

Theoretical study of the photoelectron spectra of methylketene

科學教育與應用學系 黃柏衡、謝主霖、翁偉桓

指導教授 張嘉麟 教授

Abstract

We used the density functional theory approaches M06-2X and APFD associated with the aug-cc-pVTZ basis set to obtain the equilibrium structures, harmonic and anharmonic vibrational frequencies of ethylketene and its cation. The Franck–Condon factors were computed using a hybrid model of harmonic^[1] and anharmonic oscillators, from which the photoelectron spectra of ethylketene were simulated.

Results and Discussion

Equilibrium structures

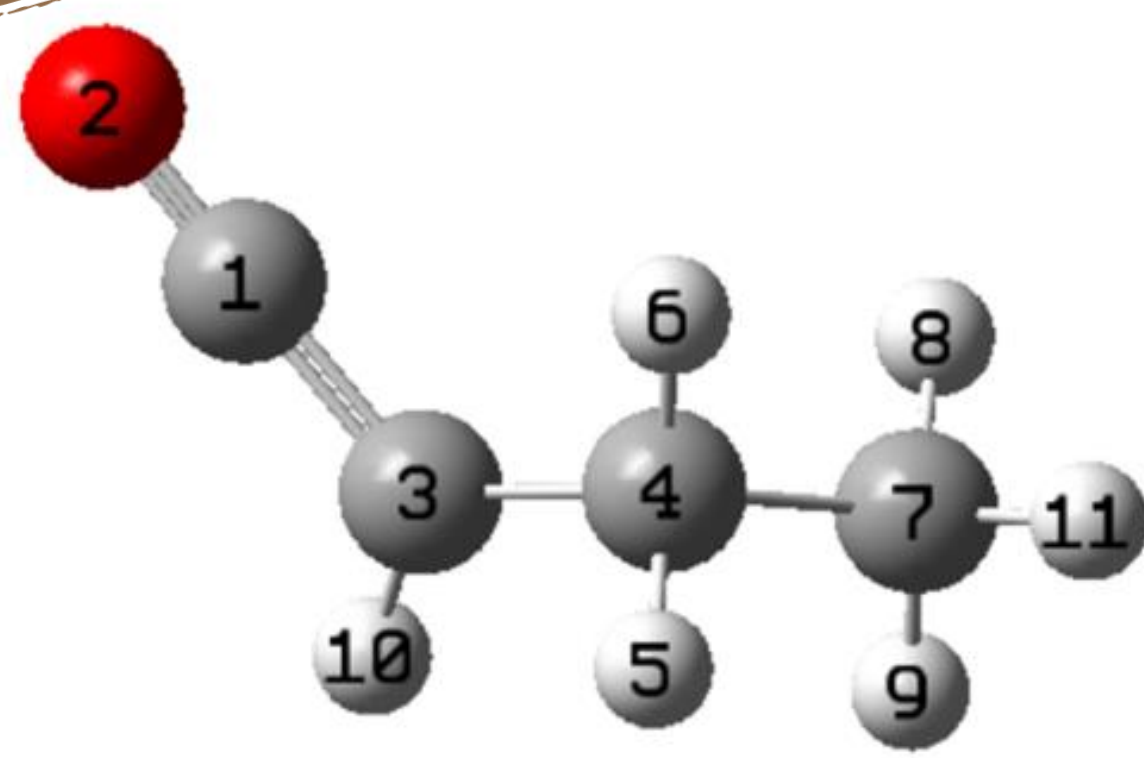


Fig. 1. The equilibrium structures of ethylketene.

