



Vibrational spectral investigations of the Fourier transform infrared and Raman spectra of 2-methyl-6-nitroquinoline

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ABSTRACT

The vibrational properties of 2-methyl-6-nitroquinoline have been investigated by FTIR and FT-Raman spectroscopies were performed according to the SQM force field method based on DFT calculation at the B3LYP/6-311+G(d,p) level. The assignments of the most of the fundamentals of the title compound provided in this work are quite comparable and unambiguous. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compound in the solid phase.

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1. Introduction

Quinoline is a heterocyclic compound and it is made up of two aromatic six membered ring. Heterocyclic compounds are worth to study for many reasons, chief among them being their prevalence among biologically active molecules. Many drugs are heterocycles, pharmacological activity requires chemical reaction and reaction requires functionality. Quinoline is more potent and better tolerated local anesthetics than common local anesthetics. The anesthetic activity is similar to those of procaine or cocaine when injected. However it is several times more potent than procaine when injected subcutaneously and about five times more toxic than cocaine when injected intravenously [1-4]. Benzene and pyridine rings are fused in this system. Like naphthalene, quinoline undergo aromatic substitution at an α - position in all carbon ring. Derivatives of quinoline have been widely used in the synthesis of antibacterial, antihypertensive and antifungicidal drugs and extensively used for the extraction and analytical determination of metal ions [5]. Also, quinoline is used in the manufacture of pharmaceutical dyes, insecticides rubber accelerator and in organic synthesis. Consideration of these factors motivated to undertake the vibrational spectroscopic studies of 2-methyl -6-nitroquinoline (2M6NQ).

The assignments of band in the vibrational spectra of molecule is an essential step in application of vibrational spectroscopy for solving various structural chemical problems. The vibrational spectra of the title compound had already been interpreted by Arivazhagan on the basis [6] of normal coordinate analysis based on semi-empirical methods. The philosophy of computational methods of vibrational spectroscopy [7,8] changed significantly after the introduction of scaled quantum mechanical (SQM) calculations. In the SQM approach, the systematic errors of the computed harmonic force field are

corrected by a few scale factors which are found to be well transferable between chemically related molecules[9-11] and were recommended for general use. In the present study, the detailed vibrational analysis of the title compound was performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based SQM approach [12].

2. Experimental

The fine polycrystalline sample of 2M6NQ was kindly provided by Lancaster Chemical Company, UK and used as such for spectral measurements. The room temperature Fourier transform infrared spectra of the title compound were measured in the 4000-50 cm^{-1} region at a resolution of $\pm 1 \text{ cm}^{-1}$ using KBr pellets on BRUKER IFS- 66V FTIR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization was used for the 250 averaged interferograms collected for the sample.

The FT-Raman Spectra were recorded on a computer interfaced BRUCKER IFS model interferometer equipped with FRA 106 FT-Raman accessory in the 3500-100 cm^{-1} Stokes region using the 1064nm line of a Nd:YAG laser for excitation operating at 200mw power. The reported wave numbers are believed to be accurate within $\pm 1 \text{ cm}^{-1}$.

3. Computational details

The molecular geometry optimization, energy and vibrational frequency calculations were carried out for 2M6NQ with GAUSSIAN 09W software package [13] using the Becke-3-Lee-Yang-Parr(B3LYP) functionals [14,15] combined with standard 6-311+G(d,p) basis set. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming Cs point group symmetry. Scaling of the force field was performed according to the SQM procedure [16,12] using selective scaling in the natural internal

coordinate representation. Transformations of the force field and subsequent normal coordinate analysis including the least square refinement of the scaling factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (Version 7.0 – G77) written by Sundius [17, 18, 19].

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using the standard procedure [20] of decomposing the traces of the symmetry operation into irreducible representation. By combining the results of GAUSSVIEW program [21] with symmetry considerations, vibrational frequency assignments were made and presented in some detail for the title compound.

