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Geometry Predictions, Vibrational Analysis and IR Intensities of XH_3Y (X=C, Si, Ge, Y=F, Cl, Br) Calculated by Hybrid Density Functional Theory, MP2 and MP4 Methods

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Abstract

Hybrid density functional theory B3LYP, B1LYP, B3P86, MPW1PW91 and B3PW91 methods as well as MP2 and MP4 methods at the 6-311++G (3df,3pd) level of theory are used for the calculations of geometrical parameters, infrared vibrational frequencies and absorption intensities of XH_3Y (X=C, Si, Ge and Y=F, Cl, Br) set of molecules. All of the calculated results are compared with the most recent experimental data. The advantages of DFT methods are exhibited from the comparison and discussion. The basis set effect is also considered and the optimal theoretical methods for the discussed systems are recommended.

Keywords: Halogenated methane, halogenated silane, halogenated germane, vibrational analysis, density functional theory

1. Introduction

Great efforts have been put in recent years into studying of the basic molecular properties of halogenated carbon family systems. Many different experimental methods have been developed to obtain thermodynamic, magnetic, spectroscopic and other properties of these compounds.[1–7] In recent few decades, with the development of quantum mechanics theory and computational technology, theoretical and computational studies on the halogenated carbon family species became more and more popular.[8–11] Computational methods are used not only due to the convenience and high efficiency, but also since satisfactory accuracy can be obtained from these methods. Due to this fact many properties of halogenated methane, silanes and germanes, such as geometry structure, vibration spectra and thermochemical properties, are available nowadays as a result of theoretical calculations.[12–20] The calculations has provides us with information about molecular physical properties as well as reactive behaviors which do not only widen our knowledge, but also may boost more creative insights and predictions.

Although the study of this topic is very popular, there are still many unsolved problems in the area of theoretical study on the properties of halogenated carbon family systems. First of all, previous computational studies have been focused mostly on one molecular system or one property of the halogenated carbon family species. Therefore comparisons of properties between different halogen-containing methanes, silanes, and germanes are scarce. On the other hand a comprehensive and systematic investigation of the similarities and differences of halogenated carbon family is indispensable for a better understanding of the chemistry of this class of compounds. Secondly, it is usually supposed that the higher level of theory used in computational studied corresponds to the higher accuracy of results. It is known, however, that for small organic systems DFT methods, and B3LYP method in particular, can give more reliable results than higher level *ab-initio* methods.[21–24] Moreover, there are many density functional methods available nowadays, and the most commonly used B3LYP functional is not always the best choice to study a certain class of molecules. Furthermore, to the best of our knowledge, previous studies in this area mainly focus on the effect of using different methods and no data from the calculation with a basis set as large as 6-311++G (3df, 3pd) are available. A comparison between the results obtained for the 6-311++G (3df, 3pd) basis set and smaller basis sets should provide more insight into the importance of the basis set effect.

To solve all above-mentioned problems, we have carried out computational studies on the geometry optimization and frequency analysis of XH_3Y, where X=C, Si, Ge and Y=F, Cl, Br. Five different DFT methods (B3LYP, B1LYP, B3P86, MPW1PW91, B3PW91) and two high level *ab-initio* methods (MP2, MP4) have been used at the 6-311++G (3df, 3pd) level of theory. From our theoretical study and the available experimental data, as well as from results of previous theoretical investigations, we collect more examples to discuss the applicability of different calculation methods (DFT and high level *ab-initio* methods). We also provide data obtained using the large 6-311++G (3df,3pd) basis set and discuss the basis set effect. Using all these approaches we have performed a systematic calculation on the geometry structure and frequency values of nine halogenated carbon family substances. It allows us to obtain important data to discuss the difference in the properties of these analogies as well as provide the reliable reference for possible future studies.

2. Computational Details

All calculations in this study have been performed with the Gaussian 03 program package.[25] Each stationary point of the nine halogenated species, CH_3F, CH_3Cl, CH_3Br, SiH_3F, SiH_3Cl, SiH_3Br, GeH_3F, GeH_3Cl and GeH_3Br, has been fully optimized with five different DFT methods (B3LYP, B1LYP, B3P86, MPW1PW91, B3PW91) and two high level *ab-initio* methods (MP2, MP4) with 6-311++G (3df,3pd) basis set. Frequencies have been calculated at the same level of theory as geometry optimizations, and each stationary point has been confirmed to be at a local minimum by frequency analysis. Thus for each system, a total of seven geometries and seven vibrational frequencies has been reported. All the reported data are unscaled.

3. Results and Discussion

Geometrical parameters of all molecules are given in Table 1, and two bond lengths (X–Y and X–H) and two angles (H–X–Y and H–X–H) are described for each molecule. Compared with the experimental data all the calculations are consistent with the experiments, except for the obvious errors in the prediction of the CH_3Cl angle value. The calculated angle values are different from experimental values by approximately 2 degrees. Surprisingly, previous investigations on this problem suggest tat the best method to predict H–C–Cl and H–C–H angle values is to use the semi empirical method (PM3) which gives values only 0.6 degree higher than experimental results.[26]