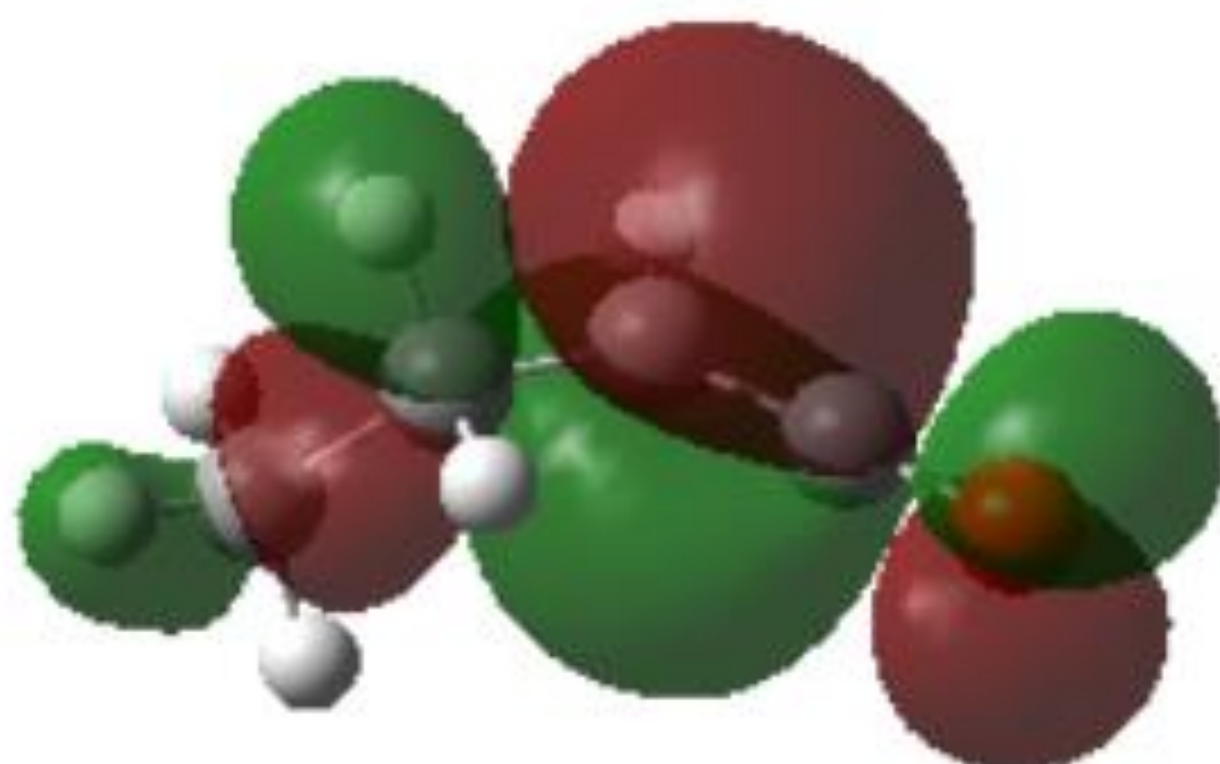


Fig. 2. The HOMO diagram of ethylketene.

Table 1. The equilibrium structures calculated by different methods.

Parameter	Method			
	M062X		APFD	
	X	X+	X	X+
R(C1,O2)	115.86	112.23	116.24	112.78
R(C1,C3)	130.73	137.70	130.79	137.16
R(C3,C4)	151.11	147.98	150.82	147.51
R(C3,H10)	108.12	108.65	108.37	108.95
R(C4,H5)	109.15	109.64	109.51	110.28
R(C4,H6)	108.98	108.72	109.27	109.00
R(C4,C7)	152.58	154.76	152.55	154.50
R(C7,H8)	108.92	108.72	109.14	108.91
R(C7,H9)	109.02	108.78	109.24	108.99
R(C7,H11)	108.98	108.73	109.25	108.97
A(C1,C3,C4)	122.9	121.8	122.9	122.0
A(C1,C3,H10)	116.1	115.4	116.3	115.7
A(C4,C3,H10)	120.9	122.7	120.8	122.3
A(C3,C4,H5)	109.0	106.4	109.0	105.9
A(C3,C4,H6)	109.3	111.5	109.4	111.8
A(C3,C4,C7)	112.2	110.0	112.5	110.8
A(H5,C4,H6)	106.5	108.5	106.0	107.7
A(H5,C4,C7)	109.7	108.5	109.7	108.1
A(H6,C4,C7)	110.0	111.7	110.0	112.2
A(C4,C7,H8)	110.7	111.0	110.9	110.9
A(C4,C7,H9)	110.7	111.0	111.0	111.5
A(C4,C7,H11)	110.9	107.7	111.0	107.9
A(H8,C7,H9)	107.8	109.4	107.6	109.2
A(H8,C7,H11)	108.6	108.9	108.3	108.8

