

Fourier transform infrared spectrum and normal coordinate analysis of chloroxylenol

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Chloroxylenol is one of the important antiseptic with the molecular formula C_8H_9ClO . A normal coordinate analysis has been carried out for chloroxylenol for the first time with a systematic set of symmetry coordinates following Wilson's F-G matrix method based on C_s point group symmetry. The frequency assignments for the bands in the Fourier transform infrared spectrum of chloroxylenol have been presented. A reasonable set of potential constants evaluated for this molecule is found to be in good agreement with literature values for similar compounds. To check whether the chosen set of vibrational frequencies contribute maximum to the normal modes of vibration of the molecule, the potential energy distribution has been evaluated. The potential energy distribution values obtained reflect the correctness of the assignments made.

[**Keywords:** Fourier transform infrared spectrum, Normal coordinate analysis, Chloroxylenol, Potential energy distribution]

1 Introduction

Chloroxylenol is an important antiseptic used commonly for treating wounds and sterilizing surgical instruments. In the present work, vibrational analysis of chloroxylenol has been carried out, using Wilson's F-G matrix method under C_s point group symmetry. For the first time, a detailed frequency assignment has been made using Fourier Transform Infrared (FTIR) spectrum of chloroxylenol. Work on related molecules and similar compounds has been referred to for solving the secular equation. Potential energy distribution obtained as an outcome of the theoretical considerations is used to confirm the frequency assignments done using the infrared spectrum.

2 Experimental Details

The sample of chloroxylenol with high-grade purity was procured from a leading pharmaceutical company SD Fine Chemicals, Chennai and was used as such without any further purification. The FTIR spectrum of the sample was recorded in the $4000\text{--}400\text{ cm}^{-1}$ range by using BRUKER IFS 66 V spectrophotometer at RSIC, IIT Chennai, India. Chloroxylenol was mixed with KBr and pressed into discs for recording the spectrum. The FTIR

spectrum of chloroxylenol is presented in Fig. 1. A detailed interpretation of the vibrational bands of the sample is summarized in Table 1.

3 Normal Coordinate Analysis

Chloroxylenol, a derivative of phenol, belongs to the C_s point group symmetry with thirty-three fundamental vibrations distributed as $\Gamma_{\text{vib}} = 23 A' + 10 A''$. All the thirty-three modes are active both in infrared and Raman. Of the twenty-three fundamentals in A' species, only fourteen, and out of ten fundamentals in A'' species, only five are considered in the present work. The structure, orientation of the principal axes and the nomenclature of the parameters of chloroxylenol molecule are presented in Fig. 2. The structural parameters have been taken from the Sutton Table.

3.1 Symmetry coordinates

The symmetry coordinates are constructed using the set of internal coordinates. The symmetry coordinates for the ring are the same as those of benzene while those for the hydroxyl group; chlorine and methyl groups are constructed satisfying the C_s point group symmetry with the knowledge of projection operators. The following are the set of symmetry coordinates for the specific

modes of vibration taken into consideration in the present case.

A' species

$$S_1 = 1/\sqrt{6} [(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6)]$$

$$S_2 = 1/\sqrt{6} [(\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4 + \Delta r_5 - \Delta r_6)]$$

$$S_3 = 1/\sqrt{6} [(\Delta r_1 - 2\Delta r_2 + \Delta r_3 + \Delta r_4 - 2\Delta r_5 + \Delta r_6)]$$

$$S_4 = \Delta D$$

$$S_5 = \Delta T$$

$$S_6 = \Delta R$$

$$S_7 = 1/\sqrt{2} [(\Delta d_1 + \Delta d_2)]$$

$$S_8 = 1/\sqrt{6} [(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3 + \Delta \alpha_4 + \Delta \alpha_5 + \Delta \alpha_6)]$$

$$S_9 = 1/\sqrt{2} [(\Delta \gamma_1 + \Delta \gamma_2)]$$

$$S_{10} = 1/\sqrt{2} [(\Delta \theta_1 + \Delta \theta_2)]$$

$$S_{11} = 1/\sqrt{2} [(\Delta t_1 + \Delta t_2)]$$

$$S_{12} = 1/\sqrt{4} [(\Delta \delta_1 + \Delta \delta_2 + \Delta \delta_3 + \Delta \delta_4)]$$

$$S_{13} = 1/\sqrt{4} [(\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 + \Delta \beta_4)]$$

$$S_{14} = \Delta \phi$$

A'' species

$$S_{15} = 1/\sqrt{2} [(\Delta d_1 - \Delta d_2)]$$

$$S_{16} = 1/\sqrt{2} [(\Delta \gamma_1 - \Delta \gamma_2)]$$

$$S_{17} = 1/\sqrt{2} [(\Delta t_1 - \Delta t_2)]$$

$$S_{18} = 1/\sqrt{6} [(\Delta \alpha_1 + \Delta \alpha_2 - \Delta \alpha_3 + \Delta \alpha_4 + \Delta \alpha_5 - \Delta \alpha_6)]$$

