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DENSITY FUNCTIONAL EFFICIENCY IN THE CALCULATIONS OF VIBRATIONAL FREQUENCIES AND MOLECULAR STRUCTURES OF β-DIKETONES

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Density functional theory (DFT) levels are employed to calculate the vibrational frequencies and geometrical data of β-diketones. We evaluate the relative performance of the different levels by comparing theoretical results to experimental values. The applied DFT levels in this work are B3LYP, BLYP, B3P86, B3PW91, BPW91, G96LYP, BP86, and G96PW91 with the standard 6-31G, 6-31G*, 6-31G**, 6-31+G**, 6-31++G**, 6-311G**, 6-311++G** basis sets. The best results are obtained at the B3LYP, B3PW91, and B3P86 levels.

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INTRODUCTION

Intra- and intermolecular hydrogen bonds are one of the important factors that govern the structure, function, thermodynamics and kinetic stability, chemical reactivity, and conformational flexibility of biologically active molecules. These types of hydrogen bonds exist in various organic compounds and biomolecules, such as hormones, coenzymes, proteins, and β-diketones (β-dicarbonyl compounds). Among these compounds, β-diketones are the simplest molecules involved in O—H…O intramolecular hydrogen bonds. These compounds of the well-known class of tautomeric compounds are important for application in organic, inorganic, and physical chemistry because of their role as important organic reagents [1, 2]. Therefore, in order to predict their physical properties or even choose one suitable for a specific application, it is necessary to make a link between the fundamental properties of the system, such as molecular interactions, electronic structure, and chemical properties of β-diketones. Different parameters, such as the conformational and structural properties of β-diketones, the possibility of diketo-enol tautomerization, and the nature of the strong intramolecular O—H···O hydrogen bond in the enol form were considered by scientists because the enol form of β-diketones is stabilized by a strong intramolecular hydrogen bond (Fig. 1). A great number of different methods, including IR, Raman, microwave, and NMR spectroscopies, X-ray and neutron diffraction measurements, combined with quantum chemical calculations, and some other techniques have been applied for the study of these compounds [3—12]. The resonance conjugation of π-electrons is enhanced due to the formation of the hydrogen bond, which causes a marked tendency for the equalization of the bond orders of valence bonds in the resulting six-membered chelate ring [13, 14]. From both

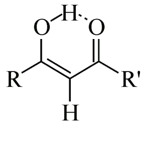

Fig. 1. The general scheme of β-diketone molecules

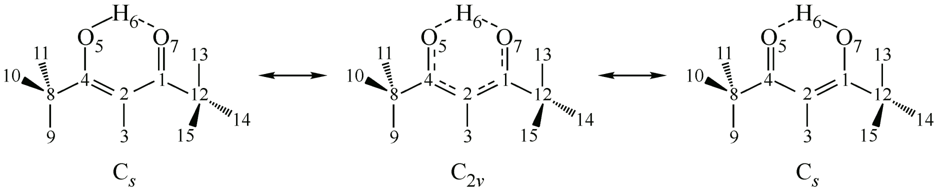

Fig. 2. Structures of enolic acetylacetone

theoretical and experimental point of view, the mobility of the hydrogen atom in these compounds determines a considerable number of interesting properties of these compounds. For instance, the vibrational spectra of these compounds have been the subject of several investigations which support the existence of a strong intramolecular hydrogen bond in the enol form of β-dicarbonyl compounds [9, 14, 15].

Acetylacetone ($CH_3C(O)CH_2C(O)CH_3$), one of the simple members of this class of compounds, has been studied both experimentally and theoretically to find that it is asymmetrical in its most stable conformation [7—9, 16]. Acetylacetone was observed in keto and enol forms of tautomers (Fig. 2). As this figure shows, the population of the enolic form of acetylacetone, which exists as a six-membered hydrogen-bonded ring, dominates the keto form in the gas phase. The enolic form of acetylacetone is usually thought to have a C_s symmetry, although in some studies the C_{2v} symmetry was obtained [4, 17]. The enolic form of acetylacetone is interesting for chemists and molecular spectroscopists because it exhibits three large amplitude motions: an intramolecular hydrogen transfer and two methyl torsions. The intramolecular hydrogen bond strength in the enol form determines a great number of the properties of acetylacetone such as the hydrogen exchange rate between the two oxygen atoms [18] and proton potentials [8]. This member of β-dicarbonyl compounds is a medium-strong hydrogen bonded system with the O—H asymmetric stretching frequency centered at 2800 cm^{-1} [9]. Compared to other compounds, in acetylacetone the system is conjugated, giving rise to a weak O—H stretching frequency. A number of experimental techniques and theoretical methods have been used to determine the structure of acetylacetone [4, 7, 10, 11]. From the theoretical point of view, the calculated structural and vibrational properties of some compounds, including hydrogen bonded systems such as β-dicarbonyls, are very sensitive to the applied level of theory. Hence, the choice of appropriate levels and basis sets makes it possible to obtain correct theoretical structural parameters for β-dicarbonyls. Currently, the most widely used theoretical quantum chemical method is DFT [19]. For the studies of various molecular properties, such as geometrical parameters, vibrational frequencies, charge distribution and ground-state properties in strongly bound systems, DFT combines accuracy with the computational speed and ease of use. The increasing usage of DFT can be understood when considering its accuracy and computational speed [20, 21]. Some of these levels have been used to calculate the geometry and vibrational spectra of the *cis*-enol form of β-diketones [14, 15, 22, 23]. It is interesting that the results are quite different and are not very similar as they are for regular molecules. This discrepancy seems to arise from the inadequacy of basis sets or defects in the calculations of systems with a resonance-assisted intramolecular hydrogen bond. Previous works comparing theoretical harmonic frequencies with the observed fundamentals have shown that the calculated frequencies generally overestimate the fundamental frequencies because of the incomplete treatment of electron correlation, the neglect of mechanical anharmonicity and basis set truncation effects. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually scaled for comparison. The scaling factor is commonly used by experimentalists in order to correct the calculated value to match the one observed experimentally, such as the vibrational frequencies and thermal contributions to the enthalpy and entropy [24].

