# Vibrational spectra and force fields for 2,3-; 2,4-; 2,5- and 3,4-dihydroxybenzaldehydes

D N Singh, I D Singh and R A Yadav*

Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Vanarasi-221 005, Uttar Pradesh, India

I-mail ravadav_a'bhu ernft in

**Abstract**      Raman and IR spectra of 2,3-; 2,4-, 2 5- and 3,4-dihydroxy benzaldehydes have been recorded. The observed frequencies have been assigned to various normal modes of vibration in light of the normal coordinate calculation using Wilson's classical FG-matrix method. All the 42 normal modes have been assigned for all the molecules for the first time

## 1. Introduction

Phenol and its derivatives have been investigated extensively using vibrational spectroscopy [1- 14]. Electronic and vibrational spectra of some tri-substituted benzenes have been studied and reported in literature [15-18]. Although several studies on the vibrational spectra of di-substituted phenols and benzaldehydes are available. complete interpretation of the entire spectra are available only for a very few of them.

The present work is in continuation of our vibrational studies on benzaldehyde derivatives [19] and deal with the vibrational spectral studies and force field calculations for 2,3-, 2,4-: 2,5- and 3,4-dihydroxy benzaldehydes (hereafter called DHBDs). To the best of our information, IR spectra of only 2,3-DHBD has so far been investigated. The purpose of this study is to (i) study the effect of the three substituents on the phenyl ring modes, (ii) study the effect of the OH group(s) on the internal modes of the CHO group and *vice-versa* and (iii) determine consistent force fields for these di-substituted benzaldehydes.

## 2. Experimental

All the four chemicals (purity > 97%) were purchased from the Aldrich Chemical Co., USA. These chemicals form solids at room temperature and were used as such for recording the IR and the Raman spectra.

Raman spectra of these four compounds were recorded in the region 50–4000 cm$^{-1}$ on a Spex model 1403 spectrometer equipped with a double monochrometer and computer datamate. Samples were placed in a quartz cell and to excite these the 4880 A line of an Ar⁺ laser was used. The laser power on the samples was in the range 400–500 mW. The Raman frequencies are accurate within ±1 cm$^{-1}$ and the resolution of the spectrometer under the present experimental conditions was of the order of 2 cm$^{-1}$.

IR spectra of the four compounds were recorded in KBr pellets in the region 180 4000 cm$^{-1}$ on a Perkin Elmer 983 spectrometer equipped with a computer datamate.

## 3. Force field calculations

An approximate geometry has been used for these molecules to calculate G-matrix elements, as no structural studies for these are available. For the benzaldehyde part, structural parameters were same as in our earlier study and for the hydroxyl group, the parameters were taken from Ref. [11] and are as follows :

$$r(C-OH) = 1.371 \text{ Å}, \quad r(O-H) = 0.81 \text{ Å},$$
$$\alpha(C-O-H) = 108.5.$$

*Corresponding Author

All the four molecules were assumed to belong to the $C_s$ point group symmetry. As these are 16 atomic molecules, the 42 normal modes of vibration are distributed between the two species of the $C_s$ point group as :

(a) phenyl ring - $21a' + 9a''$,

(b) CHO group - $4a' + 2a''$,

(c) OH group - $2(2a' + 1a'')$.

The vibrational problems were set-up in terms of the internal coordinates. Using these internal coordinates, the symmetry coordinates were constructed in the way suggested in Refs. [20,21]. The $F$ matrix was calculated assuming general valence force fields. The calculations were made using computer program of Schachtschneider [22]. The initial force constants were taken from our work on benzaldehyde [23] and the force constants related with the OH groups were taken by trial and error initially. In constructing the $F$ matrix elements, total 68, 69, 70 and 69 planar and 26, 26, 27 and 27 non-planar force constants were taken for 2,3-; 2,4-; 2,5- and 3,4-DHBDs respectively. In constructing $F$-matrix, different numbers were assigned to the principal force constants for the two C–OH groups to see if there is any significant difference between the corresponding force constants of the two C–OH groups. After calculation, it was found that the force constants for the two C–OH groups in the case of the C–OH stretching and planar bending have nearly same values whereas for the C–OH non-planar bending the force constants for the two C–OH groups differ significantly. However, for the interaction force constants for the two C–OH groups no such calculations were made and so the same number was assigned to the interaction constants for the two C–OH groups. It was observed that some of the force constants had to be left either

due to their negligible magnitudes or due to their negligibly small contributions to the potential energy distributions (PEDs).

The force constants $\gamma$(C–CHO)/$\gamma$(C–OH), $\nu$(C–C)/$\beta$(C–OH), $\tau$(C–CHO)/$\tau$(C–OH), $\phi$(CCCC)/$\tau$(C–OH), $\tau$(C–CHO)/$\omega$(C–CHO) and $\phi$(CCCC)/$\gamma$(C–OH) were left for all the isomers due to drastic changes in their values and the disturbance of the entire set of the force constants during iteration. The force constants $\nu$(O–H)/$\nu$(O–H) in 2,5-DHBD $\alpha$(CHO)/$\alpha$(COH) in 2,4- and 2,5- DHBDs and $\beta$(C–OH)/ $\beta$(C–OH) in 2,5-DHBD were also omitted due to the same reasons. The force constants $\nu$(C–CHO)/$\nu$(C–OH)$^p$ and $\beta$(C–CHO)/$\beta$(C–OH)$^p$ in 2,4- and 3,4-DHBDs were kept fixed with their values as 0.0 due to their negligibly small contributions to the PEDs.

The remaining sets of the force constants were adjusted by trial and error method with the help of damping factor. The force constants and the fundamentals were computed at perturbation 1. The calculated sets of these force constants were used as the input and again the force constants and the fundamentals were computed. During the iteration process, all the planar principal force constants and some interaction force constants were re-adjusted one by one and the remaining force constants were kept fixed with values for benzaldehyde [23]. For non-planar force fields, all the force constants had to be re-adjusted one by one and finally, all the interaction force constants were kept fixed. After 3 to 6 such cycles, a good fit between the observed and the computed fundamentals were obtained. The final values of the force constants and their despersions at perturbation 1 and their descriptions are collected in Table 1.

Table 1. Valence force constants for isomeric DHBDs.

| Sl No. | Description[#] | 2,3-DHBD[*] | | 2,4-DHBD[*] | | 2,5-DHBD[*] | | 3,4-DHBD[*] | |
|---|---|---|---|---|---|---|---|---|---|
| | | Planar principal force constants | | | | | | | |
| 1. | $\nu$(C–C) $(R)$ | 6.636 | 0.000 | 6.725 | 0 000 | 6.706 | 0 000 | 6 521 | 0.000 |
| 2 | $\nu$(C–CHO) $(l)$ | 5 002 | 0 0 | 4 937 | 0 0 | 4.968 | 0.0 | 4.955 | 0.0 |
| 3. | $\nu$(C–OH) $(t_1)$ | 3 946 | 0 221 | 3.863 | 0.186 | 4.124 | 0.139 | 4.094 | 0.149 |
| 4. | $\nu$(C–H) $(r)$ | 5 087 | 0.0 | 5 042 | 0 0 | 4.996 | 0 0 | 5.042 | 0.0 |
| 5. | $\nu$(C=O) $(u)$ | 9.144 | 0.0 | 9 179 | 0 0 | 9.074 | 0.0 | 9.113 | 0.0 |
| 6 | $\nu$(C'–H) $(v)$ | 4 030 | 0.0 | 4.045 | 0.0 | 4.045 | 0 0 | 4.335 | 0.0 |
| 7 | $\alpha$(CCC) $(a)$ | 1.409 | 0 0 | 1.179 | 0 0 | 1.416 | 0.0 | 1.168 | 0.0 |
| 8. | $\beta$(C–CHO) $(\beta_1)$ | 1.567 | 0.0 | 1.658 | 0.0 | 1.725 | 0.0 | 1.308 | 0.0 |
| 9. | $\beta$(C–OH) $(\beta_2)$ | 1.984 | 0.136 | 2 015 | 0.964 | 1.975 | 0.879 | 2.047 | 0.147 |
| 10. | $\beta$(C–H) $(\beta)$ | 0.999 | 0.0 | 0.999 | 0.0 | 1.023 | 0.0 | 0.999 | 0.0 |
| 11. | $\beta$(C=O) $(\theta_1)$ | 1.964 | 0.0 | 2.022 | 0.0 | 1.977 | 0.0 | 1.938 | 0.0 |
| 12. | $\beta$(C'–H) $(\theta_2)$ | 1.239 | 0.0 | 1.138 | 0.0 | 1.170 | 0.0 | 1.188 | 0.0 |
| 13. | $\nu$(O–H) $(s_1, s_2)$ | 5.838 | 0.042 | 5 551 | 0 047 | 6.001 | 0 069 | 5.941 | 0.053 |
| 14. | $\alpha$(C–O–H) $(\theta_3)$ | 0.351 | 0 123 | 0.360 | 0.021 | 0.365 | 0.035 | 0.361 | 0.099 |
| 15. | $\alpha$(C–O–H) $(\theta_4)$ | 0.231 | 0.224 | 0.235 | 0.021 | 0.232 | 0.035 | 0.234 | 0.071 |
| 16. | $\beta$(C–OH) $(\beta_3)$ | 1.998 | 0.117 | 2.028 | 0.809 | 2.047 | 0.792 | 2.002 | 0.109 |
| 17. | $\nu$(C–OH) $(t_2)$ | 3.889 | 0.264 | 3.804 | 0.164 | 4.199 | 0.136 | 3 961 | 0.122 |

