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Ab initio predictions of the spectroscopic parameters of the germanium halomethylidyne (Ge=C-X; X=F, Cl, Br) free radicals

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Abstract

Ab initio methods have been used to predict the spectroscopic parameters for the $\tilde{X}^2\Pi_i$ and $\tilde{A}^2\Sigma^+$ states of the unknown germanium halomethylidyne (GeCX, X=F, Cl, Br) free radicals. The predictive powers of the chosen ab initio methods have been tested on the known GeCH radical. The calculations show the linear Ge=CX (X=F, Cl, Br) isomer is the global minimum on the potential energy surface, with the cyclic XGeC isomer being between 6400 (BrGeC) and 11300 (FGeC) cm^{-1} higher in energy. The ground state geometries, vibrational frequencies, spin-orbit coupling and Renner parameters have been calculated using the cc-pVTZ basis set. The excited state geometries, vibrational frequencies and excitation energies have also been calculated, and the rotational contours of the 0_0^0 bands have been simulated at medium resolution under jet-cooled conditions. These calculations will aid in the search of these unknown radicals.

Keywords: Germanium halomethylidynes; Geometries; Vibrational frequencies; Ab initio calculations; Dipole moments; Population analysis; Spin-orbit coupling constants

1. Introduction

The linear germanium methylidyne (Ge=C–H) free radical was first observed by Smith et al. using a pulsed electric discharge source [1,2]. They showed that in the $\tilde{X}^2\Pi_i$ state, GeCH has a nominal Ge=C double bond of length 1.7758 Å, while on excitation, the G≡C bond length is shorten to 1.6737 Å and can be characterised as a germanium-carbon triple bond. Additional high-resolution spectroscopic work by Smith et al. in 2001, determined the electric dipole moment of GeCH in both the $\tilde{X}^2\Pi_i$ (0.39 D) and $\tilde{A}^2\Sigma^+$ (1.28 D) states, as well as the Fermi contact parameter for the $\tilde{A}^2\Sigma^+$ state [3]. A recent paper by He et al. looked at Renner–Teller effects and Sears resonances in the $\tilde{X}^2\Pi_i$ state of GeCH and GeCD [4].

In 2001, Sari et al. [5] published a detailed ab initio study on the $\tilde{X}^2\Pi_i$ and $\tilde{A}^2\Sigma^+$ electronic states of GeCH. Using a variety of theoretical methods, they calculated geometries, vibrational frequencies and dipole moments for each state as well as studying the Renner–Teller splitting and the importance of relativistic corrections. They concluded that the CCSD(T) method, in conjunction with a large basis set, was able to produce very reliable results and that relativistic corrections maybe necessary to make quantitative spectroscopic predictions on germanium containing species.

This present work is looking at the unknown germanium halomethylidyne (GeC–X, X=F, Cl, Br) free radicals. The work follows up an ab initio study on silicon halomethylidynes published in 2002 [6], which resulted in the successful observation of the SiCCl radical [7]. Presented in this paper are the results of ab initio studies aimed at predicting spectroscopic parameters of the GeCX(X=F, Cl, Br) free radicals with sufficient accuracy to aid in the spectroscopic detection of these species.

2. Computational methods

A number of density functional (DFT) methods were employed to calculate, equilibrium geometries, vibrational frequencies and dipole moments. The DFT methods used were: BPW91 [8,9], G96LYP [10,11], BLYP [8,11], and B3LYP [12], as implemented in MOLPRO [12,13].

Equilibrium geometries were also calculated using the restricted electron correlation methods, RCCSD and RCCSD(T), as implemented in MOLPRO [14]. The RCCSD and RCCSD(T) dipole moments where found by adding a finite dipole field along the z-axis and determining the first energy

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derivative. The ground-state spin-orbit coupling constants of GeCH and GeCX (X = F, Cl, Br) were calculated using the full Breit–Pauli Hamiltonian [15]. For all calculations, the Dunning correlation-consistent triple zeta basis sets (cc-pVTZ) were used for the Ge, H, C, F, Cl, and Br atoms [16–18].

Although Sari et al. [5] concluded that inclusion of relativistic corrections maybe important in obtaining quantitative spectroscopic predictions of GeCH, no relativistic effects were accounted for in this study due to the limitations in the employed quantum chemistry program.

3. Results and discussion

3.1. Tests on GeCH

A substantial amount of spectroscopic information is now available on the $\tilde{X}^2\Pi_i$ and $\tilde{A}^2\Sigma^+$ states of germanium methylidyne (GeCH), and subsequently this data can be used as a test of the validity of the chosen theoretical methods. A number of test calculations were performed on the $\tilde{X}^2\Pi_i$ and $\tilde{A}^2\Sigma^+$ states of GeCH using various DFT and coupled cluster methods: B3LYP, BLYP, G96LYP, BPW91, CCSD and CCSD(T). The results from these calculations are collected in Table 1. In the $\tilde{X}^2\Pi_i$ state, the calculated Ge=C bond length ranges between 1.767 and 1.795 Å, with an average difference of 0.5% from the observed r_0 value [2], while the C–H bond length ranges between 1.077 and 1.088 Å, with an average difference of 0.4% from the observed r_0 value [2]. Both of these results are in good agreement with the theoretical work of Sari et al. [5].

