

Vibrational spectral assignments of paraldehyde by *ab initio* and density functional methods

Sethu Gunasekaran · Ramadoss Arunbalaji ·
Subramanian Kumaresan · Srinivasan Seshadri ·
Sambantham Muthu

Received: 8 September 2007 / Accepted: 28 January 2008 / Published online: 26 February 2008
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Abstract The FTIR and Laser-Raman spectra of paraldehyde have been recorded in the regions 4000–400 cm^{-1} and 3500–250 cm^{-1} respectively. Molecular electronic energy, geometrical structure, harmonic vibrational spectra, infrared intensities and Raman scattering activities have been computed at the HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory. The results were compared with experimental values with the help of scaling procedures. The observed wave numbers in FTIR and Laser-Raman spectra were analyzed and assigned to different normal modes of the molecule. Most of the modes have wave numbers in the expected range and are in good agreement with computed values.

Keywords *Ab initio* · DFT · FTIR · Laser Raman spectra · Paraldehyde · Vibrational analysis

S. Gunasekaran · R. Arunbalaji (✉)
SpectroPhysics Research Laboratory, Pachaiyappa's college,
Chennai 600030, India
e-mail: arunbalaji_81@yahoo.co.in

S. Kumaresan
Department of Physics,
Arulmigu Meenakshi Amman College of Engg,
Vadamavandal 604410, India

S. Seshadri
Department of Physics,
Sri ChandraSekarendra Viswa Maha Vidyalaya,
Enathur 63156, India

S. Muthu
Department of Physics, Sri Venkateshwara College of Engg,
Sriperumbandur 602105, India

Introduction

Paraldehyde (2,4,6-trimethyl-1,3,5-trioxane) is a cyclic trimer of acetaldehyde. Pharmaceutically, it is used as Central Nervous System (CNS) depressant, anticonvulsant, hypnotic and sedative, included in some cough medicines as an expectorant. It acts as solvent for fats, oils, waxes, rubber and resins, as a substitute for acetaldehyde, as an intermediate for organic chemicals, dye stuffs and as accelerators for vulcanizations rubber oxidants, etc. [1]. The presence of lone pair of electrons in the oxygen atom of the carbonyl group imparts several characteristic features to aldehydes. Gunasekaran et al. [2] has recorded the FTIR and Laser Raman spectra of paraldehyde in the regions 4000–400 cm^{-1} and 3500–250 cm^{-1} respectively. Although spectral investigation on aldehydes has been carried out by many, not much work has been done on paraldehyde [3–7].

Density functional theory (DFT), accepted by the *ab initio* quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems [8–15], have shown promising conformity with experimental results. Therefore, in this present investigation DFT is used to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy.

Ab initio, HF and DFT calculations have been performed to support our wave number assignments. The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

Experimental

FTIR spectrum of paraldehyde was recorded in the region $4000 - 400 \text{ cm}^{-1}$, on a BRUKER IFS-66V spectrophotometer with a resolution of 0.5 cm^{-1} . All the sharp bands of the spectrum have an accuracy of $\pm 1 \text{ cm}^{-1}$. The liquid sample of paraldehyde housed in a purgeable chamber composed of KBr window. The Laser-Raman spectrum of paraldehyde was recorded on a DILOR Z 24 spectrophotometer using argon ion laser source. The monochromator consists of 3 holographic gratings having 1800 lines to a millimeter. The experimental FTIR and Laser-Raman spectra of paraldehyde are presented in Figs. 1 and 2.

Computational

The ab initio quantum mechanical calculations were performed using Gaussian 03W [16] program package, invoking gradient geometry optimization [17]. Initial geometry generated from standard geometrical parameter was minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard 6-31G(d,p) basis set. This geometry was then re-optimized at B3LYP level using 6-31G(d,p) basis set. The optimized structural parameters were used in the vibrational frequencies calculations at the HF and DFT levels to characterize all stationary points as minima. The vibrationally averaged nuclear positions of paraldehyde were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and force constants. We utilized the gradient corrected density functional theory [18] with three-parameter hybrid functional (B3)[19] for exchange part and the Lee-Yang-Parr (LYP) correlation function [20], for the computation of vibrational frequencies and energies of optimized structure. The calculated normal mode vibrational frequencies also provide thermo dynamical properties through the principle

