

**VIBRATIONAL SPECTROSCOPIC STUDY OF ACETATE GROUP****Medhat Ibrahim<sup>a</sup> and Eckhard Koglin<sup>b</sup>**<sup>a</sup> *Spectroscopy Department, National Research Center, Dokki, Cairo, Egypt*<sup>b</sup> *Institute of Physical Chemistry, Juelich Research Center, D52425, Germany**Received 12-01-2004***Abstract**

Density functional theory (DFT) was used to investigate both the structure and vibrational frequencies of acetate group. A model of B3LYP with four basis set is used to optimize and locate the energy minimum of the acetic acid molecule. The results obtained of both bond lengths and bond angles showed that B3LYP/6-31G(d,p) gave the optimal structure of acetate in acetic acid molecule. Vibrational frequencies of acetic acid at the same level of theory are calculated with assignment of each band frequency. The model B3LYP/6-31G(d,p) was used to calculate the characteristic C=O stretching of acetate group in case of acetic acid dimer, aceto-benzoic acid and aceto-polyacrylic acid respectively.

**Key words:** molecular modeling, DFT, vibrational spectra, acetate group

**Introduction**

The calculation of vibrational frequencies by computational methods is becoming increasingly important in many areas.<sup>1</sup> Molecular orbital theory was used to predict the Infrared and Raman spectra of small molecules in their ground electronic states.<sup>2</sup> The calculations were partly satisfactory as they are quite expensive, they almost invariably use the harmonic approximation, and they usually yield vibrational frequencies that need to be scaled by empirical factors in order to bring them into line with experimental measurements.<sup>1</sup> On the other hand, vibrational frequencies for species in complex environment can be computed by the combination of quantum-chemical calculations with classical molecular dynamics MD simulations.<sup>3,4</sup> The unsatisfactory state of these kinds of calculations was corrected by Density Functional Theory, DFT. DFT is concerned with predicting the properties of atomic and molecular systems.<sup>5</sup>

The infrared spectra of acetate have been studied by many researchers. Vibrational assignment of acetate ions has been obtained.<sup>6</sup> A comparison of the Fe(II) acetate spectra with sodium acetate suggests that the compound does not contain acetate ions in solid state and is best described as partly dissociated bisacetateiron (II) species.<sup>7</sup> The

correlation between the vibrational frequencies of acetate group and the types of its coordination to a metal ion<sup>8</sup> was studied. The study showed that, the frequency of COO<sup>-</sup> asymmetric stretching of the unidentate species is higher than that of ionic species and in turn higher than that of bidentate species. Acetic acid has been a subject of extensive investigation for many years. A self-consistent field study was conducted to investigate the electronic structure of acetic acid in aqueous solutions.<sup>9</sup> Both Raman and ab initio calculation were used to study the liquid structure of acetic acid.<sup>10</sup> It is stated that, the anti-conformer is less stable than the syn-conformer in gas phase. The vibrational spectrum of acetic acid monomer was studied.<sup>11</sup> A comprehensive discussion of the infrared intensity between 1150 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> was made. Electronic structures of acetic acid dimers were investigated,<sup>12</sup> in case of aqueous solution. The bond length of both C=O and O-H are long as compared with gas phase dimer. The intermolecular O-H...O=C hydrogen bonding became shorter; in addition the linear dimer was the most stable among other dimers. Harmonic vibrational analysis at HF/3-21G level was performed<sup>13</sup>, on the optimized structure of bis (*N,N*-dimethylthiocarbamoylthio) acetic acid. It was found that, the model of HF/3-21G predicts the mid-infrared spectrum of bis (*N,N*-dimethylthiocarbamoylthio) acetic acid with reasonable accuracy. The model of B3LYP/6-31G(d,p) was used to analyze five of the most stable conformers of 1-piperidineacetic acid and four of its monohydrate.<sup>14</sup>

This work presents DFT calculations for acetate group. Acetic acid is optimized at B3LYP with four basis set. The characteristic band C=O stretching is calculated for the optimized structure of acetic acid dimer, aceto-benzoic acid and aceto-polyacrylic acid.