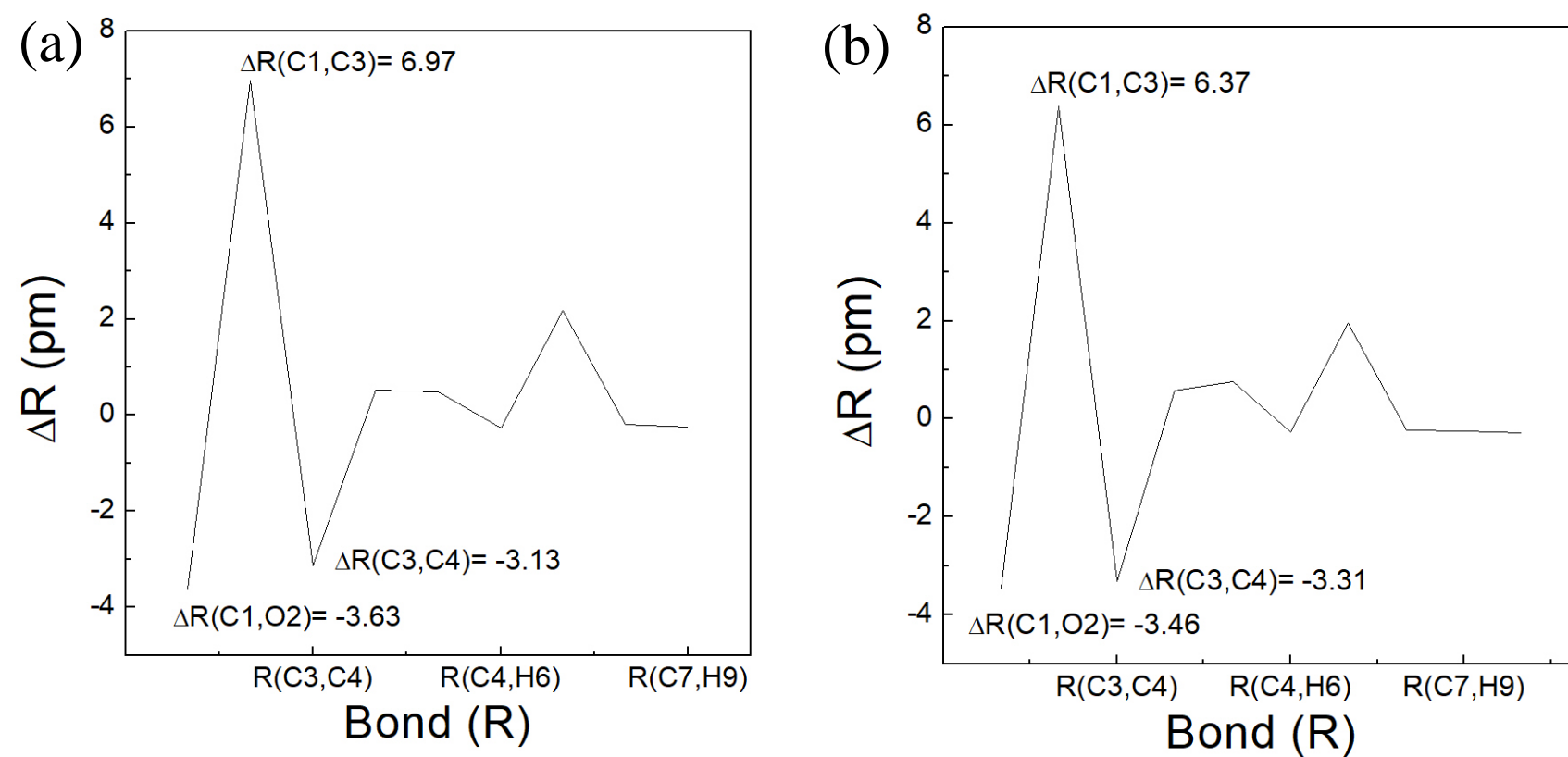


Fig. 3. The bond length variation diagram calculated by (a) M06-2X, (b) APFD.