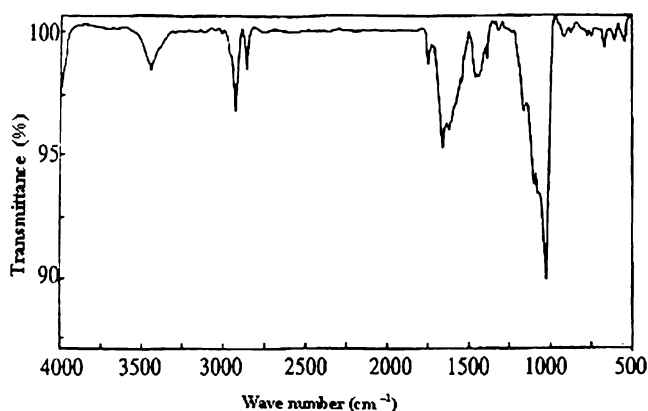


Fig. 1 FTIR spectrum of paraldehyde

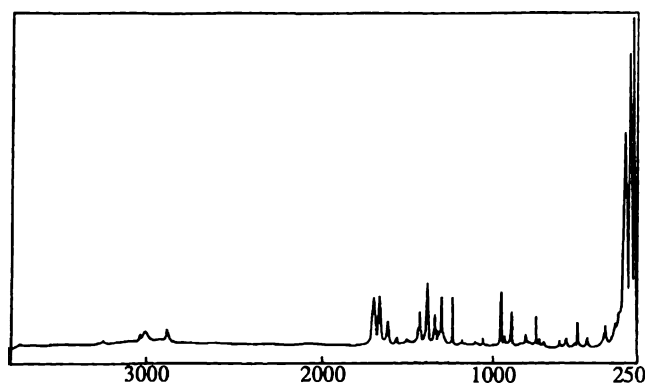


Fig. 2 Laser-Raman spectrum of paraldehyde

of statistical mechanics. To compensate errors arising from basis set incompleteness and neglect of vibrational anharmonicity we have scaled the frequencies with scaling factor, 0.9026(HF) and 0.9608(B3LYP) [21].

Results and discussion

Molecular geometry

Paraldehyde has a staggered six membered ring of alternate carbon and oxygen atoms with a hydrogen atom and methyl group attached to each of the ring carbon atoms, the methyl carbon atoms being approximately co-planar with the ring oxygen. The experimental X-ray data for paraldehyde were used to calculate geometrical parameters. The optimized structure parameters of paraldehyde calculated by ab initio HF and B3LYP levels with 6-31G(d,p) basis sets are listed in Table 1 in accordance with the numbering scheme given in Fig. 3. Table 1 compares the calculated bond lengths and bond angles for paraldehyde with those of experimental data [22]. The carbon-oxygen distance of $1.41 \pm 0.05 \text{ \AA}$, a carbon-carbon distance of $1.52 \pm 0.05 \text{ \AA}$ and the bond angle $109 \pm 5^\circ$ for paraldehyde agrees very well with the literature [23].

Vibrational band assignments

With the assumed structural model, the molecule belongs to C_1 point group and has 57 modes of fundamental vibrations. All the modes are active both in infrared (IR) and Raman (R). Paraldehyde is found to have puckered ring structure with low symmetry, coupling between normal modes increase to the level, where the application of ‘Group-Frequency’ concept becomes untenable.

We have, therefore, taken recourse to the calculation and visualization of contribution of internal co-ordinates in each normal mode; by Gaussian Package [16] and Chemcraft [24]. Figures 1 and 2 show the observed FTIR and Laser

Table 1 Optimized parameters for paraldehyde at B3LYP and RHF with 6–31G (d,p) basis set