**Table 1.** *(Cont'd.)*

| Sl. No. | Description[#] | 2,3-DHBD[*] | | 2,4-DHBD[*] | | 2,5-DHBD[*] | | 3,4-DHBD[*] | |
|---|---|---|---|---|---|---|---|---|---|
| | | Planar interaction force constants | | | | | | | |
| 18. | $(RR)^o$ | 0 777 | 0.0 | 0.820 | 0.0 | 0.777 | 0 0 | 0.777 | 0.0 |
| 19 | $(RR)^m$ | -0 349 | 0.0 | -0.394 | 0.0 | -0.349 | 0.0 | -0 349 | 0.0 |
| 20. | $(RR)^p$ | 0 272 | 0.0 | 0 237 | 0.0 | 0 272 | 0 0 | 0.272 | 0.0 |
| 21. | $(rr)^o$ | 0 091 | 0.0 | 0 124 | 0 0 | 0 147 | 0 0 | 0.038 | 0.0 |
| 22 | $(rr)^m$ | -0.003 | 0 0 | -0.001 | 0.0 | -0.032 | 0 0 | -0.005 | 0.0 |
| 23 | $(\beta\beta)^o$ | 0.001 | 0 0 | 0 001 | 0 0 | 0 001 | 0 0 | 0 001 | 0 0 |
| 24. | $(\beta\beta)^m$ | -0 054 | 0 0 | 0.026 | 0 0 | -0 026 | 0 0 | -0 026 | 0.0 |
| 25 | $(\alpha\alpha)^o$ | -0 017 | 0.0 | -0 017 | 0 0 | -0 017 | 0.0 | -0 017 | 0 0 |
| 26 | $(Rt)^o$ | 0 615 | 0 0 | 0.615 | 0.0 | 0.615 | 0 0 | 0.615 | 0.0 |
| 27 | $(Rt)^m$ | 0 208 | 0 0 | 0.208 | 0.0 | 0 208 | 0 0 | 0.208 | 0.0 |
| 28 | $(Rt)^p$ | 0.229 | 0.0 | 0.229 | 0.0 | 0.229 | 0 0 | 0 229 | 0.0 |
| 29. | $(R\alpha)^o$ | 0 404 | 0 0 | 0 404 | 0 0 | 0.404 | 0 0 | 0 404 | 0 0 |
| 30 | $(R\beta)^{o+}$ | -0 264 | 0.0 | -0 264 | 0.0 | -0.264 | 0.0 | -0.264 | 0 0 |
| 31. | $(R\beta)^{m'}$ | -0.039 | 0.0 | -0 039 | 0.0 | -0.039 | 0.0 | -0.039 | 0.0 |
| 32. | $(R\beta)^{p+}$ | 0.015 | 0.0 | 0.015 | 0 0 | 0.015 | 0.0 | 0.015 | 0.0 |
| 33. | $\beta_1 \theta_2$ | 0 364 | 0.0 | -0.364 | 0.0 | -0.364 | 0.0 | -0.364 | 0.0 |
| 34 | $\theta_1 \theta_2$ | 0 475 | 0 0 | 0 475 | 0 0 | 0 475 | 0 0 | 0.475 | 0.0 |
| 35 | $\beta_1 \theta_1$ | -0.687 | 0 0 | -0 687 | 0 0 | -0 687 | 0.0 | -0 687 | 0.0 |
| 36 | $t\theta_2$ | -0.068 | 0 0 | -0.068 | 0 0 | -0 068 | 0 0 | -0 068 | 0 0 |
| 37 | $(t\beta)^{o'}$ | 0.065 | 0.0 | 0 065 | 0 0 | 0 065 | 0 0 | 0 065 | 0.0 |
| 38. | $(t\beta)^{m+}$ | 0.058 | 0 0 | 0 058 | 0.0 | 0 058 | 0.0 | 0.058 | 0.0 |
| 39. | $(rr)^p$ | — | — | -0 072 | 0.0 | -0.072 | 0.0 | -0.072 | 0.0 |
| 40 | $u\theta_2$ | 0 289 | 0 0 | 0 289 | 0.0 | 0 289 | 0 0 | 0 289 | 0 0 |
| 41. | $(\alpha\beta)^{o+}$ | 0 132 | 0.0 | 0.132 | 0.0 | 0.132 | 0.0 | 0.132 | 0.0 |
| 42. | $(Rt_1)^o = (Rt_2)^o$ | 0.274 | 0.241 | 0 432 | 0.399 | 0 505 | 0.249 | 0.139 | 0.275 |
| 43. | $(Rt_1)^m = (Rt_2)^m$ | -0 415 | 0 251 | -0 101 | 0.331 | 0.499 | 0.206 | -0.041 | 0.235 |
| 44. | $(Rt_1)^p = (Rt_2)^p$ | -0.026 | 0.022 | -0 053 | 0.332 | -0.239 | 0 274 | -0.398 | 0 354 |
| 45. | $t_1 \theta_3 = t_2 \theta_4$ | 0.110 | 0.060 | -0.013 | 0.354 | 0.207 | 0.396 | 0 137 | 0.901 |
| 46 | $s_1 s_2$ | -0 337 | 0 042 | 0 069 | 0.047 | 0.0 | 0.0 | -0.229 | 0.053 |
| 47. | $t_1 t_2$ | 0 060 | 0 072 | -0 130 | 0.959 | -0.279 | 0.468 | 0.064 | 0.358 |
| 48 | $tt_1$ | 0.226 | 0 096 | 0 225 | 0.107 | 0.233 | 0.115 | -0.155 | 0.625 |
| 49. | $tt_2$ | -0 249 | 0 115 | 0 0 | 0.0 | -0.123 | 0.552 | 0.0 | 0.0 |
| 50 | $\beta_1 \beta_2$ | -0 093 | 0 049 | 0 402 | 0.307 | -0 036 | 0.328 | -0.244 | 0.444 |
| 51 | $\beta_1 \beta_3$ | 0 054 | 0.056 | 0.0 | 0.0 | -0.096 | 0.326 | 0.0 | 0.0 |
| 52. | $\theta_3 \theta_4$ | -0.048 | 0.038 | — | — | — | — | -0 022 | 0.0 |
| 53. | $\beta_2 \beta_3$ | -0.208 | 0.341 | -0 279 | 0.272 | 0.0 | 0.0 | 0 0 | 0.0 |
| 54. | $(\beta\beta)^p$ | — | — | 0.006 | 0 0 | 0.0 | 0.0 | 0.006 | 0.0 |
| | | Non-planar principal force constants | | | | | | | |
| 1 | $\phi(C-C-C-C) (\phi)$ | 0 692 | 0.010 | 0.073 | 0.288 | 0.069 | 0 029 | 0.064 | 0.022 |
| 2 | $\gamma(C-OH) (\delta_2)$ | 0.250 | 0.103 | 0.241 | 0 832 | 0.238 | 0.349 | 0 252 | 0.920 |
| 3. | $\gamma(C-H) (\delta)$ | 0.318 | 0.014 | 0.314 | 0.029 | 0.329 | 0.032 | 0 315 | 0.199 |
| 4 | $\tau(C-CHO) (\tau)$ | 0 009 | 0.0 | 0.009 | 0.0 | 0.009 | 0.0 | 0.009 | 0.0 |
| 5 | $\gamma(C-CHO) (\delta_1)$ | 0.285 | 0.298 | 0.282 | 0.125 | 0.283 | 0.402 | 0.294 | 0.329 |
| 6. | $\omega(CHO) (\omega)$ | 0.417 | 0.024 | 0.379 | 0.014 | 0.395 | 0.049 | 0.398 | 0.141 |
| 7. | $\tau(C-OH) (\tau_1)$ | 0.029 | 0.002 | 0.027 | 0.001 | 0.027 | 0.002 | 0.022 | 0.003 |
| 8. | $\tau(C-OH) (\tau_2)$ | 0.025 | 0.002 | 0 019 | 0.001 | 0.024 | 0.002 | 0.026 | 0 008 |
| 9. | $(C-OH) (\delta_3)$ | 0.203 | 0.290 | 0.204 | 0.099 | 0.205 | 0.290 | 0.205 | 0.330 |

