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Vibrational study on the molecular structure of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone and their radical anions by using density functional theory

Priyanka Singh^a, N. P. Singh^a, R. A. Yadav^b

^a*Lasers and Spectroscopy Laboratory Department of Physics, U P (PG) Autonomous College, Varanasi, India*

^b*Department of Physics, Banaras Hindu University, Varanasi, India*

ABSTRACT

ab initio calculations have been performed using quantum chemical method to compute optimized geometries, atomic charges, harmonic vibrational frequencies along with intensities in IR and Raman spectra and depolarization ratios of the Raman bands for the 1,4-Naphthoquinone (NQ) and 2-Methyl-1,4-Naphthoquinone (MNQ) and their corresponding radical anions (NQ^{•-} and MNQ^{•-}) species. Most of the vibrational frequencies have nearly the same magnitude for the NQ, MNQ and their radical anions; however, significant changes are noticed in their IR intensities, Raman activities and depolarization ratios of the Raman bands. For the neutral NQ molecule and its radical anions, the magnitude of the atomic charges at the atoms C₁ and C₄ are almost identical and possess more positive charge due to the attachment of O atom at the sites C₁ and C₄. But in the case of MNQ and its radical anions are found to be not identical due to the electron withdrawing nature of CH₃ group attached at the sites C₂. The present calculations predict that the thermodynamical stability order based on the total energy *E* increases in the following orders: NQ^{•-} > NQ and MNQ^{•-} > MNQ, thus, anionic form is more stable as compared to their neutral form. The magnitude of zero-point vibrational energy (ZPVE) and thermal energy correction (*E*) decreases slightly in going from NA to NA^{•-} (by 4.127/3.609), NQ to NQ^{•-} (by 1.396/1.492) and MNQ to MNQ^{•-} (by 2.536/1.569) (in Kcal/Mol) respectively.

Keywords: *ab initio* and DFT studies, optimized geometries, APT charges, vibrational characteristics, 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, their singly charged radical anion.

INTRODUCTION

The quinones and their radical anion intermediates are important in understanding their functions in various chemical and biological processes involving redox reactions processes and also because of their potential applications in various industrial processes [1-4]. 1, 4-naphthoquinone (NQ) is an organic compound and forms the central chemical structure of many natural compounds, most notably the vitamin K. Due to their aromatic stability, 1,4-naphthoquinone derivatives are known for anti-bacterial and anti-tumor properties. The medicinal point of view quinones have been attracted considerable attention in recent years and are associated with anti-tumor [5], anti-bacterial [5,6], anti-malarial [7] and anti-fungal actions [7-9]. In many cases, the biological activity is associated with the ability of the redox centre to accept electrons from donor species to the corresponding radical anion (the semiquinone). Conversion of the quinone into the semiquinone is mediated by a number of physiological protagonists, typically involving interaction with a variety of flavoenzymes or through non-enzymatic routes such as plasma thiols [5,10,11]. In either case, the semiquinone is normally returned to the native quinone state through oxidation by molecular oxygen. 2-Methyl-1,4-naphthoquinone (MNQ, menadione, vitamin K₃) is formed by synthetic intermediate of vitamin K, displays good antihemorrhagic activity, and it is an important compound in medical and dietary applications [12-13]. Vitamin K prevents bleeding by increasing hepatic biosynthesis of prothrombin and other coagulation factors. This compound has the basic structure of methylated naphthoquinone and has a synthetic form which does not have aliphatic side chain. From application point of view menadione is used in the treatment of hypoprothrombinemia (source of vitamin K) against vitamin K deficiency which does not used directly as a nutritional supplement due to high toxicity and low stability.

The crystal structure of NQ has been determined experimentally and refined analysis of three dimensional X-ray diffraction method by Gaultier et al.[14]. Singh et al.[15] have investigated the infrared spectra of NQ in solution, in solid phase ($650\text{--}4000\text{ cm}^{-1}$) as well as nujol thin films ($250\text{--}4000\text{ cm}^{-1}$). A comparative study of the properties of various fused ring quinones and their radical anions using Hartree-Fock and hybrid-Fock density functional methods were determined by Grafton et al. [16]. Analysis of vibrational spectra in the structure-sensitive region of both the NQ and MNQ radical anions using time resolved Resonance Raman and *ab initio* study have been reported by Balakrishnan et al.[17]. The absorption spectra of solution spectral region $4000\text{ to }33\text{ cm}^{-1}$ and powder samples spectral region $4000\text{--}400\text{ cm}^{-1}$ of NQ have been recorded from the polarized spectra of the (100), (010) and (001) crystal planes have also been obtained by Pecile et al. [18]. Infrared spectra of the anion radicals and dianions of a series of 1,4-benzoquinones, NQ and 9,10-anthraquinones have been recorded by Clark et al. [19]. Electrochemical and infrared-spectroscopic characterization of redox reactions of p-quinones have been studied by Bauscher et al. [20]. The contribution of the above studies are very much to our knowledge in the vibrational spectra of these molecules, however, interpretation of the observed spectral features of these molecules has not been well established.

To the best of our knowledge, there have been no theoretical calculations reported in the earlier literature to understand the structures, thermo-dynamical properties and the fundamental vibrational frequencies of the neutral NQ and MNQ molecules and their radical anionic species. In order to present a full description of the vibrational spectra of these two important molecules and their radical anionic species, we carried out DFT calculations using B3LYP/6-311++G**

basis set to obtain the geometries, thermo-dynamical properties, vibrational frequencies, IR intensities and Raman activities. The present study leads to the reassignments of some of the fundamental vibrational modes for both the molecules and their radical anionic species. Our present investigations cover not only the two neutral molecules (NQ and MNQ) but also their corresponding radical anions (NQ⁻ and MNQ⁻).

