

세 가지 3-Chloro-1-butene 이형태체들의 진동 Frequency 계산에 대한 DFT 합동법 적용 연구

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An Application of Combining DFT Methods to Calculate the Vibrational Frequencies of All Three Conformers of 3-Chloro-1-butene

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요 약. 본 연구는 진동 frequency에 대하여 양자역학적 계산 값과 분광학적 측정 값 사이에 최소의 오차를 나타내는 기저함수 세트를 찾고자 하는 것이다. 이를 위하여 3-chloro-1-butene의 세 가지 이형태체 모두에 대하여 42개의 기저함수 세트를 가지고 진동 frequency를 계산 하였고, 이 계산으로 얻은 frequency들을 실험적으로 측정된 값들과 비교 하였다. 그 결과 BLYP/6-31G(d), BLYP/6-31G(d,3p), B3LYP/6-31G(d)가 최소의 오차를 나타냄을 알 수 있었다. 이 가운데 모든 기준 진동 frequency에 대하여서는 BLYP/6-31G(d)가 0.53%로 최소의 오차를 나타내었으며, BLYP/6-31G(d,3p)는 수소 원자와 관련된 기준 진동에 대하여 그리고 B3LYP/6-31G(d)는 보다 무거운 원자와 관련된 기준 진동에 대하여 각각 0.01%의 오차를 나타내었다. 또한 BLYP/6-31G(d,3p)와 B3LYP/6-31G(d)를 합동하는 기법을 사용하면 3-chloro-1-butene의 HE, ME, CIE 이형태체들의 모든 기준 진동에 대하여 각각 0.01, 0.16, 0.37%의 오차를 갖는 좋은 frequency 계산 값을 얻을 수 있었다.

주제어: 기저함수, 진동 frequency, 3-Chloro-1-butene, DFT 계산, 합동 기법

ABSTRACT. We have determined the basis sets which give the least errors between the calculated and the observed vibrational frequencies. On this purpose we have carried out frequency calculations for the all three conformers of 3-chloro-1-butene with forty-two basis sets and these calculated frequencies were compared with the observed ones. The basis sets which give the least errors are BLYP/6-31G(d), BLYP/6-31G(d,3p) and B3LYP/6-31G(d). The BLYP/6-31G(d) gives the least error as 0.53% for all of the fundamental frequencies and the BLYP/6-31G(d,3p) and B3LYP/6-31G(d) both give the least error of 0.01% for the fundamentals related hydrogen(s) and heavier atoms, respectively. Using the combining technique with the BLYP/6-31G(d,3p) and B3LYP/6-31G(d) we have obtained the errors of 0.01, 0.16 and 0.37% for all of the fundamentals of HE, ME and CIE conformers of 3-chloro-1-butene, respectively.

Keywords: Basis Set, Vibrational Frequency, 3-Chloro-1-Butene, DFT Calculation, Combining Technique

INTRODUCTION

With the availability of fast small computers and quantum mechanical calculation programs such as Gaussian-98,¹ it is now possible to carry out rela-

tively accurate calculations on molecular structure, conformational stability and vibrational frequencies. Even though the quantum mechanical calculations are very useful to predict the structural parameters and vibrational frequencies, the calculated frequen-

cies are considerably discrepant among those obtained by different methods.²⁻⁷ Therefore, some of scientists use the scaling factors to fit the theoretical frequencies to the observed frequencies for assigning the fundamental vibrational modes of molecules.^{4,8} And also some of scientist believe that the higher basis set may give the better frequencies and use the time consuming very high basis set such as MP2/6-311++G(d,p). But the results were not as satisfactory as expected.^{1,5,9-11}

Therefore, it is necessary to find the calculation method(s) that gives very close values to the observed vibrational frequencies. For this purpose we performed forty-two sets of frequency calculations employing BLYP, B3LYP and MP2 methods on 3-chloro-1-butene. Because the 3-chloro-1-butene gives frequencies from three kinds of conformations.⁴ Therefore, this molecule will be the one of the best molecule as the representative one to find the best basis set for vibrational frequency calculation. The results of this study are reported herein.