For the SiH_3F system the calculated X–Y distances are between 1.600 and 1.611 Å, H–X–Y angles are between 108.5 and 118.6 degree, and the H–X–H angle ranges from 110.3 to 110.5 degree, depending on the computational method used. In case of the SiH_3Cl system, the X–Y distances are longer, and the calculated values are between 2.220 and 2.238Å. On the other hand the calculated H–X–Y angle of SiH_3Cl is smaller than in the previous case (ranging from 108.5 to 108.6 degrees), while the H–X–H angles are larger (110.5 to 110.6 degrees). A similar trend in variations of geometrical parameters may be observed in the case of the SiH_3Br system. The Si–H distances of the SiH_3Y systems are only slight different, with the shortest bond being present in the SiH_3Br system. The trend in GeH_3Y (Y=F, Cl, Br) class of molecules is the same as in SiH_3Y. These results can be easily explained, since when the radius of the halogen atoms increases, the X–Y distance increases as well. This in turn leads to a smaller repulsion between the X–Y bond and the lone pair of the halogen atom, resulting in the smaller value of the H–X–Y angle. Once the H–X–Y angle gets smaller, it's reasonable to assume that the H–X–H angle would get larger. The slight change of the X–H distance may be caused by the different electronegativity value of the halogen atom. If the electronegativity value of Y is decreased, the X–Y bond is weakened, while the X–H bond becomes stronger. On the other hand, for a given Y, the values of the X–Y and X–H distances as well as H–X–H angles are all increased in the C, Si and Ge order, while the H–X–Y gets shorter.

The calculated frequencies and IR intensities of all monohalogenated species as well as available experimental data are given in Table 2. Table 2a shows the absolute vibrational frequencies, whereas Table 2b shows scaled vibrational frequencies based on an important study by Scott and Radom[30] by which a comprehensive evaluation of scale factors for harmonic vibrational frequencies was performed. In that work a series of 122 molecules were computed with the Hartree-Fock, Moller-Plesset, quadratic configuration interaction (QCI), and density functional theory (DFT) methods. A scale factor of 0.9496 was reported, that can be helpful in the present computations. The present basis set used is larger but the scale factors will suffice. Therefore, we have used a scale factor of 0.9496 as recommended by Scott and Radom. However, as Table 2b shows the experimental correlations without scaling is better, this might be due to the unusual behavior of the Si, Ge atoms in the calculations. By adding this scale factor into our harmonic frequencies, we are able to include some effects of anharmonicity and should suffice the present calculations presented in this work.

Table 1. Optimized Structures of XH3Y (X=C, Si and Ge; Y=F, Cl and Br) at the [1]B3LYP, [2]B1LYP, [3]B3P86, [4]MPW1PW91, [5]B3PW91, [6]MP2, [7]MP4/6-311++G *(3df, 3pd)* level. Distances are in Å, angles are in degree.

XH_3Y	parameter	1	2	3	4	5	6	7	Expt.
CH_3F	C–F	1.389	1.388	1.379	1.376	1.380	1.383	1.388	1.3830[a]
	C–H	1.089	1.089	1.090	1.090	1.091	1.086	1.090	1.0870[a]
	H–C–F	108.7	108.7	110.0	109.0	109.0	108.7	108.6	110.20[a]
	H–C–H	110.2	110.2	110.0	109.9	110.0	110.2	110.3	108.73[a]
CH_3Cl	C–Cl	1.793	1.793	1.776	1.774	1.778	1.771	1.783	1.785[a]
	C–H	1.084	1.083	1.085	1.085	1.086	1.083	1.087	1.090[a]
	H–C–Cl	108.3	108.3	108.6	108.6	108.6	108.6	108.4	110.75
	H–C–H	110.6	110.6	110.4	110.4	110.4	110.3	110.5	108.16
CH_3Br	C–Br	1.958	1.958	1.938	1.935	1.940	1.929	1.943	1.9340[a]
	C–H	1.083	1.081	1.084	1.083	1.085	1.083	1.083	1.0823[a]
	H–C–Br	107.6	107.6	107.9	107.9	107.9	108.1	108.0	107.72[a]
	H–C–H	111.2	111.3	111.0	111.0	111.0	110.8	110.0	111.157[a]
SiH_3F	Si–F	1.611	1.610	1.606	1.605	1.608	1.60	1.613	1.595[a]
	Si–H	1.476	1.474	1.477	1.478	1.479	1.470	1.471	1.476[a]
	H–Si–F	108.2	108.2	108.2	108.2	108.2	108.3	108.3	108.269[a]
	H–Si–H	110.7	110.7	110.7	110.7	110.7	110.6	110.6	110.64[a]
SiH_3Cl	Si–Cl	2.068	2.068	2.088	2.054	2.058	2.053	2.058	2.051[a]
	Si–H	1.475	1.474	1.476	1.477	1.478	1.469	1.472	1.475[a]
	H–Si–Cl	108.5	108.5	108.5	108.5	108.6	108.6	108.6	108.295[a]
	H–Si–H	110.4	110.5	110.4	110.4	110.4	110.4	110.3	110.62[a]
SiH_3Br	Si–Br	2.238	2.238	2.220	2.220	2.223	2.222	2.228	2.2123[b]
	Si–H	1.476	1.474	1.477	1.477	1.479	1.469	1.472	1.4743[b]
	H–Si–Br	108.4	108.4	108.4	108.4	108.5	108.4	108.4	108.161[b]
	H–Si–H	110.6	110.6	110.5	110.5	110.5	110.5	110.5	
GeH_3F	Ge–F	1.760	1.757	1.748	1.747	1.752	1.791	1.798	1.7350[b]
	Ge–H	1.532	1.531	1.528	1.529	1.531	1.530	1.535	1.5220[b]
	H–Ge–F	105.9	106.0	105.9	106.0	106.0	105.6	105.5	105.92[b]
	H–Ge–H	112.8	112.7	112.7	112.7	112.7	113.1	113.1	
GeH_3Cl	Ge–Cl	2.176	2.176	2.157	2.154	2.159	2.160	2.166	2.1447[b]
	Ge–H	1.531	1.530	1.527	1.528	1.530	1.530	1.534	1.5155[b]
	H–Ge–Cl	106.9	106.9	106.9	106.9	107.0	107.1	107.2	107.10[b]
	H–Ge–H	111.9	111.9	111.9	111.8	111.8	111.7	111.6	111.0[b]
GeH_3Br	Ge–Br	2.334	2.334	2.311	2.311	2.316	2.314	2.322	2.297[b]
	Ge–H	1.531	1.530	1.527	1.528	1.530	1.530	1.536	1.527[b]
	H–Ge–Br	107.0	107.1	107.1	107.1	107.1	107.2	107.4	106.3[b]
	H–Ge–H	111.8	111.8	112.8	111.8	111.7	111.6	111.6	