### Results and discussion

Acetic acid is one of the simplest structures at which acetate can be found. The infrared spectrum of acetic acid solution is presented in Figure 1. The characteristic band of acetate group is C=O stretching which appears at 1709.0 cm<sup>-1</sup> in solution phase. The same band C=O is obtained at 1788.0 cm<sup>-1</sup> for acetic acid in the gas phase.<sup>15</sup> The acetate group is studied in case of acetic acid monomer, its optimised structure is shown in Figure 2a.

Geometry optimization predicts the equilibrium structure of the molecular system. The values of bond length in angstroms, and bond angles in degrees are presented in

Table 1. The optimization is achieved at B3LYP with four basis sets. The first basis set is 6-311G(d), which specifies the 6-311 with the polarization function d, it gives better results with neutral molecules. The second is 6-31G(d,p) it is a polarized basis set which adds d-function to heavy atoms and p-function to hydrogen atoms. Both LANL1DZ and LANL1MB are used for atoms beyond the third row of the periodic table.

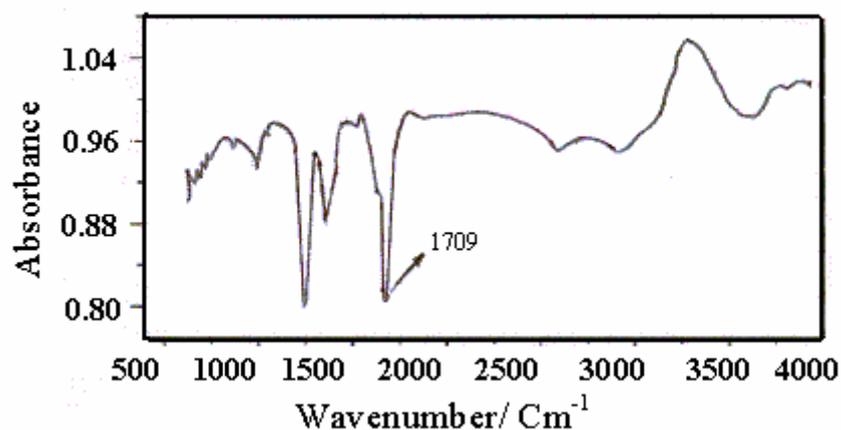


Figure 1. Infrared spectrum of acetate group in case of acetic acid solution.

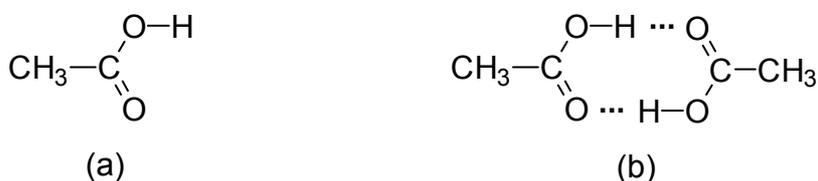


Figure 2. Structure of acetate group in case of a- acetic acid monomer and b- acetic acid cyclic dimer.

The results are compared with Hartree Fock HF, with Dunning- Huzinaga full double zeta basis set, HF/D95(d,p). Table 1 presents five bond lengths in angstroms determined experimentally.<sup>11,16</sup> The values of bond lengths  $L_{C-C}$ ,  $L_{C-H}$ ,  $L_{C-O}$ ,  $L_{C=O}$  and  $L_{O-H}$  are 1.52 Å, 1.102 Å, 1.364 Å, 1.214 Å and 0.970 Å respectively. The experimental angles of  $\angle_{C-C-O}$ ,  $\angle_{C-C=O}$ ,  $\angle_{O-C=O}$  and  $\angle_{C-C-H}$  are 113.0°~128.0°, 126.6°, 122.0°~128.0° and 107.0°, respectively. Both experimental and Hartree Fock results are used for comparison with DFT results. Generally Hartree Fock gave fairly good agreement with the experimental optimized parameters. The basis set 6-311G showed also fair agreement with experimental results. Optimized parameters of LANL1DZ basis set are

lower than those obtained with LANL1MB basis set. The basis set 6-31G(d,p) gave optimized parameters, which are in a good agreement with experimental data in one hand and better than Hartree Fock in the other hand.