Parameters	Experimental ^a	RHF/6–31G (d,p)	B3LYP/6–31G (d,p)
Bond length			
O ₁ -C ₂	1.417	1.402	1.402
O ₁ -C ₆	1.417	1.402	1.402
C ₂ -O ₃	1.417	1.402	1.402
C ₂ -C ₉	1.510	1.523	1.523
C ₂ -H ₁₀	1.107	1.113	1.113
O ₃ -C ₄	1.417	1.402	1.402
C ₄ -O ₅	1.417	1.399	1.399
C ₄ -C ₈	1.510	1.523	1.523
C ₄ -H ₁₁	1.107	1.113	1.113
O ₅ -C ₆	1.417	1.402	1.402
C ₆ -C ₇	1.510	1.523	1.523
C ₆ -H ₁₂	1.107	1.113	1.113
C ₇ -H ₁₃	1.093	1.113	1.113
C ₇ -H ₁₄	1.093	1.113	1.113
C ₇ -H ₁₅	1.092	1.113	1.113
C ₈ -H ₁₆	1.093	1.113	1.113
C ₈ -H ₁₇	1.093	1.113	1.113
C ₈ -H ₁₈	1.092	1.112	1.112
C ₉ -H ₁₉	1.093	1.113	1.113
C ₉ -H ₂₀	1.093	1.113	1.113
C ₉ -H ₂₁	1.092	1.113	1.113
Bond angle			
C ₂ -O ₁ -C ₆	111.1	106.79	106.80
O ₂ -C ₂ -O ₃	110.7	99.90	99.89
O ₁ -C ₂ -C ₉	108.7	111.78	111.78
O ₁ -C ₂ -H ₁₀	108.5	114.97	114.96
O ₃ -C ₂ -C ₉	110.6	111.78	111.78
O ₃ -C ₂ -H ₁₀	108.7	114.97	114.97
C ₉ -C ₂ -H ₁₀	108.5	103.78	103.78
C ₂ -O ₃ -C ₄	108.7	106.79	106.80
O ₃ -C ₄ -O ₅	108.5	99.77	99.77
O ₃ -C ₄ -C ₈	111.1	111.81	111.81
O ₃ -C ₄ -H ₁₁	111.7	115.04	115.03
O ₅ -C ₄ -C ₈	110.0	111.80	111.81
O ₅ -C ₄ -H ₁₁	110.0	115.03	115.04
C ₈ -C ₄ -H ₁₁	109.3	103.71	103.71
C ₄ -O ₅ -C ₆	110.6	106.83	106.83
O ₁ -C ₆ -O ₅	108.7	99.90	99.89
O ₁ -C ₆ -C ₇	108.5	111.78	111.78
O ₁ -C ₆ -H ₁₂	108.8	114.97	114.97
O ₅ -C ₆ -C ₇	108.5	111.78	111.78
O ₅ -C ₆ -H ₁₂	111.1	114.97	114.91
C ₇ -C ₆ -H ₁₂	111.7	103.77	103.78
C ₆ -C ₇ -H ₁₃	110.0	109.50	109.49
C ₆ -C ₇ -H ₁₄	110.0	109.44	109.44
C ₆ -C ₇ -H ₁₅	109.4	109.46	109.46
H ₁₃ -C ₇ -H ₁₄	108.7	109.44	109.44
H ₁₃ -C ₇ -H ₁₅	108.5	109.46	109.46
H ₁₄ -C ₇ -H ₁₅	111.7	109.51	109.51
C ₄ -C ₈ -H ₁₆	110.0	109.50	109.49
C ₄ -C ₈ -H ₁₇	110.0	109.43	109.44
C ₄ -C ₈ -H ₁₈	109.4	109.46	109.46
H ₁₆ -C ₈ -H ₁₇	109.3	109.43	109.44

Table 1 (continued)

Parameters	Experimental ^a	RHF/6–31G (d,p)	B3LYP/6–31G (d,p)
H ₁₆ -C ₈ -H ₁₈	109.1	109.46	109.46
H ₁₇ -C ₈ -H ₁₈	109.1	109.51	109.52
C ₂ -C ₉ -H ₁₉	109.3	109.49	109.49
C ₂ -C ₉ -H ₂₀	109.1	109.44	109.44
C ₂ -C ₉ -H ₂₁	109.1	109.46	109.46
H ₁₉ -C ₉ -H ₂₀	109.3	109.43	109.43
H ₁₉ -C ₉ -H ₂₁	109.1	109.45	109.46
H ₂₀ -C ₉ -H ₂₁	109.1	109.52	109.52

^a Ref [22]

Raman spectra, respectively. The harmonic vibrational frequencies calculated for paraldehyde at HF and B3LYP levels using 6-31G(d,p) have been collected in Tables 2 and 3, respectively. The observed FTIR and Laser-Raman frequencies for various modes of vibrations are presented in Table 4. Comparison of the frequencies calculated at B3LYP with the experimental values (Table 4) reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system.

Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 40 cm⁻¹. Figure 4 shows computed IR and Raman spectrum obtained by B3LYP using 6-31G(d,p) basis set for comparison.

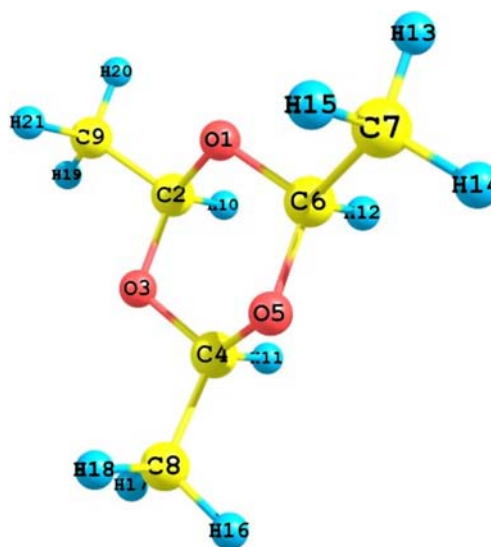
**Fig. 3** Numbering system adopted in this study (Paraldehyde)

