 2.268 Å at the DFT/TZPR(2df,2pd)) and oxygen atom distance from the GeH_2 plane (2.276 Å at HF/TZPH(2d,2p) and 2.255 Å at DFT/TZPR(2df,2pd)) are noticeably larger than the corresponding values predicted at the MP2/TZPH(2d,2p) and the MP2/TZPR(2df,2pd) (Ge−O, 2.214 Å and 2.214 Å; O−GeH_2 plane, 2.203 and 2.202 Å, respectively) levels of theory. Intermolecular angles for $GeH_2 \cdots OH_2$ predicted at the Hartree−Fock level correspond to the most nonparallel and twisted structure. The interplanar angle amounts to 40.1°, and the angles formed by the O−H bonds with the GeH_2 plane (27.5° and 17.3°) are larger than values optimized at correlated levels (interplanar angle, 29.3°, 28.7, and 27.9; O−H6 angle with GeH_2, 23.0°, 22.6°, and 22.8°; O−H5 angle with GeH_2, 11.6°, 11.3°, and 10.0° at the MP2/TZPH(2p,2d), MP2/TZPR(2df,2pd), and DFT/TZPR(2df,2pd), respectively). At all levels, the typical geometric changes of GeH_2 and H_2O upon nonplanar complex formation are observed (*i.e.*, an elongation of bond lengths, (ca. 0.01 Å) and an increase of bond angles (0.5°−3°)). Smaller distortions of the subunits that form the planar complex structure are predicted (Table 1).

The investigated complex is relatively strong. Listed in Table 2 are the calculated total electronic, zero-point vibrational, and interaction energies (ΔE) for the nonplanar and planar $GeH_2 \cdots OH_2$ complexes and its component molecules supplemented by values of dipole moments and dipole polarizablilities. The SCF interaction energy component does not differ significantly at the MP2-optimized ($\Delta E^{SCF}(CP) = -5.40$ kcal/mol (TZPH(2d,2p)) and -5.70 kcal/mol (TZPR(2df,2pd))) or HF-optimized ($\Delta E^{SCF}(CP) = -6.23$ kcal/mol (TZPH(2d,2p)) geometries of the nonplanar $GeH_2 \cdots OH_2$. These considerably large attractive values of ΔE^{SCF} originate mainly from the contribution of the deformation term. Whereas GeH_2 has practically no permanent dipole moment (0.05 D at HF/TZPH-

TABLE 2: Calculated Total Electronic (*E*), Zero-Point Vibrational (ZPE, in au), Interaction Energies (Δ*E*, in kcal/mol), Dipole Moments (*μ*, in D), and Dipole Polarizabilities (α, in au) for the $GeH_2\cdots OH_2$ Complex and Its Component Molecules