4. Results and discussion

4.1. Molecular Geometry

The molecular structure of 2M6NQ having Cs symmetry is shown in Fig.1. The global minimum energy obtained by DFT structure optimization is calculated as -645.684 Hartrees. The calculated optimized geometrical parameters obtained in this study is presented in Table 1.

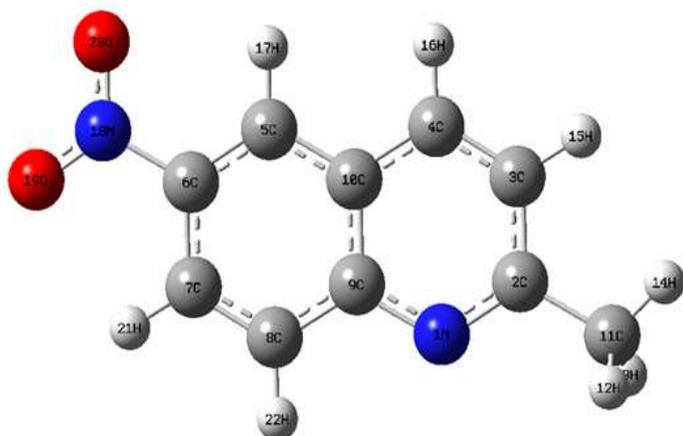


Fig. 1 Molecular structure of 2-methyl-6-nitroquinoline

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 81 standard internal coordinates (Containing 21 redundancies) were defined in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi and Pulay [7,22] are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this latter set of vibrational coordinates and used in all the subsequent calculations.

5. Vibrational Spectra

The title compound, 2M6NQ, consists of 22 atoms, has Cs symmetry and its 60 normal modes are distributed amongst the symmetry species as

$$\Gamma_{3N-6} = 40A' \text{ (in-plane)} + 20 A'' \text{ (out-of-plane)}$$

All the vibrations are active both in the Raman scattering and infrared absorption. The detailed vibrational assignments of fundamental modes of 2M6NQ along with the observed and calculated frequencies and normal mode descriptions (characterized by TED) are reported in Table 4. The FTIR and FT-Raman spectra are shown in Figs.2-4, respectively.

5.1 Effect of scaling on frequency fit and assignment

The calculated harmonic frequencies of 2M6NQ are compared with observed frequencies by normal mode analysis based on scaled quantum mechanical force field calculations are

listed in Table 4. It can be noted that the calculated results are harmonic frequencies while the observed frequencies contain anharmonic contributions. The later is generally lower than the former due to anharmonicity.