From geometry optimization point of view, one can conclude that, the model B3LYP with the basis set 6-31G(d,p) is an explorer model for studying acetic acid structure.

**Table 1.** Optimized geometry of acetic acid monomer at B3LYP with different basis sets.

	Bond Distance (Å)					Exp
	6-311(G)	6-31G(d,p)	LANL1MB	LANL1DZ	HF/D95	
L <sub>1,2</sub>	1.4954	1.5204	1.5587	1.5071	1.5511	1.520 <sup>a</sup>
L <sub>1,5</sub>	1.0850	1.0939	1.1017	1.0958	1.0888	
L <sub>1,6</sub>	1.0902	1.0938	1.1017	1.0958	1.0887	
L <sub>1,7</sub>	1.092	1.0938	1.0997	1.0912	1.0861	1.102 <sup>a</sup>
L <sub>2,3</sub>	1.3841	1.3592	1.4255	1.3933	1.2402	1.364 <sup>a</sup>
L <sub>2,4</sub>	1.2300	1.2152	1.2516	1.2390	1.2381	1.214 <sup>a</sup>
L <sub>3,8</sub>	0.9771	0.9686	1.0296	0.9846	0.949	0.970 <sup>b</sup>

	Bond Angles (deg)					Exp
	6-311(G)	6-31G(d,p)	LANL1MB	LANL1DZ	HF/D95	
A <sub>2,1,5</sub>	109.48	109.61	110.11	109.84	109.33	
A <sub>2,1,6</sub>	110.17	109.65	110.11	109.85	109.35	
A <sub>2,1,7</sub>	110.16	109.98	109.52	109.72	111.79	
A <sub>5,1,6</sub>	109.85	107.22	108.37	107.47	109.62	
A <sub>5,1,7</sub>	109.85	109.61	109.35	109.96	109.59	
A <sub>6,1,7</sub>	107.30	110.19	109.35	109.97	107.05	
A <sub>1,2,3</sub>	111.47	113.28	109.73	111.15	114.64	113 ~ 128 <sup>b</sup>
A <sub>1,2,4</sub>	126.70	125.38	127.98	127.21	116.21	126.6 <sup>a</sup>
A <sub>3,2,4</sub>	121.84	123.69	122.29	121.65	129.16	122 ~ 128 <sup>b</sup>
A <sub>2,3,8</sub>	110.35	106.65	101.78	110.64	108.93	107.0 <sup>b</sup>

<sup>a</sup> From reference 16. <sup>b</sup> From reference 11.

The vibrational Infrared frequencies were calculated for acetic acid at B3LYP/6-31G(d,p) level of theory. Acetic acid contains 8 atoms so that, it has 18 normal modes. The calculated normal modes are distributed among twelve A' and six A'' species of the C<sub>s</sub> symmetry group. For each of these modes, the infrared intensity, frequency, force constant and assignment are obtained in Table 2.

From the calculated frequencies the higher intensities correspond to the bands OCO deformation, CH<sub>3</sub> rock, C-O stretch and finally C=O stretching, with band

frequencies  $682.16\text{ cm}^{-1}$ ,  $1002.36\text{ cm}^{-1}$ ,  $1216.97\text{ cm}^{-1}$ , and  $1855.35\text{ cm}^{-1}$  respectively. Higher intensity correspond to the characteristic band C=O stretching at  $1855.35\text{ cm}^{-1}$ . The calculated force constant and IR intensity corresponding to C=O stretching were  $19.0103\text{ mdyn/\AA}$  and  $285.7071\text{ km/mol}$  respectively.

