

## Fundamental frequencies of 2 – iodo- 5 – nitro toluene from FT – Raman and FT – IR spectra

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**Abstract** FT-Raman and FT-IR spectra of 2 – iodo-5-nitro toluene have been recorded in the region 50–500  $\text{cm}^{-1}$  and 400–4000  $\text{cm}^{-1}$  respectively. The vibrational analysis is carried out in terms of fundamentals. The probable mode of vibrations have been assigned assuming  $C_{2v}$  symmetry.

**Keywords** FT-Raman, FT-IR spectrum, vibrational assignments, 2-Iodo-5-nitro toluene

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### 1. Introduction

In recent times, toluene and substituted toluene have become very important on account of their wide use in medicine and industry. Vibrational spectra of various substituted toluenes were reported earlier [1-5]. Among the halogenated nitro toluene, the vibrational spectra of chloronitro-, bromonitro-, and fluoronitro – toluenes, were reported earlier, but the vibrational spectra of iodonitro toluenes do not seem to have been investigated so far. This paper deals with the recording and analysis of the FT – Raman and FT – IR spectra of 2 – iodo – 5 nitro toluene (2 – 15 – NT) in mid and far-infrared regions.

### 2. Experimental

Commercially available (2 – 15 – NT) molecule of spec-pure grade was used without further purification for recording the FT – Raman and FT – IR spectra. The FT – Raman and FT – IR spectra of (2-I5-NT) were recorded using Bruker IFS 66V FT – IR/FT – Raman spectrometer having a resolving power of 0.1  $\text{cm}^{-1}$ . The FT – Raman spectrum of the powder sample over the

range 50 – 3500  $\text{cm}^{-1}$  are recorded using Nd : YAG laser, at wavelength 1064 nm and power 200 MW and a germanium diode detector. The FT – IR spectra in far-infrared region (FIR) are obtained over the range of 50–500  $\text{cm}^{-1}$  using polyethylene technique at a resolution of 4  $\text{cm}^{-1}$ . The FT – IR spectra in mid-infrared region (MIR) are recorded over the range of 400 – 4000  $\text{cm}^{-1}$  on a Nicolet Avtar – 360 FT – IR spectrophotometer, using KBr pellet technique. The accuracy of the measurements was estimated to be with in  $\pm 1 \text{ cm}^{-1}$  and accuracy in the assignment of the fundamental mode of the vibrations was estimated to be with in  $\pm 20 \text{ cm}^{-1}$ .

### 3. Discussion

Almost all the bands observed in the entire region, are analysed in terms of fundamental frequencies, overtones, combinations and differences. In (2-I5-NT) molecule, parent ring is a benzene ring; therefore, the same nomenclature as that used in benzene is adopted to designate the various type of fundamental modes of vibrations. The replacement of the hydrogen by the substituent groups, no doubt, changes the value of the fundamental frequencies quite appreciably. Substitution of the

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**Table 1.** Fundamental frequencies ( $\text{cm}^{-1}$ ) and assignments for 2-iodo-5-nitro toluene

