

Normal coordinate analysis of urea meta nitro benzoic acid crystal

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Urea meta nitrobenzoic acid is a crystal with the molecular formula $C_8H_7O_4N_3$. A normal coordinate analysis (NCA) has been carried out on this molecule with a systematic set of symmetry coordinates following Wilson's F-G matrix method based on C_s point group symmetry. The frequency assignments in the FTIR and FTR spectra have been presented. A reasonable set of potential constants evaluated for this molecule has been compared with those of related molecules and are in the characteristic range. The potential energy distribution has been evaluated using the vibrational spectral data and molecular parameters. The potential energy distribution value obtained reflects the correctness of the assignment mode.

Keywords: FTIR, FTR spectra, Urea meta nitrobenzoic acid crystal, Normal coordinate analysis, Potential energy distribution

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1 Introduction

Urea was the first organic chemical ever synthesized commercially. Its present commercial relevance stems from its use in plastics and as the source of nitrogen in fertilizers. Urea has the ability to form loose compounds with many organic compounds¹. An organic compound urea is added to the ADP solutions in small amounts to enhance the metastable zone width². In the present paper substitution of meta nitrobenzoic acid to urea has been made. The vibrational analysis on the molecule of meta nitrobenzoic acid crystal has been carried out using Wilson's F-G matrix method under C_s point group symmetry. A detailed frequency assignment has been made on urea meta nitro benzoic acid (UMNBA) crystal using FTIR and FTR spectra. From the spectral knowledge of wavenumber and symmetry of the molecule, the secular equation has been solved. Validation of the obtained set of force constants and frequency assignments is done through potential energy distribution (PED) calculations.

2 Experimental Details

The sample of UMNBA crystal was obtained from Crystal Growth Center, Anna University, Chennai, India. The FTIR spectrum of the sample was recorded on BRUKER IFS 66 V spectrophotometer in the range 4000-400 cm^{-1} by KBr pellet and FT Raman spectrum was recorded in the region 3500-100 cm^{-1} . The spectra were recorded at Sophisticated Analytical

Instrumentation Facility, Indian Institute of Technology, Chennai, India. A spectral width of 4.29 cm^{-1} was used and the spectra were measured with a scanning speed of 1.87 cm^{-1} per minute. The FTIR and FT Raman spectra are presented in Figs 1 and 2, respectively.

3 Normal Coordinate Analysis

Urea meta nitro benzoic acid molecule possessing C_s symmetry has sixty fundamental modes of vibration distributed as $\Gamma_{vib} = 40A' + 20A''$. All the sixty modes are active both in infrared and Raman. Of the forty fundamentals in A' species only twenty-one and out of twenty fundamentals in A'' species only fourteen are considered in the present work. The structure orientation of the principal axes and the nomenclature of the parameters of UMNBA crystal are presented in Fig. 3. The structural parameters have been taken from Sutton Table³. A systematic set of symmetry coordinates has been arrived at, using the knowledge of projection operator and the character table pertaining to the C_s symmetry point group. The symmetry coordinates, thus, obtained are as follows:

A' species

$$S_1 = (\Delta a_1 + \Delta a_2 + \Delta a_3 + \Delta a_4 + \Delta a_5 + \Delta a_6)/6^{1/2}$$

