

## Theoretical Study on the Structure and Vibrational Spectra for 4-methyl-3-penten-2-one

Dong Mei DU<sup>1</sup>, Ai Ping FU<sup>1</sup>, Zheng Yu ZHOU<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemistry, Qufu Normal University, Shandong, Qufu 273165

<sup>2</sup>State Key Laboratory of Crystal Materials, Shandong University, Shandong, Jinan 250100

**Abstract:** Density functional theory BLYP (using Becke's and Lee-Yang-Parr's correlation functionals), *ab initio* Hartree-Fock (HF) and hybrid DFT/HF B3LYP calculations were carried out to study the structure and vibrational spectra of 4-methyl-3-penten-2-one. The BLYP/6-31G\* and scaled HF/6-31G\* frequencies correspond well with each other and with available experimental assignment of the functional vibrational modes.

**Keywords:** Density functional theory, vibrational spectra, 4-methyl-3-penten-2-one.

The 4-methyl-3-penten-2-one is an important  $\alpha$ ,  $\beta$ -unsaturated ketone molecule and an important ligand of the organometallic compounds. Until now, some properties of photo-chemistry and excited states have been experimentally studied<sup>1-4</sup> and conformation of the molecule were also studied in experiments<sup>5,6</sup>. Standard infrared grating spectrum was also obtained in 1970<sup>7</sup>. However, there are no density functional theory (DFT) calculations of this molecule in the literature.

Recently, density functional theory has been accepted by the *ab initio* quantum chemistry community as a cost effective approach to molecular properties. Much effort has been devoted to refining the methodology and exploring the limits of its applicability<sup>8-11</sup>. In our previous study, we compared the calculated and experimental values of several frequencies of some small organic molecule<sup>12,13</sup>. It was found that the combination of Becke's exchange and Lee-Yang-Parr's correlation functionals (BLYP) reproduces the observed fundamental vibrational frequencies satisfactorily. The B3LYP frequencies are generally higher than observed fundamental frequencies, but appear to be closer to the available 'experimental' harmonic frequencies. In this paper, we calculate the harmonic frequencies of 4-methyl-3-penten-2-one using BLYP, HF and B3LYP methods and compare these results with experimental vibrational frequencies. It shows that since no 'experimental' harmonic frequencies are available for molecules of this size, the BLYP and scaled HF results are more useful for understanding the observed spectral features.

All calculations were carried out using the Gaussian 94 program package. The BLYP and B3LYP calculations used Becke's exchange functional and Lee-Yang-Parr's correlation functional (BLYP) was transformed by Miehlich *et al.*<sup>14</sup>. To help interpret observed spectral feature and to compare, we also calculated the vibrational frequencies by the *ab initio* HF method. The 6-31G\* basis set was used throughout. All molecular structures were fully optimized by gradient technique and confirmed by

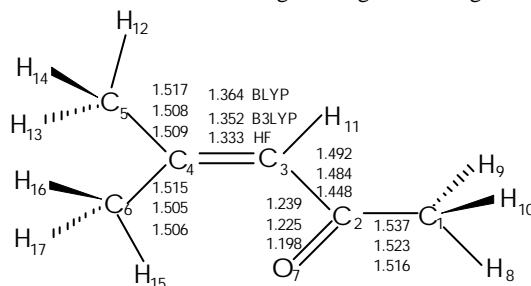
analytic second derivative calculations and vibrational analysis.

## Results and discussion

### 1. Geometric structure

4-methyl-3-penten-2-one belongs to  $C_s$  point group. A comparison of the calculated CC and CO bond lengths of 4-methyl-3-penten-2-one by different methods is presented in **Figure 1**. From experimental values of literature<sup>15</sup>, C–C single bond length is  $1.507 \text{ \AA}$  and C=O double bond length is  $1.22 \text{ \AA}$  for acetone; C=C double bond length of propene is  $1.318 \text{ \AA}$ . Taking account of the effect of conjugation, our calculated values of 4-methyl-3-penten-2-one molecule is in reasonable agreement with the above-mentioned experimental data. The HF/6-31G\* bond lengths are slightly shorter, while the BLYP/6-31G\* bond lengths are slightly longer than those found from experiments. This indicates that the BLYP method slightly exaggerated electron correlation effect while the HF theory neglected this effect. The results of hybrid DFT/HF B3LYP/6-31G\* are in good agreement with the experimental values.