Table 2 Vibrational wave numbers obtained for paraldehyde at HF/6–31G(d,p)[harmonic frequency(cm^{-1}), IR intensities (Km mol^{-1}), Raman scattering activities ($\text{A}^4 \text{amu}^{-1}$), Raman depolarization ratio and reduced masses (amu), force constants(m dyne A^{-1})]

Number	Wave number		IR intensity		Raman intensity		Depolarization ratios	Red mass	Force constants
	Unscaled	scaled	Rel	Abs	Rel	Abs			
1	166	150	64	22	37	10	0.75	2.73	0.04
2	166	150	7	3	8	2	0.75	2.73	0.04
3	176	158	7	3	8	2	0.38	2.93	0.05
4	243	219	39	13	106	30	0.74	1.01	0.04
5	253	228	39	13	106	30	0.75	1.18	0.04
6	254	229	0	0	0	0	0.75	1.18	0.04
7	288	260	0	0	344	100	0.75	2.63	0.12
8	288	260	23	8	3	0	0.75	2.63	0.12
9	452	407	23	8	3	0	0.00	2.59	0.31
10	508	458	216	77	149	43	0.75	4.22	0.64
11	508	458	5	2	4	1	0.75	4.22	0.64
12	555	501	5	2	4	1	0.04	3.45	0.63
13	623	562	22	8	7	2	0.75	3.31	0.75
14	623	562	0	0	19	5	0.75	3.31	0.75
15	837	755	0	0	19	5	0.04	5.63	2.32
16	924	834	0	0	0	0	0.34	2.01	1.02
17	953	860	5	2	17	5	0.75	1.94	1.04
18	954	862	5	2	17	5	0.75	1.94	1.04
19	1051	948	2	0	0	0	0.75	1.98	1.29
20	1051	948	61	21	1	0	0.75	1.98	1.29
21	1101	993	61	21	1	0	0.28	2.57	1.84
22	1200	1083	85	30	9	3	0.02	2.56	2.17
23	1220	1101	85	30	9	3	0.01	2.42	2.12
24	1234	1113	0	0	1	0	0.75	2.06	1.86
25	1235	1114	79	28	6	2	0.75	2.06	1.86
26	1267	1143	79	28	6	2	0.75	3.10	2.94
27	1268	1144	0	0	0	0	0.75	3.10	2.94
28	1316	1187	280	100	9	3	0.00	2.17	2.21
29	1349	1217	280	100	9	3	0.75	2.78	2.98
30	1349	1217	28	10	6	2	0.75	2.78	2.98
31	1483	1338	73	26	2	0	0.43	1.08	1.40
32	1516	1368	73	26	2	0	0.75	1.26	1.70
33	1516	1368	17	6	0	0	0.75	1.26	1.70
34	1534	1384	7	2	0	0	0.38	1.24	1.72
35	1550	1399	67	23	0	0	0.75	1.24	1.76
36	1551	1399	0	0	0	0	0.75	1.24	1.76
37	1582	1427	0	0	0	0	0.75	1.48	2.19
38	1583	1428	38	13	2	0	0.75	1.48	2.19
39	1607	1450	38	13	2	0	0.26	1.08	1.65
40	1610	1453	3	1	5	1	0.75	1.06	1.63
41	1611	1454	3	1	5	1	0.75	1.06	1.63
42	1614	1456	12	4	10	3	0.74	1.04	1.61
43	1620	1462	16	5	16	5	0.75	1.07	1.65
44	1621	1463	1	0	1	0	0.75	1.07	1.65
45	1639	1479	1	0	1	0	0.02	1.82	2.88
46	3120	2816	3	1	9	3	0.75	1.08	6.21
47	3120	2816	5	2	3	0	0.75	1.08	6.21
48	3145	2838	5	2	3	0	0.31	1.08	6.32
49	3206	2893	0	0	0	0	0.75	1.03	6.27
50	3207	2894	3	1	0	0	0.75	1.03	6.27
51	3207	2894	3	1	0	0	0.00	1.04	6.28
52	3283	2963	0	0	0	0	0.74	1.10	7.01
53	3284	2964	0	0	0	0	0.75	1.10	7.02

Table 2 (continued)

Number	Wave number		IR intensity		Raman intensity		Depolarization ratios	Red mass	Force constants
	Unscaled	scaled	Rel	Abs	Rel	Abs			
54	3284	2964	0	0	0	0	0.75	1.10	7.02
55	3293	2972	3	1	0	0	0.75	1.10	7.05
56	3293	2972	1	0	0	0	0.75	1.10	7.05
57	3294	2973	1	0	0	0	0.74	1.10	7.06