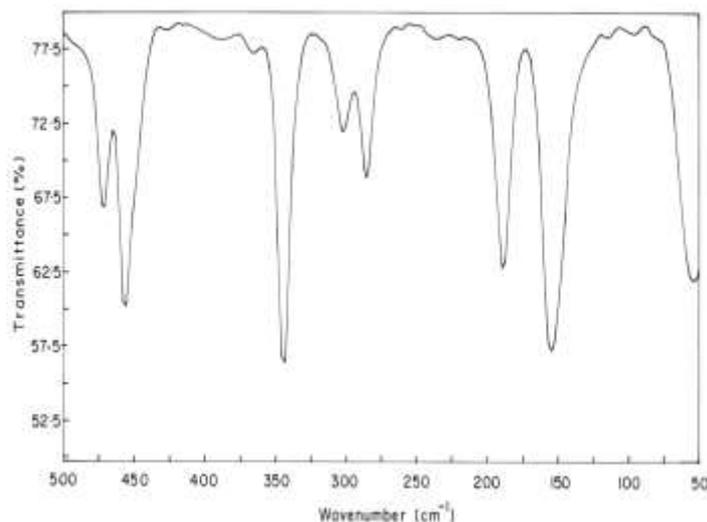


Fig. 2 Far IR Spectrum of 2-methyl-6-nitroquinoline

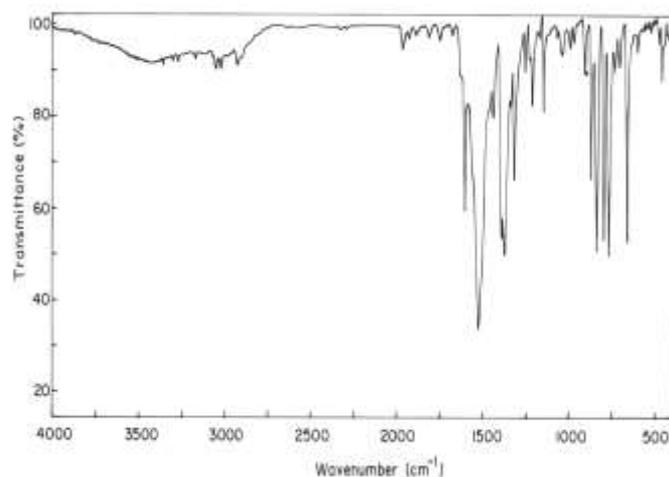


Fig. 3 FTIR Spectrum of 2-methyl-6-nitroquinoline

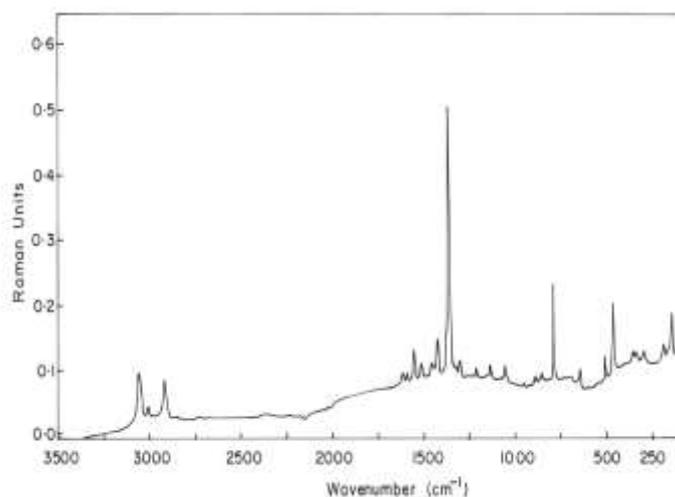


Fig. 4 FT-Raman Spectrum of 2-methyl-6-nitroquinoline

In principle, one should compare the calculated frequencies with experimental harmonic frequencies. However, as all the vibrations are more or less anharmonic, harmonic frequencies are not directly observable.

Table 1
Optimized geometrical parameters of 2-methyl-6-nitroquinoline obtained by B3LYP/6-311+G(d,p) density functional calculations

| Bond Length | Value (Å) | Bond Angle | Value (°) |
|-------------|-----------|--------------|-----------|
| N1-C2 | 1.34 | N1-C2-C3 | 120.47 |
| C2-C3 | 1.40 | C2-C3-C4 | 119.38 |
| C3-C4 | 1.39 | C3-C4-C10 | 118.82 |
| C4-C10 | 1.39 | C4-C10-C9 | 119.40 |
| C10-C9 | 1.40 | C10-C9-N1 | 120.45 |
| C9-N1 | 1.34 | C9-N1-C2 | 121.46 |
| C10-C5 | 1.40 | C8-C9-C10 | 119.77 |