CALCULATIONS

In this study all the calculations were carried out using the Gaussian-98 program¹ using Gaussian-type functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometrical parameters of molecule using the gradient method of Pulay.¹² The frequency calculations were performed analytically for the optimized structures of the conformer with the double bond eclipsing the H_i hydrogen atom (IIE; Fig. 1) of 3-chloro-1-butene using the BLYP/6-31G and BLYP/6-311G basis sets, which are known as good methods for the frequency calculation², including twelve kinds of depolarization functions of (d), (d,p), (d,2p), (d,3p), (2d), (2d,p), (2d,2p), (2d,3p), (3d), (3d,p), (3d,2p) and (3d,3p), respectively. And then the + and ++ diffuse functions were employed at the level of BLYP/6-31G and BLYP/6-311G respectively with the depolarization functions of (d), (d,3p) and (2d) that gave the least discrepant frequency differences. Finally the three basis sets that gave the best results among thirty-six BLYP

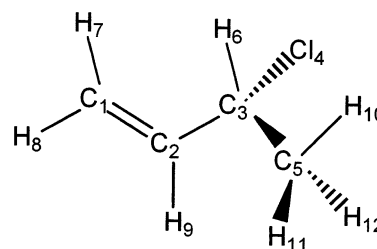


Fig. 1. Structural model and atom numbering of the HE form of 3-chloro-1-butene.

calculations have been taken and with these three basis sets the B3LYP and MP2 methods to obtain the optimized structures and frequencies for all three conformations of molecule have been performed. The percent discrepancies ($\Delta\%$) and standard deviations (σ) between the calculated and observed frequencies are listed in Table 1.

RESULT AND DISCUSSION

In Table 1 the $\Delta\%$ and σ the BLYP/6-31G(d) basis set gives best result with -0.53% discrepancy for all of the fundamental frequencies exception an asymmetric torsion for the IIE form of 3-chloro-1-butene. The BLYP/6-31G(d,3p) and B3LYP/6-31G(d) give 0.01% of $\Delta\%$ for modes related to the hydrogen(s) and C-C stretch ('Light') and the heavier atoms and =CH bend (ν_{24}) which has more potential energy distribution value of CCl stretch ('Heavy'), respectively. The calculated and observed frequencies including differences ($\Delta\nu$ and $\Delta\%$) and standard deviations (σ) are listed in Table 2.

At the BLYP/6-31G(d) level calculation the D⁰ excepting asymmetric torsion exist from -8.2 to 2.5% region and the total average error is -0.53%. And the average error for the 'Light' is 0.83% and for the one that related to the 'Heavy' is -4.09%. On the other hand the $\Delta\%$ at the BLYP/6-31G(d,3p) exist from -8.6 to 2.2% regions and the total average error is -1.29% and the average error for the 'Light' is 0.01% and for the 'Heavy' is -4.71%. And at the B3LYP/6-31G(d) the $\Delta\%$ exist from -1.9 to 5.3% region and the total average error is 2.84% and the average error for the 'Light' is 3.91% and for the 'Heavy' is 0.01%. These result clearly show that the

Table 1. Frequency percent differences ($\Delta\%$) and standard deviations (σ) between the observed and calculated frequencies with various methods for the HE form of 3-chloro-1-butene^a