$$S_2 = (\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)/2$$

$$S_3 = \Delta e$$

$$S_4 = (\Delta f_1 + \Delta f_2)/2^{1/2}$$

$$S_5 = \Delta h$$

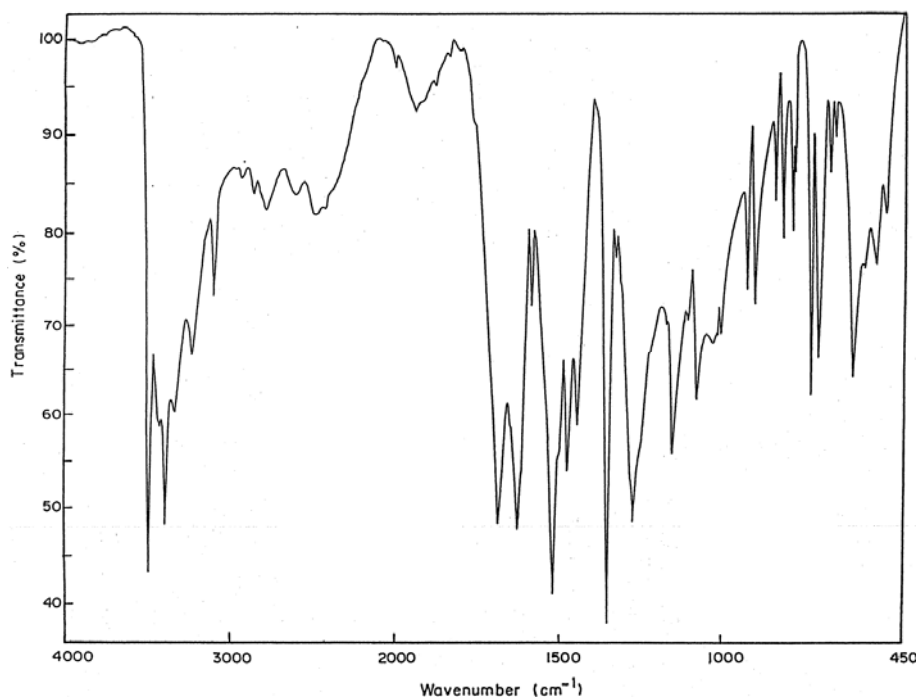


Fig. 1—FTIR spectrum of urea meta nitro benzoic acid crystal

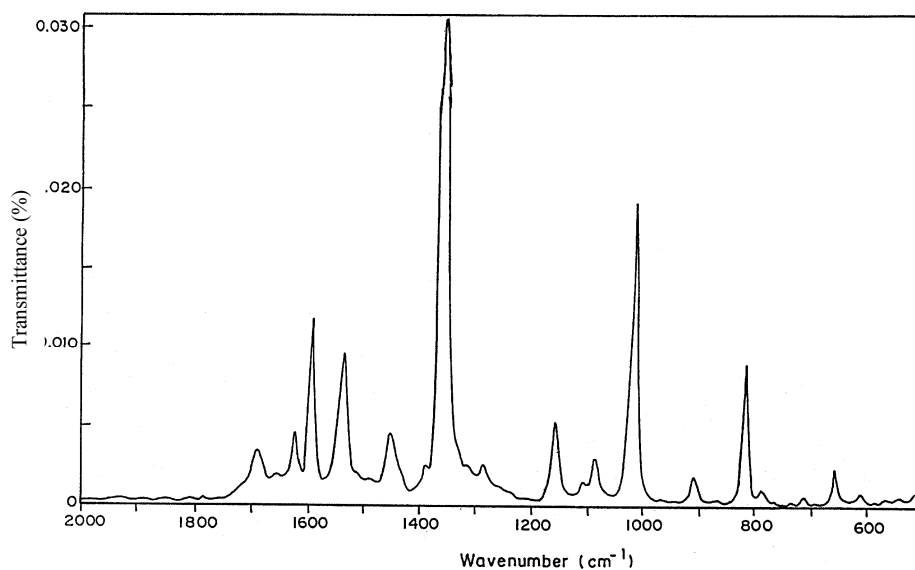


Fig. 2—FTIR spectrum of urea meta nitro benzoic acid crystal

$$S_6 = \Delta k$$

$$S_7 = \Delta p$$

$$S_8 = (\Delta q_1 + \Delta q_2)/2^{1/2}$$

$$S_9 = (\Delta r_1 + \Delta r_2)/2^{1/2}$$

$$S_{10} = (\Delta s_1 + \Delta s_2)/2^{1/2}$$

$$S_{11} = \Delta \eta$$

$$S_{12} = (\Delta \sigma_1 + \Delta \sigma_2 + \Delta \sigma_3 + \Delta \sigma_4 + \Delta \sigma_5 + \Delta \sigma_6 + \Delta \sigma_7 + \Delta \sigma_8)/8^{1/2}$$