The vibrational spectra obtained by molecular modelling has a systematic error, which can be avoided by scaling. Scaling differs from basis set to another at the same level of theory.

**Table 2.** Unscaled B3LYP/6-31G(d,p) calculations for Infrared frequencies in  $\text{cm}^{-1}$ , force constant  $\text{mdyn/\AA}$ , infrared intensities in  $\text{km/mol}$ , and band assignment of acetic acid.

Calculated Frequency	Force Constant	Infrared Intensity	Exp. Frequency	Assignment
A'' 78.94	0.0040	0.6019	75.00	CH3 torsion
A' 419.74	0.8882	4.4164	565.00	C-OH torsion
A'' 542.93	0.2832	20.6848	581.00	CCO deform
A' 581.80	0.8368	42.6642	642.00	C=O op-bend
A'' 682.16	0.3947	106.3293	657.00	OCO deform
A' 865.71	1.6641	2.6697	847.00	C-C stretch
A' 1002.36	0.9509	57.3093	989.00	CH3 rock
A'' 1070.05	1.2074	9.1360	1048.00	CH3 rock
A' 1216.97	1.6706	209.6653	1182.00	C-O stretch
A' 1355.89	1.8541	26.2089	1264.00	OB bend
A' 1422.99	1.9850	64.5742	1382.00	CH3 s-deform
A' 1484.48	1.3681	12.8528	1430.00	CH3 d-deform
A'' 1490.23	1.3685	8.2726	1430.00	CH3 d-deform
A' 1855.34	19.0103	285.7071	1788.00	C=O stretch
A' 3068.74	5.7536	2.0055	2944.00	CH3 s-stretch
A'' 3134.38	6.3700	5.2234	2996.00	CH3 d-stretch
A' 3186.15	6.6013	5.7228	3051.00	CH3d-stretch
A' 3754.75	8.8389	44.0039	3583.00	OH-stretch

Experimental frequency from reference 15.

**Table 3.** Unscaled vibrational spectra of the characteristic C=O stretching at B3LYP/6-31G(d,p) in case of acetic acid dimer.

O-H...O=C distance $\text{\AA}$	Frequency, $\text{Cm}^{-1}$
2.684	1789.36
2.741	1791.30
3.067	1798.67

As presented in Table 2 the experimental C=O band frequency of the gas phase is  $1788.00\text{ cm}^{-1}$ , which is lower than the calculated frequency. A scale factor of  $0.9614^5$  is used for our model of calculations. Then, the scaled calculated frequency became  $1783.70\text{ cm}^{-1}$  which is close to the experimental results. Again, the model B3LYP/6-31G(d,p) is the optimal from the vibrational spectra calculations point of view.

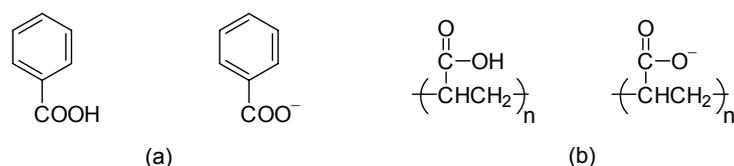
Acetate group of acetic acid dimer is also studied and the results are obtained in Table 3. The optimized structure of cyclic acetic acid dimer is shown in Figure 2b Cyclic dimer which considered to be the most stable among other dimer species. Acetic acid dimer is studied with 3 different intermolecular C=O...H-O namely,  $2.684\text{ \AA}$ ,  $2.741\text{ \AA}$  and  $3.067\text{ \AA}$  respectively. Results showed that, C=O stretching is obtained with respective values  $1789.36\text{ cm}^{-1}$ ,  $1791.29\text{ cm}^{-1}$  and  $1798.67\text{ cm}^{-1}$  for the three respective dimer intermolecular distances. From the results, the band is shifted as the distance is increased.

