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MOLECULAR STRUCTURE AND VIBRATION SPECTRA OF ANHYDROUS ZINC ACETATE AND ANHYDROUS MAGNESIUM ACETATE BY DENSITY FUNCTIONAL THEORY AND AB INITIO HARTREE-FOCK CALCULATIONS.

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The molecular geometry and vibrational frequencies of anhydrous zinc acetate and anhydrous magnesium acetate in the ground state have been calculated using the Hartree-Fock and density functional method (B3LYP) with 6-31G basic set. The optimized geometric band lengths and bond angles obtained by using HF and DFT (B3LYP) show the best agreement with the experimental data. Comparison of the observed fundamental vibrational frequencies of melamine diborate with calculated results by density functional B3LYP and Hartree-Fock methods indicate that B3LYP is superior to the scaled Hartree-Fock approach for molecular vibrational problems.

Keywords: anhydrous zinc acetate, anhydrous magnesium acetate, IR Spectra; DFT; HF, vibrational assignment.

INTRODUCTION

Magnesium acetate tetrahydrate $[\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ have been studied experimentally [1] to investigate vibrational spectroscopic properties. Monoclinic anhydrous zinc acetate has a crystal structure in which a zinc atom is tetrahedrally coordinated by four oxygens of the four bridging bidentate carboxylate groups in a syn-anti arrangement [2]. They form two-dimensional sheets along the bc plane. The space group is $C_{2/c}$ or C_{2n}^6 . The averaged Zn-O distance is $1,957 \text{ \AA}$ and C-O distance is $1,252 \text{ \AA}$. There are four symmetry species of Au and Bu of Infrared active vibrations and Ag and Bg of Raman active ones. This study was made a factor group analysis and a normal mode analysis on anhydrous zinc acetate and were assigned the vibrations of intra and inter molecular [2].

Ishioka et al. Calculated the vibrational spectra of anhydrous zinc acetate as a primitive cell containing four asymmetry units of $\text{Zn}(\text{CH}_3\text{COO})_2$ where Zn and O were assumed to be covalently bonded [3]. Koleva and Stoilova studied the infrared and Raman spectra of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and the double salt $\text{MgZn}(\text{CH}_3\text{COO})_4$ with respect to internal modes of the acetate ions and the water molecules [1].

Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to

compensate for the approximate treatment of correlation, for basis set deficiencies and for the anharmonicity [4].

Rauhant and Pulay calculated the vibrational spectra of thirty one molecules by using B3LYP method with 6-31G basis set [5]. In their work, they calculated vibrational frequencies of twenty smaller molecules whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using least-square method. The scaling factors are successfully applied to other eleven larger molecules. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31G basis can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra [6].

As far as we know, there are no complete theoretical results for anhydrous zinc acetate in the literature. In this work, by using the HF and DFT (B3LYP) methods. We calculate the vibrational frequencies of anhydrous zinc acetate and anhydrous magnesium acetate in the ground state to distinguish the fundamentals from the many experimental vibrational frequencies and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

CALCULATIONS

The molecular structure of anhydrous zinc acetate and anhydrous magnesium acetate in the ground state (in

vacou) are optimized by HF and B3LYP with 6-31G basis set. Two sets of vibrational frequencies for these species are calculated with these methods and then scaled by 0,8929 and 0,963 respectively. Molecular geometry is restricted and all the calculations are performed by using Gauss-View molecular visualisation program [7] and Gaussian 98 program package on the personal computer [8].

RESULTS AND DISCUSSION

Crystal Structure

Anhydrous zinc acetate takes different structures by different preparation methods. Before vibrational analysis, we needed to check whether a specimen have a known crystal structure. Two crystal structures of anhydrous zinc acetate have been known. One is monoclinic form in which a zinc atom is tetrahedrally coordinated by the four oxygens of the four bridging bidentate carboxylate groups and they form two-dimensional sheets along the bc plane [2]. Another is orthorhombic form in which a zinc atom is coordinated as described above, but they form three-dimensional network [9]. We haven't got crystal data of anhydrous magnesium

acetate, but it likes anhydrous zinc acetate geometric structure [1,10]. Atalay et al. showed magnesium atom is tetrahedrally coordinated by the four oxygen of the four bridging bidentate carboxylate groups [11]. Therefore, we also study anhydrous magnesium acetate as theoretically and we compare it with anhydrous zinc acetate.