Table 3 Vibrational wave numbers obtained for paraldehyde at B3LYP/6–31G(d,p)[harmonic frequency (cm^{-1}), IR intensities (Km mol^{-1}), Raman scattering activities ($\text{A}^4 \text{amu}^{-1}$), Raman depolarization ratio and reduced masses (amu), force constants(m dyne A^{-1})]

Number	Wave number		IR intensity		Raman intensity		Depolarization ratios	Red mass	Force constants
	Unscaled	scaled	Rel	Abs	Rel	Abs			
1	159	153	5	2	37	10	0.73	2.56	0.03
2	161	155	4	1	8	2	0.75	2.57	0.04
3	169	162	4	1	8	2	0.39	2.89	0.05
4	219	210	1	0	102	30	0.74	1.01	0.03
5	229	220	20	9	102	30	0.73	1.19	0.04
6	230	221	1	0	0	0	0.75	1.18	0.04
7	267	257	1	0	340	100	0.73	2.70	0.11
8	268	257	12	5	3	0	0.75	2.72	0.12
9	421	404	13	6	3	0	0.00	2.56	0.27
10	471	452	197	97	139	40	0.75	4.42	0.58
11	472	453	7	3	4	1	0.73	4.43	0.58
12	523	502	7	3	4	1	0.04	3.50	0.56
13	572	549	0	0	7	2	0.75	3.21	0.62
14	572	549	0	0	19	5	0.73	3.21	0.62
15	758	728	0	0	19	5	0.04	7.16	2.42
16	843	809	2	0	0	0	0.33	1.97	0.82
17	865	831	0	0	13	3	0.75	2.01	0.89
18	866	832	0	0	13	3	0.75	2.01	0.89
19	916	880	5	2	0	0	0.73	6.36	3.14
20	961	923	23	11	1	0	0.75	2.21	1.19
21	961	923	26	12	1	0	0.27	2.20	1.19
22	1080	1037	44	21	7	2	0.02	1.63	1.12
23	1116	1072	42	20	7	2	0.01	2.34	1.71
24	1135	1090	0	0	1	0	0.75	2.56	1.94
25	1135	1090	80	39	6	1	0.73	2.53	1.92
26	1143	1098	82	40	6	1	0.75	2.54	1.95
27	1144	1099	0	0	0	0	0.75	2.59	1.99
28	1209	1161	13	6	7	2	0.00	2.70	2.33
29	1209	1161	202	100	7	2	0.73	2.71	2.33
30	1216	1168	200	99	6	1	0.75	2.07	1.81
31	1351	1298	24	10	2	0	0.43	1.07	1.16
32	1381	1326	21	10	2	0	0.73	1.24	1.40
33	1382	1327	97	48	1	0	0.75	1.25	1.40
34	1408	1352	99	49	1	0	0.39	1.24	1.44
35	1417	1361	60	29	1	0	0.75	1.22	1.45
36	1417	1361	0	0	0	0	0.75	1.22	1.45
37	1440	1383	45	22	0	0	0.73	1.44	1.75
38	1441	1384	45	22	2	0	0.75	1.43	1.74

Table 3 (continued)

Number	Wave number		IR intensity		Raman intensity		Depolarization ratios	Red mass	Force constants
	Unscaled	scaled	Rel	Abs	Rel	Abs			
39	1481	1422	0	0	2	0	0.26	1.72	2.22
40	1496	1437	9	4	5	1	0.73	1.04	1.37
41	1496	1437	10	4	5	1	0.75	1.04	1.38
42	1499	1440	11	5	11	3	0.74	1.14	1.52
43	1503	1444	8	3	14	4	0.73	1.04	1.39
44	1507	1448	1	0	1	0	0.75	1.05	1.41
45	1507	1448	1	0	1	0	0.02	1.05	1.41
46	2925	2810	1	0	9	2	0.73	1.08	5.45
47	2925	2810	3	1	3	0	0.75	1.08	5.45
48	2945	2829	3	1	3	0	0.29	1.08	5.53
49	3069	2948	0	0	1	0	0.75	1.03	5.74
50	3069	2948	3	1	0	0	0.73	1.03	5.74
51	3070	2949	3	1	0	0	0.00	1.03	5.74
52	3152	3028	0	0	0	0	0.74	1.10	6.46
53	3152	3028	0	0	1	0	0.73	1.10	6.46
54	3152	3028	0	0	0	0	0.75	1.10	6.46
55	3155	3031	2	0	0	0	0.75	1.10	6.47
56	3155	3031	1	0	0	0	0.73	1.10	6.47
57	3155	3031	1	0	1	0	0.74	1.10	6.47