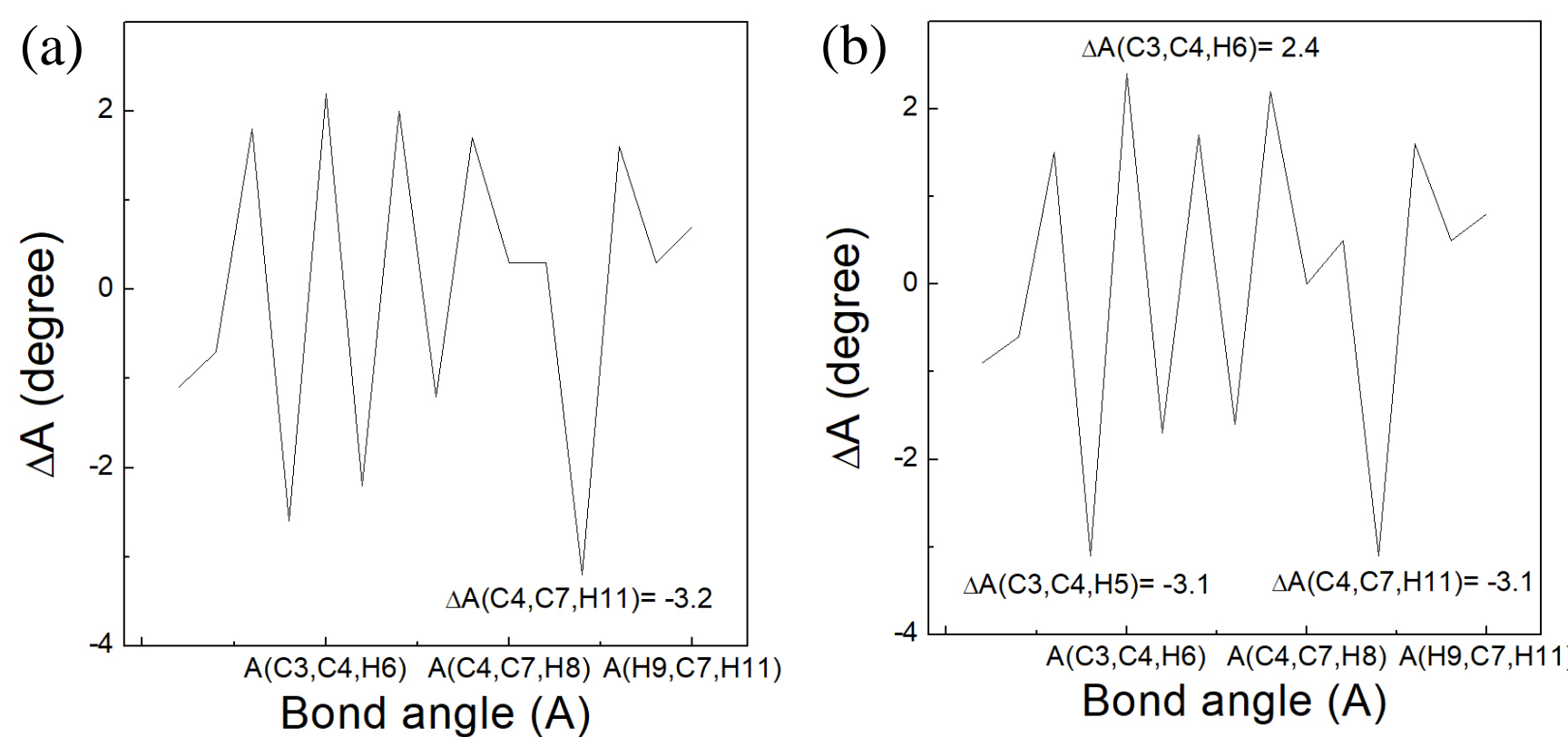


Fig. 4. The bond angle variation diagram calculated by (a) M06-2X, (b) APFD.

Vibrational frequencies

Table 2. The harmonic and anharmonic vibrational frequency calculated by M06-2X/AVTZ.

mode	M062X(harmonic)				M062X(anharmonic)			
	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species
	X		X+		X		X+	
1	3217	A	3175	A	3038	A	3100	A
2	3142	A	3173	A	3105	A	3119	A
3	3135	A	3172	A	3058	A	3176	A
4	3106	A	3145	A	3021	A	3055	A
5	3066	A	3084	A	2997	A	3040	A
6	3063	A	3028	A	3015	A	2853	A
7	2239	A	2324	A	2212	A	2290	A
8	1508	A	1501	A	1469	A	1466	A
9	1499	A	1490	A	1465	A	1454	A
10	1491	A	1466	A	1447	A	1411	A
11	1445	A	1413	A	1432	A	1382	A
12	1411	A	1372	A	1372	A	1346	A
13	1346	A	1289	A	1307	A	1274	A
14	1288	A	1217	A	1248	A	1166	A
15	1161	A	1160	A	1166	A	1133	A
16	1107	A	1103	A	1088	A	1092	A
17	1094	A	1007	A	1066	A	985	A
18	1032	A	955	A	1010	A	939	A
19	894	A	893	A	887	A	877	A
20	779	A	763	A	769	A	746	A
21	642	A	694	A	643	A	692	A
22	597	A	606	A	616	A	599	A
23	547	A	459	A	560	A	457	A
24	339	A	324	A	362	A	339	A
25	269	A	244	A	312	A	296	A
26	177	A	173	A	156	A	164	A
27	71	A	39	A	57	A	12	A