In the $\tilde{A}^2\Sigma^+$ state of GeCH, the calculated Ge≡C bond length ranges between 1.664 and 1.685 Å, with an average difference of 0.15% from the observed r_0 value [2], while the C-H bond length ranges between 1.071 and 1.084 Å, with a systematic difference of +1.7% from the observed r_0 value [2]. Again, both of these results are in good agreement with those of Sari et al. [5].

3.2. XGeC–GeCX

BPW91 calculations have been performed on the bent and linear isomers of XGeC (X = F, Cl, Br) in order to check that they are not the global minima on the potential energy surface. The results from these calculations are listed in Table 2. Stable energy minima were found for each of these species, all of which were several thousand wavenumbers above the $\tilde{X}^2\Pi_i$ state of GeCX, the global minimum. For comparison, calculations were also carried out on isomers of HGeC (see Table 2).

The ^{2}A′ state of HGeC was calculated to be 20069 cm^{-1} above the $\tilde{X}^2\Pi_i$ state of GeCH. This energy difference (ΔE) is very similar to that found for SiCH/HSiC, ca. 18000 cm^{-1} [6]. The $^2\Pi$ state of HGeC was calculated to be only slightly higher in energy than the ^{2}A′ state (20868 cm^{-1}) and has an imaginary bending frequency, which is indicative of a second order saddle point. The $^2\Sigma$ state was calculated to be 28818 cm^{-1} above the global minimum, while the ^{2}A″ state was found to be unstable and no minima were located.

The results of the XGeC(X = F, Cl, Br) species show a number of interesting features. For example, in going from HGeC to FGeC the ΔE values for the ^{2}A′ and $^2\Pi$ states decrease by ca. 7000 cm^{-1}, while the ^{2}A″ state of FGeC is found to be stable and has the lowest ΔE. In the ^{2}A′ state the ∠XGeC angle increases from 130.8° in HGeC to 147.4° in BrGeC, while the Ge–C bond length increases by ∼0.03 Å in going from HGeC to XGeC. As found for HGeC, the $^2\Pi$ state of XGeC is slightly higher in energy than the ^{2}A′ state and has an imaginary bending frequency. In the ^{2}A″ state, all of the halogenated species have a small ∠XGeC angle of ∼50°,

Table 1

Bond distances (in Å), harmonic frequencies (cm^{-1}), dipole moments (in Debye) for the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Sigma^+$ states of GeCH. The T_0 values (in cm^{-1}) for the transition, $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$, are also given

Basis	Method	r_e(Ge–C)	r_e(C–H)	ω_1	ω_2'	ω_2''	ω_3	μ_e[a]
				GeCH $\tilde{X}^2\Pi$				
cc-pVTZ	BPW91	1.786	1.088	3146.6	416.4	462.4	846.1	0.033
	G96LYP	1.792	1.087	3134.5	368.6	411.4	832.5	0.072
	BLYP	1.795	1.087	3131.2	400.5	446.3	826.6	0.085
	B3LYP	1.775	1.080	3226.5	462.9	480.5	874.5	0.114
	CCSD	1.767	1.077	–	–	–	–	−0.011
	CCSD(T)	1.779	1.080	–	–	–	–	−0.095
	Expt.[b]	1.775	1.0822					0.122

Basis	Method	r_e(Ge-C)	r_e(C-H)	ω_1	ω_2	ω_3	μ_e[a]	T_0[c]
				GeCH $\tilde{A}^2\Sigma$				
cc-pVTZ	BPW91	1.674	1.084	3199.1	660.3	1009.1	1.47	14637
	G96LYP	1.679	1.083	3178.4	600.2	992.8	1.45	15160
	BLYP	1.683	1.084	3172.8	619.5	984.7	1.42	15228
	B3LYP	1.665	1.076	3273.3	688.0	1039.5	1.63	16171
	CCSD	1.664	1.071	–	–	–	1.69	14501
	CCSD(T)	1.678	1.074	–	–	–	1.50	13124
	Expt.[c]	1.673	1.059	–	638	990	1.29	13902

[a] A positive dipole moment has the positive end of the dipole on the Ge atom and a negative dipole moment has the positive end on the hydrogen atom.

[b] Refs. [1–4].

[c] For the CCSD and CCSD(T) methods the BPW91 ZPE correction was used.