Table 4 Experimental and computed frequencies (cm^{-1}) with assignments of paraldehyde

S.No	IR	Raman	RHF	B3LYP	Assignments
57	–	–	2973	3031	CH ₃ asym stretching
56	–	–	2972	3031	CH ₃ asym stretching
55	3031w	3031vw	2972	3031	CH ₃ asym stretching
54	–	–	2964	3028	methyl C-H stretching
53	–	–	2964	3028	methyl C-H stretching
52	3010vw	3025w	2963	3028	methyl C-H stretching
51	2953vw	–	2894	2949	CH ₃ symmetric stretching
50	2944vw	–	2894	2948	CH ₃ symmetric stretching
49	2938vw	–	2893	2948	CH ₃ symmetric stretching
48	2840vw	–	2838	2829	CH stretching
47	2820w	–	2816	2810	CH stretching
46	2801vw	2815m	2816	2810	CH stretching
45	–	–	1479	1448	CH ₃ in plane bending
44	1448vw	–	1463	1448	CH ₃ in plane bending
43	–	–	1462	1444	CH ₃ in plane bending
42	–	–	1456	1440	CCH in-plane bending/CH in plane bending
41	1438w	1438w	1454	1437	CH ₃ asymmetric deformation
40	–	–	1453	1437	CH ₃ asymmetric deformation
39	–	–	1450	1422	CH ₃ opb/COC in plane bending
38	–	–	1428	1384	CH ₃ symmetric deformation
37	1384w	1384w	1427	1383	CH ₃ symmetric deformation
36	–	–	1399	1361	OCH ipb/ar CH bend/CH ₃ sym def
35	1368w	1365w	1399	1361	OCH ipb/ar CH bend/CH ₃ sym def
34	1355vw	1352w	1384	1352	CCH ipb/HCO ipb/OCC bend
33	–	–	1368	1327	CCH ipb/OCO opb
32	1330vw	1330w	1368	1326	CCH ipb/OCO opb
31	1295w	1296w	1338	1298	OCH ipb/CH opb
30	–	1182w	1217	1168	C-O stretching
29	–	–	1217	1161	C-O stretching

Table 4 (continued)

S.No	IR	Raman	RHF	B3LYP	Assignments
28	1162w	1165m	1187	1161	C-O stretching
27	1103w	–	1144	1099	COC in-plane bending
26	–	1132m	1143	1098	COC in-plane bending
25	–	1120w	1114	1090	OCO in-plane bending
24	1092m	1098m	1113	1090	OCO in-plane bending
23	1075s	1075vw	1101	1072	CH ₃ sym def/HCO opb
22	1030s	1035vw	1083	1037	CH ₃ rocking
21	–	–	993	923	C-O stretching
20	928w	930w	948	923	C-O stretching
19	890w	888m	948	880	COC in-plane bending
18	–	832w	862	832	C-CH ₃ bending
17	–	830w	860	831	C-CH ₃ bending
16	805w	806w	834	809	Ring breathing/ CCH bending
15	730w	730w	755	728	Ring deformation
14	–	564vw	562	549	Ring deformation/puckering
13	548w	560s	562	549	Ring deformation /puckering
12	–	500s	501	502	Ring breathing
11	–	458vw	458	453	C-CH ₃ out of plane bending
10	–	450vw	458	452	C-CH ₃ out of plane bending
9	–	405vw	407	404	CH ₃ wagging
8	–	271vs	260	257	C-CH ₃ in plane bending
7	–	260vs	260	257	C-CH ₃ in plane bending
6	–	–	229	221	CH ₃ twisting
5	–	–	228	220	CH ₃ twisting
4	–	–	219	210	CH ₃ twisting
3	–	–	158	162	CH ₃ torsion
2	–	–	150	155	CH ₃ torsion
1	–	–	150	153	CH ₃ torsion