$$S_{13} = \Delta \chi$$

$$S_{14} = (\Delta \theta_1 + \Delta \theta_2)/2^{1/2}$$

$$S_{15} = \Delta \delta$$

$$S_{16} = (\Delta \psi_1 + \Delta \psi_2)/2^{1/2}$$

$$S_{17} = \Delta \tau$$

$$S_{18} = \Delta \lambda$$

$$S_{19} = \Delta \omega$$

$$S_{20} = \Delta \mu$$

$$S_{21} = \Delta \Omega$$

A'' species

$$S_{22} = (\Delta a_1 - 2\Delta a_2 + \Delta a_3 + \Delta a_4 - 2\Delta a_5 + \Delta a_6)/12^{1/2}$$

$$S_{23} = (\Delta a_1 - \Delta a_2 + \Delta a_3 - \Delta a_4 + \Delta a_5 - \Delta a_6)/6^{1/2}$$

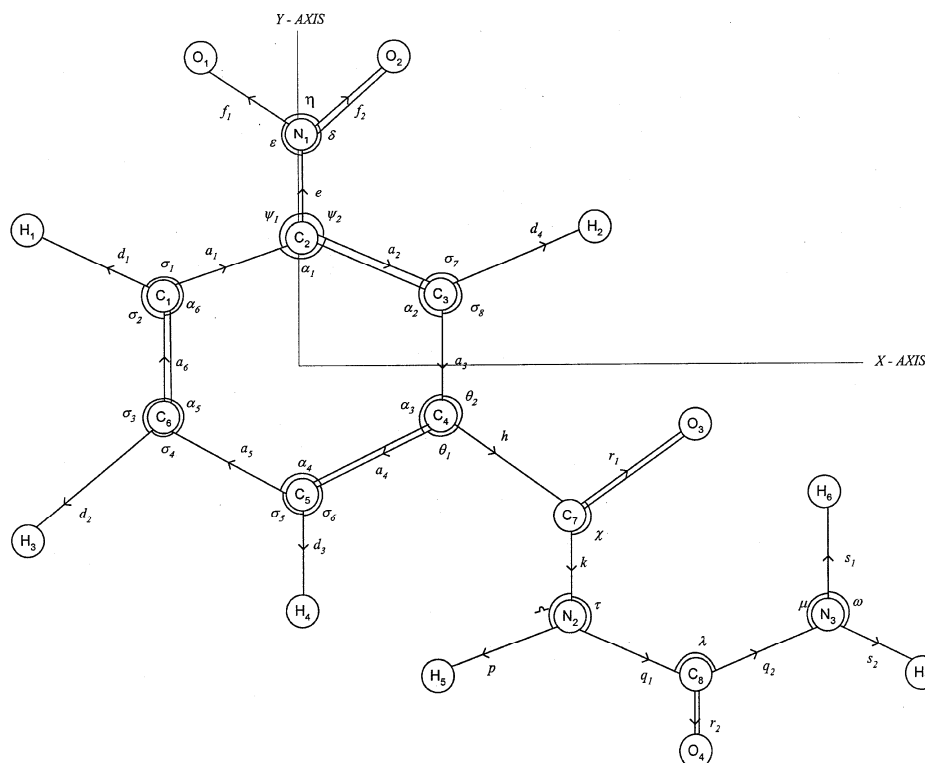


Fig. 3—Structure, nomenclature of parameters and orientations of principal axes of urea meta nitro benzoic acid crystal