[a] Taken from ref. 26. [b] Taken from ref. 27 and references therein.

There are six different vibtrational frequencies according to the six normal vibrations for species of the C_{3v} point group as depicted in Fig. 1. The first is the symmetric X–H stretch ν_1, and the second is the Y–X–H umbrella motion ν_2. They are followed by the X–Y stretch is ν_3, and the degenerate modes are the asymmetric X–H stretch ν_4, the H–X–H scissor motion ν_5 and finally the Y–X–H rock ν_6. All computational normal modes obtained in this investigation were successfully assigned to one of the six types of vibrations. As a general rule, the calculated frequency values are consistent with the experimental results, although there are small variations with different methods used. It is difficult, however, to choose one computational method as the most suitable for calculating the vibrational spectra of all compounds. The advantages of using certain methods in calculations of selected vibrational frequencies will be discussed later.

A very interesting property embedded in the molecular wavefunction is the vibrational assignment which has been developed in the valence coordinates most closely resembling normal coordinates.[31] In this technique, Bowman and co-workers use successive contractions of the expansion set that keeps the hamiltonian matrices diagonally dominant. This allows the largest component of the eigenvector to be sufficient to assign rovibrational states for many species. Such calculations can be applied to assignment of lower energy vibrational transitions, photoionization spectra and improved description of Franck-Condon factors for simple molecules. However, it is difficult to apply such a scheme to our systems due to the in-

Table 2a. Vibrational frequencies (cm^{-1}) of various species shown in Table 1 (X, Y are ligands from the table and modes shown in Figure 1) ,where I is the intensities (in parentheses, KM/mol) and the values in EXP are the experimental values (where VS=Very Strong, S=Strong, M=Medium, W=Weak, VW=Very Weak), computed at the^{1}B3LYP, ^{2}B1LYP, ^{3}B3P86, ^{4}MPW1PW91, ^{5}B3PW91, ^{6}MP2, ^{7}MP4/6-311++G (*3df*, *3pd*) level