C-H Vibrations

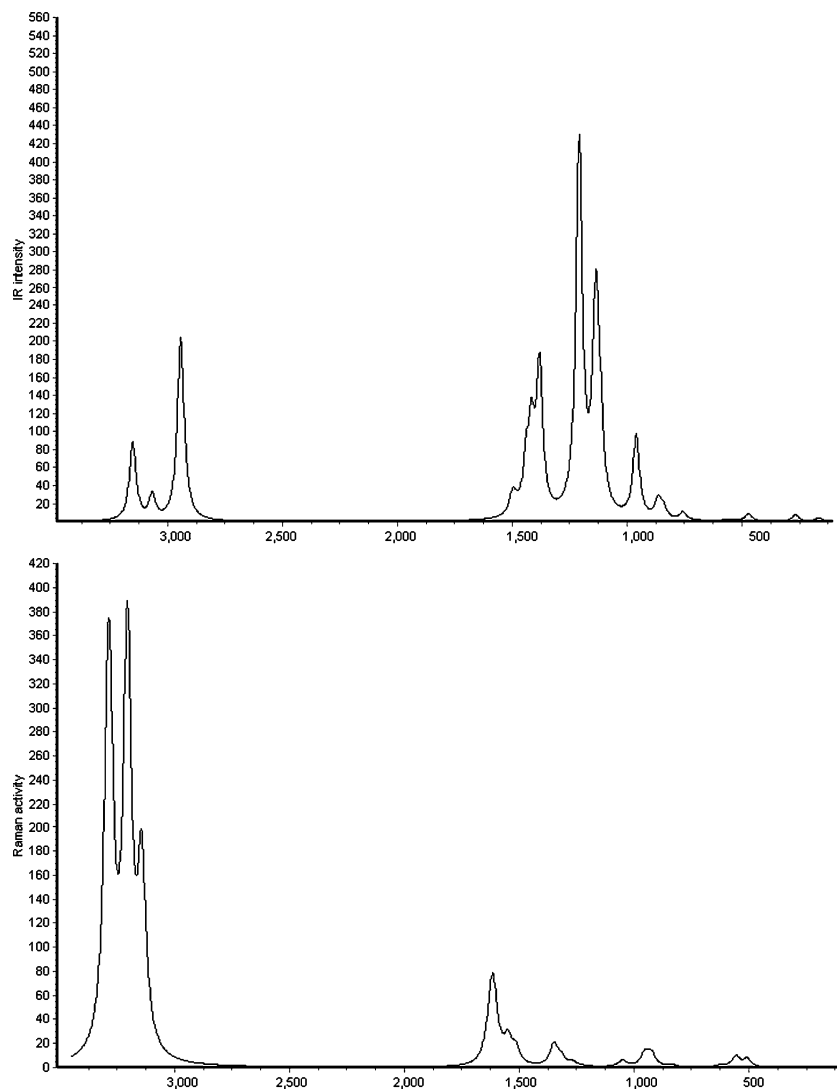
C-H stretching vibrations are highly characteristic and aldehydes show absorption in this region from the valence vibration of the hydrogen atom attached to the carbonyl group. This is found in this region 2900–2700 cm⁻¹ [25]. Many aldehydes exhibit two bands in this region one at 2720 cm⁻¹ and the other at 2820 cm⁻¹, the doubling being due to a Fermi resonance between γ_{CH} and the first overtone of the C-H deformation [26, 27]. Hence the FTIR and Laser Raman bands at 2840, 2820 and 2815 cm⁻¹ respectively in paraldehyde have been designated to C-H stretching vibrations. The scaled vibrations at 2829, 2810 and 2810 cm⁻¹ (mode nos. 46–48) correspond to stretching modes of C₂-H₁₀, C₄-H₁₁ and C₆-H₁₂.

CH₃ group vibrations

The molecule paraldehyde consists of three CH₃ groups at second, fourth and sixth position of the ring. For the assignment of CH₃ group frequencies one can expect that

there are nine fundamentals, viz., the symmetrical stretching in CH₃ (CH₃ sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode), the symmetrical (CH₃ sym. deform) and asymmetrical (CH₃ asym. deform) deformation modes; the in-plane bending (CH₃ ipb), out of plane bending (CH₃ opb), twisting (t CH₃) and bending modes. The FTIR bands at 3031 and 2953, 2938 cm⁻¹ represent asymmetric and symmetric CH₃ stretching vibrations in paraldehyde. The theoretically computed values of CH₃ asymmetric stretching gives three wave numbers which are in the same band at 3031 cm⁻¹ and CH₃ symmetric stretching exhibits three wave numbers one at 2949 cm⁻¹ and other two at 2948 cm⁻¹ shows an excellent agreement with experimental results. The identified asymmetric in-plane bending vibration at 1448 cm⁻¹, symmetric in-plane bending vibration at 1384 cm⁻¹ and rocking vibration [28] of CH₃ (ρ_r CH₃) at 1030 cm⁻¹ are well comparable with theoretically calculated values (mode no. 43–45). These assignments find support within the frequency intervals given by Varsanyi [29]. The CH₃ torsional mode assigned at 162 and 155 cm⁻¹.