The set of vibrational frequency scaling factors was evaluated by Pople *et al.* [25, 26]. They performed calculations at Hartree—Fock (HF) and second-order Møller—Plesset perturbation theory (MP2) levels. Scott and Radom [27] extended the investigation to the scaling factors for the vibrational frequencies, low-frequency vibrational modes, zero point vibrational energies (ZPVE), and thermal contributions to the enthalpy and entropy of the early generation of exchange-correlation functionals, such as BLYP, BP86, B3LYP, and B3PW91 levels. Truhlar and co-workers [28, 29] reported the scaling factors for ZPVEs of the exchange-correlation functionals, which they have developed to achieve a better prediction of thermochemical and kinetic quantities. The performance of semi-empirical, *ab initio*, and density functional methods in calculating and describing the vibrational frequencies of benzene was performed by Palafox [30]. He applied different levels in the calculations. Very recently, Vedrana Lazić and co-workers investigated the intra- and intermolecular hydrogen bonding in acetylacetone [31]. The structure and hydrogen bonding in an acetylacetone solution have been studied by a combination of experimental (NMR and UV spectroscopies) and theoretical (PM6 and DFT) methods. Schlund and co-workers [32] used a theoretical model to predict the tautomeric equilibrium of acetylacetone in solution. They studied how various components (method, basis set, and treatment of solvent effects) of a theoretical approach influence the relative energies of keto and enol forms of acetylacetone, which is an important model system to experimentally and theoretically study the solvent effects on chemical equilibria. Most of the reported vibrational frequencies of acetylacetone were in the harmonic mode, however, Matanovi and Dosli calculated the anharmonic vibrational frequencies of acetylacetone [32]. They concluded that the calculated anharmonic frequencies are in good agreement with the experimental data.

The aim of this paper is to consider: 1) DFT calculations of the optimized structure of acetylaceton and vibrational frequencies and 2) the efficiency of some regular DFT levels and basis sets in the calculation of the structural parameters and vibrational frequencies of acetylacetone as a representative of β-diketones.

METHOD

Calculations in this study were performed using the Gaussian software package [34]. Following full geometry optimizations at each level of theory, harmonic frequencies were computed analytically for various DFT methods employed in this study. The applied DFT methods are B3LYP, BLYP, B3P86, BP86, B3PW91, BPW91, G96LYP, and G96PW91 levels using 6-31G, 6-31G*, 6-31G**, 6-31+G**, 6-31++G**, 6-311G**, and 6-311++G** basis sets. Calculations of regression parameters, including the scaling factor (α), standard deviation (SD), regression coefficient (R^2), and intercept (β) were performed using the Microsoft Office Excel program. The regression coefficients and standard deviations for the calculated levels were obtained by the following equations:

$$\nu_{\text{obs}} = \alpha\nu_{\text{theo}}, \tag{1}$$

$$\nu_{\text{obs}} = \alpha\nu_{\text{theo}} + \beta, \tag{2}$$

where ν_{theo} and ν_{obs} are the *i*th calculated harmonic and *i*th experimental fundamental frequencies (in cm^{-1}), respectively (experimental frequencies were taken from [9]). In both equations, experimental frequencies of the gas phase were applied (if not available, the Raman frequencies in the liquid phase were used).

RESULTS AND DISCUSSION

Molecular geometry. The conformation of methyl groups with respect to the plane of the molecule and to each other has a great effect on the geometry of the chelated ring (Fig. 1). Similar to many investigations, after the optimization of acetylacetone we observed that the enol tautomer had the C_s symmetry with a planar ring and an asymmetric hydrogen bond [7, 10]. The molecular equilibrium geometries predicted with the B3LYP, BLYP, B3P86, BP86, B3PW91, BPW91, G96LYP, G96PW91 density functionals and corresponding to X-ray experimental data and electron diffractions studies [4, 6, 11, 12] are given in Table 1. It is apparent that the replacement of the LYP correlation functional by any other functional leads to the prediction of shorter O···O and O···H distances, corresponding to a more symmetric and also stronger hydrogen bond. A similar tendency is observed when the B3 hybrid exchange functional is replaced by other functionals. The O···H distance obtained at the B3LYP level is 0.05—0.15 Å longer than that obtained at any other levels. At the same time, a slightly more delocalized bond structure is predicted when the B3LYP level is replaced by other levels. Gene-

Table 1

Regression coefficients, scaling factors and standard deviations for vibrational frequencies of AA[a]

