Theoretical study of the photoelectron spectra of 1,3-Pentadiyne

科學教育與應用學系 陳怡茹
指導教授 張嘉麟 教授

Abstract

We used density functional theory B3LYP, PBE0, ωB97XD, and APFD methods with the aug-cc-pVTZ basis set to calculate the equilibrium structure and vibration frequency of the 1, 3-pentadiyne molecule and cation. We also calculated the Frank–Condon factor using the harmonic oscillator model developed in our laboratory. We then simulated the photoelectron spectrum of the 1, 3-pentadiyne molecule when it stripped electrons to form cations and compared it with the experimental spectrum.

Results and Discussion

Equilibrium Structures

Table 1. The equilibrium structures calculated by different methods.

	B3LYP		PBE0		ωB97XD		APFD	
Parameter	X	X+	X	X+	X	X+	X	X+
R(C1,H2)	109.16	110.24	109.24	110.32	109.00	109.12	109.27	110.36
R(C1,H3)	109.16	109.31	109.24	109.36	109.00	109.98	109.27	109.43
R(C1,H4)	109.16	109.32	109.24	109.43	109.00	109.14	109.27	109.44
R(C1,C5)	145.05	142.05	144.52	141.55	145.18	142.25	144.61	141.59
R(C5,C6)	120.69	123.58	120.69	123.61	120.12	123.18	120.69	123.61
R(C6,C7)	136.35	132.28	136.33	132.17	137.16	132.47	136.24	132.14
R(C7,C8)	120.54	122.67	120.52	122.71	120.00	122.24	120.56	122.75
R(C8,H9)	106.11	107.00	106.33	107.22	106.20	107.07	106.34	107.22
A(H2,C1,H3)	107.9	107.3	108.0	107.6	108.3	107.8	108.0	107.3
A(H2,C1,H4)	107.9	107.3	108.0	107.2	108.3	111.5	108.0	107.3
A(H2,C1,C5)	111.0	107.9	110.9	107.6	110.6	111.1	110.9	107.7
A(H3,C1,H4)	107.9	111.3	108.0	111.5	108.3	107.7	108.0	111.4
A(H3,C1,C5)	111.0	111.4	110.9	111.5	110.6	107.4	110.9	111.4
A(H4,C1,C5)	111.0	111.4	110.9	111.2	110.6	111.0	110.9	111.4

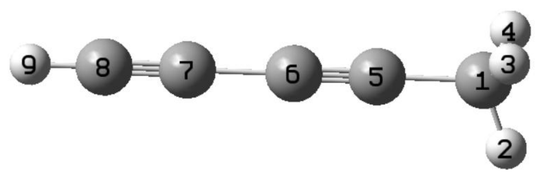

Fig. 1. The equilibrium structures of 1, 3-pentadiyne.

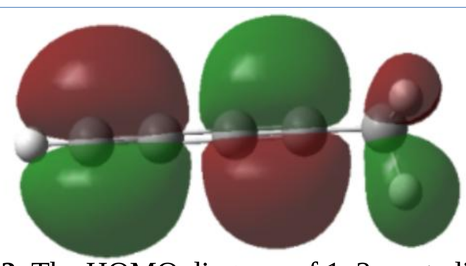

Fig. 2. The HOMO diagram of 1, 3-pentadiyne.

