

Theory Study on Structures and Vibrational Frequencies of Pyruvic acid

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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 pyruvic acid. The scaled B3LYP/6-31G* frequencies correspond well with available experimental assignment of the functional vibrational modes and the mean absolute deviation is only 12.3cm⁻¹.

Keywords: Density functional theory, vibrational spectra, pyruvic acid.

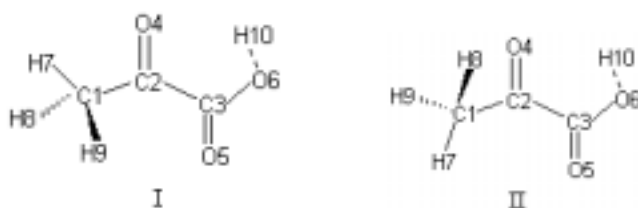
A number of theoretical studies exist for pyruvic acid. It has been studied at the semi empirical INDO and AM1 level^{1,2}. At the *ab initio* level studies of pyruvic acid range from the calculation of energies at the STO-3G level⁴ to calculations of energies using the HF/3-21G³, HF/4-21G⁵, HF/6-31G* and MP2/4-21G methods. Except for the study of Murto *et al.*, all the studies have focussed on the energies and geometries of pyruvic acid. Moreover all the existing theoretical studies have focused their attention on the orientation of the carboxyl hydrogen extensively. The orientation of the methyl group has only been dealt with by van Alsenoy *et al.*⁵ and Norris *et al.*³. The normal coordinate analysis of pyruvic acid has been done by Hollenstein *et al.*⁶ based on the microwave structure of pyruvic acid⁷. They had assigned the gas phase frequencies of pyruvic acid.

Recently, density functional theory (DFT)⁸ 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 applicability⁹. In the recent theoretical studies^{10,11}, the harmonic vibrational frequencies for a large number of molecules were computed with Hartree-Fock, Moller-Plesset and Density functional methods. On the basis of a comparison of computed and observed fundamental vibrational frequencies, the scaled B3LYP method was found to be more reliable than other ones. In the present study we have, therefore, calculated the geometries and the vibrational frequencies of two conformations (**Figure 1**) (eclipsed and staggered with respect to the methyl group) using BLYP, B3LYP and HF methods. The calculated geometries and vibrational frequencies have been compared with the experimental data.

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 correlation functional (BLYP) as transformed by Miehlich *et al.*⁷. To help interpret

observed spectral features and for comparison, we also calculated the vibrational frequencies by the *ab initio* HF and MP2 methods. The 6-31G* basis set was used in the calculations.

Figure 1. Conformers I and II of pyruvic acid.



Results and discussion

Structural parameters of pyruvic acid calculated by BLYP, B3LYP and HF methods are compared with the experimental microwave data in **Table 1**. Numbers of atoms referred to in **Table 1** is given in **Figure 1**. From **Table 1**, we can see that there is a slight overestimation of the single bond lengths and underestimation of the double bond lengths. Although of this, the present calculated geometries are in reasonable agreement with the experimental data. All of the HF/6-31G* bond lengths but the C–C

Table 1 The geometric data for pyruvic acid (bond length in Å and angle in degree) and the energies in hartree of the different conformers.

| parameter | BLYP (I) | B3LYP (I) | HF (I) | Exp. | BLYP (II) | B3LYP (II) | HF (II) |
|-----------|------------|------------|------------|-------|------------|------------|-------------|
| C2=O4 | 1.234 | 1.219 | 1.192 | 1.231 | 1.234 | 1.220 | 1.192 |
| C1–C2 | 1.508 | 1.499 | 1.498 | 1.486 | 1.513 | 1.502 | 1.502 |
| C2–C3 | 1.562 | 1.545 | 1.539 | 1.523 | 1.564 | 1.551 | 1.541 |
| C3=O5 | 1.220 | 1.207 | 1.181 | 1.215 | 1.220 | 1.207 | 1.181 |
| C3–O6 | 1.356 | 1.337 | 1.314 | 1.328 | 1.355 | 1.337 | 1.314 |
| C1–H7 | 1.098 | 1.091 | 1.080 | 1.074 | 1.097 | 1.090 | 1.078 |
| C1–H8 | 1.104 | 1.096 | 1.084 | 1.106 | 1.103 | 1.096 | 1.084 |
| O6–H10 | 0.997 | 0.983 | 0.954 | 0.983 | 0.997 | 0.983 | 0.954 |
| ∠C3C2O4 | 117.2 | 117.7 | 117.6 | 117.0 | 117.3 | 117.2 | 117.2 |
| ∠C1C2O4 | 125.0 | 125.3 | 125.2 | 124.4 | 124.6 | 124.7 | 124.1 |
| ∠C2C3O5 | 123.6 | 123.1 | 122.1 | 122.0 | 123.9 | 123.4 | 122.5 |
| ∠C2C3O6 | 111.9 | 112.3 | 113.6 | 114.5 | 111.7 | 112.0 | 113.3 |
| ∠H7C1C2 | 110.4 | 110.1 | 109.4 | 110.7 | 111.2 | 111.3 | 111.9 |
| ∠H8C1C2 | 109.8 | 109.8 | 109.8 | 109.0 | 109.2 | 109.1 | 108.6 |
| ∠H10O6C3 | 105.9 | 106.1 | 109.6 | 105.2 | 104.8 | 106.0 | 109.6 |
| Energy | -342.32016 | -342.39902 | -340.53060 | | -342.31912 | -342.39791 | -340.529112 |