Method	Basis set	All		Light		Heavy	
		$\Delta\%$ ^b	σ ^c	$\Delta\%$ ^b	σ ^c	$\Delta\%$ ^b	σ ^c
BLYP	6-31G(d)	-0.53	2.79	0.83	1.37	-4.09	2.37
	6-31G(d,p)	-0.84	2.74	0.47	1.50	-4.27	2.23
	6-31G(d,2p)	-1.05	2.73	0.25	1.51	-4.47	2.18
	6-31G(d,3p)	-1.29	2.80	0.01	1.70	-4.71	2.15
	6-31G(2d)	-1.05	2.51	0.12	1.43	-4.14	2.09
	6-31G(2d,p)	-1.08	2.64	0.16	1.55	-4.33	2.05
	6-31G(2d,2p)	-1.13	2.64	0.11	1.56	-4.37	2.07
	6-31G(2d,3p)	-1.17	2.60	0.06	1.55	-4.39	1.98
	6-31G(3d)	-1.10	2.98	0.19	2.14	-4.46	2.10
	6-31G(3d,p)	-1.09	2.98	0.19	2.21	-4.43	1.97
	6-31G(3d,2p)	-1.32	2.72	-0.20	2.07	-4.26	1.90
	6-31G(3d,3p)	-1.55	2.74	-0.42	2.06	-4.53	1.99
	6-311G(d)	-1.02	2.67	0.24	1.28	-4.35	2.53
	6-311G(d,p)	-1.30	2.60	-0.07	1.32	-4.53	2.37
	6-311G(d,2p)	-1.35	2.61	-0.12	1.36	-4.58	2.36
	6-311G(d,3p)	-1.42	2.66	-0.18	1.44	-4.67	2.37
	6-311G(2d)	-1.24	2.65	-0.02	1.47	-4.43	2.44
	6-311G(2d,p)	-1.38	2.64	-0.17	1.51	-4.58	2.30
	6-311G(2d,2p)	-1.32	2.67	-0.10	1.53	-4.54	2.36
	6-311G(2d,3p)	-1.41	2.83	-0.11	1.70	-4.80	2.35
	6-311G(3d)	-1.22	2.55	-0.04	1.44	-4.31	2.22
	6-311G(3d,p)	-1.35	2.47	-0.21	1.43	-4.32	2.13
	6-311G(3d,2p)	-1.25	2.51	-0.08	1.41	-4.32	2.13
	6-311G(3d,3p)	-1.31	2.43	-0.19	1.38	-4.26	2.12
	6-31-G(d)	-0.84	2.74	0.47	1.34	-4.28	2.49
	6-31-G(d,3p)	-1.61	2.86	-0.37	1.96	-4.85	2.26
	6-31-G(2d)	-1.47	2.55	-0.31	1.48	-4.51	2.28
	6-31+G(d)	-0.84	2.73	0.47	1.35	-4.26	2.49
	6-31+G(d,3p)	-1.60	2.84	-0.37	1.94	-4.83	2.22
	6-31+G(2d)	-1.43	2.52	-0.27	1.42	-4.48	2.25
	6-311+G(d)	-1.08	2.53	0.10	1.29	-4.19	2.37
	6-311+G(d,3p)	-1.36	2.52	-0.19	1.37	-4.45	2.26
6-311+G(2d)	-1.24	2.53	-0.06	1.34	-4.34	2.31	
6-311+-G(d)	-1.13	2.54	0.07	1.33	-4.27	2.27	
6-311+-G(d,3p)	-1.29	2.37	-0.21	1.38	-4.14	2.05	
6-311+-G(2d)	-1.26	2.52	-0.09	1.36	-4.34	2.31	
B3LYP	6-31G(d)	2.84	2.10	3.91	1.04	0.01	1.40
	6-31G(d,3p)	1.98	2.12	2.98	1.38	-0.63	1.32
	6-311G(2d)	2.08	1.86	2.99	1.02	-0.30	1.40
MP2	6-31G(d)	5.44	1.63	5.89	1.61	4.25	1.04
	6-31G(d,3p)	4.25	2.41	4.80	2.49	2.78	1.45
	6-311G(2d)	3.56	1.53	4.00	1.49	2.40	0.95

^a'All' refers to all fundamental modes of molecule excepting asymmetric torsion. 'Light' to fundamentals related to hydrogen atom(s) including C=C stretch and 'Heavy' to fundamentals related to heavier atoms including =CH bend (ν_{21}) of 3-chloro-1-butene. The asymmetric torsion is not counted for $\Delta\%$ and σ for the 'All', 'Light' and 'Heavy'.

^bPercent difference between the calculated and observed frequencies as $\nu_{\text{calc}} - \nu_{\text{obs}}$.

^cStandard deviation.

