

AB INITIO DENSITY FUNCTIONAL THEORY STUDY OF CF₂HCl AND ITS ISOTOPIC SPECIES

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ABSTRACT. The geometrical parameters, permanent dipole moments and harmonic vibrational frequencies of CF₂HCl (Freon22) and its isotopic species (D and ¹³C) has been calculated in four different basis sets (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ) at the density functional theory (DFT) method using B3LYP and B3PW91 exchange-correlation functionals. The results are compared with the experimental values. The calculated values are found to be in good agreement with the available experimental data, and explanations are offered for discrepancies. This confirms the accuracy of the ab initio DFT study in the geometry structure and other molecular parameter calculation.

1. Introduction

The experimental and computer simulation spectra of laser-induced infrared multiple photon excitations (IRMPE) of CF₂HCl for the purpose of selective isotopic enrichment have been studied [1, 2, 3] as a possible solution for laser isotope (D and ¹³C) separation. In order to understand the multiple photon excitation mechanism, an accurate study of equilibrium geometry, permanent and induced dipole moments, harmonic vibrational frequencies and their assignments is required.

The experimental geometry structure was determined very early in 1962 from microwave spectra by *McLay et al.* [4] and *Beeson et al.* [5] while the infrared (IR) and Raman spectra of CF₂HCl and their isotopic species (D and ¹³C) were obtained by *Magill et al.* [6] in 1986 and the band assignment and isotopic shifts were briefly discussed in their paper. Our aim is to obtain a good agreement for geometry and frequencies using DFT methods in order to get much more description for other molecular parameters which cannot be compared with the experimental data and which are necessary in IRMPE spectra simulation.

2. Results and Discussion

The calculations were carried out in Heidelberg on Hewlett-Packard cluster. The standard B3LYP and B3PW91 DFT type calculations (full geometry optimization and harmonic vibrational frequencies) were performed by the Gaussian98 [7] computer code using cc-pVDZ, Aug-cc-pVDZ, cc-pVTZ and Aug-cc-pVTZ Dunning's correlation consistent basis sets. The calculated results are summarized in three tables. Table 1 show the results obtained for the equilibrium, geometry and permanent dipole moments of the CF₂HCl at the DFT method. The bond distances are given in Å, the bond angles are given in Degree and the

permanent dipole moments are given in Debye. Table 2 contain the harmonic vibrational frequencies for protonated (H) and deuterated (D) species given in cm^{-1} while in Table 3 are presented the same results but for ^{12}C and ^{13}C isotopic species.

TABLE 1

The geometrical parameters (in \AA and Degree) and permanent dipole moments (in Debye) of CF_2HCl computed at DFT method, using cc-pVDZ, Aug-cc-pVDZ, cc-pVTZ, Aug-cc-pVTZ basis sets.

Basis	Method	r_1	r_2	r_3	α_1	α_2	α_3	α_4	$ \mu_a $	$ \mu_c $
cc-	B3LYP	1.099	1.797	1.343	108.44	110.40	109.54	108.54	.277	1.415
-pVDZ	B3PW91	1.099	1.785	1.340	108.59	110.30	109.56	108.53	.292	1.428
Aug-cc-	B3LYP	1.095	1.788	1.353	109.41	110.09	109.57	108.10	.012	1.498
-pVDZ	B3PW91	1.096	1.778	1.347	109.34	110.07	109.58	108.17	.060	1.461
cc-	B3LYP	1.087	1.788	1.341	108.78	110.22	109.62	108.37	.145	1.429
-pVTZ	B3PW91	1.089	1.776	1.336	108.78	110.15	109.67	108.42	.150	1.411
Aug-cc-	B3LYP	1.086	1.784	1.344	109.11	110.10	109.67	108.20	.027	1.463
-pVTZ	B3PW91	1.089	1.774	1.339	108.99	110.08	109.69	108.32	.069	1.422
Exp.		1.080	1.747	1.367	108.99	110.74	110.20	107.63	.120	1.430

TABLE 2

The harmonic vibrational frequencies (in cm^{-1}) of CF_2HCl and its deuterated species computed at DFT method, using cc-pVDZ, Aug-cc-pVDZ, cc-pVTZ, Aug-cc-pVTZ basis sets.