	TZPH (2d,2p)		TZPR (2df,2pd)					
	nonplanar		nonplanar			planar		
	MP*n*	HF	MP*n*	CCSD^a	DFT	MP*n*	DFT	CCSD^b
$E(GeH_2\cdots OH_2)$	−2151.031 170^c	−2150.647 778	−2153.035 514^c	−2153.050 379	−2154.640 625	−2153.010 228^c	−2154.617236	−2153.028124
	−2151.049 035^d		−2153.038 372^d	−2153.067 471		−2153.015 692^d		−2153.043 996
	−2051.070 820^e		−2153.071 146^e			−2153.046 957^e		
ZPE	0.039 074	0.040396	0.038831		0.037 523	0.034 808	0.033927	
μ	3.70	3.76	3.78		3.62	2.24	2.03	
$E(H_2O)$	−76.286 480^c	−76.051 109	−76.310 157^c	−76.316 757	−76.453 418			−76.316 696
	76.290 246^d		−76.315 045^d	−76.316 757				−76.323 997
	−76.299 464^e		−74.324 685^e					
ZPE	0.021 755	0.023 153	0.021 800		0.021 339			
μ	1.90	1.96			1.87			
α, $\alpha_\perp$	6.74, 8.14	6.27, 7.64	6.79, 8.16		6.93, 7.08			
$E(GeH_2)$	−2074.714 534^c	−2074.576 842	−2076.696 001^c	−2076.708 343	−2078.160 600			−2076.708 238
	−2074.731 918^d		−2076.697 065^d	−2076.716 493				−2076.716 438
	−2074.742 727^e		−2076.718 440^e					
ZPE	0.011 494	0.011 635	0.011 353		0.010 732			
μ		0.05	0.00		0.28			
α, $\alpha_\perp$	34.13, 37.40	34.76, 36.93	30.61, 35.63		31.62, 36.22			
$E(H_2O)$ dim	−76.293 096^c	−76.054 583	−76.316 100^c	−76.322 010	−76.458 810			
	−76.295 800^d		−76.320 055^d	−76.329 693		−76.315 926^d		−76.324 992
	−76.306 112^e		−76.330 597^e			−76.325 750^e		
$E(GeH_2)$ dim	−2074.717 520^c	−2074.577 654	−2076.697 411^c	−2076.709 691	−2078.160 794	−2076.696 326^c	−2078.160 596	−2076.708 664
	−2074.731 918^d		−2076.698 418^d	−2076.717 912		−2076.697 339^d		−2076.716 882
	−2074.745 786^e		−2076.719 848^e			−2076.718 724^e		
ΔE^{SCF}	−8.34	−8.92	−7.93		−13.27		1.40	
ΔE^{SCF}(CP)	−5.40	−6.23	−5.70		−9.77		2.07	
ΔE^2	−6.93		−6.93			1.01		
ΔE^2(CP)	−3.84		−4.54			1.88		
ΔE^3	2.06		−0.94					
ΔE^3(CP)	−2.33		−1.32					
ΔE^4	−1.10		−0.10					
ΔE^4(CP)	3.35		−0.54					
$\Delta E(4)$	−14.31		−14.02			1.16		
$\Delta E(4)$(CP)	−8.22		−9.43			2.05		
CCSD				−12.30				−0.84
CCSD[T]				−13.34				−1.07
CCSD(CP)				−8.16				0.01
CCSD[T](CP)				−8.90				−0.17

[a] At the MP2-optimized geometry. The first entry corresponds to CCSD, the second to CCSD[T]. Interaction energy values are corrected for ZPE(MP2). [b] At the DFT-optimized geometry. The first entry corresponds to CCSD, the second to CCSD[T]. Interaction energy values are corrected for ZPE(DFT). [c] MP2 values at the MP2-optimized geometry. [d] MP3 values at the MP2-optimized geometry. [e] MP4(SDTQ) values at the MP2-optimized geometry.

(2d,2p) and 0.03 D at HF/TZPR(2df,2pd)//MP2 /TZPR(2df,2pd) level), high values of the dipole polarizability are predicted: the average (34.76 au at the HF/TZPH(2d,2p) and 30.61 au at HF/TZPR(2df,2pd)//MP2/TZPR(2df,2pd) level) and its perpendicular component, (36.93 au and 35.63 au, respectively) are especially important due to the nonplanar orientation of the GeH_2 and H_2O planes. At the MP2/6-311G(2df,2pd)-optimized geometry, the following values of the SCF interaction energy components were obtained: $\Delta E^{(1)}(CP) = 9.49$, $\Delta E^{SCF}(def,CP) = -18.73$, and $\Delta E^{SCF}(CP) = -9.24$ kcal/mol, respectively.[15] The second-order component ($\Delta E^{(2)}$(CP)), containing dispersion and higher induction terms, contributes very significantly to the total interaction energy and is of comparable magnitude to the SCF component. It constitutes 71% (TZPH(2d,2p)) and even 80% of ΔE^{SCF}(CP) with the TZPR(2df,2pd) basis set. The higher-order terms reveal opposite basis-set dependencies. Calculated with the TZPH(2d,2p) basis set the $\Delta E^{(3)}$(CP) and $\Delta E^{(4)}$(CP) contributions are large and the $\Delta E^{(4)}$(CP) correction is noticeably larger (3.35 kcal/mol) than $\Delta E^{(3)}$(CP) (−2.33 kcal/mol). Moreover, the basis-set extension effect (*i.e.*, the difference between values obtained with monomer- and dimer-centered ($\Delta E^{(x)}$(CP)) basis sets) is enormously large (−2.33 *vs* 2.06 kcal/mol and 3.35 *vs* −1.10 kcal/mol in third- and fourth-order, respectively), and this suggests that the TZPH(2d,2p) basis set is not saturated sufficiently to describe intramolecular correlation effects. A better convergence of the MP perturbation theory is achieved with the TZPR(2df,2pd) basis set: absolute values of the second-, third-, and fourth-order corrections decrease monotonically, and the total interaction energy $\Delta E4(CP) = -9.43$ kcal/mol differs insignificantly from the value of −9.78 kcal/mol calculated at the CCSD[T](CP) level value.