$$\begin{aligned}
 S_{24} &= (-\Delta a_1 - 2\Delta a_2 - \Delta a_3 + \Delta a_4 + 2\Delta a_5 + \Delta a_6)/12^{1/2} \\
 S_{25} &= (\Delta d_1 - \Delta d_2 + \Delta d_3 - \Delta d_4)/2 \\
 S_{26} &= (-\Delta d_1 - \Delta d_2 + \Delta d_3 + \Delta d_4)/2 \\
 S_{27} &= (\Delta d_1 - 2\Delta d_2 - \Delta d_3 + 2\Delta d_4)/10^{1/2} \\
 S_{28} &= (\Delta f_1 - \Delta f_2)/2^{1/2} \\
 S_{29} &= (\Delta q_1 - \Delta q_2)/2^{1/2} \\
 S_{30} &= (\Delta r_1 - \Delta r_2)/2^{1/2} \\
 S_{31} &= (\Delta s_1 - \Delta s_2)/2^{1/2} \\
 S_{32} &= (\Delta \alpha_1 - \Delta \alpha_2 + \Delta \alpha_3 - \Delta \alpha_4 + \Delta \alpha_5 - \Delta \alpha_6)/6^{1/2} \\
 S_{33} &= (\Delta \psi_1 - \Delta \psi_2)/2^{1/2} \\
 S_{34} &= (\Delta \sigma_1 - \Delta \sigma_2 + \Delta \sigma_3 - \Delta \sigma_4 + \Delta \sigma_5 - \Delta \sigma_6 + \Delta \sigma_7 - \Delta \sigma_8)/8^{1/2} \\
 S_{35} &= (\Delta \alpha_1 + \Delta \alpha_2 - \Delta \alpha_3 - \Delta \alpha_4 + \Delta \alpha_5 - \Delta \alpha_6)/6^{1/2}
 \end{aligned}$$

where Δ 's represent the corresponding changes in bond lengths and bond angles.

A normal coordinate analysis for UMNBA molecule has been carried out, using the observed frequencies from the FTIR and FT Raman spectrum. The evaluation of the force constants has been made on the basis of general valence force field by applying Wilson's F-G matrix method. This method assumes the foreknowledge of the equilibrium molecular geometry namely, bond angles and bond lengths, vibrational frequencies and atomic masses. The master equation of Wilson method is a secular determinant $|\mathbf{FG} - \lambda \mathbf{E}| \equiv 0$, where \mathbf{F} , \mathbf{G} , \mathbf{E} are matrices. \mathbf{F} is a matrix of force constants through

which the vibrational potential energies enter the calculation. \mathbf{G} is the inverse kinetic energy matrix. \mathbf{G} matrix involves the atomic weights and equilibrium geometric relationships. Elements of the inverse kinetic energy matrix have been derived from the relation $\mathbf{G} = \mathbf{B}\mu\mathbf{B}^T$ where \mathbf{B}^T is the matrix formulated using the vectors which have been evaluated from the expression of the symmetry coordinates in terms of Cartesian displacement coordinates, μ is the diagonal matrix of the reciprocal masses of the atoms in the molecule. λ is a function of frequency coordinates, $\lambda = 4\pi^2 c^2 \nu^2$. The method of kinetic constants relates the off diagonal elements of the F matrix to its diagonal elements through the relation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$ ($i < j$, $i=1,2,3,\dots$). The basis set for an FG calculation consists of internal coordinates suitably chosen to eliminate redundancies. The calculation begins with a conjectural assignment of the peaks in the vibrational spectra.

The correctness of the 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 i_{th} symmetry coordinate to the potential energy of vibration whose frequency is ν_j . The observed frequencies along with the assignments, calculated force constants and the percentage of

Table 1—Infrared and Raman spectral assignment and potential energy distribution of UMNBA