The optimized geometric parameters (bond lengths and angles) by HF and B3LYP with 6-31G as the basis set are listed in Table 2 and compared with the experimental crystal geometry for anhydrous zinc acetate and anhydrous magnesium acetate (Table 2. geometric parameters). It is well known that HF methods underestimate some bond lengths [12,13]. We noted that the experimental results belong to solid phase. The largest difference between calculated and experimental values of bond lengths is about 0,126 Å. In Figure 1a and 1b. calculated geometric structure of Zn(CH₃COO)₂ and Mg(CH₃COO)₂ is shown.

The B3LYP method leads to geometric parameters which are much closer to experimental data. In summary, the optimized bond lengths obtained by HF method show the best agreement with the experimental values.

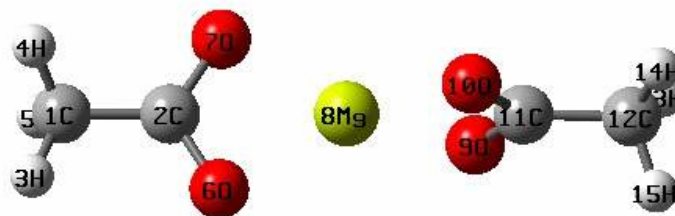


Figure 1a Calculated geometrical structure of magnesium acetate

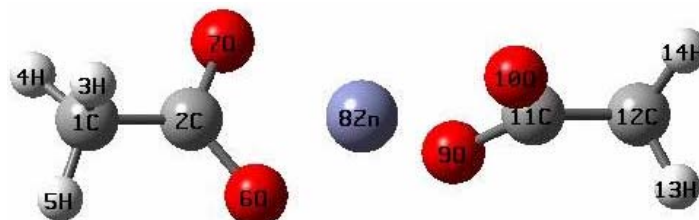


Figure 1b Calculated geometrical structure of zinc acetate

Normal Mode Analysis

A normal mode analysis was made for the monoclinic specimen as follows. The Cartesian coordinates were evaluated according to crystal structure. The CH₃ group was assumed as a unit atom. The unit cell contains eight asymmetric units. Ishoka et al. Calculated the frequencies for a primitive cell containing four asymmetry units of Zn(CH₃COO)₂ where Zn and O were assumed to be covalently bonded. The crystal belongs to the C_{2/c} or C_{2n}⁶. The asymmetric unit belongs to the C₂ point group and has 11A 10B vibrations. The site symmetry is C₂. Hence, there are (22+4R) Ag, (22+3T) Au, (20+8R) Bg and (20+6T) Bu crystal vibrations where R and T indicate rotational and translational lattice modes, respectively [3]. The fundamentals of the CH₃COO⁻ ions have been assigned in terms of a C_{2v} molecular symmetry, assigned free rotation of CH₃ about C-C bond [14]. The 15 fundamental modes of CH₃COO⁻

are classified in 5A₁, 1A₂, 5B₁, and 4B₂ modes 5A₁, 5B₁ and 4B₂ are IR and Raman active, while A₂ is Raman active only [1]. The Infrared spectra of anhydrous zinc acetate and anhydrous magnesium acetate are given in Table 1 with theoretical and experimental results. The assignments of the bonds corresponding to the acetate vibrations are mode according to those for other metal acetates [15, 16].

On the basis of our calculations and the reported infrared spectra by Koleva and Stoilova [1], we made a reliable one-to-one correspondence between our fundamentals and any of our calculated frequencies. Among calculated frequencies, the biggest difference for fundamentals between experimental and calculated frequencies is 21 cm⁻¹ (for B3LYP). Although, scaling factor for HF method is very low (0,8929), this mode is in well agreement with an experimental data.