The good performance of the DFT method should be noted, and the predicted total interaction energies of DFT(CP)/TZPR(2df,2pd) = −9.77, MP4(SDTQ)(CP)/TZPR(2df,2pd) = −9.43, and CCSD[T](CP) = −8.90 kcal/mol do not differ significantly (Table 2). As was mentioned above, the planar conformation of $GeH_2\cdots OH_2$ is predicted to be a minimum-energy isomer only at the DFT/TZPR(2df,2pd) level of theory; however, the calculated interaction energy corresponds to a repulsive ($\Delta E(CP) = 2.07$ kcal/mol) structure. On the other hand, the C_s conformation optimized at the MP2/TZPR(2df,2pd) level is a transition-state form (one imaginary harmonic frequency of 66i cm^{-1}, Table 3) that is repulsive at the both MP2 (1.88 kcal/mol) and MP4(SDTQ)(CP)/TZPR(2df,2pd)//MP2/TZPR(2df,2pd) (2.05 kcal/mol). Using the DFT-optmized planar geometry of $GeH_2\cdots OH_2$, nonbonded (0.01 kcal/mol) or very weakly attractive (−0.17 kcal/mol) structures are predicted at the CCSD(CP)/TZPR(2df,2pd) and CCSD[T](CP)/TZPR(2df,2pd) levels of approximation.

TABLE 3: Calculated Harmonic Vibrational Frequencies (Unscaled, in cm^{-1}) and Absolute IR Intensities (in km/mol) for $GeH_2\cdots{}^{16}OH_2$ at the MP2/TZPR(2df,2pd) and DFT/TZPR(2df,2pd) Levels

MP2/DFT/exptl.[a] nonplanar minimum energy form[a]	MP2/DFT planar transition form
A: 112 (37), 116 (38)[b] rotations of GeH_2 and OH_2 around Ge−O axis	A″: 66i (89), 18 (94) butterfly-like asym motion of GeH_2 and OH_2
A: 274 (42), 249 (40) Ge−O stretching	A″: 45 (5), 77 (24) libration of OH_2 against GeH_2
A: 430 (178), 400 (171) butterfly-like asym motion of OH_2 and GeH	A′: 67 (9), 82 (0) rotation of GeH_2 and OH_2 against each other, Ge−O stretching
A: 491 (11), 462 (11) butterfly-like asym motion of OH_2 and GeH	A′: 87 (0), 155 (30) libration of OH_2 against GeH_2, rotations of GeH_2 and OH_2 around Ge-O axis
A: 665 (48), 624 (50) butterfly-like sym motion of OH_2 and GeH	A′: 218 (59), 213 (31) libration of OH_2 against GeH_2, rotations of GeH_2 and OH_2 around Ge-O axis
A: 751 (33), 702 (27) butterfly-like sym motion of OH_2 and GeH_2	A″: 329 (47), 298 (29) butterfly-like sym motion of GeH_2 and OH_2
A: 956 (94), 935 (81), 897.8 GeH_2 bending	A′: 967 (90), 945 (82) GeH_2 bending
A: 1644 (71), 1629 (67), 1586.1 OH_2 bending	A′: 1675 (52), 1653 (72) OH_2 bending
A: 1949 (427), 1812 (446), 1777.2 GeH stretching	A′: 2030 (299), 1902 (320) GeH_2 stretching sym
A: 1997 (367), 1869 (392), 1813.6 GeH stretching	A″: 2039 (301), 1914 (305) GeH_2 stretching asym
A: 3830 (80), 3788 (65), 3597.4 OH_2 stretching sym	A′: 3847 (131), 3758 (137) OH_2 stretching sym
A: 3945 (134), 3885 (118), 3686.0 OH_2 stretching asym	A′: 3974 (117), 3876 (88) OH_2 stretching asym

[a] In Ar matrix, ref 2. [b] For all entries, symmetry: frequency (integration).