XH_3Y		ν_1	I_1	ν_2	I_2	ν_3	I_3	ν_4	I_4	ν_5	I_5	ν_6 I_6
CH_3F												
^{1}I	3032.706	33.639	1493.811	5.088	1047.734	110.244	3111.68	28.576	1485.097	0.911	1192.920	1.026
^{2}I	3044.911	33.474	1503.724	5.016	1053.839	111.754	3124.841	29.307	1494.857	1.032	1200.444	1.192
^{3}I	3040.286	35.129	1488.878	5.737	1078.917	109.806	3127.575	27.397	1480.935	0.665	1194.225	0.838
^{4}I	3051.952	34.021	1495.452	5.632	1088.562	110.936	3139.167	28.228	1488.823	0.725	1200.858	0.895
^{5}I	3034.949	35.323	1487.639	5.534	1073.793	110.253	3121.566	28.536	1480.214	0.748	1193.286	0.835
^{6}I	3087.626	32.204	1526.495	4.844	1084.246	105.480	3193.168	22.311	1510.283	1.357	1213.531	1.324
^{7}I	3140.294	0.000	1495.132	0.000	1060.481	0.0000	3042.339	0.000	1510.556	0.000	1200.321	0.000
^{EXP}I^a	2964	VS	1464	S	1048.6	S	3005.8	S	1466.5	M	1182.4	
CH_3Cl												
^{1}I	3070.33	22.780	1384.861	11.195	717.452	25.909	3073.504	22.873	1483.535	6.134	1030.959	2.413
^{2}I	3082	23.260	1394.292	11.913	720.097	26.962	3085.068	23.307	1493.063	6.061	1037.636	2.307
^{3}I	3080.45	22.438	1381.586	8.807	746.176	24.118	3081.847	22.184	1476.528	6.861	1032.360	2.736
^{4}I	3092.04	23.196	1388.759	8.860	754.434	24.518	3093.002	23.282	1483.276	6.679	1038.550	2.681
^{5}I	3075.28	23.134	1380.888	9.035	744.185	24.138	3076.592	23.032	1475.680	6.620	1031.851	2.743
^{6}I	3108.1	22.010	1416.413	11.258	778.977	22.586	3108.840	22.004	1510.858	5.571	1059.318	2.358
^{7}I	3071.089	0.000	1405.264	0.000	756.982	0.000	3174.764	0.000	1499.922	0.00	1048.810	0.000
^{EXP}I^a	2879.28	M	1354.9	S	732.1	S	3039.31	S	1452.1	M	1017.3	M
CH_3Br												
^{1}I	3192.553	1.264	1331.354	18.483	591.795	12.174	3087.012	15.618	1476.512	5.940	963.025	3.704
^{2}I	3205.113	1.315	1340.431	19.646	594.552	12.837	3099.315	16.149	1486.243	5.852	968.851	3.620
^{3}I	3203.389	0.859	1329.709	14.710	619.852	10.791	3092.580	14.847	1469.810	6.631	966.334	4.145
^{4}I	3214.590	1.054	1337.538	15.076	627.434	10.965	3104.095	16.120	1476.296	6.520	971.902	4.143
^{5}I	3197.989	6.684	1329.283	15.183	617.251	10.826	3087.830	15.824	1469.212	6.369	965.883	4.109
^{6}I	3235.335	0.701	1367.053	16.750	651.982	8.3	3116.225	15.749	1503.635	5.289	991.62	3.907
^{7}I	3077.104	0.000	1354.874	0.000	628.485	0.000	3189.677	0.000	1492.876	0.000	978.613	0.000
^{EXP}I^a	2972	M	1305.9	S	611.1	S	3056.35	S	1442.7	M	954.7	
SiH_3F												
^{1}I	2267.097	136.638	998.272	184.725	852.817	78.536	2262.430	32.232	973.759	85.760	728.057	52.785
^{2}I	2258.106	133.890	991.367	181.401	848.105	76.752	2251.946	31.558	967.474	83.385	723.057	51.402
^{3}I	2263.168	126.275	983.627	178.356	858.770	69.776	2255.505	30.374	959.401	78.084	719.543	50.811
^{4}I	2265.130	126.764	985.406	178.596	861.734	70.466	2258.402	30.457	961.022	78.321	721.196	51.567
^{5}I	2252.988	127.602	981.240	175.730	853.381	71.041	2245.660	31.074	957.176	77.559	718.038	50.466
^{6}I	2335.498	140.791	996.323	95.223	860.767	80.121	2332.776	34.513	996.496	95.214	739.474	57.270
^{7}I	2303.199	0.000	979.119	0.000	850.669	0.0000	2308.866	0.000	1002.660	0.000	729.681	0.000
^{EXP}I^a	2206	–	990	S	872	M	2196	M	956	M	728.1	–
SiH_3Cl												
^{1}I	2248.240	53.682	959.559	56.738	533.361	69.655	2259.531	96.168	952.550	251.673	657.685	22.826
^{2}I	2259.045	54.838	966.278	58.513	534.863	71.207	2269.248	97.889	959.379	257.626	662.338	23.520
^{3}I	2251.632	52.078	950.754	52.306	546.902	68.631	2264.017	89.129	943.423	238.490	654.623	22.446
^{4}I	2253.710	52.210	952.440	52.182	550.618	69.020	2265.107	90.492	945.408	237.920	656.555	22.804
^{5}I	2240.587	52.788	948.728	51.823	545.128	68.186	2252.787	91.257	941.936	236.074	653.750	22.343
^{6}I	2321.753	58.447	986.898	64.669	561.387	74.668	2330.588	101.285	978.722	286.458	675.741	26.117
^{7}I	2292.149	0.000	963.880	0.000	555.459	0.000	2302.334	0.000	970.810	0.000	666.318	0.000
^{EXP}I^a	2201	–	949	–	551	S	2195	S	954.4	S	664.0	M
SiH_3Br												
^{1}I	2242.121	60.507	934.849	302.548	412.972	41.807	2256.275	85.214	957.868	52.290	629.298	14.267
^{2}I	2253.500	60.829	941.516	309.309	414.344	42.619	2266.682	87.174	964.467	53.937	632.530	14.627
^{3}I	2248.585	58.506	925.677	285.551	426.408	41.170	2263.905	78.220	948.855	48.191	625.876	14.128
^{4}I	2251.594	58.192	927.508	284.767	429.298	41.412	2266.042	78.566	950.109	48.035	627.288	14.165
^{5}I	2236.190	59.154	924.521	283.036	425.261	40.902	2251.003	80.742	946.807	47.602	625.460	13.941
^{6}I	2320.444	65.329	959.709	340.908	439.605	44.851	2332.252	89.058	982.719	59.105	645.396	17.028
^{7}I	2290.032	0.000	966.547	0.000	434.576	0.000	2304.147	0.000	966.547	0.000	635.936	0.000
^{EXP}I^a	2200	–	930	S	430	M	2196	S	950.4	S	632.6	