and C1–H7 bond lengths appear to be slightly shorter than the experimental data, while all the BLYP/6-31G* bond lengths but the C1–H8 bond length are slightly longer. This indicates that the BLYP method slightly exaggerated electron correlation effect while the HF theory neglected this effect. Compared with the experimental values, the B3LYP/6-31G* bond lengths are the best. Though all the bond lengths are nearly the

same in both the conformations, it is of interest to note that two C–C single bond lengths in conformer I are shorter than the corresponding bond lengths in conformer II. The energy of conformer I is much lower than conformer II, which indicates that conformer I is more stable than conformer II.

Vibrational frequencies

Pyruvic acid molecule belongs to C_s point group, the 24 normal modes are in two symmetries as A' and A'' . An evaluation of the vibrational frequencies of both the conformations yielded imaginary frequencies for the staggered conformation indicating that it is not a minima in the potential energy hypersurface of pyruvic acid. The upper discussion in the structure also confirms this. Therefore only the vibrational frequencies of the eclipsed conformation have been used in the subsequent vibrational analysis. A comparison of harmonic vibrational frequencies calculated by BLYP, B3LYP and HF with the experimental vibrational fundamental vibrational frequencies is given in **Table 2**. From the table, we can see larger variation between the calculated and experimental frequencies were found for the CH and OH stretching vibrations. Anharmonicity may partially contribute to this, as CH and OH stretching vibrations appear more anharmonic. On the other hand, CH and OH 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 and OH stretching frequencies and the raw BLYP, B3LYP and scaled HF results are 18.9, 33.65 and 114.45cm^{-1} , respectively. It indicates that the raw BLYP and B3LYP calculations approximate the observed fundamental frequencies much better than the HF results. On the other hand, it is well known that the difference between the experimental and calculated results arise from the presence of systematic errors due to neglect of anharmonic effects, electronic correlation and because of basis set deficiencies. Though BLYP and B3LYP methods do account for certain electronic correlation effects, but they still involve errors due to the anharmonic effects and basis set deficiencies. Then it is obvious that the use of scaled factors will further improve the agreement between the DFT calculated and observed fundamental vibrational frequencies. When scaled factors are considered (0.89, 0.94, 0.99 and $0.96^{8,9}$ for HF/6-31G*, MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* respectively), the mean absolute deviations between the observed non-CH and OH stretching frequencies and scaled BLYP, B3LYP and HF results are 25.6, 23.2, 19.4 and 12.3cm^{-1} . The performance of scaled B3LYP is found to be much superior to that of HF and BLYP. We consider the relatively small deviation between the raw 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 scaled B3LYP, is a more straightforward and practical

approach to deduce the observed fundamental vibrational frequencies for many molecules whose vibrational spectra are not well understood

Table 2. Calculated and experimental frequencies for pyruvic acid.

| Sym. | No. | Exp. | BLYP | B3LYP | HF | assignment |
|------|-----|------|------|-------|------|----------------------------|
| A' | 1 | 3432 | 3350 | 3553 | 4014 | OH stretch |
| | 2 | 3033 | 3096 | 3180 | 3337 | Asym CH3 stretch |
| | 3 | 2936 | 2983 | 3065 | 3229 | Sym CH3 stretch |
| | 4 | 1800 | 1779 | 1873 | 2083 | C=O stretch |
| | 5 | 1729 | 1704 | 1802 | 2023 | C=O stretch |
| | 6 | 1424 | 1446 | 1483 | 1601 | CH3 in-plane |
| | 7 | 1384 | 1377 | 1431 | 1574 | CO str. +COH in-plane |
| | 8 | 1355 | 1346 | 1410 | 1541 | CH3 in-plane |
| | 9 | 1214 | 1210 | 1264 | 1374 | COH in-plane |
| | 10 | 1137 | 1115 | 1172 | 1274 | C–O stretch + C–C stretch |
| | 11 | 969 | 954 | 990 | 1078 | CH3 in-plane |
| | 12 | 762 | 731 | 771 | 849 | COO in plane + C–C stretch |
| | 13 | 604 | 585 | 607 | 655 | CCC wag. + COO in-plane |
| | 14 | 535 | 504 | 518 | 582 | COO wag + CCC in-plane |
| | 15 | 388 | 386 | 400 | 430 | CCC wag + COO in-plane |
| | 16 | 258 | 248 | 256 | 277 | CCC in-plane + COO wag |
| A'' | 1 | 3033 | 3034 | 3122 | 3294 | Asym CH3 stretch |
| | 2 | 1406 | 1447 | 1485 | 1607 | CH3 in-plane |
| | 3 | 1017 | 1004 | 1040 | 1149 | CH3 I-plane |
| | 4 | 720 | 753 | 754 | 797 | CCC + COO out-of-plane |
| | 5 | 664 | 663 | 691 | 688 | CO torsion |
| | 6 | 394 | 372 | 391 | 439 | COO + CCC out-of-plane |
| | 7 | 134 | 116 | 120 | 131 | CC torsion |
| | 8 | 119 | 88 | 92 | 92 | CC + CO torsion |

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