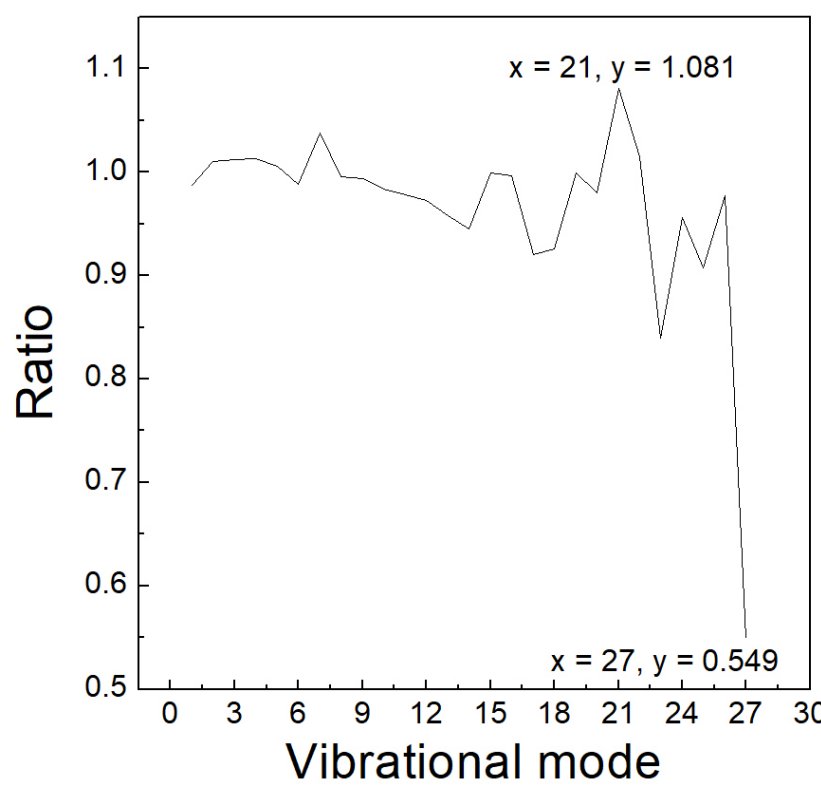


Fig. 5. The harmonic vibrational frequency variation diagram calculated by M06-2X /AVTZ.

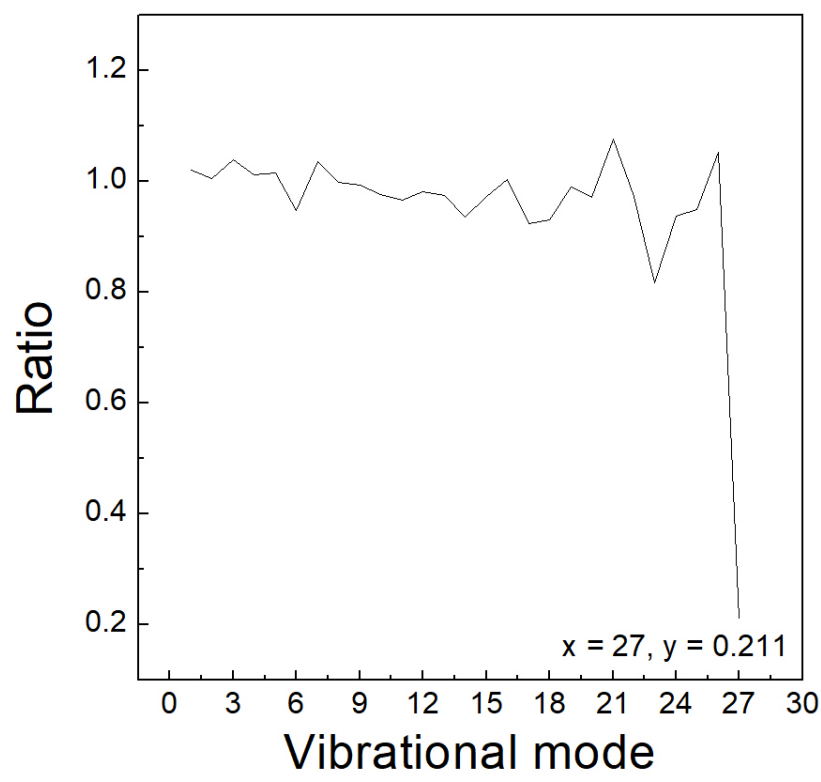


Fig. 6. The anharmonic vibrational frequency variation diagram calculated by M06-2X /AVTZ.

Table 3. The harmonic and anharmonic vibrational frequency calculated by APFD/AVTZ.

mode	APFD(harmonic)				APFD(anharmonic)			
	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species
	X		X+		X		X+	
1	3190	A	3158	A	3360	A	3042	A
2	3119	A	3154	A	3005	A	3034	A
3	3111	A	3153	A	2973	A	3000	A
4	3077	A	3119	A	2949	A	2966	A
5	3039	A	3064	A	2937	A	2953	A
6	3031	A	2965	A	2923	A	2708	A
7	2221	A	2278	A	2232	A	2237	A
8	1496	A	1487	A	1458	A	1445	A
9	1486	A	1475	A	1446	A	1440	A
10	1480	A	1441	A	1439	A	1357	A
11	1435	A	1408	A	1448	A	1391	A
12	1405	A	1369	A	1372	A	1326	A
13	1340	A	1288	A	1309	A	1265	A
14	1283	A	1193	A	1252	A	1139	A
15	1161	A	1162	A	1117	A	1126	A
16	1101	A	1099	A	1062	A	1077	A
17	1087	A	997	A	1063	A	992	A
18	1028	A	962	A	1003	A	951	A
19	895	A	894	A	883	A	872	A
20	782	A	764	A	776	A	739	A
21	640	A	694	A	637	A	635	A
22	582	A	604	A	589	A	588	A
23	538	A	454	A	517	A	447	A
24	338	A	328	A	342	A	343	A
25	266	A	239	A	335	A	268	A
26	177	A	171	A	128	A	124	A
27	69	A	36	A	59	A	45	A