COO⁻ group has got very important feature in anhydrous zinc acetate molecule and anhydrous

magnesium acetate molecule. The observed and calculated vibrational frequencies is showed Table 1. Comparison of the observed fundamental vibrational frequencies of Zn(CH₃COO)₂ and Mg(CH₃COO)₂ and the

results calculated by density functional B3LYP and Hartree-Fock methods indicates that B3LYP is superior to the scaled Hartree-Fock approach for molecular vibrational problems.

Table 1 Experimental and theoretical wavenumbers (cm⁻¹) of Zn(CH₃COO)₂ and Mg(CH₃COO)₂

Zn(CH ₃ COO) ₂			Mg(CH ₃ COO) ₂			Assignment
IR(exp)*	IR(cal.)		IR(exp)*	IR(cal.)		
	B3LYP 6-31G	HF 6-31G		B3LYP 6-31G	HF 6-31G	
	3080	3078	3020	3041	3030	(B ₁) CH asym. Stretch
-	-	-	-	3029	3028	(B ₁) CH asym. Stretch
2925	2953	2954	2932	2948	2947	(A ₁); CH sym. Stretch
2925	2953	2954	2930	2947	2947	(A ₁); CH sym. Stretch
2854	-	-	2850	-	-	?
2852	-	-	2846	-	-	?
1560	-	-	1562	1451	1449	(B ₁); CO asym. Stretch
1558	-	-	1554	1449	1448	?
1451	-	-	-	-	-	(B ₂); CH ₃ asym. Bend
1448	1488	1487	1450	-	-	?
1415	-	-	1425	1398	1394	?
1415	-	--	-	1394	1386	?
1393	1392	-	1423	1367	1368	(A ₁); CO sym. Stretch
1387	1390	-	1351	1364	1363	?
1354	1352	-	1350	1302	1301	(B ₁); CH ₃ asym. Bend
1350	1349	-	1060	1059	1058	(A ₁); CH ₃ sym. Bend
1058	1058	-	1058	1057	1058	(A ₁); CH ₃ sym. Bend
1057	1056	-	1030	1029	1028	?
1020	1021	-	1024	1025	1025	(B ₂); out of plane CH ₃ rocking
1020	1018	-	1022	1022	1021	(B ₁); in-plane CH ₃ rocking
954	955	-	949	947	947	?
954	955	-	941	940	939	?
-	-	-	672	-	-	?
-	-	-	671	-	-	?
698	699	-	-	659	658	(A ₁); OCO sym. Bend
695	695	-	628	658	659	?
-	-	-	627	-	-	?
623	622	-	-	-	-	(B ₂); out of plane OCO rocking
622	-	-	499	611	612	
477	478	-	-	609	609	(B ₁); in plane OCO rocking

*: Taken from [1].

Assignment: Taken from [15].

Table 2. Optimized and experimental geometries of Zn(CH₃COO)₂ and Mg(CH₃COO)₂ in the ground state

Parameters	Zn(CH ₃ COO) ₂			Parameters	Mg(CH ₃ COO) ₂	
	X-Ray *	B3LYP	HF		Bond Length	B3LYP
Zn-Zn	4,651	-	-	Mg-Mg	-	-
Zn-O	1,951	2,030	2,013	Mg-O	2,040	2,022
	1,953	2,030	2,013		2,040	2,022
	1,958	2,030	-		2,040	2,022
	1,965	2,040	-		2,040	2,022
Zn...C	2,708	2,380	2,376	Mg...C	2,400	2,380
	2,780	2,390	2,376		2,400	2,380
	2,920	-	-		-	-
	2,964	-	-		-	-
O-C	-	1,312	1,308	O-C	1,313	1,310
	-	1,312	1,308		1,313	1,310
C-C	-	1,500	1,493	C-C	1,501	1,500
O...C	3,446	4,200	4,180	O...C	4,250	4,240
	3,459	4,200	4,180		4,250	4,240
	3,501	4,200	4,180		4,250	4,255
	3,509	4,200	4,180		4,250	4,255

*: Taken from [3]

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