AA	Below 2000 cm^{-1}							Above 2000 cm^{-1}							All frequencies						
	Method 1			Method 2				Method 1			Method 2				Method 1			Method 2			
	R^2	α	SD	R^2	α	β	SD	R^2	α	SD	R^2	α	β	SD	R^2	α	SD	R^2	α	β	SD
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
B3LYP																					
A	0.99676	0.958	27	0.99676	0.959	–1	27	0.96748	0.957	15	0.98445	0.846	345	11	0.99933	0.957	24	0.99933	0.956	1	25
B	0.99785	0.962	22	0.99794	0.954	10	22	0.81330	0.954	36	0.83567	1.140	–581	37	0.99924	0.956	26	0.99930	0.950	13	25
C	0.99840	0.966	19	0.99843	0.961	6	19	0.97885	0.958	12	0.98035	0.922	112	13	0.99959	0.960	19	0.99966	0.955	12	18
D	0.99840	0.971	19	0.99841	0.974	–3	19	0.66014	0.954	49	0.67420	1.115	–501	52	0.99890	0.959	31	0.99901	0.951	18	30
E	0.99843	0.972	19	0.99844	0.973	–1	19	0.60889	0.953	53	0.61720	1.078	–390	56	0.99880	0.969	33	0.99893	0.950	20	31
F	0.99862	0.974	17	0.99843	0.973	–1	19	0.97677	0.965	13	0.99221	0.858	329	8	0.99964	0.968	18	0.99968	0.963	10	17
G	0.99865	0.977	17	0.99865	0.973	1	18	0.98629	0.965	10	0.98909	0.916	150	9	0.99960	0.969	19	0.99968	0.962	15	17
B3PW91																					
A	0.99754	0.954	23	0.99754	0.955	–1	24	0.76795	0.955	40	0.97879	0.652	942	13	0.99915	0.955	27	0.99915	0.955	0	28
B	0.99824	0.959	20	0.99835	0.950	12	19	0.96949	0.952	15	0.97016	0.928	76	16	0.99958	0.954	19	0.99964	0.948	13	18
C	0.99786	0.963	22	0.99789	0.958	5	22	0.61677	0.958	52	0.95974	0.600	1112	18	0.99895	0.959	31	0.99898	0.955	9	31
D	0.99742	0.967	24	0.99743	0.968	–1	24	0.08398	0.961	80	0.93028	0.492	1451	24	0.99799	0.963	42	0.99802	0.959	8	43
E	0.99742	0.967	24	0.99742	0.968	–1	24	0.10300	0.961	80	0.93102	0.495	1442	24	0.99802	0.963	42	0.99805	0.959	8	42
F	0.99835	0.971	19	0.99835	0.970	1	19	0.97574	0.959	13	0.97900	0.907	162	13	0.99953	0.963	20	0.99960	0.956	14	19
G	0.99851	0.974	18	0.99852	0.972	2	18	0.97114	0.960	14	0.98420	0.861	307	11	0.99952	0.964	21	0.99961	0.956	17	19
B3P86																					
A	0.99747	0.954	24	0.99748	0.957	–4	24	0.56471	0.955	55	0.96673	0.581	1165	17	0.99881	0.955	33	0.99881	0.956	–2	33
B	0.99808	0.959	21	0.99815	0.951	9	21	0.95219	0.953	18	0.98277	0.810	446	12	0.99953	0.955	21	0.99957	0.949	11	20
C	0.99737	0.962	24	0.99738	0.960	4	25	0.24348	0.959	73	0.93754	0.516	1374	23	0.99825	0.960	39	0.99828	0.956	8	40
D	0.99671	0.967	27	0.99672	0.969	–4	27	–0.61641	0.962	107	0.90483	0.419	1678	28	0.99672	0.964	54	0.99674	0.960	7	55
E	0.99670	0.967	27	0.99670	0.970	–4	28	–0.57608	0.962	106	0.90606	0.423	1668	28	0.99679	0.964	54	0.99680	0.960	7	54
F	0.99801	0.970	21	0.99802	0.972	–2	21	0.88159	0.960	29	0.98064	0.729	717	13	0.99935	0.963	24	0.99939	0.958	11	24
G	0.99831	0.973	19	0.99833	0.974	–1	20	0.82409	0.961	35	0.97555	0.690	840	14	0.99929	0.965	25	0.99935	0.959	13	24
BLYP																					
A	0.99519	0.988	33	0.99519	0.989	–2	33	–0.82083	0.993	113	0.91016	0.418	1723	27	0.99610	0.991	59	0.99610	0.992	–1	60
B	0.99735	0.992	24	0.99739	0.986	7	25	0.61613	0.989	52	0.95886	0.619	1112	18	0.99886	0.990	32	0.99889	0.987	8	32
C	0.99708	0.996	25	0.99708	0.994	3	26	–0.44088	0.993	101	0.90924	0.448	1632	27	0.99709	0.994	51	0.99711	0.990	8	52
D	0.99579	1.002	31	0.99582	1.006	–6	31	–1.20596	0.997	121	0.89073	0.402	1774	30	0.99582	0.998	61	0.99584	0.994	8	62
E	0.99583	1.002	30	0.99585	1.007	–6	31	–1.02703	0.997	120	0.89167	0.404	1767	30	0.99588	0.998	61	0.99590	0.994	8	61
F	0.99754	1.005	23	0.99754	1.006	–2	24	0.88719	0.993	28	0.98438	0.755	710	11	0.99924	0.996	26	0.99930	0.990	13	25
G	0.99743	1.008	24	0.99744	1.011	–4	24	0.68497	0.994	47	0.96312	0.647	1039	17	0.99887	0.998	32	0.99893	0.992	14	31
BPW91																					
A	0.99474	0.982	34	0.99478	0.988	–7	35	–4.88047	0.991	204	0.84627	0.276	2147	36	0.98935	0.988	97	0.98935	0.988	0	99
B	0.99774	0.988	22	0.99778	0.983	6	23	–0.59237	0.986	106	0.90157	0.432	1673	28	0.99697	0.987	52	0.99700	0.982	10	52
C	0.99399	0.992	36	0.99399	0.993	–1	37	–6.55635	0.994	231	0.82293	0.250	2229	38	0.98652	0.993	110	0.98657	0.987	12	111
D	0.99329	0.997	39	0.99331	1.002	–6	39	–5.95848	0.995	222	0.82857	0.258	2203	38	0.98737	0.996	106	0.98744	0.989	14	107
E	0.99328	0.997	39	0.99330	1.002	–5	39	–5.90330	0.995	221	0.82866	0.259	2201	38	0.98746	0.996	106	0.98752	0.989	14	107
F	0.99561	0.999	31	0.99564	1.004	–6	32	–2.44932	0.995	156	0.86060	0.337	1969	34	0.99352	0.996	76	0.99356	0.992	10	77
G	0.99620	1.003	29	0.99623	1.007	–6	29	–2.18813	0.995	150	0.86437	0.346	1940	33	0.99404	0.997	73	0.99409	0.991	13	74
BP86																					
A	0.99416	0.986	36	0.99420	0.992	–7	37	–5.87095	0.998	220	0.83752	0.261	2197	37	0.98759	0.994	105	0.98759	0.994	0	107
B	0.99417	0.986	36	0.99422	0.992	–7	37	–5.88127	0.997	221	0.83719	0.261	2197	37	0.98758	0.994	105	0.98758	0.994	0	107
C	0.99329	0.996	39	0.99330	0.998	–2	39	–7.67486	1.001	248	0.81709	0.238	2269	39	0.98455	0.999	117	0.98459	0.994	11	119
D	0.99262	1.001	40	0.99267	1.007	–8	41	–7.09749	1.002	239	0.82115	0.245	2249	38	0.98538	1.001	114	0.98544	0.995	12	116
E	0.99261	1.001	40	0.99267	1.008	–8	41	–7.02930	1.002	238	0.82118	0.246	2247	38	0.98549	1.002	114	0.98554	0.996	12	115
F	0.99510	1.003	33	0.99516	1.010	–9	33	–3.19472	1.002	172	0.85234	0.316	2038	35	0.99222	1.002	83	0.99224	0.999	6	84
G	0.99583	1.006	30	0.99586	1.012	–7	31	–2.98253	1.002	168	0.85405	0.322	2020	35	0.99269	1.003	81	0.99273	0.998	11	82

