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Normal coordinate analysis of the enol form of pentane-2,4-dione and its ^{2}H-isotopomers

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Abstract

The harmonic and anharmonic vibrational frequencies of the cis-enol form of pentane-2,4-dione (PD) and its ^{2}H-isotopomers were calculated by density functional theory method (DFT), performed at the B3LYP level. The results of the DFT calculations were subjected to a normal coordinate analysis, giving potential energy distribution (PED) and detailed assignments. Excellent agreement between observed and calculated anharmonic vibrational frequencies was obtained. It is well illustrated that the band frequencies resulted from movements of the enolic ring atoms are considerably coupled with the terminal groups' vibrations.

Keywords: Normal coordinate analysis; Density Functional Theory; pentane-2,4-dione; Vibrational spectra; Potential energy distribution (PED); Deuterated isotopomers; Acetylacetone

1. Introduction

Pentane-2,4-dione (PD), known as acetylacetone, is the simplest member of β-diketone compounds. PD has been the subject of a vast number of theoretical [1-11] and experimental [12-31] studies. Despite several spectroscopic studies on the vibrational spectra of PD [15-35], to the best of our knowledge, not only the quantitative analysis of vibrational spectra of this molecule has not been reported so far, but there are so many discrepancies between the vibrational band assignments of the titled molecule reported in the literature. Comparison of potential energy distribution (PED) of the vibrational normal modes of PD with those in its ^{2}H-isotopomers demonstrates the effects of the weight of methylene and terminal groups on the chelated ring vibrational frequencies of the enol forms of β-diketones. It has been shown that the density functional theory (DFT) is a powerful tool for calculating the contributions of internal coordinates in the normal modes of vibrational movements (PED) in a molecule [36]. In the present work, based on the density functional theory, a normal coordinate analysis is performed for PD and its ^{2}H-isotopomers (d_2PD, d_6PD, and d_8PD). The PED has also been calculated for the normal modes of vibrations to determine quantitatively the contribution of each internal (or symmetry) coordinate in each vibrational normal mode. As it has been previously shown, this method gives more accurately the PED of vibrational frequencies than other conventional approaches [36].

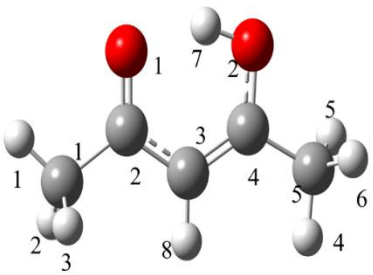

Fig. 1. Structure and atom numbering of PD.

2. Calculation methods

In the present study, all calculations for the cis-enol form of PD were performed by Gaussian-09 software [37]. The geometry optimization, harmonic vibrational frequencies, IR intensities, and Raman scattering

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calculations for the titled molecules were performed at the B3LYP [38,39] level using the 6–311++G(3df,2p) basis set. The anharmonic [40,41] vibrational frequencies were also calculated based on the optimized structure by using the B3LYP/6-311++G(P,d) level.

The calculated atomic displacements associated with the normal modes were illustrated by GaussView [42]. A normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for the cis-enol form of PD and its ^{2}H-isotopomers. By combining the displacement Cartesian coordinates of the atoms for each vibrational frequency and the Cartesian coordinates of atoms at the equilibrium position, obtained from Gaussian output, using the B3LYP/6-311++G(3df,2p) level, the displacement internal coordinates were calculated. The full sets of 49 standard internal coordinates containing 10 redundancies are defined as given in Table S1 (supplementary material). From these internal coordinates, a non-redundant set of the local symmetry coordinates was constructed by a suitable linear combination of internal coordinates (Table S1). Then all symmetry coordinates were normalized through all 39 normal coordinates, as described elsewhere [36,43,44]. The normalized symmetry coordinates were used to calculate the potential energy distributions (PEDs) for each normal mode [36,43,44].

3. Results and discussion

The structure and atom numbering of the enol form of PD are given in Fig. 1. The calculated harmonic and anharmonic and the observed [18] vibrational band frequencies of PD along with the PED of the normal modes are depicted in Table 1. The corresponding values for deuterated derivatives of PD are listed in Tables S2-S4 (supplementary materials). As it is shown in these tables, there is excellent agreement between the observed and calculated anharmonic vibrational wavenumbers, except for OH/OD stretching vibrational wavenumbers. This deviation is not surprising if we remember that the potential function for the enolic proton motion in β-diketones is the symmetric double minimum type [2,45,46], which is not considered by Gaussian calculations. The most important theoretical and observed vibrational frequencies of PD and its deuterated derivatives are compared in Table 2 and are discussed in the following sections.