$$S_{19} = 1/\sqrt{6} [(-\Delta \alpha_1 - 2\Delta \alpha_2 - \Delta \alpha_3 + \Delta \alpha_4 + 2\Delta \alpha_5 + \Delta \alpha_6)]$$

where Δr is the change in bond length C-C; ΔD the change in bond length C-O; ΔT the change in bond length O-H; ΔR the change in bond length C-Cl; Δt the change in bond length C-X; Δd the change in bond length C-H; $\Delta \alpha$ the change in bond angle C-C-C; $\Delta \beta$ the change in bond angle C-C-H; $\Delta \gamma$ the change in bond angle C-C-O; $\Delta \delta$ the change in bond angle C-C-X; $\Delta \theta$ the change in bond angle C-C-Cl; $\Delta \phi$ the change in the angle C-O-H.

3.2 Kinetic energy matrix elements and secular equation

The elements of the inverse kinetic energy matrix have been derived from the relation $G = B\mu B'$ where B is the matrix formulated using the vectors evaluated from the expression of the symmetry coordinates in terms of the Cartesian displacement coordinates, B' is the transpose of B matrix and μ is

the diagonal matrix of the reciprocal masses of the atoms in the molecule. The method of kinetic constant relates the off-diagonal elements of the F matrix to its diagonal elements through the relation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$ ($i < j$, $i = 1, 2, 3, \dots$).

Table 1 — Fourier transform infrared frequencies of chloroxylenol

Frequency (cm ⁻¹)	Description
548	ν_{13} C-C-H deformation
582	ν_{12} C-C-X deformation
625	ν_9 C-C-O symmetric bend
680	ν_{10} C-C-Cl deformation
711	ν_6 C-Cl stretch
720	ν_{16} C-C-O asymmetric bend
763	ν_8 C-C-C symmetric bend
807	ν_{18} C-C-C asymmetric bend
841	ν_{19} C-C-C asymmetric bend
1032	ν_{14} C-O-H bend
1052	ν_{11} C-CH ₃ symmetric stretch
1118	ν_1 C-C symmetric stretch
1150	ν_4 C-O stretch
1191	ν_{17} C-CH ₃ asymmetric stretch
1252	ν_3 C-C asymmetric stretch
1609	ν_2 C-C asymmetric stretch
2810	ν_7 C-H symmetric stretch
2872	ν_{15} C-H asymmetric stretch
3652	ν_5 O-H stretch

3.4 Vibrational analysis

The presence of ring in the structure of chloroxylenol along with the O-H group naturally, makes chloroxylenol to assume C_s point symmetry. The assignments for the fundamental modes of vibrations have been made in terms of band position, shape and intensity. The vibrational frequencies of benzene, phenol and pentachlorophenol are used as guidelines for the assignments of fundamental vibrations of chloroxylenol.

C-H vibrations — The band in the 3000 cm⁻¹ region in the infrared spectrum arises due to C-H stretching of aromatic ring¹. In the FTIR spectrum of chloroxylenol, the bands at 2810 cm⁻¹ and 2872 cm⁻¹ are assigned to the C-H symmetric and asymmetric stretching vibrations of the aromatic ring, respectively. The force constants for C-H symmetric and asymmetric stretching vibrations are fixed as 5.0559 × 10³ N/M and 5.5232 × 10³ N/M, respectively in the present investigation, which closely agrees with the reported values 5.0761 × 10³

N/M (Ref. 2) and 5.5253×10^2 N/M (Ref. 3) for C-H symmetric and asymmetric stretching vibrations, respectively. The C-H bending vibrations appear at two distinct regions $1300\text{--}1000\text{ cm}^{-1}$ and $700\text{--}610\text{ cm}^{-1}$, due to in-plane and out-of-plane bending vibrations, respectively⁴. The band at 1032 cm^{-1} is assigned to C-H in-plane bending vibration, which agrees well with the value reported by previous work on benzene⁵. The force constant for C-C-H in-plane bending vibration is arrived at 0.4848×10^2 N/M, the corresponding value reported being 0.4741×10^2 N/M (Ref. 3).

O-H vibrations — The hydroxyl groups of alcohols and phenols, generally give a strong absorption band in the $3650\text{--}3580\text{ cm}^{-1}$ region. The sharp band at 3652 cm^{-1} in the FTIR spectrum is assigned to O-H stretching vibration. Phenols exhibit $\text{C}_6\text{H}_5\text{--OH}$ deformation band, centered around 1200 cm^{-1} (Ref. 5). The bending of C-O-H is seen as a band at 1032 cm^{-1} in the spectrum. The O-H force constant value of 5.8880×10^2 N/M for chloroxylenol arrived at in the present work, agrees with the corresponding value of 5.8392×10^2 N/M reported for 2,4,6 trinitro phenol².