| Infrared                  |     | Raman                     |     | Probable assignments |                            |  |
|---------------------------|-----|---------------------------|-----|----------------------|----------------------------|--|
| Freq ( $\text{cm}^{-1}$ ) | Int | Freq ( $\text{cm}^{-1}$ ) | Int | Species              | Mode No. (Wilson notation) | Description                                      |
| 3077                      | 5.5 | 3085                      | 0.5 | $a'$                 | 2                          | $\nu(\text{C-H})$ stretching                     |
| 3023                      | 6.0 | 3067                      | 0.7 | $a'$                 | 20a                        | $\nu(\text{C-H})$ stretching                     |
| 3015                      | 7.0 | 3017                      | 0.3 | $a'$                 | 20b                        | $\nu(\text{C-H})$ stretching                     |
| 2984                      | 7.0 | 2973                      |     | $a''$                | —                          | $\nu_{as}$ stretching in $\text{CH}_3$ group     |
| 2938                      | 6.5 | 2922                      | 0.4 | $a''$                | —                          | $\nu_{as}$ stretching in $\text{CH}_3$ group     |
| 2892                      | 6.0 | —                         | —   | $a'$                 | —                          | $\nu_s$ stretching in $\text{CH}_3$ group        |
| 1646                      | 10  | 1639                      | 0.2 | $a'$                 | 8b                         | $\nu(\text{C-C})$ stretching                     |
| 1608                      | 4.5 | 1603                      | 0.4 | $a'$                 | 8a                         | $\nu(\text{C-C})$ stretching                     |
| 1510                      | 0.5 | 1516                      | 0.4 | $a'$                 | 19b                        | $\nu(\text{C-C})$ stretching                     |
| 1454                      | 3.0 | 1475                      | 0.3 | $a''$                | —                          | $\delta_{as}$ deformation in $\text{CH}_3$ group |
| 1423                      | 5.0 | 1420                      | 0.3 | $a'$                 | 19a                        | $\nu(\text{C-C})$ stretching                     |
| 1375                      | 3.0 | 1379                      | 0.5 | $a'$                 | —                          | $\delta_s$ deformation in $\text{CH}_3$ group    |
| 1340                      | 0.0 | 1340                      | 7.5 | $a'$                 | —                          | $\nu_s$ stretching in $\text{NO}_2$ group        |
| 1265                      | 4.0 | 1267                      | 0.3 | $a'$                 | 3                          | $\delta(\text{C-C})$ i.p. bending                |
| 1254                      | 1.5 | 1255                      | 0.3 | $a'$                 | 13                         | $\nu(\text{C-CH}_3)$ stretching                  |
| 1192                      | 5.0 | 1207                      | 1.4 | $a'$                 | 18a                        | $\delta(\text{C-C})$ i.p. bending                |
| 1130                      | 6.0 | 1125                      | 0.1 | $a'$                 | 18b                        | $\delta(\text{C-C})$ i.p. bending                |
| 1090                      | 5.0 | 1097                      | 0.5 | $a'$                 | —                          | rocking of $\text{CH}_3$ group                   |
| 1008                      | 3.0 | 1013                      | 0.2 | $a'$                 | —                          | rocking of $\text{CH}_3$ group                   |
| 992                       | 3.0 | —                         | —   | $a''$                | 17b                        | $\gamma(\text{C-H})$ o.p. bending                |
| 946                       | 8.0 | —                         | —   | $a''$                | 5                          | $\gamma(\text{C-H})$ o.p. bending                |
| 923                       | 8.0 | 920                       | 0.1 | $a'$                 | 7b                         | $\nu(\text{C-NO}_2)$ stretching                  |
| 854                       | 2.0 | —                         | —   | $a'$                 | —                          | $\delta_s$ deformation in $\text{NO}_2$ group    |
| 810                       | 1.5 | 807                       | 0.7 | $a''$                | 11                         | $\gamma(\text{C-H})$ o.p. bending                |
| 746                       | 1.0 | —                         | —   | $a'$                 | 12                         | $\delta(\text{C-C-C})$ i.p. bending              |
| 669                       | 7.0 | 680                       | 0.5 | $a'$                 | 1                          | $\gamma(\text{C-C})$ ring breathing              |
| 577                       | 7.0 | 558                       | 0.3 | $a''$                | 16a                        | $\gamma(\text{C-C-C})$ o.p. bending              |
| 515                       | 6.0 | 534                       | 0.4 | $a''$                | 16b                        | $\gamma(\text{C-C-C})$ o.p. bending              |
| 477                       | 8.0 | —                         | —   | $a'$                 | 6a                         | $\delta(\text{C-C-C})$ i.p. bending              |
| 431                       | 8.0 | —                         | —   | $a'$                 | 6b                         | $\delta(\text{C-C-C})$ i.p. bending              |
| 380                       | 6.4 | 375                       | 0.2 | $a'$                 | 9a                         | $\delta(\text{C-CH}_3)$ i.p. bending             |
| 295                       | 7.0 | 282                       | 0.4 | $a'$                 | 7a                         | $\nu(\text{C-I})$ stretching                     |
| 273                       | 6.1 | —                         | —   | $a'$                 | 15                         | $(\text{C-NO}_2)$ i.p. bending                   |
| 241                       | 7.0 | 235                       | 0.4 | $a'$                 | 9b                         | $\delta(\text{C-I})$ i.p. bending                |
| 207                       | 7.2 | 211                       | 0.8 | $a''$                | 10b                        | $\gamma(\text{C-CH}_3)$ o.p. bending             |
| 187                       | 7.5 | 185                       | 0.2 | $a''$                | 17a                        | $\gamma(\text{C-I})$ o.p. bending                |
| 167                       | 6.8 | —                         | —   | $a''$                | 17b                        | $\gamma(\text{C-NO}_2)$ o.p. bending             |
| 147                       | 7.7 | —                         | —   | $a''$                | —                          | torsion in $\text{CH}_3$ group                   |
| 110                       | 8.0 | —                         | —   | $a''$                | —                          | torsion in $\text{NO}_2$ group                   |