TABLE 4: Calculated (MP2/TZPR(2df,2pd) Vibrational Frequencies upon Isotopic Substitution for GeH_2 and H_2O Subunits of the $GeH_2\cdots OH_2$ Complex[a]

	GeH_2 submolecule		
mode	GeH_2	GeHD	GeD_2
δ(H−Ge−H)	956 (897.8)	833, 831	690 (646.4)
ν(Ge−H)	1949, 1997 (1777.2, 1813.6)	1388, 1422, 1948, 1997 (1287.0, 1307.4, 1782.0, 1811.6)	1387, 1442 (1281.6, 1308.9)

	H_2O submolecule		
mode	$H_2{}^{16}O/H_2{}^{18}O$	HDO	D_2O
δ(H−O−H)	1644/1638 (1586.1/1580.1)	1443, 1445 (1398.4)	1204 (1173.6)
ν_s (O−H)	3830/3822 (3597.4/3590.3)	2822, 2825 (2682.3)	2760 (2627.8)
ν_{as} (O−H)	3945/3929 (3686.0/3672.5)	3888, 3892 (3637.3)	2892 (2738.5)

[a] In cm^{-1}. Experimental data in parentheses (Ar matrix, ref 2).

Calculated harmonic vibrational frequencies and IR intensities for the $GeH_2\cdots OH_2$ complex are listed in Table 3. Low-frequency vibrations corresponding to intermolecular motions for planar and nonplanar forms differ substantially due to their different molecular symmetries. Intramolecular stretching and bending modes of component subunits predicted at both the MP2 and the DFT/TZPR(2df,2pd) levels for nonplanar conformation are lower and closer to experimental data than corresponding values calculated for the planar $GeH_2\cdots OH_2$ (Table 3). As usual, the calculated (unscaled) harmonic vibrational frequencies, especially for higher-lying stretching vibrations, are larger than the corresponding measured anharmonic values. However, measured and calculated shifts of frequencies for isotopic nonplanar $GeH_2\cdots OH_2$ systems are very close. For example, observed diagnostic values of the ^{18}O red shift of the O−H stretching modes (7.1 and 13.4 cm^{-1}) and the MP2/TZPR(2df,2pd)-predicted (8 and 16 cm^{-1}) values agree very well (Table 4).

4. Conclusions

Molecular parameters and interaction energy of the $GeH_2\cdots OH_2$ complex detected by Whitnall and Andrews in argon matrices[2] were calculated using the Hartree−Fock and post-Hartree−Fock quantum-mechanical methods. The obtained results strongly support a nonplanar geometry of the complex; its nonplanar structure corresponds to a relatively strongly bonded system for which the interaction energy insignificantly varies at the applied correlated levels of theory (*e.g.*, ΔE(CP) = −9.43 kcal/mol at the MP4(SDTQ)(CP)/TZPR(2df,2pd)//MP2/TZPR(2df,2pd), −9.77 kcal/mol at the DFT(CP)/TZPR(2df,2pd)//DFT/TZPR(2df,2pd), and −8.90 kcal/mol at the CCSD[T](CP)/TZPR(2df,2pd)//MP2(2df,2pd)/TZPR(2df,2pd) levels). The optimized molecular structure obtained assuming planarity corresponds to a transition-state repulsive form (1.88 kcal/mol) at the MP2(CP)/TZPR(2df,2pd)//MP2/TZPR(2df,2pd) and 2.05 kcal/mol at the MP4(SDTQ)(CP)/TZPR(2df,2pd)//MP2/TZPR(2df,2pd) levels). The planar structure of the title complex is predicted to be a minimum-energy but also repulsive (2.07 kcal/mol) conformation at the DFT(CP)/TZPR(2df,2pd) level. Results of coupled-cluster calculations based on the DFT-optimized geometry are not conclusive: 0.01 kcal/mol at the CCSD(CP) and −0.17 kcal/mol at the CCSD[T](CP).

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(15) A discrepancy between cited above $\Delta E^{\mathrm{SCF}}(\mathrm{CP}) = -5.70$ kcal/mol (HF/TZPR(2df,2pd)//MP2/TZPR(2df,2pd)) and here (-9.24 kcal/mol), which are the results from different size of the basis sets used: spherical (5d and 7f, Gaussian 92/94) and pure cartesian (6d and 10f, GAMESS) Gaussian-type orbitals.