XH_3Y	ν_1	I_1	ν_2	I_2	ν_3	I_3	ν_4	I_4	ν_5	I_5	ν_6	I_6
						GeH_3F						
[1]I	2154.843	25.680	865.958	65.778	667.185	104.507	2166.739	122.048	865.958	65.778	628.143	36.201
[2]I	2164.580	32.297	876.224	65.426	673.228	106.758	2173.078	124.352	871.051	66.041	630.701	37.398
[3]I	2168.948	37.025	865.537	58.925	683.570	105.565	2182.164	105.478	870.726	58.160	627.839	36.340
[4]I	2177.874	30.321	868.845	60.893	686.758	107.461	2193.203	111.945	873.606	61.618	629.572	37.267
[5]I	2163.700	29.240	868.948	59.265	678.775	104.768	2174.969	118.148	863.965	59.813	626.978	36.258
[6]I	2235.889	22.971	892.957	75.686	738.329	154.334	2232.867	131.666	892.957	75.686	635.794	40.505
[7]I	2193.716	0.000	875.666	0.000	728.836	0.000	2199.086	0.000	877.538	0.000	623.501	0.000
EXPI[b]	2120.6	S	859.0	VS	689.1	S	2131.7	S	874.0	S	624.6	M
						GeH_3Cl						
[1]I	2150.816	47.597	843.756	164.019	406.513	54.466	2164.156	98.140	871.551	46.105	591.816	15.681
[2]I	2157.763	51.052	851.401	168.007	407.99	55.547	2167.861	100.009	878.860	47.453	596.876	16.316
[3]I	2166.886	49.089	843.021	152.159	420.072	54.589	2185.186	92.325	870.053	42.671	595.831	15.701
[4]I	2173.003	50.688	847.562	154.920	423.685	55.482	2189.300	93.663	873.485	43.310	598.601	16.467
[5]I	2160.173	47.590	842.237	153.936	417.765	54.383	2175.691	94.380	870.031	42.894	594.969	15.819
[6]I	2231.680	57.714	873.858	199.143	608.571	20.791	2232.132	106.184	896.933	54.880	433.193	60.802
[7]I	2196.527	0.000	858.485	0.000	598.571	0.000	2199.906	0.000	881.248	0.000	428.853	0.000
EXPI[b]	2119.9	S	847.5	VS	421.7	S	2128.9	S	874.1	S	602.2	
						GeH_3Br						
[1]I	2148.268	53.753	829.336	213.569	294.152	27.101	2163.497	90.527	871.769	43.215	569.974	10.049
[2]I	2153.914	59.216	837.249	219.436	295.125	27.614	2167.140	88.735	875.750	44.400	574.380	10.539
[3]I	2163.073	54.254	829.638	199.376	305.906	27.027	2185.006	83.239	870.208	39.299	570.518	10.331
[4]I	2173.380	52.990	832.306	202.993	307.277	27.614	2187.211	85.561	873.141	40.078	570.015	10.381
[5]I	2155.804	56.421	828.326	200.721	303.623	27.054	2169.929	84.383	868.348	39.451	569.100	10.343
[6]I	2225.913	62.544	861.330	251.476	314.744	30.247	2227.435	98.264	896.378	51.291	588.031	14.163
[7]I	2188.916	0.000	846.592	0.000	310.434	0.000	2191.258	0.000	881.017	0.000	578.270	0.000
EXPI[b]	2115.2	–	832.7	–	307.7	–	2126.7	–	870.9	–	578.2	–

[a] Taken from ref. 28. [b] Taken from ref. 29.

creased level of complexity associated with such calculations. We do believe that by using high level *ab initio* methods with an extended basis set experimentally reliable calculations can be obtained.

The results suggest that it is difficult to choose the most reliable method for all studied systems. Several trends in results are, however, clear. In the geometry optimization, both DFT methods, MP2 and MP4 methods can get very accurate results (except for the CH_3Cl angles). Since MP2 and MP4 calculations are much more time consuming and have no obvious advantages for geometry optimization, we believe that DFT calculations are more favorable for geometry optimizations of these systems. For frequency analysis, in some cases the MP4 approach can give more accurate results than DFT methods (see for example ν_4 of CH_3F, or ν_1 of CH_3Br). In most cases DFT calculations are, however, also accurate and give better results than MP2 and MP4 calculations. For almost all frequency calculations MP2 results are the least accurate. Our calculations reveal that in many cases the accuracy of DFT methods is very high, with the average error of only 30 cm^{-1}. This is, however, not true for the ν_1 vibration, where we usually obtain larger variations (of more than 50 cm^{-1}).

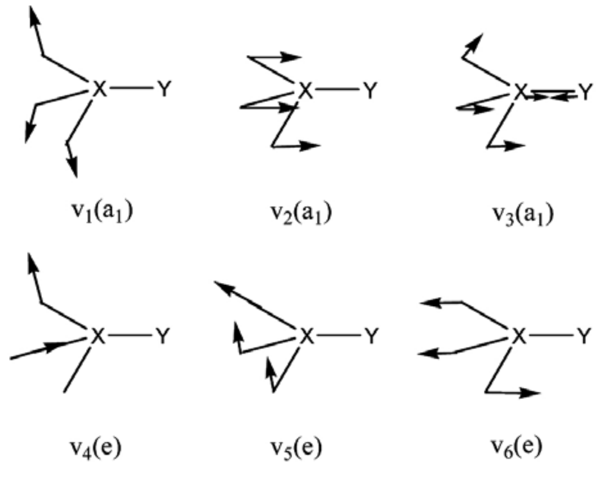

Fig. 1. Vibrational modes of the XH_3Y molecules that belong to the C_{3v} point group.