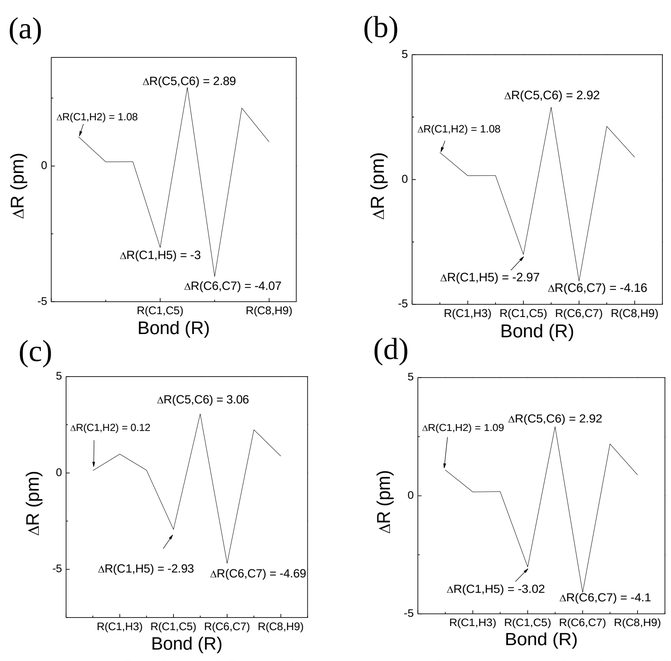

Fig. 3. The bond length variation diagram calculated by (a) B3LYP, (b) PBE0, (c) ωB97XD, (d) APFD.

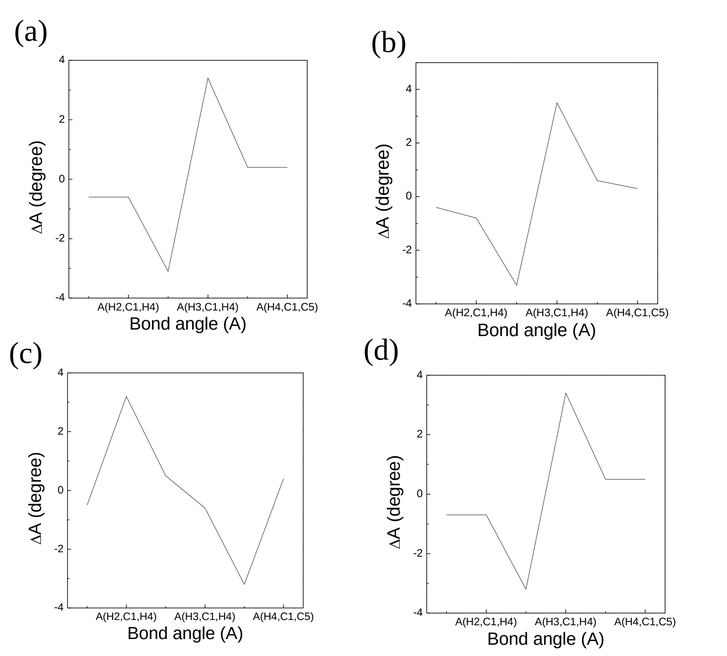

Fig. 4. The bond angle variation diagram calculated by (a) B3LYP, (b) PBE0, (c) ωB97XD, (d) APFD.

Vibrational Frequencies

Table 2. The harmonic vibrational frequency calculated by B3LYP, PBE0, ωB97XD, and APFD /aug-cc-pVTZ.

	B3LYP				PBE0				ωB97XD				APFD			
mode	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species	frequency	Symmetry species
	X		X+		X		X+		X		X+		X		X+	
1	3468	A	3383	A	3480	A	3393	A	3480	A	3393	A	3476	A	3390	A
2	3078	A	3044	A	3112	A	3084	A	3128	A	3104	A	3102	A	3070	A
3	3078	A	3040	A	3112	A	3066	A	3128	A	3088	A	3102	A	3059	A
4	3022	A	2958	A	3042	A	2982	A	3055	A	3001	A	3035	A	2972	A
5	2343	A	2285	A	2371	A	2313	A	2403	A	2343	A	2365	A	2307	A
6	2165	A	1997	A	2184	A	2009	A	2203	A	2017	A	2179	A	2006	A
7	1473	A	1433	A	1462	A	1423	A	1481	A	1443	A	1462	A	1422	A
8	1473	A	1349	A	1462	A	1339	A	1481	A	1364	A	1462	A	1337	A
9	1415	A	1286	A	1402	A	1282	A	1420	A	1321	A	1403	A	1278	A
10	1179	A	1229	A	1198	A	1246	A	1180	A	1233	A	1194	A	1242	A
11	1050	A	955	A	1039	A	940	A	1056	A	962	A	1039	A	937	A
12	1050	A	756	A	1039	A	755	A	1056	A	775	A	1038	A	754	A
13	680	A	694	A	690	A	703	A	682	A	697	A	688	A	701	A
14	645	A	643	A	657	A	654	A	682	A	677	A	653	A	651	A
15	645	A	516	A	657	A	528	A	681	A	639	A	653	A	518	A
16	529	A	514	A	533	A	510	A	538	A	516	A	531	A	512	A
17	529	A	455	A	533	A	464	A	538	A	497	A	531	A	458	A
18	340	A	347	A	344	A	347	A	346	A	348	A	341	A	346	A
19	340	A	261	A	344	A	266	A	346	A	310	A	341	A	260	A
20	147	A	139	A	148	A	139	A	147	A	141	A	147	A	138	A
21	147	A	138	A	148	A	136	A	147	A	138	A	147	A	136	A