Table 1

Theoretical and experimental vibrational frequencies (cm^{-1}) and PED of PD.[a]

sym	Theoretical					Experimental [18]				PED (%)[b]
	F1	F_{an}	F2	I_{IR}	R_A	IR(gas) I		R (liq.)	I	
A'	3204	3055	3202	3	60			3096	5	νCHα(81)
A'	3140	3005	3136	14	64	3017	10	3007	7	vaCH_3(74), vsCH_3(15)
A'	3135	2994	3132	10	50	3017		3007		vaCH_3(73), vsCH3(15)
A"	3090	2948	3085	5	98	2976	6	2966	10	va'CH_3(92)
A"	3088	2901	3083	7	61	2976		2966		va'CH_3(91)
A'	3066	2540	3048	355	100	2800				νOH(71), vsCH_3(21)
A'	3036	2924	3033	0	210	2941		2923	100	vsCH_3(71), vaCH_3(16), νOH(9)
A'	3030	2925	3029	11	201	2941		2923		vsCH_3(69), vaCH_3(17), νOH(11)
A'	1676	1641	1678	351	8	1642	19	1628	sh	νC=C(17),νC=O(17),δCHα(10), δOH(8),νC-CH_3(8)
A'	1637	1612	1643	292	50	1624	77	1601	13	νC=C(11), νC=O(17), νC-C(7),δOH(18), νC-CH_3(9)
A'	1490	1445	1492	54	12	1464	10	1468	sh	δaCH_3(27), δCH(16), νC-C(8),νC-O(8)
A"	1477	1407	1479	7	6			1401	1	δa'CH_3(72), πCH_3(17)
A"	1471	1434	1473	10	4	1427	17	1446	3	δa'CH_3(70), πCH_3(18)
A'	1470	1424	1472	6	8	1427		1426	8	δaCH_3(43), δOH(11), δCH(9)
A'	1456	1433	1460	141	2	1427				δsCH_3(14),δaCH_3(29),δCHα(10),δOH(8),νCC(7),νCO(7)
A'	1412	1376	1412	14	3			1370	8	δsCH_3(37), ρCH_3(11), νC-CH_3(10)
A'	1389	1350	1391	66	3	1365	10	1364	5	δsCH_3(48)

A'	1377	1315	1377	82	44	1302	47	1306	13	δsCH$_3$(20),δOH(14),δaCH$_3$(11),νC=C(12),νC=O(10),νCO(9)
A'	1268	1240	1268	145	6	1250	17	1247	13	νC-CH$_3$(18),νC=C(12),νC-C(11),δsCH$_3$(14),δC=O(9),δOH(8)
A'	1191	1167	1195	16	7	1171	6	1169	7	δCHα(23),νC=O(8),δsCH$_3$(8),νC-CH$_3$(14), δC-O(8)
A"	1059	1038	1062	1	2			1036	2	πCH$_3$(42), γC-CH$_3$(17), δa'CH$_3$(14), γCHα(8),
A"	1043	1031	1045	8	0	1025	1			πCH$_3$(37), γC=O(16), δ'CH$_3$(14), gCH(10)
A'	1033	1012	1033	10	1	1005	sh	1000	4	ρCH$_3$(31),δaCH$_3$(16)
A'	1008	968	1009	14	9			993	4	ρCH$_3$(19), νC-CH$_3$(15),δsCD$_3$(13),νC-O(10)
A"	968	949	999	66	0	952	10			γOH(60), γC=O(8)
A'	942	930	943	2	4			930	7	δCCC(13), νC-C(19), ρCH$_3$(16), νC-CH$_3$(12)
A'	917	866	917	37	2	913	9	915	2	νC-CH$_3$(28), νC-O(11), ρCH$_3$(11), νC=C(8)
A"	790	773	794	32	1	768	40	785	5	γCHα(46), πCH$_3$(12), γC-CH$_3$(12), γC=O(10),γC-O(19)
A"	650	553	651	0	0					πCH$_3$(26),γC=O(28), γC-O(22),γC-CH$_3$(13)
A'	642	700	647	13	12	636	9	641	35	νC-CH$_3$(22), δC=O(18), δC-O(12), δC-CH$_3$(11)
A"	553	564	559	0	2			554	15	γC-CH$_3$(38), πCH$_3$(24), γOH(11), γC-O(9), γC=O(8)
A'	510	508	512	11	3	508	20	508	4	δC=O(15), δC-O(20), δC-CH$_3$(19), ρCH$_3$(10)
A'	397	382	397	3	0	397	s			δC-CH$_3$(41),ρCH$_3$(17)
A'	369	362	372	7	4	362	s	369	5	δC-CH$_3$(30), δC-O(17) ,δCCC(13), ρCH$_3$(11)
A'	229	224	231	3	0	210	w	227	7	δC-CH$_3$(30), δCCC(19), ρCH$_3$(10)
A"	180	174	182	0	0					τCH$_3$(20), γCH$_3$(38), γC-O(14)
A"	148	142	148	0	0			140	sh	τCH$_3$(50), γC-CH$_3$(18),γC=O(11), γC-O(9)
A"	118	115	119	1	0	120	w	104	w	γC-CH$_3$(35),τCH$_3$(30), γC=O(12), γC-O(11)
A"	15	NC	21	0	0					τCH$_3$(82)