**Table 1.** *(Cont'd)*

| SI No. | Description[#] | 2,3-DHBD[*] | | 2,4-DHBD[*] | | 2,5-DHBD[*] | | 3,4-DHBD[*] | |
|---|---|---|---|---|---|---|---|---|---|
| | | Non-planar interaction force constants | | | | | | | |
| 10 | $(\phi\phi)''$ | -0 012 | 0 0 | -0 012 | 0 0 | 0 012 | 0.0 | -0.012 | 0.0 |
| 11 | $(\delta\delta)''$ | 0 001 | 0 0 | 0 001 | 0 0 | 0.001 | 0 0 | 0.001 | 0 0 |
| 12 | $(\delta\delta)'''$ | -0.001 | 0 0 | -0 001 | 0 0 | 0.001 | 0.0 | -0.001 | 0 0 |
| 13 | $(\phi\delta)''^+$ | 0 019 | 0 0 | 0 019 | 0 0 | 0.019 | 0 0 | 0.019 | 0 0 |
| 14 | $\phi_1\delta_1 = -\phi_6\delta_1$ | 0.010 | 0 0 | 0 010 | 0 0 | 0.010 | 0 0 | 0.010 | 0 0 |
| 15 | $(\delta\delta_1)''$ | 0 001 | 0 0 | 0.001 | 0 0 | 0 001 | 0 0 | 0.001 | 0.0 |
| 16 | $(\delta\delta_1)'''$ | -0 001 | 0 0 | -0 001 | 0 0 | 0.001 | 0 0 | -0.001 | 0 0 |
| 17 | $(\delta\delta_1)^y$ | -0 001 | 0 0 | -0 001 | 0 0 | 0 001 | 0 0 | -0.001 | 0.0 |
| 18 | $\delta_1\omega$ | 0.001 | 0 0 | 0.001 | 0.0 | 0.001 | 0 0 | 0.001 | 0 0 |
| 19 | $(\phi\tau)''$ | 0 001 | 0 0 | 0 001 | 0 0 | 0 001 | 0 0 | 0.001 | 0.0 |
| 20 | $\phi_1\omega = -\phi_6\omega$ | 0 001 | 0 0 | 0 001 | 0 0 | 0 001 | 0 0 | 0 001 | 0.0 |
| 21 | $(\phi\tau_1)'' = (\phi\tau_2)$ | 0 007 | 0 0 | 0 007 | 0 0 | 0 007 | 0.0 | 0 007 | 0 0 |
| 22 | $\delta_2\delta_1$ | -0 027 | 0 077 | -0 015 | 0 04 | 0 025 | 0 032 | -0.032 | 0 083 |
| 23 | $(\delta\delta)^y$ | | | | | 0 001 | 0 0 | - . - | |

# *v*. Stretching, *α* : Angle bending, *β* : In-plane bending, *φ* . Ring-torsion, *γ* Out-of-plane bending, *τ* Torsion of a top, *ω* Wagging; *o,m,p* stand for ortho, meta and para respectively

†$(R\beta)''$ means $R_i\beta_i = -R_i \;_1\beta_i$ Similar convention is adopted for all interaction terms bearing symbol †

* Units of force constants are as follows mdyne/Å for stretch and stretch-stretch interaction, mdyne/rad for stretch-band interaction and mdyne Å/rad² for the other

## 4. Results and discussion

All the frequencies observed in the IR and Raman spectra together with their relative intensities, the calculated frequencies corresponding to the fundamentals alongwith the PEDs and the proposed mode assignments are presented in Tables 2–5 for the 2,3-; 2,4-; 2,5- and 3,4-DHBDs molecules respectively. The presently proposed vibrational assignments are based on the intensities and magnitudes of the observed frequencies and PEDs for the calculated fundamentals. Assistance has also been taken from the vibrational assignments proposed for benzene derivatives containing the CHO [24–34] and the OH [1,10,12 and 15] groups. The discussion of the vibrational mode assignments has been divided into the following three sections : (i) the phenyl ring modes, (ii) the CHO group modes and (iii) the OH group modes.

### (i) Phenyl ring modes

As the phenyl ring moeds are mostly well discussed in literature and can be easily assigned, here only controversial modes are discussed in the following.

The ring-breathing the trigonal planar ring-bending the Kekule C=C stretching and the umbrella C–H non-planar bending modes are some of the controversial and substituent sensitive ring modes.

In di-substituted and symmetrically tri-substituted (1,3,5-$C_6H_3X_3$) benzenes the ring-breathing and the trigonal planar ring-bending modes usually give rise to Raman lines with

characteristic features. However, in non-symmetrically tri-substituted benzenes no such lines are observed. For 1,3-dibromo-5-fluorobenzene the ring breathing and the trigonal bending are assigned at 519 and 996 cm⁻¹ whereas for 2,4-di-bromo-1-fluorobenzene these modes are assigned at 1018 and 596 cm⁻¹ by Belgaum *et al* [15]. Rastogi *et al* [16] have assigned the frequencies 1078 and 570 cm⁻¹ respectively to these modes. Varsanyi [35] has argued that for the 1,2,3-trisubstituted benzenes the trigonal bending mode has higher magnitude than the ring breathing mode whereas reverse is the case for the other tri-substituted benzenes. He has further argued that, owing to strong mixing of different symmetrically permissible modes, the two frequencies cannot be uniquely labelled as a C–C stretching mode and a C-C–C angle bending modes.

In the present case, in light of the force field calculations the frequencies 638, 758, 780 and 766 cm⁻¹ could be assigned to the ring breathing mode for the 2,3-; 2,4-; 2,5- and 3,4-DHBDs respectively. Similarly, the trigonal ring bending mode is assigned at 840, 646, 713, 643 cm⁻¹ respectively for the isomers 2,3-; 2,4-; 2,5- and 3,4-DHBDs. It is to be noted here that the presently assigned frequencies for the ring breathing and trigonal bending modes fall in the spectral ranges suggested by Varsanyi [35] for all the four isomeric HBDs.

The Kekule C=C stretching mode appears in the region 1200–1400 cm⁻¹ in substituted benzenes. The force field calculations suggest that this is a pure C=C stretching mode.