| C5-C6 | 1.40 | C9-C10-C5 | 120.24 |
| C6-C7 | 1.40 | C10-C5-C6 | 119.91 |
| C7-C8 | 1.40 | C5-C6-C7 | 119.96 |
| C8-C9 | 1.40 | C6-C7-C8 | 120.00 |
| C2-C11 | 1.54 | C7-C8-C9 | 120.05 |
| C11-H12 | 1.07 | N1-C2-C11 | 119.76 |
| C11-H13 | 1.07 | C3-C2-C11 | 119.76 |
| C11-H14 | 1.07 | C2-C3-H15 | 120.31 |
| C3-H15 | 1.07 | C4-C3-H15 | 120.31 |
| C4-H16 | 1.07 | C3-C4-H16 | 120.58 |
| C5-H17 | 1.07 | C10-C4-H16 | 120.58 |
| C6-H18 | 1.07 | C10-C5-H17 | 120.04 |
| C7-H19 | 1.07 | C6-C5-H17 | 120.04 |
| C8-N20 | 1.47 | C5-C6-H18 | 120.01 |
| N20-O21 | 1.36 | C7-C6-H18 | 120.06 |
| N20-O22 | 1.36 | C6-C7-H19 | 119.98 |
| | | C8-C7-H19 | 119.98 |
| | | C7-C8-N20 | 119.97 |
| | | C9-C8-N20 | 119.97 |
| | | C8- N20-O21 | 109.47 |
| | | C8- N20-O22 | 109.47 |
| | | O21- N20-O22 | 109.47 |
| | | C2- C11-H12 | 109.47 |
| | | C2- C11-H13 | 109.47 |
| | | C2- C11-H14 | 109.47 |
| | | H12- C11-H13 | 109.47 |
| | | H12- C11-H14 | 109.47 |
| | | H13- C11-H14 | 109.47 |