[a] F1 and F_{an}, stand for harmonic and anharmonic vibrational wavenumbers obtained with the B3LYP/6-311++G** level, respectively; F2 stands for harmonic wavenumbers calculated at the B3LYP/6-311++(3df,2p) level; $I_{IR,}$ IR intensity (in km/mol); R_A, Raman activity (in Å^4/amu); I stands for relative intensity; ν, δ, γ, and τ stand for stretching, in-plane bending, out-of-plane bending, and torsion vibrations, respectively; ρ and π in-plane and out-of-plane rocking modes; ν' and δ' stands for out-of plane stretching and bending vibrations, respectively; NC, not converged. [b] The PEDs are only includes the contributions larger than 7%.

Table 2

Comparison of some important vibrational modes in PD and its 2H-isotopomers. a

Experimental [18]				Theoretical			
d_0	d_2	d_6	d_8	d_0	d_2	d_6	d_8
3096	2300	3098	2303	3055	2279	3084	2303
2800	2027	2761	1970	2540	2000	2487	1912
1642	1633	1628	1614	1641	1640	1615	1598
1624	1544	1606	1524	1612	1536	1593	1497
1464	1448	1446	1371	1445	1442	1434	1359
1302	1082	1294	1078	1315	1094	1302	1078
1250	1273	1265	1274	1240	1270	1254	1271
952	707	952	691	949	706	952	718
362	360	337	335	362	356	335	330

[a] All values are in cm^{-1}

3.1. OH/OD vibrations

It has been shown that the enol form of β-diketones exhibits an extremely broad band in the 3500–2200 cm^{-1} region, which upon deuteration of the enolic proton appears as a new narrower band at the 2200–1800 cm^{-1} region [46-51]. Upon increasing of hydrogen bond strength, the position of this bond shifts towards lower frequencies, its bandwidth increases, and its intensity decreases. The low

intensity of this band is not surprising since its significant intensity is spread over a wide wavenumber region. Therefore, the estimation of the position of the band in the stronger intramolecular hydrogen bond of these compounds is not easily determined. However, the observed vibrational band frequencies of PD in the gas phase are reported to be occurring at about 2800 cm^{-1} [18,27]. The corresponding band for d_6PD occurs at 2761 cm^{-1} [18], about 40 cm^{-1} lower than that of the light compound. The calculated anharmonic wavenumber for the OH stretching vibration in PD and d_6PD is 2540 and 2487 cm^{-1}, respectively, which, its frequency shift is in agreement with the observed results. This frequency shift may be attributed to the effect of coupling between the OH stretching and CH_3/CD_3 vibrational modes. Our PED calculations show that 21% of symmetric CH_3 stretching contributes to this normal mode, which explains the frequency shifts upon deuteration. The OD stretching in the IR spectra of d_2PD and d_8PD appears at about 2027 and 1970 cm^{-1}, respectively, which indicates that the OD stretching is also coupled with the CH_3/CD_3 vibrations.

The broad IR band at 1302 cm^{-1} is mainly OH bending, which is strongly coupled with asymmetric C-C=O and asymmetric C=C-O stretching and also weakly coupled to the symmetric CH_3 deformation. The corresponding band in the IR spectrum of d_6PD occurs at 1294 cm^{-1} [18]. In d_2PD and d_8PD this band disappears and a new band appears at 1082 and 1078 cm^{-1}, respectively. The 1302 cm^{-1} band was not considered by Ogoshi and Nakamoto [27] instead they assigned a shoulder at 1460 cm^{-1} to the OH in-plane bending mode. The 1082 cm^{-1} band in d_2PD is mainly OD in-plane bending vibration that is coupled with the C=C stretching and CH_3 rocking mode, which is in agreement with the Matanović and Došlić assignment [23]. However, the 1082 cm^{-1} band in the IR spectrum of d_2PD was solely assigned by Gutiérrez-Quintanilla *et al*. [34] and Ogoshi and Nakamoto [27] to the OD in-plane bending mode.