Table 2. Frequency fitting for the HE conformer of 3-chloro-1-butene

No. ^a	Description	Obs. ^b	BLYP/6-31G(d)			BLYP/6-31G(d,3p)			B3LYP/6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$
1	=CH ₂ antisymmetric stretch	3097	3159	62	2.0	3152	55	1.8	3244	147	4.7	3152	55	1.8
2	=CH stretch	3027	3085	58	1.9	3078	51	1.7	3171	144	4.8	3078	51	1.7
3	CH ₃ antisymmetric stretch	3002	3077	75	2.5	3067	65	2.2	3161	159	5.3	3067	65	2.2
4	=CH ₂ symmetric stretch	2995	3066	71	2.4	3059	64	2.1	3147	152	5.1	3059	64	2.1
5	CH ₃ antisymmetric stretch	2983	3044	61	2.0	3038	55	1.8	3129	146	4.9	3038	55	1.8
6	CH stretch	2967	3031	64	2.2	3024	57	1.9	3115	148	5.0	3024	57	1.9
7	CH ₃ symmetric stretch	2935	2976	41	1.4	2968	33	1.1	3057	122	4.2	2968	33	1.1
8	C=C stretch	1650	1661	11	0.7	1655	5	0.3	1727	77	4.7	1655	5	0.3
9	CH ₃ antisymmetric deformation	1459	1486	27	1.9	1468	9	0.6	1523	64	4.4	1468	9	0.6
10	CH ₃ antisymmetric deformation	1452	1478	26	1.8	1460	8	0.6	1516	64	4.4	1460	8	0.6
11	=CH ₂ deformation	1430	1440	10	0.7	1422	-8	-0.6	1478	48	3.4	1422	-8	-0.6
12	CH ₃ symmetric deformation	1380	1396	16	1.2	1376	-4	-0.3	1437	57	4.1	1376	-4	-0.3
13	CH bend	1300	1317	17	1.3	1305	5	0.4	1353	53	4.1	1305	5	0.4
14	=CH bend	1285	1295	10	0.8	1287	2	0.2	1330	45	3.5	1287	2	0.2
15	CH bend	1237	1228	-9	-0.7	1209	-28	-2.3	1274	37	3.0	1209	-28	-2.3
16	CCC antisymmetric stretch	1178	1169	-9	-0.8	1158	-20	-1.7	1206	28	2.4	1206	28	2.4
17	CH ₃ rock	1092	1078	-14	-1.3	1070	-22	-2.0	1116	24	2.2	1070	-22	-2.0
18	CH ₃ rock	1029	1015	-14	-1.4	1007	-22	-2.1	1050	21	2.0	1007	-22	-2.1
19	=CH ₂ twist	988	996	8	0.8	989	1	0.1	1031	43	4.4	989	1	0.1
20	=CH ₂ rock	970	962	-8	-0.8	954	-16	-1.6	990	20	2.1	954	-16	-1.6
21	=CH ₂ wag	932	911	-21	-2.3	909	-23	-2.5	955	23	2.5	909	-23	-2.5
22	CCC symmetric stretch	866	844	-22	-2.5	839	-27	-3.1	875	9	1.0	875	9	1.0
23	CCl stretch	715	685	-30	-4.2	684	-31	-4.3	716	1	0.1	716	1	0.1
24	=CH bend	631	579	-52	-8.2	577	-54	-8.6	619	-12	-1.9	619	-12	-1.9
25	C=CC bend	458	431	-27	-5.9	431	-27	-5.9	453	-5	-1.1	453	-5	-1.1
26	CCC bend	319	312	-7	-2.2	308	-11	-3.4	322	3	0.9	322	3	0.9
27	CCl bend	305	294	-11	-3.6	292	-13	-4.3	304	-1	-0.3	304	-1	-0.3
28	CCl bend	283	268	-15	-5.3	265	-18	-6.4	280	-3	-1.1	280	-3	-1.1
29	CH ₃ torsion	247	248	1	0.4	239	-8	-3.2	256	9	3.6	239	-8	-3.2
30	Asymmetric torsion	92	104	12	13.0	101	9	9.8	104	12	13.0	104	12	13.0

No. ^a	Description	Obs. ^b	BLYP/6-31G(d)			BLYP/6-31G(d,3p)			B3LYP/6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%d$
'All'	Average		11.0	-0.53		2.7	-1.29		56.0	2.84		10.3	0.01	
	Standard deviation		34.1	2.79		32.9	2.80		56.3	2.10		28.1	1.60	
'Light'	Average		23.4	0.83		13.3	0.01		76.3	3.91		13.3	0.01	
	Standard deviation		31.0	1.37		32.0	1.70		53.0	1.04		32.0	1.70	
'Heavy'	Average		-21.6	-4.09		-25.1	-4.71		2.5	0.01		2.5	0.01	
	Standard deviation		14.9	2.37		13.6	2.15		12.0	1.40		12.0	1.40	

^a'All' refer to the all modes; 'Light' to the modes related to the H atom(s) and C=C stretch; 'Heavy' to the modes related to the heavier atoms and =CH bend (ν_{23}). 'All', 'Light' and 'Heavy' all together not include the asymmetric torsion.

^bTaken from reference 4 and frequencies are in cm⁻¹.

^cFrequency difference between the calculated and observed frequencies as $\nu_{\text{calc.}} - \nu_{\text{obs.}}$.

^dPercent difference between the calculated and observed frequencies as $\nu_{\text{calc.}} / \nu_{\text{obs.}}$.

^eValues for the 'Light' are taken from BLYP/6-31G(d,3p) and those for the 'Heavy' from B3LYP/6-31G(d).