Comparison

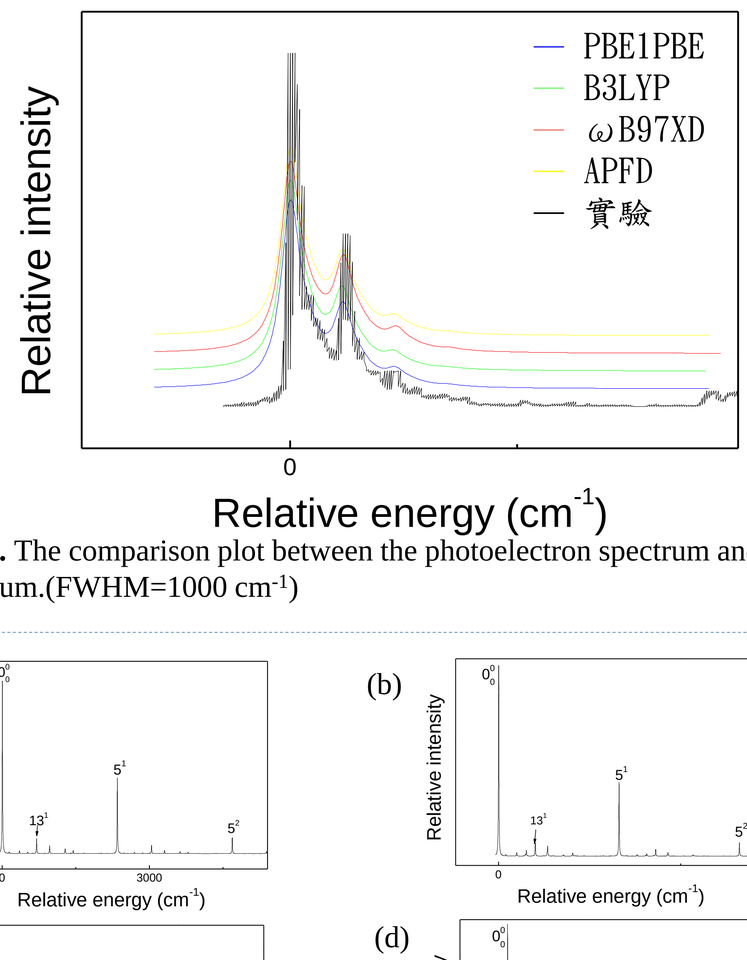

Fig. 5. The comparison plot between the photoelectron spectrum and experimental spectrum.(FWHM=1000 cm^{-1})

Franck-Condon Factor

Table 3. The Franck-Condon factors calculated by B3LYP, PBE0, ωB97XD, and APFD method.