$\nu$  = stretching,  $\delta$  = in-plane bending,  $\gamma$  = out-of-plane bending,  $\nu_{as}$  = asymmetric stretching,  $\nu_s$  = symmetric stretching,  $\delta_s$  = symmetric deformation,  $\delta_{as}$  = asymmetric deformation.

Visual estimates of the intensities have been given in the visual scale of 1 to 10.

hydrogen also changes the point group symmetry from  $D_{6h}$  corresponding to benzene to  $C_{2v}$ , if  $\text{NO}_2$  and  $\text{CH}_3$  are regarded as point masses. (2-I-5-NT) will have in addition to 30 benzene like vibrations, six  $\text{NO}_2$  vibrations and nine  $\text{CH}_3$  vibrations, making up a total of 45 fundamental vibrations. As the molecule belongs to  $C_{2v}$  point group, there is only one plane of symmetry *ie* plane of molecule. There will be only two types of vibrations that are  $a'$  (planar) and  $a''$  (non planar). The observed fundamental frequencies and probable assignments are presented in Table 1. All the assignments are made by comparison of the experimental frequencies and assignments reported earlier [1-3] in similar molecules.

### 3.1 Stretching vibrations ( $\nu$ )

#### 3.1.1. C-H and C-X stretching

Benzene has six modes of (C-H) stretching vibrations denoted by the numbers 2, 20a, 20b, 7a, 7b, and 13; in Wilson's notations, these have the frequencies 3062 ( $a_{1g}$ ), 3080 ( $e_{1u}$ ), 3046 ( $e_{2g}$ ), and 3060  $\text{cm}^{-1}$  ( $b_{1u}$ ) respectively. In case of tri-substituted benzenes, out of six (C-H) stretching vibrations, three remain pure (C-H) stretching vibrations while the remaining three frequencies would be (C-X) stretching (X = substitution for H atom) and will be depending on the masses of the substituents. The three (C-H) stretching frequencies do not change due to substitution and lie in the range of 3000–3100  $\text{cm}^{-1}$ . The (C-X) stretching frequencies decrease considerably [6] below 1200  $\text{cm}^{-1}$ . If the substituents, are light (atomic mass less than 25), these frequencies will lie above 1000  $\text{cm}^{-1}$ . Thus utilizing the mode of

assignments in the tri-substituted benzene by Syam Sundar and Kanna Rao [1], Rai *et al* [2] and Rangacharyulu and Premaswarup [3] for (2-I 5- NT) molecule, the frequencies (R 3085, IR 3077), (R 3067, IR 3023), (R 3017, IR 3015)  $\text{cm}^{-1}$  have been assigned as (C-H) stretching frequencies, corresponding to modes 2, 20a and 20b respectively. The frequencies (R 1255, IR 1254), (R 920, IR 923) and (R 282, IR 295)  $\text{cm}^{-1}$  have been assigned as (C-CH<sub>3</sub>), (C-NO<sub>2</sub>) and (C-I) stretching frequencies. These frequencies correspond to the modes 7a, 7b and 13 respectively. All these assignments agree well with the results of the earlier workers. [1-3, 6-8].

### 3.1.2. C-C stretching vibrations

According to Singh and Singh [6], there are six normal modes of benzene, which belong to the groups namely 8a, 8b, 19a, 19b, 14 and 1. The  $\nu(\text{C-C})$  stretching vibrations of benzene come around 1600  $\text{cm}^{-1}$  and correspond to a degenerate  $e_{2g}$  mode 8 (8a and 8b). In substituted benzenes, the degeneracy should be removed and the two components should appear near 1600  $\text{cm}^{-1}$  giving rise to fairly strong bands in infrared and Raman spectra. Thus, the strong bands at (R 1639, IR 1646) and (R 1603, IR 1608)  $\text{cm}^{-1}$  are assigned to modes 8a and 8b respectively. It could be seen that we have taken 8a > 8b. This is done in order to be in accordance with the results of normal mode analysis of tri-substituted benzenes [9, 10].