Table 3. Frequency fitting for the ME conformer of 3-chloro-1-butene

No. ^a	Description	Obs. ^b	BLYP/6-31G(d)			BLYP/6-31G(d,3p)			B3LYP/6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$
1	=CH ₂ antisymmetric stretch	3085	3168	83	2.7	3161	76	2.5	3253	168	5.4	3161	76	2.5
2	=CH stretch		3096			3088			3182			3088		
3	CH ₃ antisymmetric stretch		3086			3076			3171			3076		
4	=CH ₂ symmetric stretch	3036	3074	38	1.3	3065	29	1.0	3156	120	4.0	3065	29	1.0
5	CH ₃ antisymmetric stretch		3050			3043			3134			3043		
6	CH stretch		3010			3008			3094			3008		
7	CH ₃ symmetric stretch	2945	2982	37	1.3	2974	29	1.0	3062	117	4.0	2974	29	1.0
8	C=C stretch		1662			1655			1727			1655		
9	CH ₃ antisymmetric deformation		1494			1475			1530			1475		
10	CH ₃ antisymmetric deformation	1461	1481	20	1.4	1462	1	0.1	1520	59	4.0	1462	1	0.1
11	=CH ₂ deformation		1435			1417			1472			1417		
12	CH ₃ symmetric deformation		1396			1377			1437			1377		
13	CH bend	1330	1349	19	1.4	1339	9	0.7	1387	57	4.3	1339	9	0.7
14	=CH bend	1292	1310	18	1.4	1303	11	0.9	1344	52	4.0	1303	11	0.9
15	CH bend	1225	1212	-13	-1.1	1192	-33	-2.7	1263	38	3.1	1192	-33	-2.7
16	CCC antisymmetric stretch	1157	1147	-10	-0.9	1139	-18	-1.6	1183	26	2.2	1183	26	2.2
17	CH ₃ rock	1029	1018	-11	-1.1	1008	-21	-2.0	1046	17	1.7	1008	-21	-2.0
18	CH ₃ rock	1078	1076	-2	-0.2	1067	-11	-1.0	1108	30	2.8	1067	-11	-1.0
19	=CH ₂ twist	996	1005	9	0.9	997	1	0.1	1040	44	4.4	997	1	0.1
20	=CH ₂ rock		964			958			997			958		
21	=CH ₂ wag	927	911	-16	-1.7	910	-17	-1.8	954	27	2.9	910	-17	-1.8
22	CCC symmetric stretch	856	826	-30	-3.5	824	-32	-3.7	860	4	0.5	860	4	0.5
23	CCl stretch	600	556	-44	-7.3	554	-46	-7.7	588	-12	-2.0	588	-12	-2.0
24	=CH bend	721	693	-28	-3.9	690	-31	-4.3	725	4	0.6	725	4	0.6
25	C=CC bend	511	487	-24	-4.7	484	-27	-5.3	511	0	0.0	511	0	0.0
26	CCC bend	245	263	18	7.3	260	15	6.1	272	27	11.0	272	27	11.0
27	CCl bend	344	324	-20	-5.8	322	-22	-6.4	340	-4	-1.2	340	-4	-1.2
28	CCl bend	302	273	-29	-9.6	264	-38	-12.6	284	-18	-6.0	284	-18	-6.0
29	CH ₃ torsion	319	299	-20	-6.3	297	-22	-6.9	314	-5	-1.6	297	-22	-6.9
30	Asymmetric torsion	96	106	10	10.4	104	8	8.3	110	14	14.6	110	14	14.6

No. ^a	Description	Obs. ^b	BLYP/6-31G(d)			BLYP/6-31G(d,3p)			B3LYP/6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$	cm ⁻¹	$\Delta\nu^c$	$\Delta^0_{o,d}$
'All'	Average		0.2	-0.85		-6.6	-1.69		36.4	2.80		4.0	-0.16	
	Standard deviation		29.8	4.68		28.8	4.69		47.6	4.35		24.8	3.55	
'Light'	Average		13.5	0.00		4.3	-0.70		60.3	3.25		4.3	-0.70	
	Standard deviation		29.6	2.37		29.9	2.46		49.9	1.80		29.9	2.46	
'Heavy'	Average		-20.9	-3.54		-24.9	-4.42		3.4	0.65		3.4	0.65	
	Standard deviation		18.4	5.12		18.3	5.37		16.2	4.85		16.2	4.85	

^a'All' refer to the all modes; 'Light' to the modes related to the H atom(s) and C=C stretch; 'Heavy' to the modes related to the heavier atoms and =CH bend (ν_{23}). 'All', 'Light' and 'Heavy' all together not include the asymmetric torsion.

^bTaken from reference 4 and frequencies are in cm⁻¹.

^cFrequency difference between the calculated and observed frequencies as $\nu_{calc} - \nu_{obs}$.

^dPercent difference between the calculated and observed frequencies as $\nu_{calc} - \nu_{obs}$.

^eValues for the 'Light' are taken from BLYP/6-31G(d,3p) and those for the 'Heavy' from B3LYP/6-31G(d).