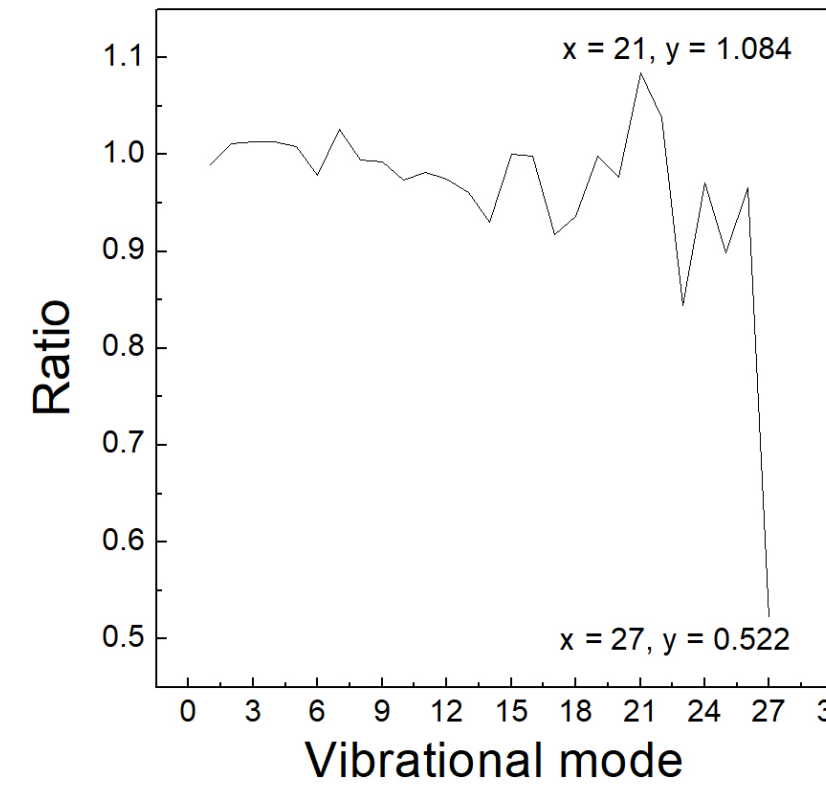


Fig. 7. The harmonic vibrational frequency variation diagram calculated by APFD/AVTZ.

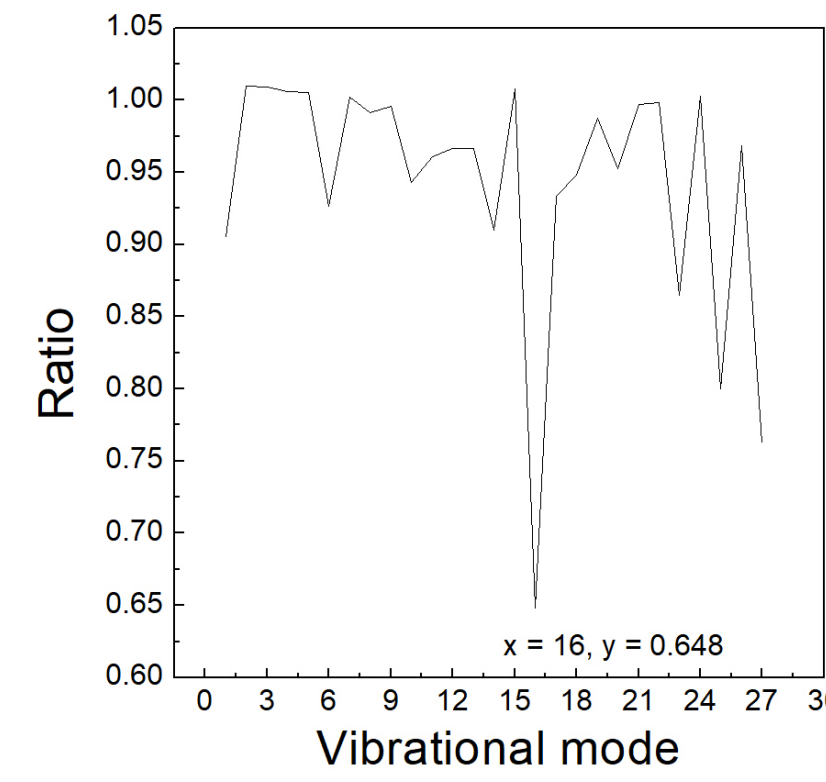


Fig. 8. The anharmonic vibrational frequency variation diagram calculated by APFD/AVTZ.

Franck-Condon factor

Table 4. The Franck-Condon factors calculated by M06-2X method.