Continued Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
											G96LYP										
A	0.99393	0.983	37	0.99396	0.988	–6	37	–2.50788	0.995	157	0.87371	0.336	1971	32	0.99303	0.991	79	0.99304	0.994	–7	80
B	0.99741	0.988	24	0.99743	0.984	5	24	0.38778	0.990	66	0.94480	0.560	1291	21	0.99851	0.989	36	0.99851	0.988	3	37
C	0.99585	0.991	30	0.99586	0.994	–3	31	–3.02903	0.997	169	0.85605	0.319	2023	34	0.99262	0.995	81	0.99262	0.994	2	82
D	0.99511	0.997	33	0.99515	1.003	–7	33	–2.42910	0.997	156	0.86633	0.339	1965	33	0.99348	0.997	76	0.99349	0.995	5	77
E	0.99512	0.998	33	0.99516	1.003	–7	33	–2.39084	0.997	155	0.86628	0.340	1961	33	0.99354	0.997	76	0.99355	0.995	5	77
F	0.99695	1.000	26	0.99698	1.005	–7	26	0.00427	0.996	84	0.92358	0.499	1484	25	0.99778	0.997	44	0.99779	0.995	4	45
G	0.99730	1.003	24	0.99732	1.008	–6	25	0.16371	0.995	77	0.93063	0.522	1414	24	0.99808	0.997	41	0.99810	0.993	8	42
											G96PW91										
A	0.99331	0.981	38	0.99333	0.985	–5	39	–6.18156	0.991	225	0.83706	0.255	2210	37	0.98694	0.987	108	0.98694	0.986	2	110
B	0.99666	0.985	27	0.99668	0.981	5	28	–2.50762	0.989	157	0.86136	0.333	1974	34	0.99363	0.988	75	0.99365	0.984	7	76
C	0.99042	0.990	46	0.99042	0.989	0	47	–9.07989	0.995	267	0.81065	0.222	2312	40	0.98171	0.993	128	0.98179	0.986	15	129
D	0.98993	0.994	47	0.98994	0.997	–3	48	–8.75355	0.995	263	0.81244	0.226	2302	39	0.98217	0.993	128	0.98227	0.987	17	128
E	0.98992	0.994	47	0.98993	0.997	–3	48	–8.70937	0.995	262	0.81276	0.226	2301	39	0.98224	0.995	126	0.98234	0.987	17	127
F	0.99313	0.997	39	0.99315	1.001	–5	40	–4.42466	0.996	196	0.83969	0.285	2124	36	0.98984	0.996	95	0.98987	0.992	10	96
G	0.99372	0.999	37	0.99374	1.003	–5	38	–4.24268	0.996	192	0.84073	0.289	2113	36	0.99024	0.997	93	0.99030	0.991	12	94

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[a] A, B,C, D, E, F, and G stand for 6-31G, 6-31G*, 6-31G**, 6-31+G**, 6-31++G**, 6-311G**, and 6-311++G** basis sets, respectively.

rally, the geometrical parameters predicted by B3LYP are in excellent agreement with the experimental data, except for the O—H distance. The main problem in the prediction of the O—H bond length by theoretical methods arises from the double minimum potential nature with a relatively low barrier in these systems [22, 35, 36]. Theoretically we obtain the H atom at the bottom of the potential well, whereas experimentally it is to be found at the vibrational ground state which, in the case of a low barrier double minimum potential, may be quite different from that in the electronic minima. Table 1 also indicates that the 6-31G* basis set gives the longest O···O and O···H distances and the shortest O—H bond length. The addition of a polarized orbital on H considerably changes the geometry of the hydrogen bond. According to Table 1, the results of the calculations are in good agreement with the electron diffraction data [4, 12], unlike those obtained by X-ray diffraction [11]. The predicted geometrical parameters by the 6-31G basis set are far from those obtained by other basis sets and experimental ones.

VIBRATIONAL FREQUENCIES

The fundamental wavenumbers obtained for acetylacetone using different DFT methods were compared with the experimental ones by means of two different regression analyses (Eq. 1 and 2). In the first regression analysis, we consider the intercept equivalent zero (Eq. 1). In this method, the computed harmonic frequencies for the acetylacetone molecule were compared with the corresponding experimental values to obtain regression parameters. In the second method, the intercept (β) was added to the calculations. The average values of regression parameters for three regions (all frequencies below and above 2000 cm^{-1}) of the vibrational modes of acetylacetone obtained by two methods are presented in Table 2. In order to relate the O—H vibrational modes to the obtained regression parameters, the O—H vibrational frequencies, including stretching, in-plane bending, and out-of-plane bending modes, were excluded. Similar to Table 2, the average values of the regression parameters, after the O—H vibrations were removed for acetylacetone, are presented in Table 3. From these tables some points have been concluded:

a) the obtained *SD* values for Eq. 1 have a high accuracy as compared to Eq. 2.

b) Table 3 shows that when O—H vibrations were excluded, good agreement was obtained between the calculated and experimental frequencies corresponding to smaller SD values.

c) good agreement between the experimental and calculated frequencies were obtained at the B3LYP level.