	B3LYP										
	cc-pVDZ		Aug-cc-pVDZ		cc-pVTZ		Aug-cc-pVTZ		Exp.		
	H	D	H	D	H	D	H	D	H	D	
ν_1	3125.7	2306.9	3175.0	2321.6	3129.5	2307.5	3130.2	2309.2	3020.5	2260.5	
ν_2	1295.1	1107.6	1289.6	1071.0	1319.5	1097.1	1314.5	1085.1	1313.2	1102.8	
ν_3	1119.2	993.7	1082.7	988.7	1125.6	1009.1	1097.8	1004.9	1109.0	1012.7	
ν_4	776.2	716.9	781.1	722.7	794.2	722.0	777.7	722.1	809.3	750.0	
ν_5	591.1	586.3	578.4	573.9	600.4	589.4	590.7	586.0	596.3	592.1	
ν_6	398.9	395.8	397.3	394.2	400.9	397.8	400.3	397.3	412.9	410.9	
ν_7	1364.9	1198.4	1335.0	1123.8	1374.0	1164.9	1362.7	1142.0	1351.3	1161.0	
ν_8	1153.2	961.7	1094.9	952.0	1128.8	974.5	1109.7	969.2	1127.5	969.0	
ν_9	357.5	354.7	355.3	352.6	359.2	356.4	358.3	355.5	365.4	365.0	
	B3PW91										
	ν_1	3137.7	2316.0	3150.3	2323.5	3129.5	2307.8	3130.2	2308.2	3020.5	2260.5
	ν_2	1300.3	1121.9	1293.5	1089.0	1319.8	1113.4	1315.2	1104.1	1313.2	1102.8
	ν_3	1133.2	999.4	1100.1	993.9	1125.6	1012.0	1116.3	1008.3	1109.0	1012.7
	ν_4	791.7	729.8	797.1	735.6	794.2	734.9	793.6	734.6	809.3	750.0
	ν_5	597.3	592.4	585.5	580.3	600.4	595.6	597.4	592.6	596.3	592.1
	ν_6	406.1	402.9	403.9	400.6	407.6	404.4	406.9	403.7	412.9	410.9
	ν_7	1367.0	1214.8	1336.8	1145.6	1372.3	1183.2	1362.2	1164.3	1351.3	1161.0
	ν_8	1170.6	964.6	1118.1	955.1	1149.5	975.9	1134.1	971.3	1127.5	969.0
	ν_9	362.4	359.6	359.5	356.8	363.3	360.5	362.2	359.4	365.4	365.0

As it can be observed from Table 1, the calculated geometry parameters (bonds and angles) are in a very good agreement with the experimental values. Increasing the number of the basis functions, the bond lengths and bond angles do

not change that much, but the values of the permanent dipole components (μ_a and μ_c) have an important basis set dependence.

The CF₂HCl is an asymmetric top molecule having C_s molecular symmetry with two types of vibrational bands (ν_1 - ν_6 : A' and ν_7 - ν_9 : A''). The A' symmetry vibrations give rise to polarized Raman and IR absorption bands of mixed *a/c* type, which in general have well defined central Q branch. While the A'' vibrations give rise to *b* type bands having central minima (only P and R branch) in IR absorption and Raman bands of similar shape.

In case of deuterated species (Table 2) it can be observed an important isotopic shift in vibrational frequencies especially for higher values, but at the same time we have to mention that this frequency values and their isotopic shifts are quite sensitive on the applied functional and basis set. As we are interested in IRMPD using CO₂ laser the two most important values are ν_3 and ν_8 . Both frequency values are well separated in the absorption band from their isotopic species.