Symmetry Coordinate	Frequency (cm ⁻¹)		Band Assignment	Force Constant (10 ² N/m)	PED (%)
	FTIR	FTR			
S ₁	1351(mw)	—	Ring C= C sym. stretching	6.5843	51
S ₂	2788 (w)	—	C-H sym. stretching	5.0116	98
S ₃	1300 (mw)	—	C-NO ₂ stretching	5.0318	71
S ₄	1318 (mw)	—	NO ₂ sym. stretching	9.0244	70
S ₅	1612 (s)	1616(m)	Ring-acid C-C stretching	6.5843	82
S ₆	1148 (s)	1157(m)	C-N stretching	5.0318	97
S ₇	3439 (vs)	—	N-H stretching	6.4454	98
S ₈	1012 (m)	1014(w)	N-C-N sym. stretching	5.0318	71
S ₉	1686 (s)	1657(m)	C=O sym. stretching	10.2103	86
S ₁₀	3393 (s)	—	N-H sym. stretching	6.4454	96
S ₁₁	809 (w)	—	NO ₂ bending	1.4951	98
S ₁₂	987 (m)	—	C-H deformation	0.5111	83
S ₁₃	664 (vw)	650(vw)	O=C-N deformation	0.9932	78
S ₁₄	779 (w)	784(vw)	Ring-acid C-C deformation	0.9143	66
S ₁₅	649 (vw)	650(vw)	O=N-C deformation	0.9881	67
S ₁₆	494 (w)	—	N-C-C sym. deformation	0.9426	68
S ₁₇	768 (vw)	784(vw)	C-N-C deformation	1.3576	42
S ₁₈	531 (mw)	—	N-C-N deformation	1.5298	88
S ₁₉	1506 (s)	—	N-H bending	0.4445	94
S ₂₀	897 (mw)	—	H-N-C deformation	0.5849	57
S ₂₁	919 (mw)	907(w)	C-N-H deformation	0.5849	51
A" species					
S ₂₂	1627 (s)	1623(m)	Ring C= C asym. stretching	6.5843	87
S ₂₃	1585 (mw)	1591(w)	Ring C= C asym. stretching	6.5843	98
S ₂₄	1506 (s)	1534(m)	Ring C= C asym. stretching	6.5843	93
S ₂₅	3231 (m)	—	C-H asym. stretching	5.0116	86
S ₂₆	3106 (mw)	3115(w)	C-H asym. stretching	5.0116	80
S ₂₇	2951 (w)	—	C-H asym. stretching	5.0116	78
S ₂₈	1520 (vs)	—	NO ₂ asym. stretching	9.0244	99
S ₂₉	1473 (s)	1484(s)	N-C-N asym. stretching	5.0318	84
S ₃₀	1937 (vw)	—	C=O asym. stretching	10.2103	78
S ₃₁	3493 (s)	—	N-H asym. stretching	6.4454	98
S ₃₂	831 (w)	816(w)	Ring C- C-C deformation	1.4734	53
S ₃₃	559 (mw)	507(vw)	N-C-C asym. deformation	0.9881	33
S ₃₄	1162 (m)	—	C-H deformation	0.5111	67
S ₃₅	702 (m)	707(w)	Ring C- C-C deformation	1.4734	66

vs-very strong, s-strong, m-medium, w-weak, mw-medium weak, vw-very weak

potential energy distribution for UMNBA crystal are presented in Table 1. The initial set of force constants for the UMNBA molecule has been taken from related molecules. This set of force constants was, subsequently refined by keeping a few interaction constants fixed, throughout the refinement process.

4 Vibrational Band Assignment

IR and Raman spectra contain a number of bands at specific wavenumbers. The aim of the vibrational analysis is to decide which of the vibrational modes give rise to each of these observed bands. The presence of ring in the structure of UMNBA molecule along with the NO₂ group makes UMNBA molecule

to assume *C_s* point symmetry. The assignment for the fundamental modes of vibrations has been made in terms of band position, shape and intensity. The vibrational frequencies of di-substituted benzene, urea were used as guidelines for the assignments of fundamental vibrations of UMNBA molecule^{4,5}.