Table 2

The calculated R^2, SD *and* α *by excluding the* OH *stretching*, *in-plan and out-of-plane bending modes for* AA[a]

AA By excluding OH Freq	Below 2000 cm^{-1}							Above 2000 cm^{-1}							All frequencies						
	Method 1			Method 2				Method 1			Method 2				Method 1			Method 2			
	R^2	α	SD	R^2	α	β	SD	R^2	α	SD	R^2	α	β	SD	R^2	α	SD	R^2	α	β	SD
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
B3LYP																					
A	0.99676	0.958	27	0.99676	0.959	–1	28	0.91046	0.956	16	0.97245	0.763	604	10	0.99928	0.957	25	0.99928	0.956	2	26
B	0.99800	0.961	21	0.99807	0.954	9	22	0.94922	0.958	12	0.96969	0.836	380	10	0.99955	0.959	20	0.99958	0.955	8	20
C	0.99854	0.967	18	0.99858	0.961	7	18	0.93926	0.958	13	0.96647	0.820	430	11	0.99960	0.961	19	0.99966	0.955	13	18
D	0.99889	0.973	16	0.99889	0.974	–1	16	0.94744	0.959	12	0.97221	0.827	412	10	0.99959	0.963	19	0.99966	0.957	15	17
E	0.99886	0.974	16	0.99886	0.973	0	17	0.94594	0.959	12	0.97410	0.820	435	9	0.99957	0.964	19	0.99966	0.956	16	18
F	0.99863	0.974	18	0.99864	0.973	2	18	0.95726	0.964	11	0.97710	0.844	374	9	0.99962	0.968	18	0.99967	0.962	11	17
G	0.99866	0.977	18	0.99866	0.975	2	18	0.95908	0.965	11	0.97767	0.848	363	9	0.99958	0.969	19	0.99966	0.962	14	18
B3PW91																					
A	0.99763	0.955	23	0.99763	0.955	0	24	0.87235	0.951	19	0.95246	0.737	673	13	0.99943	0.952	22	0.99944	0.950	4	23
B	0.99824	0.959	20	0.99836	0.950	12	20	0.91771	0.953	15	0.94951	0.805	463	13	0.99956	0.955	20	0.99962	0.949	13	19
C	0.99877	0.965	17	0.99882	0.959	8	17	0.89886	0.953	17	0.94311	0.783	533	14	0.99958	0.957	19	0.99968	0.949	16	17
D	0.99919	0.970	14	0.99919	0.969	1	14	0.91140	0.953	16	0.94907	0.795	497	13	0.99957	0.959	20	0.99969	0.950	18	17
E	0.99919	0.970	14	0.99919	0.969	1	14	0.91266	0.954	16	0.95021	0.795	497	13	0.99957	0.959	20	0.99969	0.950	19	17
F	0.99881	0.973	17	0.99882	0.971	3	17	0.92738	0.959	14	0.95557	0.819	439	12	0.99957	0.964	20	0.99966	0.956	16	18
G	0.99889	0.976	16	0.99891	0.973	4	16	0.92864	0.959	14	0.95630	0.820	435	12	0.99953	0.964	20	0.99966	0.955	19	18
B3P86																					
A	0.99769	0.955	23	0.99769	0.957	–3	24	0.87440	0.950	19	0.95423	0.737	672	12	0.99943	0.951	22	0.99944	0.949	4	23
B	0.99810	0.959	21	0.99818	0.951	10	21	0.91811	0.951	15	0.94849	0.807	455	13	0.99952	0.954	21	0.99958	0.948	13	20
C	0.99868	0.965	17	0.99871	0.960	6	18	0.90059	0.952	17	0.94311	0.785	524	14	0.99953	0.956	20	0.99964	0.948	17	18
D	0.99906	0.970	15	0.99906	0.971	–1	15	0.91052	0.952	16	0.94878	0.793	501	13	0.99949	0.958	21	0.99963	0.949	19	18
E	0.99906	0.971	15	0.99906	0.971	–1	15	0.91231	0.952	16	0.94990	0.794	497	13	0.99949	0.958	21	0.99962	0.949	19	18
F	0.99888	0.973	16	0.99888	0.972	0	16	0.92801	0.958	14	0.95685	0.816	443	12	0.99956	0.963	20	0.99965	0.955	16	18
G	0.99902	0.975	15	0.99902	0.975	1	15	0.93025	0.958	14	0.95790	0.819	435	12	0.99953	0.963	20	0.99965	0.954	19	18
BLYP																					
A	0.99557	0.989	32	0.99557	0.990	0	33	0.91738	0.982	15	0.97284	0.793	577	9	0.99900	0.984	30	0.99903	0.980	8	30
B	0.99736	0.992	25	0.99742	0.986	8	25	0.95484	0.984	11	0.97270	0.867	357	10	0.99938	0.987	23	0.99944	0.981	12	23
C	0.99801	0.999	21	0.99803	0.995	5	22	0.94587	0.983	12	0.96946	0.851	404	10	0.99939	0.988	23	0.99951	0.980	18	21
D	0.99784	1.005	22	0.99785	1.008	–3	23	0.96178	0.985	10	0.97951	0.868	355	8	0.99923	0.991	26	0.99937	0.982	19	24
E	0.99785	1.006	22	0.99786	1.008	–3	23	0.96171	0.985	10	0.97951	0.868	356	8	0.99923	0.991	26	0.99937	0.982	20	24
F	0.99800	1.006	21	0.99800	1.006	0	22	0.96748	0.990	9	0.98116	0.885	316	8	0.99937	0.995	24	0.99948	0.987	17	22
G	0.99787	1.009	22	0.99787	1.011	–2	23	0.97620	0.989	8	0.98541	0.902	264	7	0.99926	0.996	26	0.99940	0.986	20	23
BPW91																					
A	0.99640	0.986	29	0.99642	0.989	–5	29	0.90317	0.973	16	0.96205	0.780	594	11	0.99909	0.977	28	0.99913	0.972	11	28
B	0.99815	0.990	21	0.99822	0.983	9	21	0.92252	0.976	15	0.94992	0.834	435	13	0.99943	0.980	22	0.99956	0.972	19	20
C	0.99853	0.997	18	0.99854	0.997	1	19	0.92214	0.974	15	0.95167	0.829	448	13	0.99926	0.982	25	0.99948	0.970	24	22
D	0.99855	1.003	18	0.99856	1.006	–3	19	0.92131	0.976	15	0.95402	0.823	468	12	0.99910	0.984	28	0.99936	0.971	27	24
E	0.99855	1.003	18	0.99856	1.006	–3	19	0.92229	0.976	15	0.95404	0.825	462	12	0.99910	0.985	28	0.99937	0.971	27	24
F	0.99891	1.004	16	0.99892	1.007	–4	16	0.95007	0.981	12	0.96656	0.867	346	11	0.99934	0.988	24	0.99952	0.977	23	21
G	0.99883	1.007	16	0.99884	1.010	–3	17	0.94919	0.981	12	0.96544	0.868	344	11	0.99923	0.989	26	0.99947	0.977	25	22
BP86																					
A	0.99644	0.990	29	0.99645	0.994	–5	29	0.91017	0.978	16	0.96526	0.790	577	11	0.99911	0.982	28	0.99915	0.977	11	28
B	0.99645	0.990	29	0.99647	0.994	–5	29	0.91075	0.978	16	0.96502	0.791	574	11	0.99911	0.982	28	0.99915	0.977	11	28
C	0.99843	1.002	19	0.99843	1.002	0	19	0.92869	0.980	14	0.95836	0.833	448	12	0.99928	0.987	25	0.99947	0.976	23	22
D	0.99849	1.008	19	0.99852	1.013	–6	19	0.92917	0.981	14	0.95994	0.832	455	12	0.99914	0.990	28	0.99936	0.978	25	24
E	0.99849	1.008	19	0.99852	1.013	–7	19	0.92940	0.982	14	0.95927	0.834	449	12	0.99914	0.990	27	0.99935	0.978	24	24
F	0.99894	1.008	16	0.99897	1.013	–6	16	0.95177	0.986	12	0.97067	0.865	367	10	0.99940	0.993	23	0.99954	0.983	20	20
G	0.99883	1.011	16	0.99884	1.014	–4	17	0.94992	0.986	12	0.96783	0.868	359	10	0.99928	0.994	25	0.99949	0.982	24	22