C ₂ H ₅ (CHCO)→C ₂ H ₅ (CHCO) ⁺ +e ⁻					
Method			Method		
M062X(harmonic)			M062X(anharmonic)		
ΔE	FCF	State	ΔE	FCF	State
0	3.1252E-01	0 ⁰	-17	5.6606E-05	27 ^s
1007	2.0808E-02	17 ¹	0	2.4968E-01	0 ⁰
1103	7.1767E-02	16 ¹	2	1.7595E-02	27 ⁴
1289	3.0627E-02	13 ¹	17	5.4117E-02	27 ²
1372	4.8464E-02	12 ¹	985	1.6116E-02	17 ¹
2324	1.4944E-01	7 ¹	1092	5.6586E-02	16 ¹
3427	2.8507E-02	7 ¹ 16 ¹	1274	2.3961E-02	13 ¹
3696	1.9809E-02	7 ¹ 12 ¹	1346	3.8282E-02	12 ¹
4648	4.0154E-02	7 ²	2290	1.1797E-01	7 ¹
			2303	2.5568E-02	7 ¹ 27 ²
			3375	2.2165E-02	7 ¹ 16 ¹
			3629	1.5463E-02	7 ¹ 12 ¹
			4542	3.1191E-02	7 ²

Table 5. The Franck-Condon factors calculated by APFD method.

C ₂ H ₅ (CHCO)→C ₂ H ₅ (CHCO) ⁺ +e ⁻					
Method			Method		
APFD(anharmonic)			APFD(anharmonic)		
ΔE	FCF	State	ΔE	FCF	State
0	2.7988E-01	0 ⁰	0	2.8402E-01	0 ⁰
36	4.2747E-02	27 ¹	45	4.0120E-02	27 ¹
1099	6.0549E-02	16 ¹	1077	7.0600E-02	16 ¹
1288	2.8157E-02	13 ¹	1124	1.4554E-02	16 ¹ 27 ¹
1369	3.9366E-02	12 ¹	1265	2.6684E-02	13 ¹
2278	1.2062E-01	7 ¹	1326	3.8616E-02	12 ¹
2313	1.6137E-02	7 ¹ 27 ¹	2237	1.2277E-01	7 ¹
3377	2.1358E-02	7 ¹ 16 ¹	2280	1.4773E-02	7 ¹ 27 ¹
3647	1.4309E-02	7 ¹ 12 ¹	3313	2.6685E-02	7 ¹ 16 ¹
4555	2.9003E-02	7 ²	4448	2.8100E-02	7 ²