**Figure 1.** Comparison of the calculated structure parameters of 4-methyl-3-penten-2-one by different methods. The bond lengths are given in Angstroms.



### 2. Vibrations

Under  $C_s$  point group, the 45 fundamental vibrational modes of 4-methyl-3-penten-2-one are distributed into the following symmetry species:  $28A' + 17A''$ . A comparison of harmonic vibrational frequencies calculated by BLYP, B3LYP and HF with the observed fundamental vibrational frequencies is given in **Table 1**. Mode descriptions given in this **Table** are based on total vibrational energy distribution calculated by using the BLYP force field. To account for errors due to neglecting electron correlation and basis set incompleteness, the HF/6-31G\* frequencies have been scaled by 0.8900. The scaled HF/6-31G\* frequencies of non-CH stretching modes correspond well with BLYP/6-31G\* and the observed results, indicating that the density functional theory recovers electron correlation effectively. Larger variations between the BLYP and scaled HF frequencies were found for the CH stretching vibrations. It appears that the scaled HF results of the CH stretching vibrations are closer to the observed results. Anharmonicity may partially contribute to this, as CH stretching vibrations appear more anharmonic. On the other hand, CH stretching vibrations are much higher than other fundamental modes and they are less important than modes of the fingerprint region for chemical analysis.

The mean absolute deviations between the observed non-CH stretching frequencies and the BLYP, B3LYP and scaled HF results are  $10.4 \text{ cm}^{-1}$ ,  $38.3 \text{ cm}^{-1}$  and  $17.9 \text{ cm}^{-1}$ , respectively. It indicates that both the BLYP and scaled HF calculations reproduce the observed fundamental

**Table 1** Calculated and experimental<sup>7</sup> frequencies for 4-methyl-3-penten-2-one

No.	Sym.	BLYP	B3LYP	HF(scal.)	Exp.(IR)	Exp.(Ram)	Assignment
45	A'	3115	3204	3014			Asym. CH <sub>3</sub> stretch
44	A'	3084	3168	2971	3003w sh	3012s sh	CH stretch
43	A'	3063	3154	2958	2978w	2981	Asym. CH <sub>3</sub> stretch
42	A'	3047	3132	2930	2939w		Asym. CH <sub>3</sub> stretch
41	A''	3013	3101	2902			Asym. CH <sub>3</sub> stretch
40	A''	2993	3081	2892	2914w	2914s	Asym. CH <sub>3</sub> stretch
39	A''	2986	3073	2879			Asym. CH <sub>3</sub> stretch
38	A'	2962	3045	2852			Sym. CH <sub>3</sub> stretch
37	A'	2954	3037	2849	2855		Sym. CH <sub>3</sub> stretch
36	A'	2948	3030	2842			Sym. CH <sub>3</sub> stretch
35	A'	1691	1779	1768	1689s	1688w	C=O stretch
34	A'	1616	1690	1647	1619s	1618m	C=O stretch
33	A''	1499	1536	1470		1482	Asym. CH <sub>3</sub> deform
32	A'	1478	1417	1456			Asym. CH <sub>3</sub> deform
31	A''	1468	1505	1444			Asym. CH <sub>3</sub> deform
30	A''	1467	1504	1442			Asym. CH <sub>3</sub> deform
29	A'	1459	1497	1440	1449s	1448m	Asym. CH <sub>3</sub> deform
28	A'	1454	1494	1435			Asym. CH <sub>3</sub> deform
27	A'	1440	1443	1398	1425m sh		Sym. CH <sub>3</sub> deform
26	A'	1392	1437	1395			Sym. CH <sub>3</sub> deform
25	A'	1370	1411	1377	1380m	1378w	Sym. CH <sub>3</sub> deform
24	A'	1363	1404	1357	1357m		CH in-plane
23	A'	1211	1256	1201	1220m		CH <sub>3</sub> rock
22	A'	1159	1201	1156	1166m	1172vw	CH in-plane
21	A''	1089	1122	1089			CH <sub>3</sub> rock
20	A'	1079	1122	1068	1069w	1070vw	CH <sub>3</sub> rock
19	A''	1018	1053	1028			CH <sub>3</sub> rock
18	A''	991	985	1019 <sub>w</sub>			CH out-of-plane
17	A'	948	981	950	965m	864w	CH <sub>3</sub> rock
16	A'	940	970	929			CH <sub>3</sub> rock
15	A'	886	920	875	900w		CH out-of-plane
14	A''	837	862	834	822w	817w	C-C stretch
13	A'	802	831	783			C-C stretch
12	A'	606	629	603	622w	622w	C-C stretch
11	A''	585	604	583			C-C stretch
10	A''	454	467	449	459w		C-C deform
9	A'	429	441	417			CH deform
8	A'	368	377	356			C-C deform
7	A'	331	340	322			C-C deform
6	A'	210	215	200			C-C deform
5	A''	202	209	199			C-C deform
4	A''	146	150	141			CH <sub>3</sub> twist
3	A''	104	113	124			CH <sub>3</sub> twist
2	A''	98	97	124			CH <sub>3</sub> twist
1	A''	60	55	31			CH <sub>3</sub> twist