Continued Table 2

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
G96LYP																					
A	0.99492	0.986	34	0.99494	0.989	–4	35	0.93844	0.980	13	0.98184	0.810	520	8	0.99890	0.982	31	0.99891	0.980	4	32
B	0.99751	0.989	24	0.99754	0.984	6	24	0.95179	0.983	12	0.97236	0.858	380	10	0.99944	0.985	22	0.99947	0.980	9	22
C	0.99839	0.996	19	0.99839	0.996	0	20	0.95661	0.981	11	0.97649	0.859	374	9	0.99950	0.986	21	0.99957	0.979	15	20
D	0.99819	1.002	20	0.99821	1.006	–4	21	0.95384	0.983	11	0.97709	0.851	400	9	0.99933	0.989	24	0.99944	0.980	18	22
E	0.99821	1.002	20	0.99822	1.006	–4	21	0.95573	0.983	11	0.97744	0.855	388	9	0.99932	0.989	24	0.99945	0.980	18	22
F	0.99845	1.003	19	0.99846	1.006	–4	19	0.97125	0.987	9	0.98382	0.887	304	7	0.99949	0.992	21	0.99956	0.985	14	20
G	0.99822	1.005	20	0.99823	1.008	–4	21	0.97194	0.987	9	0.98383	0.889	297	7	0.99938	0.993	23	0.99949	0.985	17	22
G96PW91																					
A	0.99603	0.985	30	0.99604	0.987	–3	31	0.89201	0.971	17	0.95930	0.768	627	12	0.99898	0.976	30	0.99905	0.969	13	29
B	0.99796	0.988	22	0.99800	0.982	7	22	0.93171	0.974	14	0.95586	0.841	411	12	0.99940	0.979	23	0.99951	0.970	18	21
C	0.99701	0.997	26	0.99702	0.995	2	27	0.91575	0.973	15	0.95176	0.815	488	13	0.99891	0.981	31	0.99916	0.968	26	28
D	0.99712	1.001	26	0.99712	1.003	–2	26	0.91429	0.974	15	0.95121	0.813	493	13	0.99879	0.982	33	0.99907	0.969	28	29
E	0.99714	1.002	26	0.99714	1.003	–2	26	0.91483	0.974	15	0.95179	0.813	493	13	0.99879	0.982	33	0.99908	0.969	28	29
F	0.99802	1.003	21	0.99803	1.005	–3	22	0.93941	0.979	13	0.96317	0.846	406	11	0.99913	0.986	28	0.99933	0.975	23	25
G	0.99796	1.005	22	0.99797	1.007	–2	22	0.94082	0.979	13	0.96294	0.850	394	11	0.99905	0.987	29	0.99929	0.974	26	25

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[a] See footnote of Table 1.

Since the functional groups replaced by the CH_3 group of acetylacetone have only a negligible effect on the position of all vibrations, we can also apply this results to other β-dicarbonyls [14, 37, 38].

The tabulated scaling factors have values in the range of 0.950—1.003. For each given functional, a change in the basis set causes only a slight change in the scaling factor. The scaling factor depends on the exchange-correlation functional more than the basis sets. The change in the regression coefficient R^2 caused by the applied basis sets calculated at the B3LYP level using Eq. 1 is as follows:

6-311G** > 6-311++G** > 6-31G** > 6-31+G > 6-31G* > 6-31++G** > 6-31G.