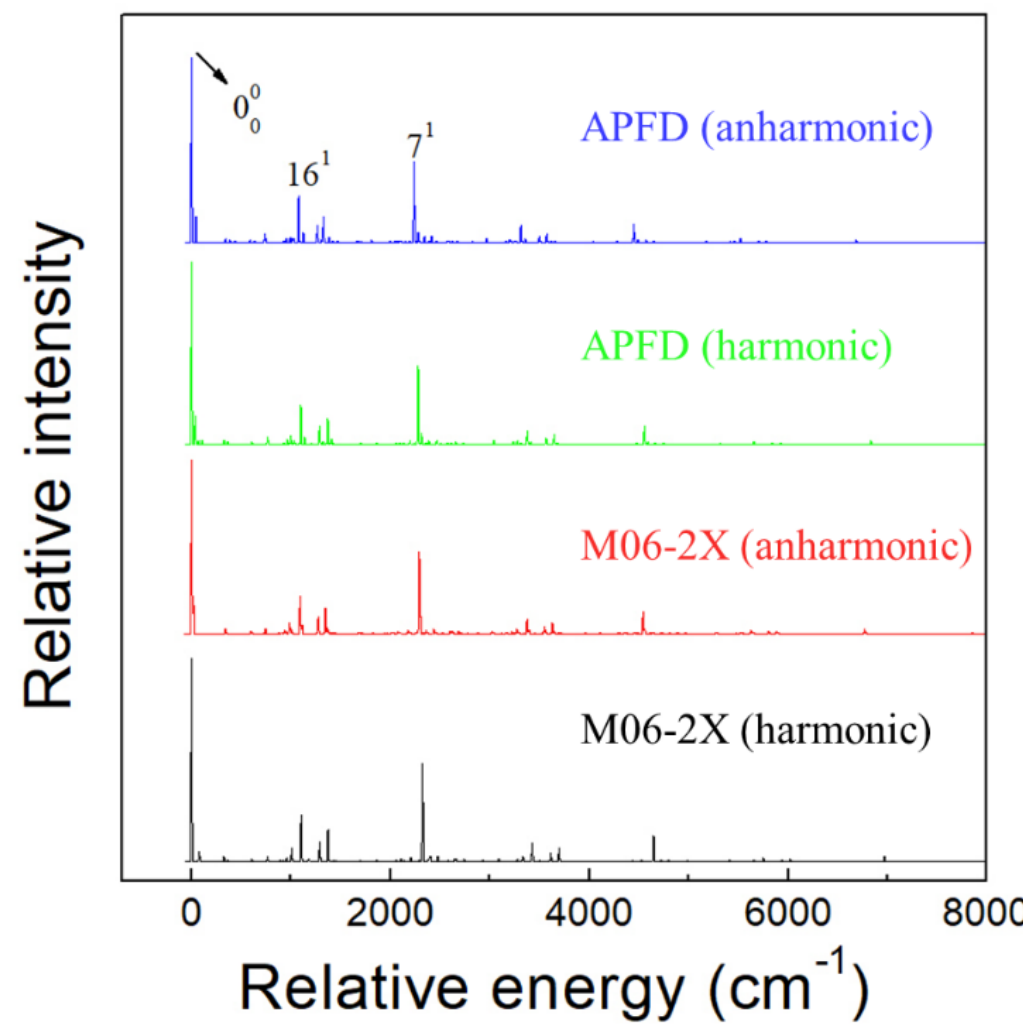


Fig. 9. The photoelectron spectra simulated by different methods.(FWHM=10 cm⁻¹)

Comparison

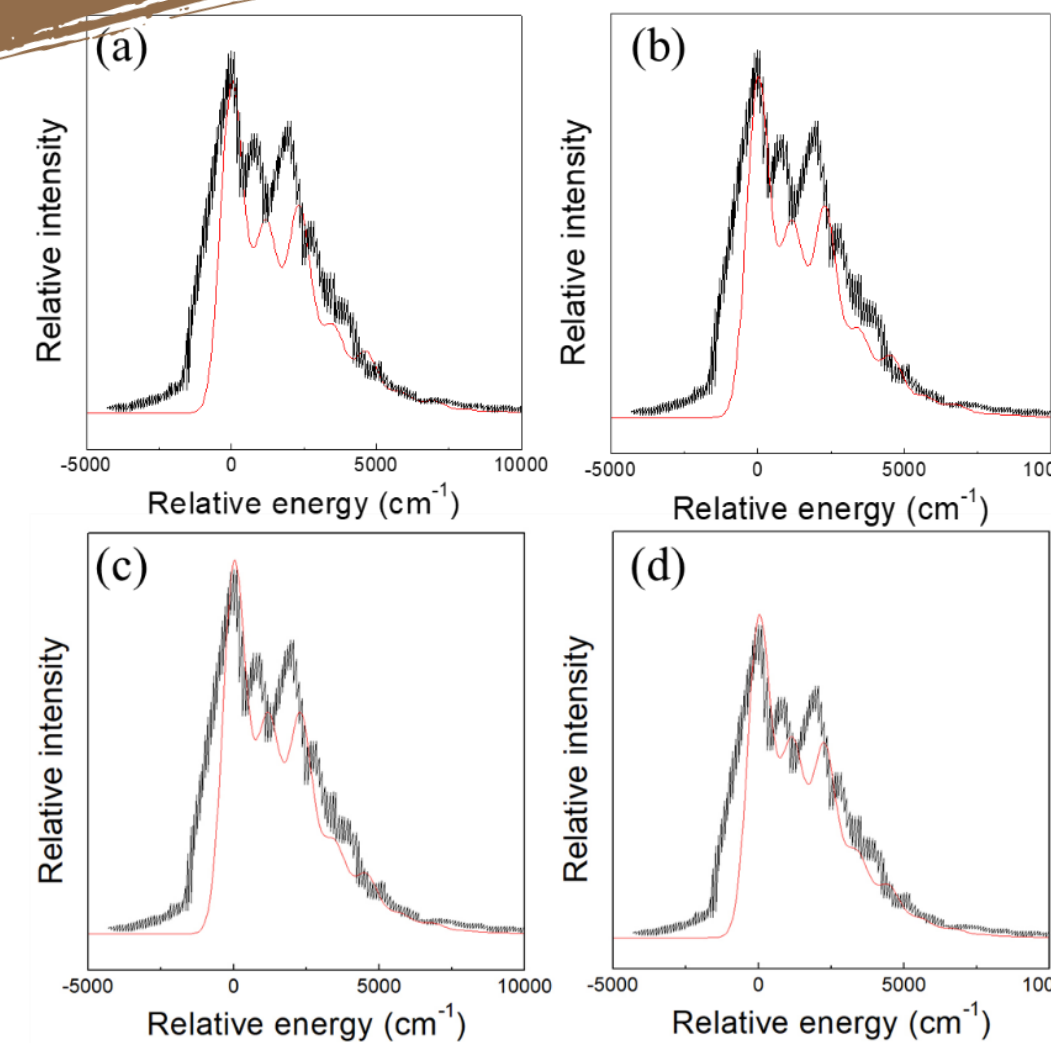


Fig. 10. The comparison plot between the photoelectron spectrum and experimental spectrum.(FWHM=900 cm⁻¹)
(a) M06-2X/harmonic · (b) M06-2X/anharmonic · (c) APFD/harmonic · (d) APFD/anharmonic

Conclusion

The equilibrium structure of ethylketene is changed only slightly upon ionization, leading to simple vibrational structures in its photoelectron spectrum. The simulated photoelectron spectra of ethylketene are consistent with the experimental spectrum.