Further calculation of C=O band is carried out for both acetate and acetate ion which were coordinated with benzoic acid and polyacrylic acid. The coordination of the acetate group into both acid structures occurs through hydrogen bonding. Benzoic acid represents acetate group which coordinated with aromatic compound, while polyacrylic acid represents acetate group among aliphatic compound. The optimized structure of aceto-benzoic and aceto-polyacrylic acid are shown in Figure 3.

Table 4 presents the results of both acetate and acetate ion in case of aceto-benzoic acid and aceto-polyacrylic acid at B3LYP/6-31G(d,p) level of theory. Acetate group showed a shift of  $4.0\text{ cm}^{-1}$  in C=O ongoing from aceto-benzoic,  $1819.22\text{ cm}^{-1}$  to aceto-polyacrylic acid,  $1823.22\text{ cm}^{-1}$ . Similarly the same shift in case of acetate ion is  $23.34\text{ cm}^{-1}$ , ongoing from aceto-benzoic,  $1748.33\text{ cm}^{-1}$  to aceto-polyacrylic acid,  $1724.99\text{ cm}^{-1}$ . The calculated band frequency of C=O indicate that, the observed shift in acetate group is smaller as compared to that in case of acetate ion.

**Table 4.** Unscaled vibrational spectra of C=O of both acetate and acetate ion at B3LYP/6-31G(d, p) in case of both aceto-benzoic acid and aceto-polyacrylic acid.

Structure	Acetate	Acetate ion
Aceto-benzoic acid	1819.22	1748.33
Aceto-polyacrylic acid	1823.22	1724.99



**Figure 3.** Structures of both acetate and acetate ion in case of a-Benzoic acid, and b-Polyacrylic acid.

### Conclusions

Both structure and vibrational spectra of acetate group in different states are examined by the DFT method using four different basis sets. The results indicate that, the exchange functional proposed by Becke and the correlation functional of Lee, Yang, and Parr with 6-31G(d,p) basis set is the optimal model for studying acetate group.

### Experimental

#### IR-Spectroscopy

The IR-Spectra is measured with BRUKER EQUINOX 55 Fourier Transform Interferometer, at Juelich Research Center, Germany. The spectral range of which is 370-7500  $\text{cm}^{-1}$ . With a direct attachment of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT).

#### Calculation details

All calculations were performed with the Gaussian 98<sup>17</sup> suite of programs on the CRAY supercomputer at Juelich Research Center, Germany. The geometries were fully optimized without imposing external symmetry constraints using Density Functional Theory, DFT correlation functionals Becke's three parameters methods with the Lee, Yang and Parr correlation functional, B3LYP.<sup>18,19,20</sup> The geometry was optimized using four basis set namely, 6-311G, 6-31G(d,p), LANL1MB, and LANL1DZ. Optimization with Hartree-Fock model, HF/D95(d,p), was used only for comparison with DFT. Vibrational spectra was calculated at B3LYP/6-31G(d,p). Since normally the errors within this type of calculation are normally systematic, all calculations are carried out in gas phase.

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### Povzetek

Pri študiju strukture in vibracijskih spektrov acetatne skupine smo uporabili teorijo gostotnih funkcionalov (DFT). Z modelom B3LYP in štirimi nabori baznih funkcij smo z optimizacijo določili energijski minimum molekule očetne kisline. Bazni set 6-31G(d,p) je geometrijo acetatne skupine v očetni kislini zadovoljivo opisal. Na istem nivoju teorije smo izračunali vibracijske frekvence molekule in asignirali vibracijski spekter. Model B3LYP/6-31G(d,p) smo uporabili tudi za izračun frekvenc karakterističnega valenčnega nihanja O=O v acetatni skupini dimera očetne kisline ter molekul acetobenzojske in acetopoliakrilne kisline.