TABLE 3

The harmonic vibrational frequencies (in cm⁻¹) of ¹²CF₂HCl and its ¹³C isotope computed at DFT method, using cc-pVDZ, Aug-cc-pVDZ, cc-pVTZ, Aug-cc-pVTZ basis sets.

B3LYP										
	cc-pVDZ		Aug-cc-pVDZ		cc-pVTZ		Aug-cc-pVTZ		Exp.	
	¹² C	¹³ C	¹² C	¹³ C	¹² C	¹³ C	¹² C	¹³ C	¹² C	¹³ C
ν_1	3125.7	3111.3	3175.0	3137.6	3129.3	3116.7	3130.2	3120.9	3020.5	3010.6
ν_2	1295.1	1289.0	1289.6	1286.3	1319.5	1312.7	1314.5	1310.2	1313.2	1307.2
ν_3	1119.2	1091.1	1082.7	1054.7	1125.6	1083.5	1097.8	1073.3	1109.0	1083.5
ν_4	776.2	754.9	781.1	755.7	794.2	754.5	777.7	755.6	809.3	788.9
ν_5	591.1	586.7	578.4	574.2	600.4	589.4	590.7	586.8	596.3	592.3
ν_6	398.9	397.8	397.3	395.9	400.9	398.9	400.3	399.1	412.9	412.8
ν_7	1364.9	1357.5	1335.0	1331.6	1374.0	1366.9	1362.7	1359.4	1351.3	1346.0
ν_8	1153.2	1125.9	1094.9	1064.7	1128.8	1101.2	1109.7	1083.4	1127.5	1101.0
ν_9	357.5	355.1	355.3	354.0	359.2	357.1	358.3	356.7	365.4	363.0
B3PW91										
ν_1	3137.7	3125.6	3150.3	3137.9	3129.5	3116.2	3130.2	3118.1	3020.5	3010.6
ν_2	1300.3	1293.0	1293.5	1289.6	1319.8	1313.4	1315.2	1310.8	1313.2	1307.2
ν_3	1133.2	1102.9	1100.1	1072.1	1125.6	1099.5	1116.3	1090.7	1109.0	1083.5
ν_4	791.7	769.9	797.1	771.7	794.2	771.4	793.6	772.4	809.3	788.9
ν_5	597.3	592.2	585.5	580.4	600.4	595.5	597.4	593.2	596.3	592.3
ν_6	406.1	404.6	403.9	402.8	407.6	406.1	406.9	405.8	412.9	412.8
ν_7	1367.0	1357.0	1336.8	1332.9	1372.3	1364.8	1362.2	1358.7	1351.3	1346.0
ν_8	1170.6	1140.3	1118.1	1087.9	1149.5	1121.9	1134.1	1107.0	1127.5	1101.0
ν_9	362.4	359.9	359.5	358.5	363.3	361.4	362.2	360.8	365.4	363.0

In case of ¹²C and ¹³C isotopes (Table 3) this frequency shifts are much smaller. Only ν_3 and ν_8 give considerable isotopic shift.

On the other hand it can be observed an important discrepancy between the theoretical and experimental frequency values due to the anharmonic effects. Taking into account the experimental anharmonic corrections [8] the calculated

values are in a very good agreement with the experimental results. Moreover comparing only the calculated and measured isotopic shifts this agreement is more accurate.

Considering the above results we found that in case of geometry parameters the method and basis set dependence are not so important that in case of permanent dipole moments and harmonic vibrational frequencies, the best approach for all these parameters can be obtained with B3LYP exchange-correlation functional using cc-pVTZ basis set. Comparing theoretical results with the experimental values we could establish the accuracy of the applied *ab initio* calculation (the choice of a suitable method and basis set). Using this calculation we are able to get other important molecular parameters (force constants, induced dipole moments, etc.) which cannot be easily obtained by experimental methods. The knowledge of these molecular data are necessary as starting data to model the infrared multiphoton process in CF₂HCl and their isotopic species.

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