Table 4. Frequency fitting for the CIE conformer of 3-chloro-1-butene

No. ^a	Description	Obs. ^b	BLYP:6-31G(d)			BLYP:6-31G(d,3p)			B3LYP:6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d
1	=CH ₂ antisymmetric stretch	3110	3176	66	2.1	3169	59	1.9	3261	151	4.9	3169	59	1.9
2	=CH stretch		3096	3096		3083			3179			3083		
3	CH ₃ antisymmetric stretch		3072	3072		3064			3154			3064		
4	=CH ₂ symmetric stretch		3048	3048		3045			3139			3045		
5	CH ₃ antisymmetric stretch		3043	3043		3037			3128			3037		
6	CH stretch		2990	2990		2985			3080			2985		
7	CH ₃ symmetric stretch		2976	2976		2968			3057			2968		
8	C=C stretch		1675	1675		1669			1738			1669		
9	CH ₃ antisymmetric deformation		1489	1489		1471			1525			1471		
10	CH ₃ antisymmetric deformation		1479	1479		1460			1517			1460		
11	=CH ₂ deformation		1427	1427		1407			1466			1407		
12	CH ₃ symmetric deformation		1395	1395		1376			1436			1376		
13	CH bend	1304	1307	3	0.2	1299	-5	-0.4	1347	43	3.3	1299	-5	-0.4
14	=CH bend	1295	1230	-65	-5.0	1292	-3	-0.2	1337	42	3.2	1292	-3	-0.2
15	CH bend	1258	1247	-11	-0.9	1228	-30	-2.4	1294	36	2.9	1228	-30	-2.4
16	CCC antisymmetric stretch	1082	1067	-15	-1.4	1059	-23	-2.1	1106	24	2.2	1106	24	2.2
17	CH ₃ rock	977	958	-19	-1.9	952	-25	-2.6	993	16	1.6	952	-25	-2.6
18	CH ₃ rock	1113	1101	-12	-1.1	1090	-23	-2.1	1137	24	2.2	1090	-23	-2.1
19	=CH ₂ twist		985	985		978			1065			978		
20	=CH ₂ rock	1025	1036	11	1.1	1028	3	0.3	1021	-4	-0.4	1028	3	0.3
21	=CH ₂ wag	927	910	-17	-1.8	910	-17	-1.8	956	29	3.1	910	-17	-1.8
22	CCC symmetric stretch	866	837	-29	-3.3	833	-33	-3.8	872	6	0.7	872	6	0.7
23	CCl stretch	703	679	-24	-3.4	677	-26	-3.7	707	4	0.6	707	4	0.6
24	=CH bend	628	600	-28	-4.5	597	-31	-4.9	626	-2	-0.3	626	-2	-0.3
25	C=CC bend	511	475	-36	-7.0	475	-36	-7.0	501	-10	-2.0	501	-10	-2.0
26	CCC bend	366	357	-9	-2.5	355	-11	-3.0	369	3	0.8	369	3	0.8
27	CCl bend		235	235		233			245			245		
28	CCl bend		315			313			326			326		
29	CH ₃ torsion		253			242			261			242		
30	Asymmetric torsion	90	93	3	3.3	91	1	1.1	98	8	8.9	98	8	8.9

No. ^a	Description	Obs. ^b	BLYP:6-31G(d)			BLYP:6-31G(d,3p)			B3LYP:6-31G(d)			Combined ^c		
			cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d	cm ⁻¹	$\Delta\nu^c$	$\Delta^0\%$ ^d
'All'	Average		-13.2	-2.10		-14.4	-2.28		25.9	1.63		-1.1	-0.37	
	Standard deviation		29.1	2.46		24.3	2.27		40.0	1.83		22.5	1.57	
'Light'	Average		-5.5	-0.92		-5.1	-0.91		42.1	2.60		-5.1	-0.91	
	Standard deviation		36.6	2.18		28.4	1.57		46.6	1.53		28.4	1.57	
'Heavy'	Average		-23.5	-3.69		-26.7	-4.10		4.2	0.34		4.2	0.34	
	Standard deviation		9.9	1.94		9.0	1.72		11.3	1.39		11.3	1.39	

^a'All' refer to the all modes; 'Light' to the modes related to the H atom(s) and C=C stretch; 'Heavy' to the modes related to the heavier atoms and =CH bend (ν_{CH}). 'All', 'Light' and 'Heavy' all together not include the asymmetric torsion.

^bTaken from reference 4 and frequencies are in cm⁻¹.

^cFrequency difference between the calculated and observed frequencies as $\nu_{calc} - \nu_{obs}$.