Scaling factor = 0.8900; w, m, sh, s, v = weak, middle, shoulder, strong, very.

frequencies satisfactorily. It should be pointed out that these results do not mean BLYP is a better theoretical method than B3LYP. There have been many theoretical studies indicating that B3LYP yields superior results for many molecular properties. The small deviation between the BLYP and observed frequencies may be a result of error

cancellation. As BLYP slightly exaggerates electron correlation effects and gives longer bond distances, it tends to underestimate harmonic vibrational frequencies. On the other hand, the observed fundamental vibrational frequencies are generally lower than true harmonic frequencies because of the anharmonic nature of molecular vibrations.

Therefore, the high level of conformity between the observed and calculated spectral features indicates that BLYP, without any empirical adjustment, is a more straightforward and practical approach to deduce the observed fundamental vibrational frequencies for many molecules whose vibrational spectra are not well understood.

### Conclusions

We have carried out density functional and *ab initio* calculations on the structure and vibrational spectrum of 4-methyl-3-penten-2-one. The calculated bond lengths of carbon skeleton are in reasonable agreement with the experimental data. Harmonic vibrational frequencies of the non-CH stretching calculated by both BLYP/6-31G\* and scaled HF/6-31G\* corresponding well with each other and with the observed frequencies. A high level of conformity between the BLYP/6-31G\* and experimental results indicates that the density functional theory is a very promising method for molecular vibrational analysis.

### Acknowledgments

This work was supported by the Natural Science Foundation of Shandong Province, the National Key Laboratory Foundation of Crystal Material and the National Natural Science Foundation of China (2967305)

### References

1. R. Ricard, P. Sauvage, *J. Org. Chem.* **1986**, *51*, 62.
2. R. M. Duhaim, A. C. Weedon, *J. Am. Chem. Soc.* **1987**, *109*, 2479.
3. A. Bienrenue, *J. Am. Chem. Soc.* **1973**, *95*, 7345.
4. A. C. Weedon, D. F. Wong, *J. Photochem.* **1987**, *38*, 289.
5. G. Montaudo, V. Librando, *J. Am. Chem. Soc.* **1978**, *95*, 6365.
6. F. A. Carey, R. Sundberg, *Advanced Organic Chemistry*, Part A, Plenum Press in New York and London, **1990**.
7. Sadtler Research Laboratory, Inc. Sadtler Standard Spectra, *Commercial Composite Infrared Indexes*, ISOOIK, **1978**.
8. B. G. Johnson, P. M. W. Gill and J. A. Pople, *J. Chem. Phys.*, **1993**, *98*, 5612.
9. N. C. Handy, C. W. Murry, R. D. Amos, *J. Phys. Chem.*, **1993**, *97*, 4392.
10. X. F. Zhou, J. A. Krauser, D. R. Tate, A. S. Vanburen, *J. Phys. Chem.*, **1996**, *100*, 16822.
11. J. Higgins, X. F. Zhou, R. F. Liu, T. S. Huang, *J. Phys. Chem.*, **1997**, *A101*, 2702.
12. A. P. Fu, D. M. Du and Z. Y. Zhou, *Chin. Chem. Lett.*, in press.
13. Z. Y. Zhou, D. M. Du and A. P. Fu, *Chem. Phys. Lett.*, to be published.
14. B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, **1989**, *157*, 200.
15. W. J. Hehre, J. A. Pople, P. V. R. Schleyer and L. Radom, *ab initio molecular Orbital Theory*, Wiley, New York, **1986**.

Received 9 May 1999