C-O vibrations — In the case of phenols, the C-O stretching vibration produces a strong band in the $1200\text{--}1000\text{ cm}^{-1}$ region. The band at 1150 cm^{-1} in the spectrum is assigned to C-O stretching vibration. This is in good agreement with the

literature value⁷. The C-O force constant is fixed at 5.5867×10^2 N/M. For paracetamol, the C-O force constant is reported to be 5.0135×10^2 N/M (Ref. 3).

Table 2 — Potential constants and PED for chloroxylenol

Symmetry coordinates	Frequency (cm^{-1})	Potential constants (10^2 N/M)	PED %
S_1	1118	6.5843	85
S_2	1609	6.7905	98
S_3	1252	6.8143	82
S_4	1150	5.5867	45
S_5	3652	5.8880	75
S_6	711	3.7562	40
S_7	2810	5.0559	99
S_8	763	1.2556	41
S_9	625	1.0429	60
S_{10}	680	1.1041	54
S_{11}	1052	4.5644	40
S_{12}	582	0.2787	99
S_{13}	548	0.4848	99
S_{14}	1032	0.7763	30
S_{15}	2872	5.5232	79
S_{16}	720	0.2732	40
S_{17}	1191	4.7325	40
S_{18}	807	0.9364	65
S_{19}	841	0.9463	30

C-C vibrations — Gunasekaran *et al.*⁸ have reported the ring C-C stretching vibration in the $1625\text{--}1530\text{ cm}^{-1}$ region. The C-C stretching vibration of the ring has been reported at 1325 cm^{-1} (Ref. 3). The sharp band observed at 1118 cm^{-1} in

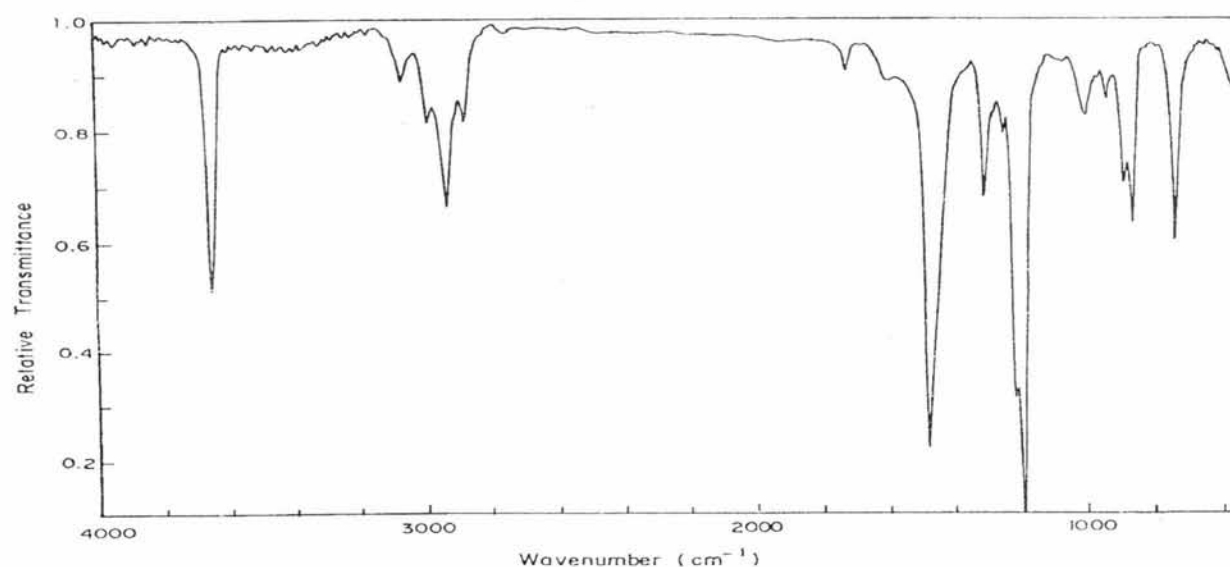


Fig. 1 — FTIR spectrum of chloroxylenol

the spectrum is assigned to C-C symmetric stretching and the bands at 1252 and 1609 cm^{-1} to C-C asymmetric stretching vibrations. The C-C symmetric and asymmetric stretching force constants reported earlier as $6.5783 \times 10^2 \text{ N/M}$ and $6.7905 \times 10^2 \text{ N/M}$, respectively³ agree well with the respective $6.5843 \times 10^2 \text{ N/M}$ and $6.8143 \times 10^2 \text{ N/M}$ values of the present investigation. The ring symmetric bending results in a band at 963 cm^{-1} and the respective asymmetric bendings are seen as bands at 841 and 807 cm^{-1} . For paracetamol molecule, the C-C-O bending vibration has been assigned to the band at 607 cm^{-1} (Ref. 3). In the present case, the C-C-O symmetric and asymmetric bending vibrations are assigned to the 625 and 720 cm^{-1} bands, respectively.