For numbering of atom refer Fig. 1

Table 2
Definition of internal Coordinates of 2-methyl-6-nitroquinoline

| No (i) | Symbol | Type | Definition |
|------------------------------|------------|--------------------|---|
| Stretching | | | |
| 1 – 5 | r_i | C-H | C3-H15, C4 – H16, C5 – H17, C6 – H18, C7-H19 |
| 6 – 8 | r_i | C-H (methyl) | C11-H12, C11-H13, C11-H14 |
| 9 – 11 | Q_i | C-N | C2-N1, C9-N1, C8-N20 |
| 12 – 21 | R_i | C-C | C2-C3, C3-C4, C4-C10, C10-C9, C10-C5, C5-C6, C6-C7, C7-C8, C8-C9, C2-C11 |
| 22– 23 | P_i | N-O | N20-O21, N20-O22 |
| Bending | | | |
| 24 – 29 | β_i | Ring1 | N1-C2-C3, C2-C3-C4, C3-C4-C10, C4-C10-C9, C10-C9-N1, C9-N1-C2 |
| 30-35 | β_i | Ring2 | C10-C5-C6, C5-C6-C7, C6-C7-C8, C7-C8-C9, C8-C9-C10, C9-C10-C5 |
| 36-45 | α_i | C-C-H | C2-C3-H15, C4-C3-H15, C3-C4-H16, C10-C4-H16, C10-C5-H17, C6-C5-H17, C5-C6-H18, C7-C6-H18, C6-C7-H19, C8-C7-H19 |
| 46-48 | δ_i | C-C-H (Methyl) | C2-C11-H12, C2-C11-H13, C2-C11-H14 |
| 49-51 | δ_i | H-C-H | H12-C11-H13, H12-C11-H14, H13-C11-H14 |
| 52-53 | ν_i | C-C-N | C9-C8-N20, C7-C8-N20 |
| 54 | θ_i | C-C-C | C3-C2-C11 |
| 55 | θ_i | N-C-C | N1-C2-C11 |
| 56-57 | σ_i | C-N-O | C8-N20-O21, C8-N20-O22 |
| 58 | σ_i | O-N-O | O21-N20-O22 |
| Out –of-plane bending | | | |
| 59-63 | ω_i | C-H | H15-C3-C2-C4, H16-C4-C3-C10, H17-C5-C10-C6, H18-C6-C5-C7, H19-C7-C6-C8 |
| 64 | π_i | C-N | N20-C8-C7-C9 |
| 65 | ψ_i | C-C | C11-C2-N1-C3 |
| Torsion | | | |
| 66-71 | τ_i | t Ring1 | N1-C2-C3-C4, C2-C3-C4-C10, C3-C4-C10-C9, C4-C10-C9-N1, C9-N1-C2-C3, C10-C9-N1-C2 |
| 72-77 | τ_i | t Ring2 | C10-C5-C6-C7, C5-C6-C7-C8, C6-C7-C8-C9, C7-C8-C9-C10, C8-C9-C10-C5, C9-C10-C5-C6 |
| 78 | τ_i | tC-NO ₂ | C8-N20-O21-O22 |
| 79 | τ_i | tC-CH ₃ | (N1-C3)-C2-C11-(H12,H13,H14) |
| 80-81 | τ_i | Butterfly | N1-C9-C10-C5, C8-C9-C10-C4 |