Considering the applicability of different DFT methods, one can see that some of the functionals tend to be superior to the commonly used B3LYP method. Taking the frequency analysis of SiH_3F as an example, the experimental value of ν_1 is 2206 cm^{-1}, and the result of MPW1PW91 calculation is 2252.988 cm^{-1} while the result of B3LYP calculation is 2267.097 cm^{-1}. Similarly, B1LYP predicts ν_2 better than B3LYP, and MPW1PW91 predicts ν_3 better than B3LYP. Unfortunately it is impossible to find a single DFT method which will accurately predict all of the six vibrational frequencies. The differen-

Table 2b. Scaled vibrational frequencies (cm^{-1}) by a factor of 0.9496 (which are represnted as the ν^{SC} values) for various species shown in Table 1 (X, Y are ligands from the table and modes shown in Figure 1) ,where I is the intensities (in parentheses, KM/mol) and the values in EXP are the experimental values computed at the^{1}B3LYP, ^{2}B1LYP, ^{3}B3P86, ^{4}MPW1PW91, ^{5}B3PW91, ^{6}MP2, ^{7}MP4/6-311++G (*3df, 3pd*) level.

XH$_3$Y	ν_1	ν_1^{SC}	ν_2	ν_2^{SC}	ν_3	ν_3^{SC}	ν_4	$\nu4_1^{SC}$	ν_5	ν_5^{SC}	ν_6	ν_6^{SC}
CH$_3$F												
^{1}I	3032.706	2879.857	1493.811	1418.522	1047.734	994.928	3111.68	2954.851	1485.097	1410.248	1192.920	1132.796
^{2}I	3044.911	2891.447	1503.724	1427.936	1053.839	1000.725	3124.841	2967.349	1494.857	1419.516	1200.444	1139.941
^{3}I	3040.286	2887.055	1488.878	1413.838	1078.917	1024.539	3127.575	2969.945	1480.935	1406.295	1194.225	1134.036
^{4}I	3051.952	2898.133	1495.452	1420.081	1088.562	1033.698	3139.167	2980.952	1488.823	1413.786	1200.858	1140.334
^{5}I	3034.949	2881.987	1487.639	1412.661	1073.793	1019.673	3121.566	2964.239	1480.214	1405.611	1193.286	1133.144
^{6}I	3087.626	2932.009	1526.495	1449.559	1084.246	1029.600	3193.168	3032.232	1510.283	1434.164	1213.531	1152.369
^{7}I	3140.294	2982.023	1495.132	1419.777	1060.481	1007.032	3042.339	2889.005	1510.556	1434.423	1200.321	1139.824
^{EXP}I^a	2964		1464		1048.6		3005.8		1466.5		1182.4	
CH$_3$Cl												
^{1}I	3070.33	2915.585	1384.861	1315.064	717.452	681.292	3073.504	2918.599	1483.535	1408.765	1030.959	978.999
^{2}I	3082	2926.667	1394.292	1324.020	720.097	683.804	3085.068	2929.581	1493.063	1417.813	1037.636	985.339
^{3}I	3080.45	2925.195	1381.586	1311.954	746.176	708.569	3081.847	2926.522	1476.528	1402.111	1032.360	980.329
^{4}I	3092.04	2936.201	1388.759	1318.766	754.434	716.411	3093.002	2937.115	1483.276	1408.519	1038.550	986.207
^{5}I	3075.28	2920.285	1380.888	1311.291	744.185	706.678	3076.592	2921.532	1475.680	1401.306	1031.851	979.846
^{6}I	3108.1	2951.451	1416.413	1345.026	778.977	739.717	3108.840	2952.154	1510.858	1434.711	1059.318	1005.928
^{7}I	3071.089	2916.306	1405.264	1334.439	756.982	718.830	3174.764	3014.756	1499.922	1424.326	1048.810	995.950
^{EXP}I^a	2879.28		1354.9		732.1		3039.31		1452.1		1017.3	
CH$_3$Br												
^{1}I	3192.553	3031.648	1331.354	1264.254	591.795	561.969	3087.012	2931.427	1476.512	1402.096	963.025	914.489
^{2}I	3205.113	3043.575	1340.431	1272.873	594.552	564.587	3099.315	2943.110	1486.243	1411.336	968.851	920.021
^{3}I	3203.389	3041.938	1329.709	1262.692	619.852	588.611	3092.580	2936.714	1469.810	1395.732	966.334	917.631
^{4}I	3214.590	3052.575	1337.538	1270.126	627.434	595.811	3104.095	2947.649	1476.296	1401.891	971.902	922.918
^{5}I	3197.989	3036.810	1329.283	1262.287	617.251	586.142	3087.830	2932.203	1469.212	1395.164	965.883	917.202
^{6}I	3235.335	3072.274	1367.053	1298.154	651.982	619.122	3116.225	2959.167	1503.635	1427.852	991.62	941.642
^{7}I	3077.104	2922.018	1354.874	1286.588	628.485	596.809	3189.677	3028.917	1492.876	1417.635	978.613	929.291
^{EXP}I^a	2972		1305.9		611.1		3056.35		1442.7		954.7	
SiH$_3$F												
^{1}I	2267.097	2152.835	998.272	947.959	852.817	809.835	2262.430	2148.404	973.759	924.682	728.057	691.363
^{2}I	2258.106	2144.297	991.367	941.402	848.105	805.361	2251.946	2138.448	967.474	918.713	723.057	686.615
^{3}I	2263.168	2149.104	983.627	934.052	858.770	815.488	2255.505	2141.828	959.401	911.047	719.543	683.278
^{4}I	2265.130	2150.967	985.406	935.742	861.734	818.303	2258.402	2144.579	961.022	912.586	721.196	684.848
^{5}I	2252.988	2139.437	981.240	931.786	853.381	810.371	2245.660	2132.479	957.176	908.934	718.038	681.849
^{6}I	2335.498	2217.789	996.323	946.108	860.767	817.384	2332.776	2215.204	996.496	946.273	739.474	702.205
^{7}I	2303.199	2187.118	979.119	929.771	850.669	807.795	2308.866	2192.499	1002.660	952.126	729.681	692.905
^{EXP}I^a	2206		990		872		2196		956		728.1	
SiH$_3$Cl												
^{1}I	2248.240	2134.929	959.559	911.197	533.361	506.480	2259.531	2145.651	952.550	904.541	657.685	624.538
^{2}I	2259.045	2145.189	966.278	917.578	534.863	507.906	2269.248	2154.878	959.379	911.026	662.338	628.956
^{3}I	2251.632	2138.150	950.754	902.836	546.902	519.338	2264.017	2149.911	943.423	895.874	654.623	621.630
^{4}I	2253.710	2140.123	952.440	904.437	550.618	522.867	2265.107	2150.946	945.408	897.759	656.555	623.465
^{5}I	2240.587	2127.661	948.728	900.912	545.128	517.654	2252.787	2139.247	941.936	894.462	653.750	620.801
^{6}I	2321.753	2204.737	986.898	937.158	561.387	533.093	2330.588	2213.126	978.722	929.394	675.741	641.684
^{7}I	2292.149	2176.625	963.880	915.300	555.459	527.464	2302.334	2186.296	970.810	921.881	666.318	632.736
^{EXP}I^a	2201		949		551		2195		954.4		664.0	
SiH$_3$Br												
^{1}I	2242.121	2129.118	934.849	887.733	412.972	392.158	2256.275	2142.559	957.868	909.591	629.298	597.581
^{2}I	2253.500	2139.924	941.516	894.064	414.344	393.461	2266.682	2152.441	964.467	915.858	632.530	600.650
^{3}I	2248.585	2135.256	925.677	879.023	426.408	404.917	2263.905	2149.804	948.855	901.033	625.876	594.332
^{4}I	2251.594	2138.114	927.508	880.762	429.298	407.661	2266.042	2151.833	950.109	902.224	627.288	595.673
^{5}I	2236.190	2123.486	924.521	877.925	425.261	403.828	2251.003	2137.552	946.807	899.088	625.460	593.937
^{6}I	2320.444	2203.494	959.709	911.340	439.605	417.449	2332.252	2214.706	982.719	933.190	645.396	612.868
^{7}I	2290.032	2174.614	966.547	917.833	434.576	412.673	2304.147	2188.018	966.547	917.833	635.936	603.885
^{EXP}I^a	2200		930		430		2196		950.4		632.6	