^dPercent difference between the calculated and observed frequencies as $\nu_{calc} - \nu_{obs}$.

^eValues for the 'Light' are taken from BLYP:6-31G(d,3p) and those for the 'Heavy' from B3LYP:6-31G(d).

BLYP/6-31G(d,3p) gives the best frequencies for the 'Light' modes of HE conformer of 3-chloro-1-butene and the B3LYP/6-31G(d) does for the 'Heavy' ones. Therefore, with combining the frequencies from the BLYP/6-31G(d,3p) and the B3LYP/6-31G(d) for the 'Light' and 'Heavy' modes the total average error comes down from -1.29 and 2.84, respectively, to 0.01% with standard deviation 1.60%. With this error and standard deviation the calculated frequencies are in excellent agreement with the observed ones (Table 2).

With these BLYP/6-31G(d,3p) and B3LYP/6-31G(d) basis sets the frequency calculations for the higher energy conformers, the conformer with the double bond eclipsing the methyl group (ME) and the conformer with the double bond eclipsing the chlorine atom (CIE), of 3-chloro-1-butene also carried out and the results are listed in Table 3 and 4. The error, $\Delta\%$, of the 'Light' modes at the BLYP/6-31G(d,3p) obtained as -0.70 and -0.91% and the $\Delta\%$ of the 'Heavy' ones at the B3LYP/6-31G(d) as 0.65 and 0.34% for the ME and CIE form, respectively. By applying the combining method for the ME and CIE the $\Delta\%$ s for all modes come down to -0.16 and -0.37%, respectively. And we found most of the calculated frequencies with this combining method of all three conformers are in fairly good agreement with the observed ones within about $\pm 2\%$ errors with exception of those of CCC bend and two CCl bends of ME form. Therefore, the combining the frequen-

cies from BLYP/6-31G(d,3p) and B3LYP/6-31G(d) will be very useful to predict and assign the vibrational frequencies of molecules such as 3-chloro-1-butene. And it would be interest to reassign the CCC bend and two CCl bends of ME conformer of 3-chloro-1-butene using the frequencies from the B3LYP/6-31G(d) calculation.

The enthalpy differences, ΔH , among the HE, ME and CIE conformers of 3-chloro-1-butene in the vapor phase were also estimated from the BLYP/6-31G(d), BLYP/6-31G(d,3p) and B3LYP/6-31G(d). The ΔH values between the HE and ME form were obtained of 390 cm^{-1} (4.67 kJ/mol), 320 cm^{-1} (3.83 kJ/mol) and 353 cm^{-1} (4.22 kJ/mol) and those between the HE and CIE form were 685 cm^{-1} (8.19 kJ/mol), 600 cm^{-1} (7.18 kJ/mol) and 565 cm^{-1} (6.76 kJ/mol) with the HE being the most stable form from the BLYP/6-31G(d), BLYP/6-31G(d,3p) and B3LYP/6-31G(d), respectively (Table 5). These values are not significantly different from those obtained from the MP2/6-31G(d) and MP2/6-311++G(d).⁴

The structural parameters obtained from the BLYP/6-31G(d), BLYP/6-31G(d,3p) and B3LYP/6-31G(d) calculations are not significantly different from those experimentally obtained by electron diffraction (see Table 6).¹³ At the B3LYP/6-31G(d) level, the C-C and C-Cl bond lengths are about 0.6 and 1.8% shorter, respectively, than those at the BLYP/6-31G(d,3p) and closer to those of electron diffraction. The C-H bond lengths at the BLYP/6-

Table 5. Comparison of the conformational energy differences obtained for 3-chloro-1-butene

Method		Conformation		
		HE	ME	CIE
BLYP/6-31G(d)	E/Hartree	-616.702487	-616.700712	-616.699365
	$\Delta E/\text{cm}^{-1}$	0	390	685
BLYP/6-31G(d,3p)	E/Hartree	-616.716810	-616.715354	-616.714077
	$\Delta E/\text{cm}^{-1}$	0	320	600
B3LYP/6-31G(d)	E/Hartree	-616.819022	-616.817414	-616.816449
	$\Delta E/\text{cm}^{-1}$	0	353	565
MP2/6-31G(d) ^a	E/Hartree	-615.684110	-615.682398	-615.682046
	$\Delta E/\text{cm}^{-1}$	0	376	453
MP2/6-311++G(d) ^a	E/Hartree	-615.930539	-615.928735	-615.928196
	$\Delta E/\text{cm}^{-1}$	0	396	514
Raman (temperature variance) ^a	$\Delta E/\text{cm}^{-1}$	0	75(8)	197(37)

^aTaken from reference 4.