Fig. 4 Calculated infrared and Raman spectra of paraldehyde using B3LYP/6-31G(d,p)



C-O stretching

From the data available in literature, it is found that the intensities of the carbonyl bands of aldehyde vary with structural features. In alcoholic solution, there is a distinct fall in the intensity of aldehyde due to carbonyl absorptions. Ashdown and Kletz [30] have reported number of such cases and the range of frequencies 1020–1110 cm^{-1} to be associated with the C-O linkage. In the present case, the experimental frequencies at 1162 cm^{-1} and at 928 cm^{-1} in FTIR spectrum of paraldehyde are assigned to C-O stretching vibrations. This is in excellent agreement with B3LYP/6-31G(d,p) predicted frequencies at 1161 cm^{-1} and at 923 cm^{-1} (Table 4). The above conclusions are in good agreement with the literature values [31, 32].

Conclusions

Attempts have been made in the present work, for the proper frequency assignments of paraldehyde from FTIR and Laser Raman spectra. The equilibrium geometries, harmonic frequencies and IR spectra of paraldehyde were determined and analyzed both at HF and DFT levels of theory utilizing 6-31G(d,p) basis set. Comparison between calculated and experimental vibrational frequencies indicates that both the methods B3LYP/6-31G(d,p) and HF/6-31G(d,p) can predict the IR and Laser Raman spectra of title compound well. Any discrepancy noted between the observed and calculated frequency may be due to the fact that the calculations have been done on single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions.

The optimized geometry parameters calculated at both B3LYP/6-31G(d,p) and HF/6-31G(d,p) values coincides well with experimental data.

Acknowledgements The authors are thankful to Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai for the spectral measurements.

References

1. <http://www.chemicaland21.com/arokorhi/industrialchem/solalc/PARALDEHYDE.html>
2. Gunasekaran S, Leela A (2004) *Indian J Phys* 78(6):485–488
3. Jungnickel JL, Reilly CA (1965) *J Mol Spectroscopy* 16:135–157
4. King JF, Vig B (1962) *Can J Chem* 40:1023–1025
5. Powers RM, Harper JL, Tai H (1960) *Anal Chem* 32:1287–1290
6. Liu J, Feng Y, Chen L, Wu G-S, Yu Z-W (2004) *Vibrational spectroscopy* 36:203–206. DOI 10.1016/j.vibspec.2004.01.006
7. Pobiner H (1960) *Anal Chem* 32:1899–1905
8. Adzelm J, Wimmer E (1992) *J Chem Phys* 96:1280–1284
9. Johnson BG, Gill PMW, Pople JA (1993) *J Chem Phys* 98:5612–5626
10. Handy NC, Murray CW, Amos RO (1993) *J Phys Chem* 97:4392–4396
11. Chan DP, Ree AV (1993) *Chem Phys Lett* 210:443–457
12. Berces A, Ziegler T (1993) *J Chem Phys* 98:4793–8040
13. Sim F, St-Amat A, Salahub DR (1992) *J Am Chem Soc* 114:4391
14. Krishnakumar V, Balachandran V, Chithambarathanu T (2005) *Spectrochim Acta A* 62:918–925
15. Fan L, Zeigler T (1992) *J Phys Chem* 96:6937–6941
16. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) *Gaussian 03*. Gaussian Inc, Wallingford CT
17. Schlegel HB (1982) *J Comput Chem* 3:214–218
18. Hohenberg P, Kohn W (1964) *Phys Rev B* 136:864–871
19. Becke AD (1993) *J Chem Phys* 98:5648–5652
20. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
21. NIST, <http://srdata.nist.gov/cccbdb>
22. <http://www.Chemsoft.com>
23. Ackermann PG, Mayer JE (1936) *J Chem Phys* 4:377–381
24. <http://chemcraft.com>
25. Colthup NB (1950) *J Opt soc Amer* 40:397–400
26. Lucczeau G, Sandorfy C (1970) *Can J Chem* 48:3694–3698
27. Rock SL, Hammaker RM (1971) *Spectrochim Acta* 23a:1899–1907
28. Sundaraganesan N, Anand B, Dominic Joshua B (2006) *Spectrochim Acta A*:1386–1425
29. Varsanyi G (1973) *Assignments for vibrational spectra of seven hundred Benzene derivatives*, 1/2. Academic Kiado, Budapest, p 44,22
30. Ashdown A, Kletz TA (1948) *J Chem Soc* 1454–1456. DOI 10.1039/JR9480001454
31. Silverstein RM, Clayton Bassler G, Morrill TC (1991) *Spectrometric identification of organic compounds*, 5th edn. Wiley, New York, p 111
32. Abkowicz-Bienko AJ, Latajka Z, Bienko DC, Michalska D (1999) *Chem phys* 250:123–129