**Table 2.** Observed and calculated frequencies for 2,3-DHBD[#].

| Raman cm⁻¹ | Rel. Int. | Infrared cm⁻¹ | Rel. Int. | Calculated cm⁻¹ | Potential energy distribution* | Proposed assignments | Species |
|---|---|---|---|---|---|---|---|
| – | | 3327 | (9) | 3327 | 13(94) | O–H stretch | $a'$ |
| 3140 | (1) | – | | 3140 | 13(106) | O–H stretch | $a'$ |
| 3101 | (1) | – | | 3100 | 4(97) | C–H stretch | $a'$ |
| 3060 | (5) | 3062 | (9) | 3062 | 4(99) | C–H stretch | $a'$ |
| 3018 | (1) | 3024 | (9) | 3025 | 4(101) | C–H stretch | $a'$ |
| – | | 2978 | (8) | | | 1628 + 1355 | $A'$ |
| – | | 2878 | (8) | | | 1650 + 1234 | $A'$ |
| – | | 2725 | (8) | 2725 | 6(99) | C–H stretch CHO group | $a'$ |
| 1774 | (1) | – | | | | 1628 + 148 | $A''$ |
| 1754 | (1) | 1746 | (3) | | | 1420 + 330 | $A'$ |
| 1696 | (2) | – | | 1695 | 5(31), 1(22), 2(24), 1(22), 11(10), 1(7) | C=O stretch (II) | $a'$ |
| 1657 | (7) | 1650 | (10) | | | C–O stretch (I) | |
| 1628 | (2) | 1611 | (9) | 1618 | 1(64), 5(13), 12(12), 7(9), 10(7) | C=C stretch | $a'$ |
| 1597 | (2) | 1586 | (9) | 1586 | 1(81), 7(14), 10(14) | FR between 1585, | $a'$ |
| 1574 | (3) | | | | | C–C stretch | |
| | | | | | | and 1243 + 330 | |
| 1481 | (1) | 1481 | (9) | 1475 | 1(47), 10(32) | C=C stretch | $a'$ |
| 1465 | (1) | – | | 1461 | 10(45), 1(43) | C=C stretch | $a'$ |
| 1417 | (3) | 1397 | (8) | 1394 | 12(45), 5(36), 11(34) | C–H i.p.b. CHO group | $a'$ |
| 1355 | (2) | 1355 | (8) | 1344 | 1(142), 10(16) | C=C stretch | $a'$ |
| 1292 | (3) | 1280 | (9) | 1289 | 7(34), 3(16), 17(14) | C–OH stretch | $a'$ |
| | | 1261 | (8) | | | 783 + 482 | $A'$ |
| 1243 | (5) | 1235 | (10) | 1240 | 10(35), 1(28), 3(13), 17(11) | C–OH stretch | $a'$ |
| 1204 | (1) | – | | 1207 | 10(51), 1(25) | C–H i p b. | $a'$ |
| 1176 | (5) | 1161 | (8) | 1170 | 10(55), 1(23) | C–H i.p.b | $a'$ |
| 1143 | sh | | | | | 790 + 350 | $A'$ |
| 1129 | sh | | | | | 638 + 494 | $A'$ |
| 1080 | (5) | 1076 | (5) | 1065 | 1(46), 10(26) | C–H i p.b | $a'$ |
| | | 1063 | (5) | | | 733 + 330 | $A''$ |
| 1031 | (1) | – | | 1035 | 14(55), 1(24) | C–O–H angle bending | $a'$ |
| | | 1021 | (4) | 1022 | 3(73), 1(20), 6(18) | C–H o p b | $a''$ |
| 988 | (0) | – | | 994 | 6(70), 3(21), 1(8) | CHO wagging | $a''$ |
| 976 | (1) | 969 | (8) | 972 | 17(15), 1(14), 2(14), 7(10) | C–CHO stretch | $a'$ |
| 902 | (1) | 909 | (4) | 904 | 3(84), 1(26) | C–H o.p.b. | $a''$ |
| 840 | (2) | 840 | (6) | 825 | 7(58), 3(13) | C–C–C i p b | $a'$ |
| 800 | (1) | 795 | (5) | 780 | 3(82), 1(14) | C–H o.p.b | $a''$ |
| 790 | (1) | 783 | (8) | 781 | 15(82), 14(14) | C–O–H angle bending | $a'$ |
| 751 | (0) | 754 | (6) | | | 550 + 199 | $A'$ |
| 724 | (1) | 733 | (8) | 700 | 1(26), 2(21), 5(13), 3(12) | C–C–C–C torsion | $a''$ |
| 649 | (1) | | | | | 450 + 199 | $A'$ |
| 638 | (3) | 632 | (7) | 638 | 1(26), 3(17), 7(13), 17(11) | C=C stretch | $a'$ |
| 620 | (1) | 622 | (6) | 620 | 7(92) | C–OH torsion | $a''$ |
| 584 | (1) | 590 | (5) | 583 | 8(85), 1(6) | C–OH torsion | $a''$ |
| 560 | (3) | 550 | (7) | 546 | 7(34), 11(11), 1(13), 8(10), 9(10) | C–C–C i.p.b | $a'$ |

Table 2. *(Cont'd)*

| Observed | | | | Calculated | | Proposed | |
|---|---|---|---|---|---|---|---|
| Raman | | Infrared | | | | assignments | Species |
| cm⁻¹ | Rel Int | cm⁻¹ | Rel Int | cm⁻¹ | Potential energy distribution* | | |

| Raman cm⁻¹ | Rel Int | Infrared cm⁻¹ | Rel Int | Calc cm⁻¹ | Potential energy distribution* | Proposed assignments | Species |
|---|---|---|---|---|---|---|---|
| 500 | (2) | 497 | (4) | 490 | 2(29), 1(24), 9(12), 3(8) | C–OH o.p.b. | |
| 494 | (10) | 482 | (4) | 480 | 16(34), 9(23), 1(15), 7(10) | C–OH i.p.b. | |
| 450 | (9) | – | | 434 | 7(48), 17(19), 3(14), 1(8), 8(8) | C–C–C i.p.b | |
| | | 442 | (6) | 447 | 5(40), 9(29), 1(23) | C–OH o.p.b. | |
| 350 | (0) | 351 | (3) | 335 | 11(44), 8(18), 2(15), 7(15), 12(7) | C=O i.p.b. | |
| 330 | (1) | 328 | (3) | 315 | 9(35), 16(33), 1(13) | C–OH i.p.b. | |
| 253 | (1) | | | 256 | 1(45), 4(30), 1(7) | C–C–C–C torsion | |
| 234 | (1) | | | 233 | 2(36), 9(35), 1(18), 5(14) | C–CHO o.p.b. | |
| 199 | (2) | | | 180 | 8(64), 1(8) | C–CHO i.p.b. | |
| 148 | (2) | | | 172 | 1(52), 2(29) | C–C–C–C torsion | |
| 136 | (0) | | | | | Lattice mode | |
| 110 | sh | | | 108 | 1(42), 4(34), 5(11), 7(9) | C–CHO torsion | |

*Abbreviations used . Rel. int. = Relative intensity; sh. = shoulder; i.p.b. = in-plane bend; o.p.b. = out-of-plane bend; FR = Fermi resonance.
* The numbers out side the brackets are the force constants number defined in Table 1 and those within the brackets are the corresponding contributions

Table 3. Observed and calculated frequencies for 2,4-DHBD#

| Raman n⁻¹ | Rel Int | Infrared n⁻¹ | Rel Int | Calc cm⁻¹ | Potential energy distribution* | Proposed assignments | Species |
|---|---|---|---|---|---|---|---|
| 3174 | (2) | | | 3174 | 13(99) | O–H stretch | |
| 3135 | (1) | 3123 | (9) | 3125 | 13(101) | O-H stretch | |
| 3088 | (2) | | | 3091 | 4(96) | C–H stretch | |
| 3053 | sh | 3055 | (9) | 3050 | 4(99) | C–H stretch | |
| 3001 | (1) | 3028 | (9) | 3004 | 4(102) | C–H stretch | |
| – | | 2730 | (7) | 2730 | 6(99) | C–H stretch CHO group | |
| 1643 | (4) | 1630 | (10) | 1676 | 5(36), 2(25), 1(20), 12(18) | C=O stretch (II) ⎫ | |
| 1627 | (6) | 1613 | (10) | | | C=O stretch (I) ⎭ | |
| 1590 | (6) | 1597 | (9) | 1614 | 1(82), 7(10) | C=C stretch | a' |
| | | 1576 | (9) | 1588 | 1(69), 10(19), 7(10) | C=C stretch | a' |
| 1545 | (0) | – | | | | 1130 + 410. | A" |
| 1511 | (3) | 1494 | (10) | 1493 | 10(43), 1(38), 5(9), 12(5) | C=C stretch | a' |
| 1477 | (1) | | | | | 1398 + 79 | A' |
| 1465 | (1) | | | | | 1428 + 136 | A' |
| 1442 | sh. | 1441 | (9) | 1444 | 1(55), 10(22), 3(6), 7(6) | C=C stretch | a' |
| – | | 1428 | (9) | | | 1129 + 301 | A' |
| 1398 | (5) | 1393 | (9) | 1375 | 12(48), 11(40), 5(30) | C–H i.p.b. CHO group | a' |
| 1340 | (6) | 1328 | (10) | 1332 | 1(142), 10(16) | C=C stretch | a' |
| 1239 | (5) | 1230 | (10) | 1230 | 10(75), 1(17) | C–H i.p.b. | a' |
| 1223 | (5) | | | 1220 | 7(33), 3(21), 17(17), 1(15), 10(6) | C–OH stretch | a' |
| 1185 | (3) | | | | | FR between 1165, C–CHO stretch and 758 + 410 | a' |
| 1145 | (5) | 1164 | (10) | 1159 | 1(39), 2(27), 10(14) | | |
| 1130 | (0) | 1129 | (10) | 1139 | 10(54), 1(23), 7(6) | C–H i.p.b. | a' |
| 1110 | (0) | | | | | 758 + 361 | A' |
| 1088 | (0) | | | 1106 | 10(32), 1(19), 17(17), 3(10) | C–H i.p.b. | a' |
| 1035 | (0) | | | 1031 | 14(64), 1(16), 7(13) | C–O–H angle bending | a' |
| 1000 | (0) | 1010 | (5) | 995 | 3(76), 1(22), 6(13) | C–H o.p.b. | a" |