Table 6. Structural parameters, rotational constants, dipole moments and total energies for HE form of 3-chloro-1-butene.^a

Parameter ^b	BLYP/6-31G(d)	BLYP/6-31G(d,3p)	B3LYP/6-31G(d)	ED ^c
$r(C_2=C_1)$	1.344	1.343	1.333	1.337(6)
$r(C_5-C_2)$	1.502	1.502	1.496	1.503(4)
$r(Cl-C_3)$	1.890	1.888	1.854	1.813(4)
$r(C_5-C_3)$	1.534	1.534	1.525	1.522(5)
$r(H_6-C_3)$	1.100	1.098	1.092	1.089(18)
$r(H_7-C_1)$	1.095	1.094	1.088	1.089(18)
$r(H_8-C_1)$	1.094	1.092	1.086	1.089(18)
$r(H_9-C_2)$	1.097	1.096	1.090	1.089(18)
$r(H_{10}-C_3)$	1.102	1.100	1.095	1.089(18)
$r(H_{11}-C_3)$	1.104	1.103	1.097	1.089(18)
$r(H_{12}-C_3)$	1.101	1.099	1.094	1.089(18)
$\angle(C_3-C_2=C_1)$	123.8	123.9	123.8	122.9(2.1)
$\angle(Cl-C_3-C_2)$	108.6	108.6	108.8	109.9(0.2)
$\angle(C_5-C_3-C_2)$	114.0	114.0	113.5	112.6(2.2)
$\angle(H_6-C_3-C_2)$	110.8	110.6	110.5	110.0(1.3)
$\angle(H_7-C_1=C_2)$	121.8	121.8	121.8	121.9
$\angle(H_8-C_1=C_2)$	121.6	121.6	121.6	121.9
$\angle(H_9-C_2=C_1)$	120.4	120.3	120.5	121.9
$\angle(H_{10}-C_3-C_3)$	111.0	111.1	110.9	110.0(1.3)
$\angle(H_{11}-C_3-C_3)$	109.1	109.1	109.2	110.0(1.3)
$\angle(H_{12}-C_3-C_3)$	111.1	111.2	111.0	110.0(1.3)
$\tau(Cl-C_3-C_2=C_1)$	114.8	114.4	116.2	119.4
$\tau(C_5-C_3-C_2=C_1)$	-124.6	-124.7	-122.8	
$\tau(H_6-C_3-C_2=C_1)$	1.7	1.5	2.4	
$\tau(H_7-C_1=C_2-C_3)$	-2.0	-1.8	-1.9	0.0
$\tau(H_8-C_1=C_2-C_3)$	180.0	178.0	178.1	180.0
$\tau(H_9-C_2=C_1-C_3)$	-178.5	-178.8	-178.6	180.0
$\tau(H_{10}-C_3-C_3-Cl)$	64.1	63.9	63.7	
$\tau(H_{11}-C_3-C_3-H_{10})$	119.4	119.3	119.4	
$\tau(H_{12}-C_3-C_3-H_{10})$	-120.9	-120.9	-120.7	
A	5427	5424	5569	5737
B	2686	2692	2729	2724
C	1957	1959	1996	2015
μ	2.4	2.3	2.4	
-E	616.702487	616.716810	616.819022	

^aBond length in Å, bond angle in degrees, rotational constant (*A*, *B*, *C*) in MHz, dipole moment (μ) in Debyes and energy (*E*) in Hartrees.

^bFor the definition of atom numbers, see Fig. 1.

^cReference 13.

31G(d,3p) are about 0.5% longer than those at the B3LYP/6-31G(d). This could explain the reason why the B3LYP/6-31G(d) gives the better frequencies of fundamentals on heavier atoms and the BLYP/6-31G(d,3p) gives the better frequencies of fundamentals related to hydrogen(s).

By utilizing combining density functional calculations with the BLYP/6-31G(d,3p) and B3LYP/6-31G(d) basis sets, we have found an excellent agreement between the calculated vibrational frequencies and those obtained experimentally for the 3-chloro-1-butene. Therefore, it is believed that the

very high basis set, such as 6-311++G(d,3p), is not necessary to predict frequencies of this molecule and the combining method with the BLYP and B3LYP employing not a very high basis set, such as BLYP/6-31G(d,3p) and B3LYP/6-31G(d), can be valuable assigning the fundamental modes of 3-chloro-1-butene. And we found the combining technique presently discussed provides excellent estimates for the vibrational frequencies from the low to the high frequency modes of this molecule.

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