For numbering of atom refer Fig..1

Table 3
Definition of local Symmetry coordinates and values of corresponding scale factors used to correct the refined B3LYP/6-311+G(d,p) force field for 2-methyl-6-nitroquinoline

| No (i) | Symbol ^a | Definition ^b | Scale factors used in the calculation B3LYP/ 6-311+G(d,p) |
|--------|-----------------------|---|---|
| 1-5 | CH | r_1, r_2, r_3, r_4, r_5 | 0.928 |
| 6 | CH ₃ ss | $(r_6+r_7+r_8)/\sqrt{3}$ | 0.919 |
| 7 | CH ₃ ips | $(2r_6+r_7+r_8)/\sqrt{6}$ | 0.919 |
| 8 | CH ₃ ops | $(r_7-r_8)/\sqrt{2}$ | 0.919 |
| 9-11 | CN | Q_9, Q_{10}, Q_{11} | 0.928 |
| 12-21 | CC | $R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}$ | 0.928 |
| 22 | NO ₂ ss | $(P_{22}+P_{23})/\sqrt{2}$ | 0.904 |
| 23 | NO ₂ ass | $(P_{22}-P_{23})/\sqrt{2}$ | 0.904 |
| 24 | R1trigd | $(\beta_{24}-\beta_{25}+\beta_{26}-\beta_{27}+\beta_{28}-\beta_{29})/\sqrt{6}$ | 0.965 |
| 25 | R1symd | $(-\beta_{24}-\beta_{25}+2\beta_{26}-\beta_{27}-\beta_{28}+2\beta_{29})/\sqrt{12}$ | 0.965 |
| 26 | R1asymd | $(\beta_{24}-\beta_{25}+\beta_{27}-\beta_{28})/\sqrt{2}$ | 0.965 |
| 27 | R2trigd | $(\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33}+\beta_{34}-\beta_{35})/\sqrt{6}$ | 0.965 |
| 28 | R2symd | $(-\beta_{30}-\beta_{31}+2\beta_{32}-\beta_{33}-\beta_{34}+2\beta_{35})/\sqrt{12}$ | 0.965 |
| 29 | R2asymd | $(\beta_{30}-\beta_{31}+\beta_{33}-\beta_{34})/\sqrt{2}$ | 0.965 |
| 30-34 | bCH | $(\alpha_{36}-\alpha_{37})/\sqrt{2}, (\alpha_{38}-\alpha_{39})/\sqrt{2}, (\alpha_{40}-\alpha_{41})/\sqrt{2},$ $(\alpha_{42}-\alpha_{43})/\sqrt{2}, (\alpha_{44}-\alpha_{45})/\sqrt{2}$ | 0.978 |
| 35 | CH ₃ sb | $(-\alpha_{46}-\alpha_{47}-\alpha_{48}+\delta_{49}+\delta_{50}+\delta_{51})/\sqrt{6}$ | 0.940 |
| 36 | CH ₃ ipb | $(-\delta_{49}-\delta_{50}-2\delta_{51})/\sqrt{6}$ | 0.940 |
| 37 | CH ₃ opb | $(\delta_{49}-\delta_{50})/\sqrt{2}$ | 0.940 |
| 38 | CH ₃ ipr | $(2\alpha_{46}-\alpha_{47}-\alpha_{48})/\sqrt{6}$ | 0.940 |
| 39 | CH ₃ opr | $(\alpha_{47}-\alpha_{48})/\sqrt{2}$ | 0.940 |
| 40 | bCN | $(v_{52}-v_{53})/\sqrt{2}$ | 0.978 |
| 41 | bCC | $(\theta_{54}-\theta_{55})/\sqrt{2}$ | 0.928 |
| 42 | NO ₂ rock | $(\sigma_{56}-\sigma_{57})/\sqrt{2}$ | 0.904 |
| 43 | NO ₂ twist | $(\sigma_{56}+\sigma_{57})/\sqrt{2}$ | 0.904 |
| 44 | NO ₂ sciss | $(2\sigma_{58}-\sigma_{56}-\sigma_{57})/\sqrt{6}$ | 0.904 |
| 45-49 | ω CH | $\omega_{59}, \omega_{60}, \omega_{61}, \omega_{62}, \omega_{63}$ | 0.962 |
| 50 | π CN | π_{64} | 0.962 |
| 51 | ψ CC | ψ_{65} | 0.962 |
| 52 | t R1trigd | $(\tau_{66}-\tau_{67}+\tau_{68}-\tau_{69}+\tau_{70}-\tau_{71})/\sqrt{6}$ | 0.896 |
| 53 | t R1symd | $(\tau_{66}-\tau_{68}+\tau_{69}-\tau_{71})/\sqrt{2}$ | 0.896 |
| 54 | t R1asymd | $(-\tau_{66}+2\tau_{67}-\tau_{68}-\tau_{69}+2\tau_{70}-\tau_{71})/\sqrt{12}$ | 0.896 |
| 55 | t R2trigd | $(\tau_{72}-\tau_{73}+\tau_{74}-\tau_{75}+\tau_{76}-\tau_{77})/\sqrt{6}$ | 0.896 |
| 56 | t R2symd | $(\tau_{72}-\tau_{74}+\tau_{75}-\tau_{77})/\sqrt{2}$ | 0.896 |
| 57 | t R2asymd | $(-\tau_{72}+2\tau_{73}-\tau_{74}-\tau_{75}+2\tau_{76}-\tau_{77})/\sqrt{12}$ | 0.896 |
| 58 | NO ₂ wag | τ_{78} | 0.962 |
| 59 | tCH ₃ | τ_{79} | 0.962 |
| 60 | Butterfly | $(\tau_{80}-\tau_{81})/\sqrt{2}$ | 0.902 |