Table 3. *(Cont'd.)*.

| Raman | | Infrared | | Calculated | | Proposed | |
| cm⁻¹ | Rel. Int. | cm⁻¹ | Rel Int. | cm⁻¹ | Potential energy distribution* | assignments | Species |
|---|---|---|---|---|---|---|---|
| 994 | (2) | 973 | (7) | 963 | 1(26), 17(14), 7(13), 3(10), 15(10) | C–OH stretch | *a'* |
| 936 | (0) | – | | 950 | 6(77), 3(14), 1(6) | CHO wagging | *a"* |
| 907 | (0) | - | | 920 | 3(86), 1(22) | C–H o.p.b | *a"* |
| 860 | (0) | 856 | (7) | | | 699 + 160 | *A'* |
| 838 | (3) | 823 | (7) | 826 | 15(72), 7(13) | C–O–H angle bending | *a'* |
| 817 | (0) | 805 | (8) | 815 | 3(85), 1(20) | C–H o p b. | *a"* |
| 758 | (5) | 756 | (6) | 780 | 1(28), 7(16), 3(13), 2(11) | C=C stretch | *a'* |
| 738 | (0) | 726 | (6) | | | 425 + 301 | *A'* |
| 699 | (0) | 693 | (7) | 670 | 1(35), 2(17), 5(20) | C–C–C–C torsion | *a"* |
| 666 | (0) | | | | | 566 + 99 | *A"* |
| 646 | (8) | 640 | (9) | 660 | 7(49), 17(14), 2(7), 1(6) | C–C–C i.p b | *a'* |
| 599 | (0) | 597 | (7) | 599 | 7(87), 1(6) | C–OH torsion | *a"* |
| 566 | (1) | 551 | (6) | 540 | 16(31), 9(23), 8(19), 1(15) | C–OH i.p.b | *a'* |
| 509 | (1) | – | | 507 | 8(90) | C–OH torsion | *a"* |
| 497 | (1) | 497 | (7) | 480 | 7(50), 3(23), 17(12), 1(7) | C–C–C i p b | *a'* |
| 474 | (0) | 458 | (5) | 480 | 2(27), 9(18), 1(18), 5(12), 7(6) | C–OH o p.b | *a"* |
| 439 | (6) | 425 | (6) | 445 | 7(40), 11(22), 12(9), 17(9), 16(8), 9(6) | C–C–C i p b | *a'* |
| 410 | (1) | - | | 404 | 1(37), 9(16), 2(13), 5(13), 3(6) | C–OH o.p.b | *a"* |
| 383 | (0) | 383 | (4) | | | 248 + 136 | *A"* |
| 361 | (0) | 367 | (5) | 346 | 16(36), 9(24), 1(23) | C–OH i p b | *a'* |
| | | 344 | (4) | | | 248 + 99 | *A'* |
| 301 | (0) | – | | 307 | 11(34), 7(31), 2(14), 8(13), 12(7) | C=O i.p.b. | *a'* |
| | | 280 | (4) | 309 | 5(32), 1(34), 9(19), 2(5), 3(5) | C–CHO o.p b | *a"* |
| 248 | (1) | – | | 218 | 1(45), 4(18), 2(10), 9(5) | C–C–C–C torsion | *a"* |
| 160 | (2) | – | | 173 | 8(75), 9(27), 1(7) | C–CHO i.p b. | *a'* |
| – | | – | | 193 | 4(36), 1(20), 2(14), 9(14), 3(8) | C–C–C–C torsion | *a"* |
| 136 | (1) | | | | | Lattice mode | |
| 122 | (1) | - | | 99 | 1(44), 4(28), 5(11), 3(5) | C–CHO torsion | *a"* |
| 99 | (10) | | | | | Lattice mode | |
| 79 | (9) | | | | | Lattice mode | |

Notations as explained in Table 2

Table 4. Observed and calculated frequencies for 2,5-DHBD[#].

| Raman | | Infrared | | Calculated | | Proposed | |
| cm⁻¹ | Rel. Int | cm⁻¹ | Rel. Int | cm⁻¹ | Potential energy distribution* | assignments | Species |
|---|---|---|---|---|---|---|---|
| - | | 3861 | (5) | | | 3090 + 772 | *A'* |
| – | | 3710 | (4) | | | 2990 + 719 | *A'* |
| – | | 3280 | (9) | 3280 | 13(100) | O–H stretch | *a'* |
| – | | – | | 3280 | 13(100) | O–H stretch | *a'* |
| 3090 | (2) | – | | 3088 | 4(96) | C–H stretch | *a'* |
| 3027 | (3) | – | | 3029 | 4(99) | C–H stretch | *a'* |
| 2991 | (3) | – | | 2990 | 4(102) | C–H stretch | *a'* |
| | | 2876 | (6) | | | 1486 + 1380 | *A'* |
| | | 2772 | (5) | | | 1486 + 1281 | *A'* |
| – | | 2730 | (7) | 2730 | 6(99) | C–H stretch CHO group | *a'* |
| 1749 | (1) | 1756 | (3) | | | 1430 + 320 | *A'* |
| | | 1722 | (4) | | | 952 + 772 | *A'* |