XH_3Y	ν_1	ν_1^{SC}	ν_2	ν_2^{SC}	ν_3	ν_3^{SC}	ν_4	$\nu4_1^{SC}$	ν_5	ν_5^{SC}	ν_6	ν_6^{SC}
						GeH_3F						
^{1}I	2154.843	2046.239	865.958	822.314	667.185	633.559	2166.739	2057.535	865.958	822.314	628.143	596.485
^{2}I	2164.580	2055.485	876.224	832.062	673.228	639.297	2173.078	2063.555	871.051	827.150	630.701	598.914
^{3}I	2168.948	2059.633	865.537	821.914	683.570	649.118	2182.164	2072.183	870.726	826.841	627.839	596.196
^{4}I	2177.874	2068.109	868.845	825.055	686.758	652.145	2193.203	2082.666	873.606	829.576	629.572	597.842
^{5}I	2163.700	2054.650	868.948	825.153	678.775	644.565	2174.969	2065.351	863.965	820.421	626.978	595.378
^{6}I	2235.889	2123.200	892.957	847.952	738.329	701.117	2232.867	2120.331	892.957	847.952	635.794	603.750
^{7}I	2193.716	2083.153	875.666	831.532	728.836	692.103	2199.086	2088.252	877.538	833.310	623.501	592.077
^{EXP}I^b	2120.6		859.0		689.1		2131.7		874.0		624.6	
						GeH_3Cl						
^{1}I	2150.816	2042.415	843.756	801.231	406.513	386.025	2164.156	2055.083	871.551	827.625	591.816	561.988
^{2}I	2157.763	2049.012	851.401	808.490	407.99	387.427	2167.861	2058.601	878.860	834.565	596.876	566.793
^{3}I	2166.886	2057.675	843.021	800.533	420.072	398.900	2185.186	2075.053	870.053	826.202	595.831	565.801
^{4}I	2173.003	2063.484	847.562	804.845	423.685	402.331	2189.300	2078.959	873.485	829.461	598.601	568.432
^{5}I	2160.173	2051.300	842.237	799.788	417.765	396.710	2175.691	2066.036	870.031	826.181	594.969	564.983
^{6}I	2231.680	2119.203	873.858	829.816	608.571	577.899	2232.132	2119.633	896.933	851.728	433.193	411.360
^{7}I	2196.527	2085.822	858.485	815.217	598.571	568.403	2199.906	2089.031	881.248	836.833	428.853	407.239
^{EXP}I^b	2119.9		847.5		421.7		2128.9		874.1		602.2	
						GeH_3Br						
^{1}I	2148.268	2039.995	829.336	787.537	294.152	279.327	2163.497	2054.457	871.769	827.832	569.974	541.247
^{2}I	2153.914	2045.357	837.249	795.052	295.125	280.251	2167.140	2057.916	875.750	831.612	574.380	545.431
^{3}I	2163.073	2054.054	829.638	787.824	305.906	290.488	2185.006	2074.882	870.208	826.350	570.518	541.764
^{4}I	2173.380	2063.842	832.306	790.358	307.277	291.790	2187.211	2076.976	873.141	829.135	570.015	541.286
^{5}I	2155.804	2047.151	828.326	786.578	303.623	288.320	2169.929	2060.565	868.348	824.583	569.100	540.417
^{6}I	2225.913	2113.727	861.330	817.919	314.744	298.881	2227.435	2115.172	896.378	851.201	588.031	558.394
^{7}I	2188.916	2078.595	846.592	803.924	310.434	294.788	2191.258	2080.819	881.017	836.614	578.270	549.125
^{EXP}I^b	2115.2		832.7		307.7		2126.7		870.9		578.2	