R^2 results at the BLYP level with 6-311G** are very close. They also show a clear difference between the results of B3LYP, B3P86, B3PW91, and BLYP with those obtained at other levels. From these tables it follows that B3PW91, B3P86, and B3LYP functionals predict the harmonic vibrational frequencies closest to the experimental fundamental frequencies. It is clear that least SDs are obtained with R^2 closer to 1 and the least of them belong to B3LYP, B3PW91, and B3P86. The best α values were obtained using Eq. 1 at the BP86, BPW91, and G96PW91 levels. After the O—H vibrations were removed, almost all calculation levels gave reasonably good results, as presented in Tables 3. As shown in these Tables, we can observe that the obtained results of both equations have not great differences. These calculations indicate that the most deviation in frequencies belongs to O—H vibrational frequencies.

In the region below 2000 cm^{-1} (the fingerprint region), quantum chemical predictions can be most useful in making vibrational band assignments that may not be otherwise interpretable. Also, high-energy modes can be expected to be more anharmonic, leading to greater errors because of using the harmonic approximation [39]. In order to investigate the utility of separated scaling factors (duel scaling) for the two ranges < 2000 cm^{-1} and > 2000 cm^{-1}, we reanalyzed the agreement between the theoretical harmonic frequencies and experimental fundamentals for two ranges (Tables 2 and 3). The theoretical description of the fundamental vibrations in the region above 2000 cm^{-1} is not straightforward; one problem is the strong anharmonicity of the O—H stretching vibration, as discussed below. Another problem is the difficulty in determining the exact position of the O—H stretching wavenumber because of its weakness and broadness. Other factors which affect the measurement of the position of this band are its overlapping with the C—H stretching, combination, and overtone bands. Additionally the estimation of the hydrogen bond strength highly depends on the applied level and basis sets. Thus, we have removed the O—H stretching from our regression analysis. Tables 2 and 3 also indicate that in the calculations of frequencies below 2000 cm^{-1}, by increasing the basis set size the scaling fac-

Table 3

Bond distances (Å) *and bond angles* (deg.) *of* AA[a]

	$O_5...O_7$	$O_5—H_6$	$H_6...O_7$	$C_1=O_7$	$C_4—O_5$	$C_1—C_2$	$C_2=C_4$	OHO	CCC	$C_2C_1O_7$	CCO
1	2	3	4	5	6	7	8	9	10	11	12
Exp [19]	2.535	1.030	1.660	1.238	1.331	1.412	1.338	141.0	122.2	120.5	122.8
Exp [20]	2.512	1.049	—	1.243	1.319	1.430	1.382	137.0	119.7	123.0	121.0
Exp [21]	2.381	—	—	—	1.315	—	1.416	—	118.0	120.0	—
Exp [22]	2.592	1.003	1.683	—	1.321	1.443	1.359	148.4	120.4	—	—
					B3LYP						
A	2.5412	1.0189	1.63507	1.27938	1.35298	1.44095	1.37579	145.5	121.0	121.2	121.7
B	2.5558	1.0092	1.63708	1.25002	1.32818	1.44483	1.37238	149.0	120.6	121.9	122.3
C	2.5187	1.0135	1.58561	1.25238	1.32473	1.44214	1.37405	150.7	120.0	121.6	121.9
D	2.5107	1.0164	1.57691	1.25672	1.32496	1.44054	1.37816	150.3	120.2	121.2	121.5
E	2.5146	1.0152	1.57983	1.25612	1.32565	1.44136	1.37752	150.2	120.3	121.3	121.5
F	2.5411	1.0033	1.62723	1.24397	1.32469	1.44449	1.36974	149.1	120.5	121.7	122.2
G	2.54440	1.00300	1.63477	1.24555	1.32608	1.44444	1.37028	148.5	120.8	121.5	122.0
					B3P86						
A	2.50480	1.02700	1.58159	1.27878	1.34467	1.43424	1.37531	146.8	120.5	121.0	121.5
B	2.51850	1.01630	1.58374	1.24937	1.31980	1.43778	1.37192	150.5	120.0	121.7	122.0
C	2.47250	1.02560	1.51618	1.25279	1.31518	1.43396	1.37455	152.6	119.3	121.4	121.9
D	2.45920	1.03210	1.49610	1.25747	1.31415	1.43119	1.37896	152.7	119.4	121.0	121.0
E	2.45970	1.03190	1.49701	1.25741	1.31429	1.43129	1.37889	152.7	119.3	121.0	121.0
F	2.48940	1.01580	1.54906	1.24532	1.31440	1.43499	1.37085	151.5	119.7	121.5	121.7
G	2.48630	1.01710	1.54613	1.24730	1.31448	1.43398	1.37213	151.2	119.9	121.3	121.5
					B3PW91						
A	2.51740	1.02390	1.59940	1.27869	1.34682	1.43697	1.37609	146.5	120.6	121.1	121.5
B	2.53140	1.01340	1.60144	1.24918	1.32185	1.44071	1.37274	150.2	120.2	121.8	122.1
C	2.48590	1.02160	1.53576	1.25241	1.31745	1.43708	1.37519	152.3	119.5	121.5	121.6
D	2.47370	1.02690	1.51826	1.25677	1.31666	1.43460	1.37931	152.3	119.6	121.1	121.2
E	2.47410	1.02680	1.51890	1.25675	1.31676	1.43465	1.37928	152.2	119.6	121.1	121.2
F	2.50630	1.01120	1.57338	1.24445	1.31725	1.43879	1.37085	151.0	119.9	121.6	121.8
G	2.50320	1.01240	1.57787	1.24567	1.31814	1.43870	1.37131	150.5	120.2	121.4	121.7
					BLYP						
A	2.53870	1.04920	1.58443	1.30015	1.36496	1.44525	1.39118	148.5	120.8	121.0	121.3
B	2.55740	1.03280	1.60483	1.26870	1.34012	1.44884	1.38672	151.0	120.5	121.7	121.9
C	2.51560	1.04070	1.54443	1.27178	1.33592	1.44560	1.38883	152.8	119.9	121.4	121.5
D	2.50620	1.04480	1.53277	1.27685	1.33695	1.44436	1.39307	152.5	120.1	121.0	121.0
E	2.50660	1.04460	1.53360	1.27681	1.33703	1.44440	1.39304	152.4	120.1	121.0	121.0
F	2.54400	1.02520	1.59849	1.26233	1.33684	1.44857	1.38362	151.0	120.4	121.6	121.8
G	2.53450	1.02890	1.58642	1.26640	1.33664	1.44590	1.38647	150.8	120.6	121.3	121.4
					BPW91						
A	2.48890	1.06820	1.50306	1.30207	1.35294	1.43592	1.39391	150.5	120.1	120.8	120.8
B	2.52050	1.04130	1.54997	1.26770	1.33052	1.44219	1.38690	152.6	120.0	121.5	121.6
C	2.45310	1.06840	1.43971	1.27538	1.32147	1.43376	1.39349	155.7	118.9	121.1	120.9
D	2.45640	1.06580	1.44884	1.27719	1.32434	1.43526	1.39439	155.0	119.3	120.8	120.6
E	2.45680	1.06550	1.44947	1.27717	1.32444	1.43530	1.39437	155.0	119.3	120.8	120.6
F	2.47760	1.04850	1.49118	1.26614	1.32257	1.43616	1.38779	154.2	119.4	121.3	121.1
G	2.47970	1.04730	1.49709	1.26738	1.32404	1.43649	1.38804	153.7	119.7	121.0	120.9