**Table 4.** *(Cont'd)*

| Raman cm⁻¹ | Raman Rel Int. | Infrared cm⁻¹ | Infrared Rel. Int. | Calculated cm⁻¹ | Potential energy distribution* | Proposed assignments | Species |
|---|---|---|---|---|---|---|---|
| 1661 | (2) | 1660 | (7) ⎫ | 1687 | 1(32), 5(24), 2(24), 12(14), 7(10) ⎤ | C=O stretch (II) ⎫ | a' |
| 1642 | (2) | 1646 | (9) ⎭ | | ⎦ | C=O stretch (I) ⎭ | |
| 1631 | (2) | 1623 | (9) | 1632 | 1(63), 5(15), 12(10), 7(9) | C=C stretch | a' |
| 1579 | (10) | 1577 | (10) | 1584 | 1(69), 10(22), 7(13), 5(8) | C=C stretch | a' |
| 1485 | (3) | 1486 | (10) | 1489 | 10(43), 1(38), 5(9), 12(5) | C=C stretch | a' |
| 1422 | (1) | 1430 | (9) | 1449 | 1(55), 10(16), 17(9), 7(7) | C=C stretch | a' |
| ⎡ | | 1397 | (6) | | | ⎤ FR between 1389, | |
| | | | | | | ⎬ C–H i.p b CHO | a' |
| ⎣ 1385 | (2) | 1380 | (6) | 1376 | 12(48), 11(38), 5(33) | ⎦ group and 1281 + 109 | |
| 1365 | (2) | 1359 | (7) | 1350 | 1(133) | C=C stretch | a' |
| 1302 | (2) | 1300 | (10) | 1310 | 7(48), 17(16), 10(14), 3(6) | C·OH stretch | a' |
| 1285 | (2) | 1281 | (10) | 1278 | 10(54), 1(17), 3(5), 7(5) | C–H i p.b. | a' |
| 1261 | (4) | 1251 | (8) | 1257 | 1(38), 3(24), 10(11), 17(10) | C–OH stretch | a' |
| ⎡ 1190 | (1) | | | | | ⎤ FR between 1179, | |
| | | | | | | ⎬ C–H i.p.b. | a' |
| ⎣ 1167 | (2) | 1160 | (9) | 1146 | 10(54), 1(29) | ⎦ and 682 + 499 | |
| 1118 | (2) | – | | 1111 | 10(39), 1(23), 2(12), 17(13) | C–H i p b | a' |
| 1030 | (2) | – | | 1010 | 3(89), 1(22) | C–H o p b | a" |
| 1017 | (2) | – | | 1008 | 14(92), 1(8) | C–H–O angle bending | a' |
| – | | 1000 | (4) | 985 | 6(70), 3(20), 1(5) | CHO wagging | a" |
| 954 | (2) | 952 | (5) | 952 | 1(34), 7(21), 2(18), 10(7) | C–CHO stretch | a' |
| 895 | (1) | – | | 920 | 3(70), 6(21), 1(17) | C–H o p b. | a" |
| – | | 881 | (5) | | | 487 + 393 | A' |
| – | | 865 | (5) | | | 682 + 179 | A" |
| – | | 832 | (7) | 832 | 3(88), 1(20) | C–H o p b. | a" |
| 809 | (1) | 803 | (9) | 809 | 15(91) | C–O–H angle bending | a' |
| 780 | (5) | 772 | (7) | 780 | 1(31), 7(30), 3(14), 15(9) | C=C stretch | a' |
| 713 | (1) | 719 | (6) | 699 | 7(33), 17(24), 3(21) | C–C–C i p b | a' |
| 670 | (1) | 682 | (8) | 674 | 1(37), 2(18), 5(16) | C–C–C–C torsion | a" |
| – | | 651 | (8) | | | 499 + 152 | A" |
| – | | – | | 604 | 7(32), 11(17), 12(11), 1(10), 8(10), 9(9) | C–C–C i.p.b | a' |
| – | | 597 | (5) | 597 | 7(89), 1(5) | C–OH torsion | a" |
| – | | 568 | (5) | 568 | 8(94) | C–OH torsion | a" |
| 499 | (4) | – | | 503 | 16(38), 9(26), 7(14), 1(5) | C–OH i.p.b | a' |
| – | | 487 | (7) | 462 | 5(33), 9(20), 1(18), 2(12) | C–OH o.p.b. | a" |
| 444 | (10) | 439 | (5) | 432 | 7(46), 17(22), 3(21), 1(16) | C–C–C i p.b. | a' |
| – | | 393 | (3) | 402 | 1(39), 2(20), 9(19), 3(5) | C–OH o.p.b | a" |
| 380 | (2) | 373 | (3) | 356 | 9(31), 11(26), 16(15), 1(11), 12(6) | C–OH i p.b. | a' |
| – | | 346 | (3) | | | 234 + 109 | A' |
| 320 | (2) | – | | 309 | 16(24), 11(21), 1(15), 8(13), 2(10), 9(7) | C=O i.p b | a' |
| 290 | (1) | – | | 315 | 1(33), 2(24), 9(22), 3(5) | C–C–C–C torsion | a" |
| 244 | (4) | – | | 234 | 4(43), 1(20), 2(11), 9(11), 5(10) | C–CHO o.p.b. | a" |
| 179 | (1) | – | | 191 | 8(62), 9(9), 1(7) | C–CHO i.p.b. | a' |
| 152 | (0) | – | | 151 | 1(59), 3(9), 2(9) | C–C–C–C torsion | a" |
| 109 | (6)ᵣ | – | | 112 | 4(46), 1(28), 5(13) | C–CHO torsion | a" |
| 79 | (2) | | | | | Lattice mode | |

*Notations as explained in Table 2.

Table 5. Observed and calculated frequencies for 3,4-DHBD[#].

| Observed | | | | Calculated | | Proposed | |
|---|---|---|---|---|---|---|---|
| Raman | | Infrared | | | | | |
| cm⁻¹ | Rel. Int. | cm⁻¹ | Rel. Int. | cm⁻¹ | Potential energy distribution* | assignments | Species |
| 3349 | (2) | 3326 | (9) | 3326 | 13(96) | O–H stretch | *a'* |
| 3200 | (2) | – | | 3200 | 13(103) | O–H stretch | *a'* |
| – | | – | | 3072 | 4(97) | C–H stretch | *a'* |
| 3054 | (2) | – | | 3047 | 4(99) | C–H stretch | *a'* |
| 3017 | (1) | – | | 3023 | 4(100) | C–H stretch | *a'* |
| – | | 2825 | (5) | 2825 | 6(99) | C–H stretch CHO group | *a'* |
| 1660 | (10) | 1656 | (9) | 1676 | 5(37), 2(25), 12(22), 8(15) | C=O stretch | *a'* |
| 1608 | (10) | – | | 1607 | 1(79), 7(10) | C=C stretch | *a'* |
| 1595 | (10) | 1595 | (10) | 1587 | 1(69), 10(16), 7(11) | C=C stretch | *a'* |
| 1540 | (2) | 1530 | (6) | 1511 | 1(38), 10(37), 5(13) | C=C stretch | *a'* |
| 1450 | (9) | 1442 | (10) | 1430 | 1(54), 10(18), 3(8), 7(7) | C=C stretch | *a'* |
| | | 1420 | (6) | | | 1302 + 114 | *A"* |
| 1394 | (1) | 1388 | (7) | 1375 | 12(50), 11(37), 5(32) | C–H i.p.b. CHO group | *a'* |
| 1355 | (1) | | | | | 1202 + 155 | *A'* |
| 1302 | (3) | 1298 | (10) | 1321 | 1(146), 10(15) | C=C stretch | *a'* |
| 1284 | sh | | | | | 1175 + 106 | *A'* |
| 1276 | (1) | – | | 1265 | 10(79), 1(9) | C–H i p.b | *a'* |
| 1202 | (3) | 1192 | (8) | 1212 | 7(33), 10(21), 1(10), 3(10), 17(10), 2(7) | C–H i.p.b. | *a'* |
| 1175 | (7) | 1167 | (10) | 1178 | 10(35), 1(28), 3(15), 17(17) | C–OH stretch | *a'* |
| 1130 | (3) | 1119 | (6) | 1134 | 1(32), 10(32), 2(13), 7(9) | C–CHO stretch | *a'* |
| 1065 | (3) | – | | 1072 | 10(28), 1(24), 2(19), 7(14), 17(11), 3(5) | C–H i p.b. | *a'* |
| 1040 | (3) | – | | 1023 | 3(77), 1(14), 6(6) | C–H o.p.b. | *a"* |
| 1018 | (3) | – | | 1018 | 14(88), 1(10) | C–H–O angle bending | *a'* |
| 986 | (3) | 974 | (3) | 950 | 1(44), 7(16), 3(11), 2(6), 10(6) | C–OH stretch | *a'* |
| 966 | (1) | – | | 979 | 6(48), 3(44), 1(12) | CHO wagging | *a"* |
| 944 | (1) | – | | 936 | 3(65), 6(27), 1(12) | C–H o.p.b. | *a"* |
| – | | 877 | (5) | | | 766 + 114 | *A"* |
| 847 | (1) | – | | 843 | 3(89), 1(16) | C–H o.p.b. | *a"* |
| 823 | (2) | 813 | (6) | 813 | 15(93) | C–O–H angle bending | *a'* |
| – | | 776 | (3) | | | 670 + 106 | *A"* |
| 766 | (3) | 755 | (5) | 735 | 1(27), 7(32), 3(17), 17(9) | C=C stretch | *a'* |
| 724 | (0) | | | | | 643 + 74 | *A'* |
| 674 | (0) | 670 | (4) | 663 | 1(38), 2(18), 9(14), 5(8) | C–C–C–C torsion | *a"* |
| 643 | (4) | 631 | (6) | 653 | 7(35), 17(23), 2(12), 1(8), 12(6), 11(5) | C–C–C i.p.b. | *a'* |
| 606 | (1) | 592 | (4) | 592 | 8(83), 1(7) | C–OH torsion | *a"* |
| 543 | (1) | – | | 543 | 7(94) | C–OH torsion | *a"* |
| 515 | (2) | – | | 524 | 16(32), 7(22), 9(16), 1(12), 3(11) | C–OH i.p.b. | *a'* |
| 488 | (1) | – | | 478 | 7(33), 11(13), 1(10), 12(6), 17(5) | C–C–C i.p.b. | *a'* |
| – | | – | | 503 | 2(33), 9(15), 1(10), 8(10) | C–OH o.p.b. | *a"* |
| 465 | (1) | 452 | (3) | | | 2 * 235 | *A'* |
| 419 | (3) | 410 | (3) | 429 | 7(38), 8(18), 11(18), 3(11), 9(7) | C–C–C i.p.b. | *a'* |
| 402 | (1) | 390 | (3) | 401 | 1(46), 2(12), 5(11), 3(6), 9(5) | C–OH o.p.b. | *a"* |
| – | | – | | 318 | 7(30), 11(20), 9(15), 16(9), 1(6) | C=O i.p.b. | *a'* |
| – | | 362 | (2) | | | 290 + 74 | *A'* |