The broad band in about 950 cm^{-1} in PD and d_6PD, which disappears in d_2PD and d_8PD is assigned to the OH out-of-plane bending slightly coupled to the C=O and C-O stretching vibrations. The corresponding band in d_2PD and d_8PD appears at 707 and 691 cm^{-1}, respectively, which OD out-of-plane bending is coupled with the CH_3 and CD_3 out-of-plane rocking vibrations, respectively.

3.2. C=C, C-C, C=O, and C-O stretching vibrations

The two strong bands at 1642 and 1624 cm^{-1} (Table 2), which could only be identified either by deconvolution [18] or using matrices [16,34,35], in the IR spectrum of gaseous PD are very close to those predicted by the calculated anharmonic wavenumbers (1641 and 1612 cm^{-1}, respectively) and are shown to be media sensitive. In the H_2 matrix, these are observed at 1638 and 1618 cm^{-1} [16] and in the liquid phase appear at 1625 and 1600 cm^{-1} [18], respectively. According to our calculations, the former is assigned to the asymmetric C=C-C=O stretching vibrations (40%), which is somewhat coupled to the C-H_α and O-H in-plane bending and C-CH_3 stretching vibrations, and the latter is assigned to the symmetric C=C-C=O stretching (36%) strongly coupled to the OH in-plane bending (19%) and weakly coupled to the C-CH_3 stretching (9%). In d_6PD the corresponding bands appear at 1628 and 1606 cm^{-1}, in d_2PD shift to 1633 and 1544 cm^{-1}, and in d_8PD are observed at 1614 and 1524 cm^{-1}, respectively [18]. These band frequency shifts are in agreement with our calculated results. By considering the corresponding bands in the gas phase IR spectra of d_2PD, d_6PD, and d_8PD (see Table 2), it results that the deuteration of methyl groups causes a redshift for the higher and lower band frequencies of 14-19 and 18-20 cm^{-1}, respectively, whereas, the deuteration of H_α and enol proton, shifts the higher and lower band frequencies of 9-14 and 80-82 cm^{-1} towards lower frequencies, respectively, which confirms the results of our normal coordinate analysis. Ogoshi and Nakamoto [27] reported only a single band as the superposition of these two bands at 1623 cm^{-1}, which solely assigned one of them to the C=O and the other to the C=C stretching vibrations. Gutiérrez-Quintanilla *et al*. [34] assigned the corresponding bands in d_2PD to the asymmetric and symmetric C=C+C=O stretching, respectively, which is almost in agreement with our results. Matanović and Došlić [23] assigned the 1642 cm^{-1} to the asymmetric C=C-C=O stretching and OH in-plane bending, while the 1624 cm^{-1} band was considered solely as C=O stretching and OH in-plane bending vibrations. Lozada-Garcia *et al.* [35] assigned the former to the C=O and asymmetric C=C-O stretching and OH in-plane bending vibrations. However, according to our calculations, the contribution of C-O stretching in this normal mode is not significant and the contribution of OH bending is considerably low (8%).

The 1464 cm^{-1} band is assigned to the asymmetric C-C=C-O stretching vibrations, which is coupled to the CH_3 deformation and CH_α in-plane bending modes. The corresponding band in d_2PD and d_6PD appears at 1448 and 1446 cm^{-1}, respectively, whilst in d_8PD, because of decoupling from both CH_3 deformation and CH_α bending, considerably shifts downward and appears at 1381 cm^{-1}. This band was assigned by Ogoshi and Nakamoto [27] to the OH in-plane bending mode and assigned by Gutiérrez-Quintanilla *et al*. [34] and Matanović and Došlić [23] to the CH_3 deformation, while Lozada-Garcia *et al.* [35] considered this band as CH_α in-plane bending and asymmetric CH_3 deformation.

The IR band at 1250 cm^{-1} is also a complicated vibrational mode which includes C-CH_3, C=C, C-C, and C-O stretching and CH_3 deformation and OH in-plane bending vibrations. Ogoshi and Nakamoto [27] considered this band solely as C-C stretching, while assigned by Lozada-Garcia *et al*. [35] to the symmetric C-C=C-C stretching and by Matanović and Došlić [23] assigned to the ν_sC-C=C coupled with OH in-plane bending and C-CH_3 stretching, which is in agreement with our results, while ignored by Gutiérrez-Quintanilla *et al*. [34]. In d_2PD, d_6PD, and d_8PD this band moves to 1273, 1265, and 1271 cm^{-1}, respectively, which are also in agreement with our calculations.