[a] Taken from ref. 28. [b] Taken from ref. 29.

ces between the results for different DFT methods are, on the other hand, not very large and, compared with experimental values, rather small. Thus, we believe that any of the five tested DFT methods is a reliable tool to perform vibrational analysis of monohalogenated species. The IR intensities are predicted accurately, although for some systems there is not a single method reproducing ideally all the experimental data.

The last question concerns the necessity of using a large, 6-311++G(3df,3pd) basis set. Table 3 shows the relative error in frequency assignments using different computational approaches and basis sets for the CH_3Cl system. Clearly, the larger basis set improves the results obtained at the B3LYP level of theory. The results for the largest basis set are also more accurate then in the case of more sophisticated *ab-initio* methods using smaller basis sets. Thus we believe that DFT calculations can provide us with more reliable results than high level *ab-initio* methods for the frequency analysis of small organic molecules, and a large basis set of 6-311++G (3df,3pd) is crucial for the improvement of accuracy.

4. Conclusions

From theoretical studies we provide the geometrical structures, vibrational frequencies as well as IR intensities of monohalogenated carbon family species using five

Table 3. Δν values ($\Delta\nu = \nu_{calculated} - \nu_{experimental}$) for the frequency analysis of CH_3Cl at different levels of theory.

	B3LYP 6–311++(3df,3pd)	**B3LYP 6–31G***	**B3LYP 6–311+G(3df,2p)**	**MP4 6–311G***	**CISD 6–31G***	**QCISD 6–311G****	**CCSD 6–311G***
$\Delta\nu_1$	191	216 [a]	191 [a]	193 [a]	288 [a]	218 [a]	209 [a]
$\Delta\nu_2$	30	59 [a]	26 [a]	80 [a]	120 [a]	83 [a]	89 [a]
$\Delta\nu_3$	–14.7	–11.1 [a]	–17.1 [a]	30 [a]	58 [a]	41 [a]	38 [a]
$\Delta\nu_4$	34	156 [a]	125 [a]	137 [a]	229 [a]	156 [a]	149 [a]
$\Delta\nu_5$	31	49 [a]	34 [a]	51 [a]	102 [a]	44 [a]	58 [a]
$\Delta\nu_6$	14	28 [a]	12 [a]	44 [a]	74 [a]	43 [a]	51 [a]

[a] Taken from ref. 26.

DFT methods (B3LYP, B1LYP, B3P86, MPW1PW91, B3PW91) and two high level of *ab-initio* methods (MP2, MP4) at 6-311++G (3df,3pd) level of theory. DFT methods are shown to be as accurate as MP2 and MP4 methods in geometry optimization. The advantages of DFT methods over MP2 and MP4 approaches in frequency analysis are presented. In comparison with the available data, we conclude that for the frequency analysis of a small organic systems there is no need to use high level *ab-initio* methods, since DFT methods with large basis set of 6-311++G (3df,3pd) can provide more reliable results.

Other attempts to estimate the anharmonicity have been attempted. Recently, a Car-Parrinello simulation of a Mannich base, (4,5-dimethyl-2(N,N-dimethylaminemethyl)phenol) was performed. This system has been shown to be troublesome due to the internal hydrogen bonding network[32]. Mavri and co-workers proposed a package that uses *ab initio* or DFT calculated points and fits them to calculate accurate expectation values, and IR spectra[33]. The advantage to such a technique is that it accounts for anharmonicity effects. Future prospects in this work include the use of such models to study the systems described herein.

While we have only considered fundamental modes there is some knowledge available on the overtones and hot transitions for certain species[34] from a theoretical perspective. Experimentally, there is very little knowledge known about the hot transitions and overtones in molecules of this type. However, other investigations have shown that hot transitions and overtones can be adequately accounted for (in correlation to experiments) by using DFT methods and gaussian basis sets[35]. To the best of our knowledge limited information on these data points are available for the compounds investigated herein.

The results from all tested DFT methods are all similar. At this point it is difficult to choose a method, which would be the most accurate in all cases. A benchmark study of various density functionals to evaluate the performance of more density functional techniques for the frequency analysis of the discussed systems is in process.

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Povzetek

Z metodami gostotnostnega funkcionala B3LYP, B1LYP, B3P86, MPW1PW91 in B3PW91 kot tudi z MP2 in MP4 z uporabo baznega seta 6-311++G (3df,3pd) smo izračunali geometrijske parametre, valovna števila infrardečih nihanj in njihove intenzitete za molekule XH_3Y (X=C, Si, Ge in Y=F, Cl, Br). Izračune smo primerjali z opaženimi vrednostmi iz literature. Prednosti DFT metod so razvidne iz primerjav izračunanih in opaženih vrednosti. V članku predlagamo najustreznejše metode in bazne sete.