The pair of vibrations 19a and 19b arises from  $e_{1u}$  mode of benzene. They are usually strong in infrared and are expected in the range of 1400- 1500  $\text{cm}^{-1}$ . There are two bands at (R 1420, IR 1423) and (R 1510, IR 1516)  $\text{cm}^{-1}$ , whose origin can be attributed to modes 19a and 19b respectively.

The vibration mode 14, called the kekule mode, belongs to  $b_{2u}$  species of benzene, expected near 1300  $\text{cm}^{-1}$ , in di-substituted benzenes. A correct assignment of this band is complicated by the fact that the  $\delta(\text{C-C})$  in-plane-bending mode 3 also occurs in this region. The frequencies (R 1267 IR 1265)  $\text{cm}^{-1}$  observed in (2-I 5-NT) have been assigned to mode 3. Our assignment is in agreement with the assignments made in fluoro nitro toluenes by Syam Sundar and Kanna Rao [1]. The frequencies (R 680, IR 669)  $\text{cm}^{-1}$  have been assigned to the mode 1 in accordance to assignments made by earlier workers [1-5] and the frequency range agrees with that given by Shukla *et al* [11].

### 3.2. In-plane Bending vibrations :

#### 3.2.1. (C-H) and (C-X) $\delta$ vibrations

The C-H in-plane bending modes lie in the region 1000 – 1300  $\text{cm}^{-1}$ . These arise due to  $a_{2g}$  (1340  $\text{cm}^{-1}$ ),  $e_{2g}$  (1178  $\text{cm}^{-1}$ ),  $b_{2u}$  (1152  $\text{cm}^{-1}$ ) and  $b_{1u}$  (1037  $\text{cm}^{-1}$ ) modes of benzene denoted by Wilson's numbers 3, 9a, 9b, 15, 18a and 18b, respectively. In tri-substituted benzene derivatives, three modes of vibrations remain almost unchanged and are called (C-H)  $\delta$  vibrations, while three modes change considerably in frequency and are

called (C-X)  $\delta$  vibrations. The frequencies for (C-H)  $\delta$  modes have been assigned at (R 1267, IR 1265), (R 1207, IR 1192), and (R 1125, IR 1130)  $\text{cm}^{-1}$  in agreement with the observations of several workers [1-3] and following the suggestions of Varsanyi [12]. These frequencies will originate from the mode 3, 18a, and 18b. The frequencies for (C-X)  $\delta$  modes have been assigned at (R 375, IR 380), (IR 273) and (R 235, IR 241)  $\text{cm}^{-1}$  as C-CH<sub>3</sub>, C-NO<sub>2</sub> and C-I vibrations respectively corresponding to the mode 9a, 15 and 9b respectively. These assignments are in good agreement with those of Refs. [13-15] and the frequency range with that given by Rao [16], Varsanyi [12].

#### 3.2.2. C-C-C in-plane bending

The normal modes 6a, 6b, and 12 are regarded as the (C-C-C)  $\delta$  vibrations. The frequencies (IR 477), (IR 431), (IR 746)  $\text{cm}^{-1}$ , have been identified as (C-C-C) in-plane bending vibrations. The above assignments are within frequency range given by Varsanyi [12], for similar compounds and find support from the studies of other workers. [17, 18].

### 3.3. Out-of-plane bending :

#### 3.3.1 (C-H) and (C-X) out-of-plane bending vibrations

The modes 5, 17a, 17b, 10a, 10b and 11 with frequencies (958)  $b_{2g}$ , (975)  $e_{2u}$ , (849)  $e_{1g}$ , (673)  $a_{2u}$ , represent (C-H)  $\gamma$ . These vibrations have been observed at (IR 946), (IR 992), (R 807, IR 810)  $\text{cm}^{-1}$  in (2-I 5NT) corresponding to modes 5, 17b, and 11 respectively. The frequencies (R 185, IR 187), (R 211, IR 207)  $\text{cm}^{-1}$  have been identified as C-I and C-CH<sub>3</sub> out-of-plane bending vibrations corresponding to modes 17b, and 10b respectively. Our assignments find support from the work of Green *et al* [17] and are within frequency range given by Varsanyi. [12].