3.3. *CH_3/CD_3 vibrations*

Three bands at about 3017, 2970, and 2940 cm^{-1} were observed in the IR spectrum of gaseous PD and d_2PD [18] are attributed to the in-plane asymmetric, out-of-plane asymmetric, and symmetric CH_3 stretching vibrations, respectively, which is in agreement with the Lozada-Garcia *et al*. [35] and Matanović and Došlić [23] assignments. Ogoshi and Nakamoto [27] did not consider the CH_3 stretching vibrations.

The relatively broad IR band at 1427 cm^{-1} seems to be the superposition of four bands, include mainly the degenerate CH_3 deformation vibrations, δaCH_3. In the H_2 matrix, four distinct bands are distinguished at 1462.6, 1431.7, 1427.3, and 1424.2 cm^{-1} [35]. In the IR spectrum of d_2PD, because of decoupling from OH and CH in-plane bending, the δaCH_3 band shifts to 1448 cm^{-1}. The corresponding bands in d_6PD occur at about 1050 cm^{-1}, whilst in d_8PD appear at about 1033 cm^{-1}.

The symmetric CH_3 deformations in PD and d_2PD were observed at 1365 and 1371 cm^{-1} [18], respectively. The IR spectra of the H_2 matrix of PD shows two distinct bands for symmetric CH_3 deformation at 1375.2 and 1360.8 cm^{-1}, which are in agreement with the calculated anharmonic wavenumbers, 1376 and 1350 cm^{-1}. The symmetric CD_3 deformations in the IR spectrum of PD appear at 1076 and 1051 cm^{-1} [18], which are very close to the calculated anharmonic wavenumbers, 1082 and 1055 cm^{-1}. In d_8PD the higher frequency band is strongly coupled to the OD in-plane bending and appears at 1112 cm^{-1} [18].

For PD, the Raman bands at 1036 and 1000 cm^{-1} and IR bands at 1025 and 1005 cm^{-1} are mainly caused by CH_3 rocking vibrations. The corresponding bands in d_6PD were observed at 914, 904, 812, 803 cm^{-1} and in d_8PD occur at 902, 890, and 802 cm^{-1} [18].

3.4. *CH_α vibrations*

The weak Raman band at 3096 cm^{-1} [18], which disappears upon deuteration, is assigned to the CH_α stretching (81%). The corresponding band in the IR spectrum is very weak, so it is reported neither by Matanović and Došlić [23] nor by Lozada-Garcia *et al*. [35], while Ogoshi and Nakamoto [27] considered the 2960 cm^{-1} band as CH_α stretching vibration.

The weak IR band at 1171 cm^{-1} is mainly resulted from CH_α in-plane bending (23%), although it is highly coupled to other vibrational movements. Matanović and Došlić [23], Lozada-Garcia *et al*. [35] and Ogoshi and Nakamoto [27] also considered this band as δCH_α. The corresponding band in d_6PD is observed at 1186 cm^{-1}. Upon deuteration of the proton at the α-position, this band disappears and a new band appears at about 830-820 cm^{-1} [18] at the α-position, this band disappears and a new band appears at about 830-820 cm^{-1} [18].

3.5. *O…O stretching vibration*

In the Far-IR spectra of PD and d_2PD, the O···O stretching mode appears as a strong band at 362 and 360 cm^{-1}, respectively, which is strongly coupled with the C-CH_3 bending and CH_3 rocking vibrations. The corresponding band in the Far-IR spectra of d_6PD and d_8PD is observed at 337 and 335 cm^{-1}, respectively. Therefore, the O···O stretching vibration does not precisely reflect the hydrogen bond strength since it is considerably coupled to the terminal groups' vibrations.

4. Conclusions

The vibrational band frequencies of PD and its ^{2}H-isotopomers were assigned by using the calculated harmonic and anharmonic vibrational wavenumbers performed at the B3LYP level and normal coordinate analysis. Excellent agreement between experimental and calculated anharmonic wavenumbers obtained with the B3PLYP/6-311++G(p,d) level. A normal coordinate analysis, using the eigenvectors calculated at the B3PLYP/6-311++G(3df,2p), was performed for the titled molecules. The results of the normal coordinate analysis indicate that the vibrational modes related to the enolic ring atoms are highly coupled with the movements of terminal groups' atoms. The discrepancies between previously reported assignments were also discussed.

5.Conflicts of interest

There are no conflicts to declare.

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