^a These symbols are used for description of normal modes by TED in Table 4

^b The internal coordinates used here are defined in Table 2.

Table 4

Assignment of fundamental vibrations of 2-methyl-6-nitroquinoline by normal mode analysis based on SQM force field calculations using selectively scaled B3LYP/6-311+G(d,p) force field

| Symmetry Species C_s | Observed fundamentals (cm^{-1}) | | Calculated frequencies using B3LYP/6-311+G(d,p)force field (cm^{-1}) | | TED (%) among types of internal coordinates ^b |
|------------------------|--|-----------|---|---------------------|--|
| | FTIR | FT-Raman | Unscaled | Scaled ^a | |
| A' | 3142 (vw) | -- | 3314 | 3145 | vCH (99) |
| A' | 3096 (vw) | -- | 3232 | 3094 | vCH (96) |
| A' | -- | 3064 (w) | 3219 | 3068 | vCH(94) |
| A' | 3049 (w) | -- | 3198 | 3043 | vCH(90) |
| A' | 3015 (w) | -- | 3162 | 3011 | vCH(90) |
| A' | -- | 3005 (w) | 3138 | 3003 | CH ₃ ips(98) |
| A' | -- | 2912 (w) | 3069 | 2912 | CH ₃ ss (96) |
| A' | 1659 (w) | -- | 1800 | 1656 | vCC (89) |
| A' | -- | 1618 (w) | 1755 | 1617 | vCC (88) |
| A' | 1605 (w) | -- | 1745 | 1600 | vCC (87) |
| A' | 1589 (s) | 1589 (w) | 1714 | 1587 | NO ₂ ass (95) |
| A' | -- | 1565 (w) | 1694 | 1566 | vCC (86) |
| A' | -- | 1527 (w) | 1603 | 1527 | vCC (85) |
| A' | 1524 (ms) | -- | 1596 | 1522 | vCC (86) |
| A' | -- | 1467 (w) | 1534 | 1474 | CH ₃ ipb (82) |
| A' | 1435 (w) | 1435 (w) | 1498 | 1432 | vCC (83) |
| A' | -- | 1388 (vw) | 1453 | 1384 | vCC (85) |
| A' | -- | 1373 (vs) | 1429 | 1370 | vCC (84) |
| A' | 1372 (w) | -- | 1422 | 1378 | CH ₃ sb(80) |
| A' | 1334 (w) | -- | 1382 | 1332 | vCC (81) |
| A' | -- | 1325 (w) | 1368 | 1321 | vCN (80) |
| A' | 1315 (s) | -- | 1354 | 1306 | NO ₂ ss (82) |
| A' | -- | 1312 (w) | 1339 | 1315 | vCN (79) |
| A' | 1254 (w) | -- | 1287 | 1254 | vCN (77) |
| A' | -- | 1223 (w) | 1252 | 1222 | bCH (74) |
| A' | 1208 (ms) | -- | 1248 | 1206 | bCH (72) |
| A' | 1186 (w) | -- | 1215 | 1196 | bCH (70) |
| A' | 1178 (w) | -- | 1201 | 1171 | bCH (68) |
| A' | -- | 1165 (w) | 1191 | 1160 | bCH (67) |
| A' | -- | 1125 (w) | 1160 | 1134 | R1synd (62) |
| A' | 1112 (w) | -- | 1151 | 1103 | R1 trigd (59) |
| A' | 1065 (w) | 1065 (w) | 1099 | 1057 | R2 trigd (60) |
| A' | -- | 1059 (w) | 1086 | 1062 | R2 asymd (58) |
| A' | 1004 (w) | -- | 1026 | 1004 | CH ₃ ipr (71) |
| A' | 964 (vw) | -- | 983 | 962 | bCN (61) |
| A' | 866 (s) | 866 (ms) | 889 | 869 | R1 asymd (60) |
| A' | 795 (vs) | 796 (s) | 816 | 792 | NO ₂ sciss (73) |
| A' | 765 (vs) | -- | 783 | 772 | bCC (62) |
| A' | 728 (w) | -- | 750 | 731 | R2synd (61) |
| A' | 552 (vw) | -- | 568 | 548 | NO ₂ rock (63) |
| A'' | 2866 (w) | -- | 3027 | 2865 | CH ₃ ops (86) |
| A'' | 1145 (w) | -- | 1181 | 1144 | CH ₃ opb (84) |
| A'' | 982 (w) | -- | 1005 | 983 | CH ₃ opr (76) |
| A'' | 896 (w) | 896 (w) | 916 | 896 | ω CH (68) |
| A'' | 835 (vs) | -- | 845 | 838 | ω CH (66) |
| A'' | -- | 703 (w) | 711 | 698 | NO ₂ wag (70) |
| A'' | 689 (w) | -- | 698 | 692 | ω CH (65) |
| A'' | 680 (w) | -- | 673 | 678 | ω CH (63) |
| A'' | 658 (vs) | 658 (w) | 664 | 656 | ω CH (61) |
| A'' | -- | 625 (w) | 618 | 624 | tRI Symd (57) |
| A'' | -- | 539 (ms) | 539 | 538 | ω CN (53) |
| A'' | 525 (vw) | -- | 529 | 528 | tR1 trigd (55) |
| A'' | 516 (w) | -- | 523 | 516 | tR2 asymd (52) |
| A'' | 472 (vw) | 472 (ms) | 476 | 474 | tR2 symd (54) |
| A'' | 456 (w) | -- | 463 | 459 | tR1 asymd (59) |
| A'' | -- | 358 (w) | 364 | 357 | ω CC (52) |
| A'' | 344 (s) | 344 (w) | 347 | 348 | tR2 symd (58) |
| A'' | 302 (w) | 320 (w) | 318 | 323 | Butterfly (57) |
| A'' | 283(ms) | -- | 283 | 283 | NO ₂ twist (59) |
| A'' | 238 (w) | -- | 241 | 236 | τ CH ₃ (56) |