**Table 5.** *(Cont'd.)*

| Observed | | | | Calculated | | Proposed | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Raman | | Infrared | | | | assignments | Species |
| cm⁻¹ | Rel. Int | cm⁻¹ | Rel Int | cm⁻¹ | Potential energy distribution* | | |
| 290 | (0) | – | | 297 | 16(27), 9(27), 11(18), 1(13), 7(10), 8(10) | C–OH i.p.b. | $a'$ |
| 270 | (0) | – | | 280 | 9(28), 1(33), 5(13), 2(10) | C–C–C–C torsion | $a''$ |
| 253 | (1) | – | | | | Lattice mode | |
| 235 | (1) | – | | 214 | 1(46), 2(18), 5(11), 3(7), 9(7) | C–CHO o.p.b. | $a''$ |
| – | | – | | 192 | 4(54), 1(25), 9(7) | C–C–C–C torsion | $a''$ |
| 155 | (3) | – | | 186 | 8(75), 1(10) | C–CHO i.p.b. | $a'$ |
| 114 | (3) | – | | 102 | 1(47), 4(26), 5(10) | C–CHO torsion | $a''$ |
| 106 | (3) | – | | | | Lattice mode | |
| 74 | (5) | – | | | | Lattice mode | |

Notations as explained in Table 2

For the three isomeric methoxy benzaldehydes [MBDs] this mode is assigned in the range 1280–1310 cm⁻¹ [20]. In the present case, the frequencies 1355, 1340, 1365 and 1302 cm⁻¹ are assigned to the Kekule mode for the 2,3-; 2,4-; 2,5- and 3,4-DHBDs respectively. It is to be noted that the PED for this mode has only contribution from the ring C–C stretching force constant for the 2,5-isomer whereas for the rest three there is a very small contribution from the planar ring C–H bending force constants, in addition to large contribution from the ring C–C stretching force constant.

The umbrella mode has been observed as a strong IR band in benzene at 670 cm⁻¹ [36]. As mentioned earlier its magnitude is substituent sensitive. For the isomeric MBDs this mode is assigned in the range 740–775 cm⁻¹. In the present case this mode is assigned in the range 850–780 cm⁻¹ for all the four isomers.

In addition to the above four phenyl ring modes the two C–OH and the C–CHO stretching modes also deserve some discussion. For the isomeric MBDs [20], the C–CHO stretching mode is assigned in a very narrow frequency range 1150–1170 cm⁻¹. However, in the present case the C–CHO stretching mode appears to be affected drastically for the 2,3- and 2,5-DHBDs for which it appears in the range 950–980 cm⁻¹ whereas for the 2,4- and 3,4-DHBDs this mode has magnitude very close [1130–1170 cm⁻¹] to that for the isomeric MBDs [20]. It is interesting to note that in case of the isomers which have the C–CHO stretching mode in the region 950–980 cm⁻¹ [2,3- and 2,5-isomers], the two C–OH stretching modes appear in the region 1240–1305 cm⁻¹ whereas in case of those isomers which have the C–CHO stretching mode in the region 1130–1170 cm–1 [2,4- and 3,4-isomers], one of the two C–OH stretching frequency appears in the region 1170–1240 cm⁻¹ and the other C–OH stretching mode appears in the region 980–1000 cm⁻¹.

## (ii) CHO group modes :

Out of the six CHO internal modes, the CH stretching mode has its characteristic magnitude in the range 2700–2850 cm⁻¹. In the present case, this mode is assigned at 2725, 2730 and 2730 cm⁻¹ for the 2,3-; 2,4- and 2,5-DHBDs whereas for the 3,4-DHBD it is observed at 2825 cm⁻¹. For 2,3-; 2,4- and 2,5-DHBDs there appear two frequencies whereas for 3,4-DHBD only one frequency is observed in the C=O stretching region. All these four molecules may have two conformations (Figures 1 and 2). It can be seen that for the 3,4-DHBD, the CHO group modes are expected to
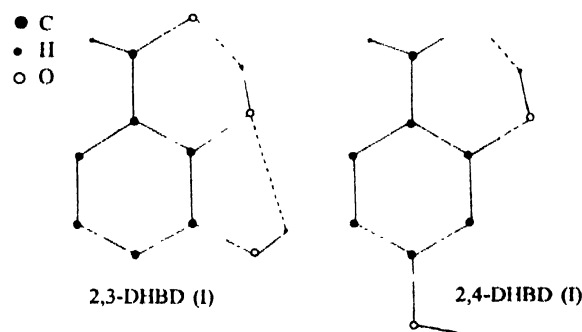


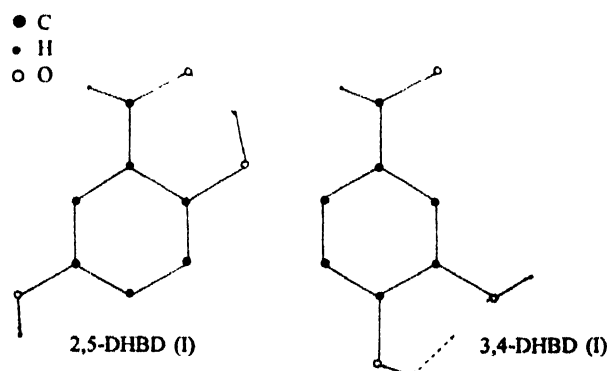**Figure 1a.** 2,3-DHBD (I); 2,4-DHBD (I)



**Figure 1b.** 2,5-DHBD (I); 3,4-DHBD (I)

have the same magnitudes in the two conformations, as the CHO group is not expected to be involved in intramolecular hydrogen bonding. However, for the other three isomers the CHO group is expected to be involved in the intramolecular
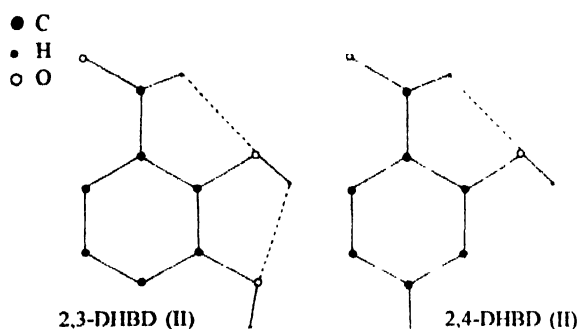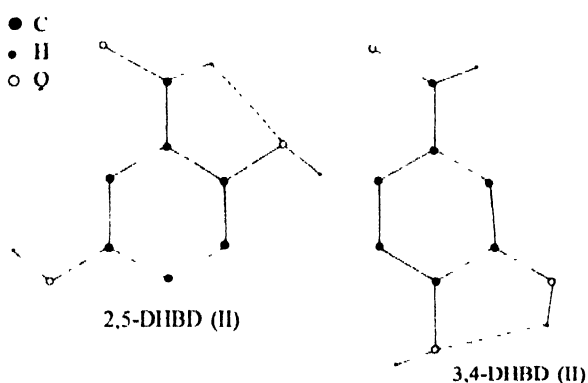
• C
• H
o O



2,3-DHBD (II)        2,4-DHBD (II)

Figure 2a. 2,3-DHBD (II); 2,4-DHBD (II)

• C
• H
o O



2,5-DHBD (II)

3,4-DHBD (II)

Figure 2b. 2,5-DHBD (II); 3,4-DHBD (II)

hydrogen bonding and the magnitude of the (C=O) mode in the configuration II is excepted to have higher magnitude compared to that in the configuration I because the O atom of the CHO group in the configuration II is non-bonded whereas that in configuration I is bounded with the H atom of the OH group. Hence, we assign the frequencies 1696, 1643 and 1660 cm⁻¹ to the (C=O) mode corresponding to the configuration II and the frequencies 1657, 1627 and 1646 cm⁻¹ corresponding to the configuration I for the 2,3-; 2,4- and 2,5-DHBDs respectively. One could expect similar behaviour for the CHO group CH stretching mode. However, the region of the CH stretching mode is masked by the presence of strong ν(O–H) modes of the OH groups. The other CHO group modes fall in the regions crowded by the other modes and so behaviour similar to the ν(C=O) mode is not expected to be obvious for these modes.