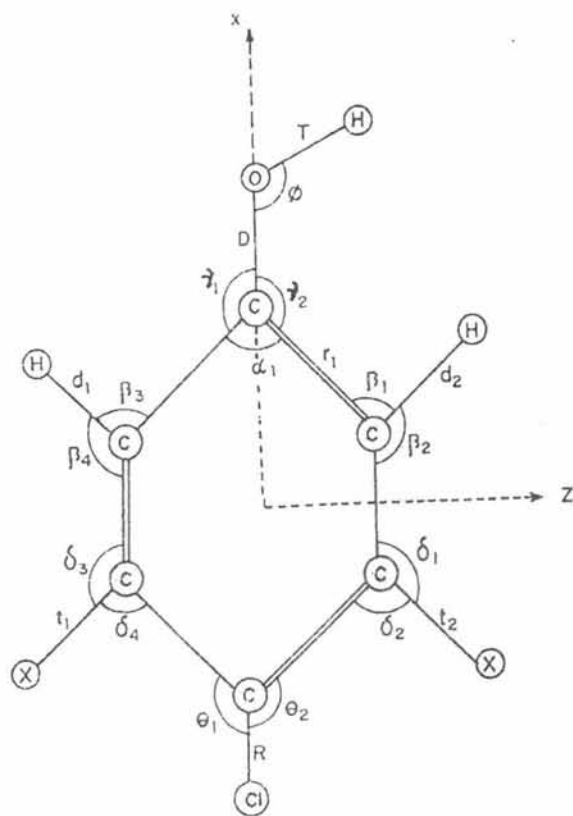


Fig. 2 — Structure, nomenclature of parameters and orientation of the principal axes of chloroxylenol molecule

C-CH₃ vibrations — The C-CH₃ stretching vibrations have been identified in the 950-1160 cm^{-1} region⁹. The C-CH₃ symmetric stretching vibration in chloroxylenol occurs at 1052 cm^{-1} whereas, the corresponding asymmetric stretching gives rise to a band at 1191 cm^{-1} . This is in tune with the reported values³. The deformation of C-CH₃ has resulted in a

band at 582 cm^{-1} , which agrees well with earlier workers⁹. The deformation of C-C-H is seen as a band at 548 cm^{-1} in the spectrum of the sample².

C-Cl vibrations — Strong characteristic absorptions due to the C-Cl stretching are observed, the position of the band being affected by neighbouring atoms or groups- the smaller the halide atom, the greater the influence of the neighbour. The C-Cl stretching gives generally strong bands in the 760-505 cm^{-1} region. The sharp band at 711 cm^{-1} in the spectrum of chloroxylenol is assigned to C-Cl stretching vibration. The C-Cl stretching force constant in the present work is arrived at $3.7562 \times 10^2 \text{ N/M}$. This is in good agreement with the literature value⁹. The C-Cl deformation has resulted in a band at 680 cm^{-1} . This band at 680 cm^{-1} appears as a shoulder to the band at 711 cm^{-1} . This agrees well with literature reports that, there appears to be no pure C-Cl stretching vibration for aromatic halogen compounds. The C-Cl deformation force constant value of $1.1041 \times 10^2 \text{ N/M}$ is a good one; the value obtained by earlier workers being $1.1084 \times 10^2 \text{ N/M}$.

3.5 Potential Energy Distribution

A knowledge of the transformation matrix L and the kinetic constant matrix K leads to the solution of the secular equation due to Wilson, yielding the elements of the force constant matrix F . The frequency assignment is verified by evaluating the potential energy distribution (PED) using the relation, $\text{PED} = F_{ij} L_{ij}^2 / \lambda_j$, where PED is the contribution of the symmetry coordinate to the potential energy of the vibration whose frequency is ν_j , F_{ij} is the force constant, L_{ij} is the L matrix element and $\lambda_j = 4\pi^2 c^2 \nu_j^2$.

3.6 Results and Discussion

In the present case, only the diagonal force constants have been taken into consideration. Solving the secular equation and fixing the appropriate force constants have been carried out through several cycles with suitable increments without fixing any of the force constants. The PED for the various fundamental modes is given in Table 1, and the force constants values are presented in Table 2. The PED values for the fundamental modes indicate the correctness of the frequency assignments made. The value of force constants presented in the current work agrees very

well with those reported by earlier workers on similar compound^{2,3,9}. Thus, a complete vibrational band assignment has been made available for the first time for chloroxylenol, using FTIR spectrum on the basis of C_s point group symmetry. The PED evaluated for the normal modes of vibration provide strong support to the work carried out.

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