#### 3.3.2. C-C-C out of plane bending vibrations

The normal modes 4, 16a and 16b are regarded as the (C-C-C)  $\gamma$  vibrations. The frequencies (R 558, IR 577), (R 534, IR 515)  $\text{cm}^{-1}$  have been identified as C-C-C out-of-plane bending vibrations. Our assignments find support from the work of several workers. [1, 19, 20].

### 3.4. Internal vibrations of methyl group (CH<sub>3</sub> group) :

There must be three C-H stretching modes (two asymmetric and one symmetric type). The frequencies of asymmetric vibrations are higher than that of symmetric one. According to Colthup *et al* [21], these frequencies appear around fairly constant regions of 2960  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$  respectively. Singh *et al* [22] have assigned symmetric and asymmetric C-H stretching modes in CH<sub>3</sub> group in o-m-p- methoxy benzaldehydes within the frequency range (2829–2863)  $\text{cm}^{-1}$  and (2945–2965)  $\text{cm}^{-1}$  respectively. In the present case, the frequencies (R 2973, IR 2984) and (R 2922, IR 2938)  $\text{cm}^{-1}$  are taken as asymmetric C-H stretching modes and (IR 2892  $\text{cm}^{-1}$ ) as symmetric C-H stretching mode in CH<sub>3</sub>. These assignments find support from the work of Fusion *et al* [23] and Rangacharyulu and Premaswarup [3].

The rocking vibrations of  $\text{CH}_3$  group interact with other modes. As a result of this interaction, the rocking mode frequencies do not appear consistently. Several workers [24, 25] have assigned these vibrations at about  $1170 \pm 40 \text{ cm}^{-1}$ . Rangacharyulu and Premaswarup [3] have assigned out-of-plane rocking mode of  $\text{CH}_3$  group at  $1050 \text{ cm}^{-1}$  in 2-bromo-5-nitro toluene, at  $1090 \text{ cm}^{-1}$  in 2-bromo-4-nitro toluene and  $1080 \text{ cm}^{-1}$  in 4-chloro-3-nitro toluene, respectively. In the present case, the frequencies at (R 1090, IR 1097), (R 1008, IR 1013)  $\text{cm}^{-1}$ , are assigned to this mode. Our assignments find support from the work of several workers. [3, 11, 17].

A literature survey [26-28] reveals that in xylene, the  $\text{CH}_3$  torsional mode appears at about  $180 \text{ cm}^{-1}$ . We have observed tentatively this vibration at about (IR 147)  $\text{cm}^{-1}$ .

### 3.5. Internal mode of vibration of $\text{NO}_2$ group :

The symmetric stretching of the substituent  $\text{NO}_2$  group have been assigned in the region (1338-1351)  $\text{cm}^{-1}$  by various workers. In the present case, the frequencies (R1340, IR 1340)  $\text{cm}^{-1}$  have been assigned to the symmetric stretching mode in  $\text{NO}_2$  group, in accordance with the assignments made by previous workers. [29-32].

$\text{NO}_2$  deformation vibration has been assigned to the band observed at (IR 854)  $\text{cm}^{-1}$ , these vibrations have been reported in the region 824–890  $\text{cm}^{-1}$  by many workers [29-33]. The band observed at (IR 167)  $\text{cm}^{-1}$  has been assigned to C- $\text{NO}_2$  out-of-plane bending vibration in (2-I-5-NT). Rai *et al* [2] have identified this vibration at  $150 \text{ cm}^{-1}$  in 4-chloro 2-nitro toluene. Torsion mode vibration in  $\text{NO}_2$  group has been observed at  $110 \text{ cm}^{-1}$  in (2-I-5-NT), Syam Sundar and Kanna Rao [1] have suggested this vibration in the region 111-120  $\text{cm}^{-1}$  in fluoro nitrotoluenes.

## 4. Conclusion

Vibrational assignments of such complicated molecules have been performed by taking the help of similar vibrations observed in similar molecules. These studies will be helpful to identify ground state vibrations of the above benzene derivative, and to enable us to propose a consistent assignment for C-X modes and the internal modes of the substituent groups and to study the effects of these substituents on the phenyl ring modes. These frequencies observed in FT-Raman and FT-IR spectra can be used as ground state vibrations, to confirm excited state vibrations of (2-I-5-NT) with the help of the electronic spectra.

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