The C–H planar bending mode is assigned in the region 1370–1420 cm⁻¹. It is a pure group mode as all the force constants involved in the PED of this mode are the CHO group force constants only. The CH non-planar bending mode of the CHO group appears in the region 900–1010 cm⁻¹. In the present work, this mode is assigned in the region

930–1100 cm⁻¹. This shows some mixing with other ring non-planar modes.

The C=O planar bending is observed in the region 550–625 cm⁻¹ for the isomeric MBDs [20]. It has been observed in the neighbourhood of 650 cm⁻¹ for the isomeric trifluoromethyl benzaldehydes [23]. In the present case, this mode is assigned in the region 300–350 cm⁻¹ for all the isomers. However, due to strong mixing of this mode with the other planar modes unambiguous labelling is not possible. Hence, no conclusion could be drawn from the assignment of this mode regarding the hydrogen bonding. As expected, the CHO torsional mode has lowest magnitude of all the modes. It is observed in the region 100–120 cm⁻¹ for all the four isomers. It shows mixing with the ring torsion and CHO wagging mode for all the molecules.

*(iii) OH group modes :*

An OH group has three normal modes of vibration, namely, the OH stretching, the C–O–H angle bending and the C–OH torsion. For substituted phenols, a very sharp line like band appears in the neighbourhood of 3600 cm⁻¹ in very dilute solution prepared using non-polar solvents if intramolecular hydrogen bonding is absent [13]. In bonded form, a broad and intense band appears in the region 2500–3500 cm⁻¹. Presently, the region 2000–3000 cm⁻¹ is masked by a broad and intense band for all the four isomers. This band is obviously due to the ν(O–H) mode in bonded form. The magnitudes of the two ν(O–H) modes could be ascertained on the basis of calculation.

It is also to be mentioned that for an OH containing benzene derivatives, the C–OH stretching and C–O–H angle bending modes interact strongly to give rise to two frequencies in the range 1100–1350 cm⁻¹. However, in the present case, the calculations do not indicate the presence of any such interaction for all the four isomers. However, it may be noted that the two C–O–H angle bending modes appear to interact for the 2,3-isomer only, as for this molecule one of the two C–O–H angle bending frequencies involves constants of both the C–O–H angle bending motions. For the remaining three isomers the two C–O–H angle bending modes do not interact. It appears that the interaction between the two C–O–H angle bending modes is induced by the presence of the CHO group in the juxtaposition of one of the two OH groups. It is further to be noted that the C–O–H angle bending mode of the OH group at the position 2 has higher magnitude than that at the position 3(for 2,3-isomer) or 4 (for 2,4-isomer) or 5(for 2,5-isomer) and for the 3,4-isomer the mode due to the OH group at the position 3 has a magnitude higher than that due to the OH group at the position 4. For the 2,3-; 2,4- and 2,5-DHBDs it could be due to intramolecular hydrogen bonding between the hydrogen of the OH group at the position 2 and the oxygen atom of the CHO group.

However, the above observation for the 3,4-isomer is not understandable from the present study.

The torsional mode of the OH group appears around 500 cm⁻¹ in bonded form. In the present case, it has been assigned in the region 500–625 cm⁻¹. Surprisingly enough, these modes appear to be pure OH torsional modes for all the isomers. Moreover, the two OH torsional modes do not appear to interact with each other even for 2,3- and 3,4-DHBDs

## Acknowledgments

Two of the authors (DNS and IDS) are grateful to the Banaras Hindu University for the financial support in the form of fellowships during the course of the work.

### References

[1] H Zeiss and M Tsutsui *J Am Chem Soc* **75** 897 (1953)

[2] G L Carlson, W G Fateley, A S Manocha and F F Bentley *J. Phys Chem.* **76** 1553 (1972)

[3] R A Nyquist *Spectrochim Acta* **19** 1655 (1963)

[4] R Mecke and G Rossmy *Z Electrochem* **59** 866 (1955)

[5] S Krimm, C Y Liang and G B B M Sutherland *J Chem Phys* **25** 778 (1956)

[6] A V Stuart and G B B M Sutherland *J Chem Phys* **24** 559 (1956)

[7] G L Carlson and W B Fateley *J Phys Chem* **77** 1157 (1973)

[8] A S Manocha, G L Carlson and W G Fateley *J Phys Chem* **77** 2094 (1973)

[9] W G Fateley, G L Carlson and F F Bentley *J Phys Chem* **79** 199 (1975)

[10] H Takeuchi, N Watanabe and I Harada *Spectrochim Acta* **44A** 749 (1988)

[11] H Tylli and H Konschin *J Mol Struct* **57** 13 (1979)

[12] R A Yadav and I S Singh *J Sci Res (India)* **33** 133 (1982-83)

[13] R A Yadav and I S Singh *Indian J. Pure Appl Phys* **23** 626 (1985)

[14] J H S Green, D J Harrison and W Kynaston *Spectrochim Acta* **27A** 2199 (1971)

[15] S C Belgaum, M S Navati and M A Shashidhar *Indian J. Pure Appl Phys* **34** 576 (1996)

[16] V K Rastogi, C B Arora, S K Singhal, D N Singh and R A Yadav *Spectrochim. Acta* **53A** 2505 (1997)

[17] N G Dongre, B P Asthana and P C Mishra *Spectrochim. Acta* **47A** 673 (1991)

[18] M K Aralakkanavar, N R Katti, Rekha Rao, P R Jeergal and M A Shashidhar *Indian J Pure Appl. Phys.* **29** 569 (1991)

[19] D N Singh, I D Singh and R A Yadav (Submitted to *Indian J Phys.*)

[20] R A Yadav *Spectrochim. Acta* **49A** 891 (1993)

[21] D H Whiffen *Phil Trans Roy Soc.* **248A** 131 (1955)

[22] J H Schachtschneider *Vibrational Analysis of Polyatomic Molecules* Parts V and VI Tech Emery Ville, C A (1964 and 1965)

[23] D N Singh and R A Yadav *Asian Chem. Lett* **2** 65 (1998)

[24] R Zwarich, J Smolarek and L Goodman *J Mol Spectrosc.* **38** 336 (1971)

[25] L O Pietila, B Mannfors and K Palmo *Spectrochim Acta* **44A** 141 (1988)

[26] S N Garg *J Sci Res B H U (India)* **4** 68 (1953-54)

[27] S N Garg *J. Sci Res B H U (India)* **4** 83 (1953-54)

[28] R A Yadav and I S Singh *Indian J Phys* **58B** 556 (1984)

[29] R A Yadav and I S Singh *Spectrochim. Acta* **41A** 191 (1985)

[30] B B Lal, M P Srivastava and I S Singh *Indian J Pure Appl. Phys.* **11** 615 (1973)

[31] M P Srivastava, B B Lal and I S Singh *Indian J Pure Appl Phys* **9** 857 (1971)

[32] M P Srivastava and I S Singh *Indian J. Pure Appl Phys* **10** 50 (1972)

[33] M P Srivastava, B B Lal and I S Singh *Indian J. Pure Appl. Phys* **10** 570 (1972)

[34] R A Yadav, Ramakant, P C Mishra and I S Singh *Pramana* **18** 311 (1982)

[35] G Varasanyi *Vibrational Spectra of Benzene Derivatives* (New York : Academic) (1969)

[36] P C Painter and J L Koening *Spectrochim. Acta* **33A** 1003 (1977)