$HC{\equiv}C-C{\equiv}C-CH_3 \rightarrow HC{\equiv}C-C{\equiv}C-CH_3^+ + e^-$

Method												
B3LYP			PBE0			ωB97XD			APFD		
ΔE	FCF	State	ΔE	FCF	State	ΔE	FCF	State	ΔE	FCF	State
0	4.8954E-01	0^0	0	4.8276E-01	0^0	0	4.9582E-01	0^0	0	4.8060E-01	0^0
347	7.2356E-03	18^1	347	9.0544E-03	18^1	348	8.5035E-03	18^1	346	8.9461E-03	18^1
522	1.6487E-02	19^2	533	1.4196E-02	19^2	516	4.9702E-03	16^1	512	4.9610E-03	16^1
694	3.3554E-02	13^1	703	3.3672E-02	13^1	697	4.3055E-02	13^1	519	1.6185E-02	19^2
910	7.5663E-03	17^2	928	5.6807E-03	17^2	962	2.2618E-02	11^1	701	3.3185E-02	13^1
955	2.3680E-02	11^1	940	2.5108E-02	11^1	1279	1.3250E-02	15^2	916	6.3144E-03	17^2
1433	8.7232E-03	7^1	1423	8.3584E-03	7^1	1443	8.8871E-03	7^1	937	2.4415E-02	11^1
2285	1.8106E-01	5^1	2313	1.8717E-01	5^1	2343	2.1745E-01	5^1	1422	8.1276E-03	7^1
2807	6.0978E-03	$5^1 19^2$	2846	5.5041E-03	$5^1 19^2$	3040	2.3843E-02	$5^1 13^1$	2307	1.8396E-01	5^1
2979	1.6221E-02	$5^1 13^1$	3017	1.7035E-02	$5^1 13^1$	3305	9.0679E-03	$5^1 11^1$	2826	6.1951E-03	$5^1 19^2$
3240	8.0505E-03	$5^1 11^1$	3253	8.9363E-03	$5^1 11^1$	3622	5.8112E-03	$5^1 15^2$	3008	1.6583E-02	$5^1 13^1$
4570	3.1744E-02	5^2	4626	3.4509E-02	5^2	4686	4.5624E-02	5^2	3244	8.5484E-03	$5^1 11^1$
						5383	6.2191E-03	$5^2 13^1$	4614	3.3436E-02	5^2
						7029	6.0874E-03	5^3			

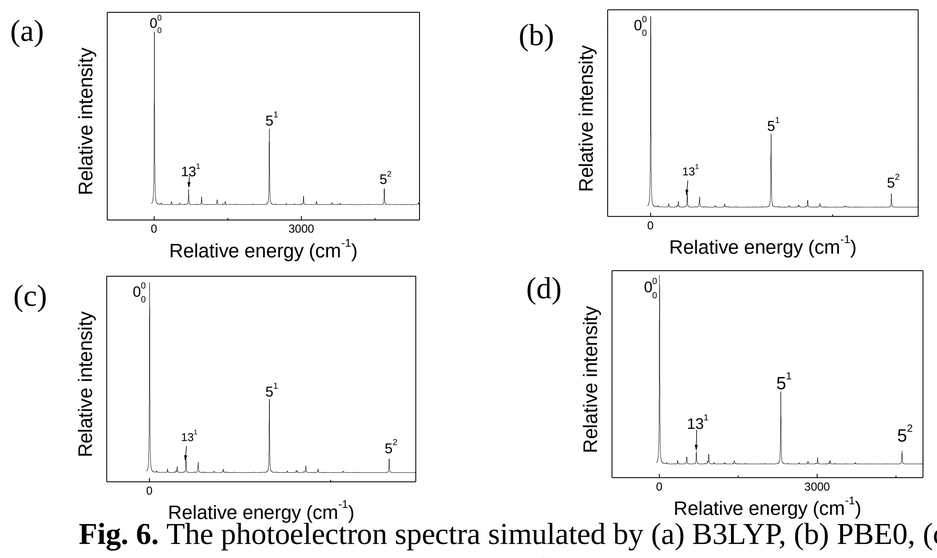

Fig. 6. The photoelectron spectra simulated by (a) B3LYP, (b) PBE0, (c) ωB97XD, (d) APFD.(FWHM=10 cm^{-1})

Conclusion

The simulated photoelectron spectrum of 1,3-pentadiyne is consistent with the experimental results. The harmonic oscillator hybrid model developed by our laboratory can be used as a research tool for theoretical spectroscopy.

References

1.Chang, J.-L.; Huang, C.-H.; Chen, S.-C.; Yin, T.-H.; Chen, Y.-T., An analytical approach for computing Franck-Condon integrals of harmonic oscillators with arbitrary dimensions. *Journal of Computational Chemistry* **2013**, *34*, 757-765.

2.Chang, J.-L.; Chen, H.-Y.; Huang, Y.-J., Reassignment of the Photoelectron Spectrum of Methylketene Using a Hybrid Model of Harmonic and Anharmonic Oscillators to Compute Franck–Condon Factors. *ACS Omega* **2023**, *8*, 40685-40694.

3.Brogli, F.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E., Die Photoelektronen-Spektren methyl-substituierter Acetylene. Helv. Chim. Acta 1973, 56 (7), 2171-2178.