Ring C-H vibrations—The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm⁻¹. In the FTIR spectrum of UMNBA, the bands at 3231, 3106 and 2788 cm⁻¹ are assigned to the C-H asymmetric stretching vibrations of the aromatic ring, respectively. In the laser Raman spectrum, the band observed at 3115 cm⁻¹ is attributed

to the C-H stretching vibrations. The C-H deformation vibrations appear at two distinct regions 1300-1000 and 700-610 cm⁻¹ due to in-plane and out-of-plane bending vibrations respectively⁶. The band at 1162 and 987 cm⁻¹ assigned to C-H in-plane bending vibrations agrees well with the value reported by previous work on benzene⁷.

Ring C=C vibrations—Gunasekaran *et al.*⁸ have reported the ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm⁻¹ region. In general, the bands are of variable intensity and observed in the range 1625-1590, 1590-1575, 1540-1470, 1465-1430 cm⁻¹ and 1380-1280 cm⁻¹ form the frequency ranges given by Varsanyi⁹ for the five bands in the region. The sharp band observed at 1627 and 1506 cm⁻¹ in the spectrum are assigned to C-C asymmetric stretching and the band at 1351 cm⁻¹ to symmetric stretching vibrations. The weak bands observed at 831 and 702 cm⁻¹ are assigned to C-C-C deformations.

NO₂ vibrations—Asymmetric NO₂ stretching vibration for singly substituted aromatic meta nitro compound⁹ is in the range 1540-1525 cm⁻¹ and for symmetric vibration in the range 1355-1345 cm⁻¹. The observed peaks in the spectrum at 1520 cm⁻¹ and 1318 cm⁻¹ are due to asymmetric and symmetric stretching vibrations of the NO₂ group respectively. Due to the in-plane deformation of NO₂ group, a band of variable intensity is in the region 810-695 cm⁻¹. The band seen at 809 cm⁻¹ is assigned corresponding to this deformation.

C-N vibrations—Ureas have a strong characteristic band in the range 1490-1465 cm⁻¹ due to asymmetric stretching vibrations of the N-C-N group, the band due to symmetric vibration of N-C-N group is of medium intensity occurring at about 1010 cm⁻¹. The bands observed at 1473 cm⁻¹ and 1012 cm⁻¹ are representative of the N-C-N asymmetric and symmetric stretching vibrations respectively.

C=O stretching vibrations—The band due to the stretching vibrations of the carbonyl group of ureas occurs in the range 1705-1635 cm⁻¹. The presence of ring strain and strong electron accepting groups raise this frequency^{10,11}. On this basis, the bands seen at 1937 cm⁻¹ and 1686 cm⁻¹ are assigned to carbonyl stretching.

N-H vibrations—The bands due to the NH₂ asymmetric and symmetric stretching vibrations of urea are at about 3515 cm⁻¹ and 3415 cm⁻¹. The bands observed at 3393 cm⁻¹ and 3493 cm⁻¹ are assigned to N-H symmetric and asymmetric vibrations respectively¹². The amide II band due to the N-H bending motion of ureas is found at 1555-1515 cm⁻¹. This band is identified in the spectrum to be at 1506 cm⁻¹.

5 Results and Conclusion

A complete vibrational analysis has been made for the UMNBA molecule, using FTIR and FTR spectra on the basis of C_s point group symmetry. Fixing appropriate ranged force constants through iterations with sufficiently small increments the secular equations have been solved. A detailed band assignment, evaluated potential constants and potential energy distribution have been presented in Table 1. The different functional groups significant in the molecule give rise to very strong and strong bands in the expected region. The force constants calculated for the twenty-one A' species and fourteen A'' species provide a clarity on the force constants, which is further supported by the high values of PEDs. The NO₂ stretch force constant is found to be 9.0244×10² N/m, N-H stretch force constant is 6.4454×10² N/m, C=O stretch force constant is 10.2103×10² N/m and ring C=C stretch force constant is 6.5843×10² N/m (Table 1). These results are consistent with that found in literature. Also the corresponding calculated PED are greater than 80% reinforcing the correctness of the frequency assignment. Thus, a force constant refinement calculation using the observed frequencies allows the normal coordinates for the planar modes of UMNBA to be determined in terms of the independent force constants, thus providing a strong support to the present work.

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