^a For optimized values of scale factors see Table 3

^b For the notation see Table 2

Although they can be deduced theoretically it requires detailed knowledge of both quadratic and anharmonic force constants and is only feasible for very small molecules. It should be pointed out that reproduction of observed fundamental frequencies is more desirable because they are directly observable in a vibrational spectrum. Therefore, the combination of the calculated and the observed vibrational spectra helps to understand the observed spectral features.

Root mean square values were obtained in this study using the following expression.

$$RMS = \sqrt{\frac{1}{(n-1)} \sum_i^n (v_i^{calc} - v_i^{exp})^2} \quad \dots 7.1$$

The RMS error of the frequencies (unscaled) observed for 2M6NQ is found to be 75.28 cm⁻¹. In order to reproduce the observed frequencies, the scale factors were applied and optimized via least square refinement algorithm which resulted in the mean deviation of 3.65 cm⁻¹ between the experimental and calculated frequencies (scaled) for the title compound.

Methyl group vibrations

For the assignments of CH₃ group frequencies, nine fundamental vibrations can be associated to each CH₃ group. Three stretching, three bending, two rocking modes and a single torsional mode describe the motion of the methyl group. The above modes are defined in Table 4. The CH₃ symmetric stretching frequency is established at 3005 cm⁻¹ and CH₃ in-plane stretching is assigned at 2912 cm⁻¹ in Raman. The CH₃ symmetric bending and CH₃ in-plane bending frequencies are attributed at 1372 and 1467 cm⁻¹, respectively. These assignments are also supported by literature [5]. The in-plane rocking and out-of-plane rocking modes of CH₃ group are found at 1004 and 982 cm⁻¹ in IR, respectively. The bands obtained at 2866 and 1145 cm⁻¹ in IR are assigned to CH₃ out-of-plane stretching and CH₃ out-of-plane bending modes, respectively. The assignment of band at 238 cm⁻¹ is attributed to methyl twisting mode.

Nitro group vibrations

The characteristics group frequencies of nitro group are relatively independent of the rest of the molecule, which makes this group convenient to identify. Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO₂ group at 1570–1485 cm⁻¹ and 1370–1320 cm⁻¹, respectively [23]. Hydrogen bonding has little effect on the NO₂ asymmetric stretching vibrations [24, 25]. The infrared and Raman bands both at 1589 cm⁻¹ and infrared bands both at 1589 cm⁻¹ and infrared band at 1315 cm⁻¹ have been designated to asymmetric and symmetric stretching modes of NO₂ group, respectively. The scissoring modes of NO₂ group have been designated to the bands at 795 cm⁻¹ in IR and 796 cm⁻¹ in Raman. The band at 552 cm⁻¹ in Raman is attributed to NO₂ rocking mode.

5.4. Ring vibrations

Many ring modes are affected by the substitutions in the aromatic ring of 2M6NQ. In the present study, the bands identified at 1125, 1112, 1065, 1059, 866 728 cm⁻¹ and 625, 525, 516, 472, 456, 344 cm⁻¹ have been designated to ring in-plane and out-of-plane bending modes, respectively, by careful consideration of their quantitative descriptions. The reduction in frequencies of these modes are due to the changes in force constant, resulting mainly from addition of methyl group to 2M6NQ and from different extents of mixing between the ring and constituent groups vibration.

6. Conclusion

The vibrational properties of 2-methyl-6-nitroquinoline have been investigated by FTIR and FT-Raman spectroscopies and were performed according to the SQM force field method based on DFT calculation at the B3LYP/6-311+G(d,p) level. The assignments of the most of the fundamentals of the title compound provided in this work are quite comparable and unambiguous. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compound in the solid phase.

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