Continued Table 1

1	2	3	4	5	6	7	8	9	10	11	12
BP86											
A	2.48330	1.07560	1.48858	1.30453	1.35317	1.43595	1.39585	150.8	119.9	120.8	120.7
B	2.50190	1.05320	1.53010	1.27063	1.33014	1.44118	1.38943	153.0	119.7	121.5	121.5
C	2.44890	1.07600	1.42705	1.27779	1.32160	1.43357	1.39543	155.9	118.8	121.1	120.8
D	2.45190	1.07340	1.43594	1.27979	1.32460	1.43524	1.39649	155.2	119.2	120.7	120.5
E	2.45220	1.07290	1.43680	1.27973	1.32473	1.43533	1.39644	155.1	119.2	120.7	120.5
F	2.47270	1.05480	1.47910	1.26842	1.32276	1.43633	1.38983	154.4	119.2	121.3	121.1
G	2.47460	1.05390	1.48431	1.26979	1.32448	1.43671	1.38996	153.9	119.5	121.0	120.9
G96LYP											
A	2.51220	1.05810	1.54263	1.30181	1.35950	1.44104	1.39368	149.5	120.4	120.9	120.9
B	2.51054	1.04895	1.58658	1.26794	1.33710	1.44721	1.38663	151.5	120.4	121.6	121.7
C	2.48140	1.05440	1.48878	1.27458	1.32911	1.43967	1.39231	154.3	119.4	121.2	121.0
D	2.48630	1.05160	1.50073	1.27663	1.33242	1.44127	1.39329	153.4	119.8	120.9	120.8
E	2.48660	1.05140	1.50139	1.27660	1.33250	1.44130	1.39326	153.4	119.8	120.9	120.8
F	2.51190	1.03490	1.54878	1.26445	1.33047	1.44275	1.38632	152.4	120.0	121.4	121.4
G	2.51510	1.03370	1.55659	1.26585	1.33218	1.44295	1.38648	151.7	120.3	121.2	121.2
G96PW91											
A	2.47350	1.07380	1.47863	1.30177	1.34948	1.43409	1.39443	151.1	119.9	120.6	120.6
B	2.49220	1.05120	1.50576	1.26957	1.32500	1.43738	1.38940	153.7	119.6	121.4	121.2
C	2.43420	1.07910	1.40624	1.27611	1.31700	1.43065	1.39466	156.5	118.6	120.9	120.6
D	2.43660	1.07720	1.41282	1.27766	1.31934	1.43167	1.39527	156.0	119.0	120.6	120.4
E	2.43680	1.07700	1.41328	1.27766	1.31943	1.43169	1.39524	156.0	119.0	120.6	120.4
F	2.45750	1.05750	1.45733	1.26666	1.31807	1.43286	1.38857	155.2	119.1	121.1	120.9
G	2.45840	1.05660	1.46103	1.26760	1.31906	1.43300	1.38870	154.8	119.4	120.9	120.7

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[a] See footnote of Table 1.

tor increases, SD decreases, and the regression coefficient approaches 1. The most deviations of theoretical frequencies from the experimental frequencies are observed for O—H stretching, in-plane bending and out-of-plane bending modes, and this deviation for the stretching mode is more pronounced than for the others. Since the greatest deviation observed for the range 2000—3100 cm^{-1} containing the O—H stretching, we could not obtain reasonable results for this region using several levels and basic sets. The calculated deviations, obtained at the B3LYP, B3PW91, and B3P86 levels, are less than those obtained at the other calculation levels. Applying Eq. 2 for the calculation of regression parameters, we obtained the reasonable results specially for the region > 2000 cm^{-1}. As shown in Tables 2 and 3, we obtained the superior results at the BLYP, BP86, BPW91, G96LYP, and G96PW91 levels in the region above 2000 cm^{-1}. Table 3 and reports the scaling factors for the vibrational frequencies in the separated regions after the removal of O—H frequencies. Therefore, we concluded that B3LYP, B3PW91, and B3P86 levels predict the hydrogen bond strength better than other levels and all the other levels suggested a stronger hydrogen bond than B3LYP, B3PW91, and B3P86. These results are in good agreement with those obtained for the calculation of proton tunnelling and potential function for malonaldehyde ($C_3H_4O_2$) [35,40,41] and 6-hydroxy-2-formylfulvene ($C_7H_6O_2$) [36].

CONCLUSIONS

We have performed *ab initio* and density functional theory calculations of the molecular properties of acetylacetone, such as frequencies and geometric data, with various combinations of exchange correlation functionals. The obtained results indicate that the applied DFT methods can be used for β-diketones to predict the molecular properties with good accuracy. The best results were obtained at the B3LYP, B3PW91, and B3P86 levels.

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