1. Computational details

The theoretical calculations present in this work have been carried out using Gaussian 03 [21] program package. The computations have been performed using density functional theory (DFT) [22] at the B3LYP level. The B3LYP functional, consists of Becke's three-parameter (B3) hybrid exchange functional [23] was combined with Lee-Yang-Parr correlation functional (LYP) [24] with the standard 6-311++g** basis set, accepted as a cost effective approach, for the computation of molecular structure, vibrational fundamental frequencies and energies of optimized structures. The basis set used as a Valence triple-zeta with the addition of diffuse and polarization functions for each atom in the molecules. The calculations on the anionic species have been performed using restricted B3LYP formalism. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints [25]. For the NQ molecule, the initial parameters were taken from the work of Gaultier *et al.* [14] and calculations were performed at the B3LYP/6-311++g** level taking charge 0 and multiplicity 1. In the optimized geometry at the B3LYP/6-311++g** level for the NQ molecule, the H₁₂ atoms was replaced by CH₃ group at the sites C₂ with the geometrical parameters as $r(\text{C-C}) = 1.521 \text{ \AA}$, $r(\text{C-H}) = 1.092 \text{ \AA}$ and angle $\text{C-C-H} = 110.5^\circ$ and $\text{H-C-H} = 108.8^\circ$ and with this modification the optimized geometry at the B3LYP/6-311++g** level for the NQ molecule was taken as the input structure for the neutral MNQ molecule for the DFT calculations at the B3LYP/6-311++g** level by taking charge 0 and multiplicity 1. For the radical anions of the two (NQ⁻ and MNQ⁻) species, the input structure was taken from the geometries of their corresponding neutral molecules optimized at the B3LYP/6-311++g** level and the DFT calculations were performed using the B3LYP/6-311++g** level by taking the charge as -1 and multiplicity as 2. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics. The assignments of the normal modes of vibrational frequencies were made with a high degree of accuracy along with available related molecules (NQ and MNQ) and their radical anions are made by visual inspection of the individual mode using the Gauss View software [26].

RESULTS AND DISCUSSION

3.1. Molecular structures

The optimized molecular geometries for the neutral NQ and MNQ molecules and their radical anions calculated using the method B3LYP/6-311++g** are given in Table-1. The experimental parameters [14] for the crystal structure of the neutral NQ obtained from the X-ray diffraction study are also included in the same Table. The present calculation predicts the neutral NQ molecule and its radical anions possess planar structures with C_{2v} point group symmetry while the neutral MNQ molecule and its radical anions possess non-planar structures with C_s point group symmetry. The same atomic numbering label scheme has been followed for the neutral NQ and MNQ molecules and their radical anionic species are shown in Figs. 1-4.

The bond lengths obtained for the neutral NQ and MNQ molecules and their radical anions show that the NQ molecule consist of the two parts, namely enedione structure (O₁₁-C₁-C₂-O₁₄) and benzenoid structure. The optimized bond lengths of two C=O and one C₂=C₃ bonds clearly show their double bond character are almost identical with values of 1.221 Å and 1.343 Å, for the neutral NQ and MNQ molecules respectively. The C₁-C₂ bond length in the enedione part increased by the magnitude 0.015 Å in going from the neutral NQ to MNQ molecules which is strongly affected by the methyl group. The benzenoid part can be visualized from the almost identical C-C bond lengths (1.391Å – 1.407Å) for the neutral NQ and MNQ molecules. The description of enedione and benzenoid parts for the NQ molecule structure is consistent with the experimental values reported [14] as compared to the calculated values at B3LYP/6-311++g** level. It can be seen from the Table-1 that in most of the cases the bond angles changes with 1° in going from the NQ to MNQ molecules. The bond angle C₁-C₂-C₃ decreases by 2.4° in going from NQ to MNQ molecules due to the presence of the CH₃ group at the site C₂ for the neutral MNQ molecule. For the neutral NQ molecule, the calculated values of the bond angle are found to be good agreement (within 1°) with the experimental values [14].

No experimental data for the determinations of the geometrical structures of these radical anions are available for the NQ^{•-} and MNQ^{•-} radical anionic species as well as neutral MNQ molecule. The ab initio electron density distribution data for the radical anionic NQ^{•-} and MNQ^{•-} species confirms that the most of the added electron is found with the enedione part of the radical anion species. This is reflected in the relative changes of the bond lengths for the NQ^{•-} and MNQ^{•-} species. It can be obtained that the one C=C and two C=O are consistent with the double bond nature of these bonds for the four (NQ, NQ^{•-}, MNQ and MNQ^{•-}) molecules. It is found that enedione and benzendione part in the radical anions shows the bond loses its bond length character.

On the basis of calculation, the carbonyl C=O and ethylene C=C bond lengths for the radical anions of the NQ and MNQ are found to be ~1.262 Å and ~1.380 Å, respectively. The C=O and C₂=C₃ bonds are elongated by 0.042 Å and 0.035 Å, respectively, for the radical anions as compared to those of the neutral NQ and MNQ molecules. The C₁-C₂ bond length in the radical anion of the NQ and MNQ molecule is reduced. This process of radicalization leads to decrease in C₁-C₂ and C₃-C₄ bond to such an extent that in the radical anion these bonds lose its single/doubled bond character. The other bond lengths in the benzenoid part such as C₅-C₆, C₇-C₈ and C₉-C₁₀ are found to be increase in magnitude by ~0.012 Å in going from the two neutral molecules to their respective radical anions. The geometrical changes associate with benzenoid part of the radical anion NQ^{•-} and MNQ^{•-} shows, its less aromatic character compared to that of the corresponding neutral NQ and MNQ molecules. The magnitude of the C₁-C₂-C₃ angle increases by 1.0° and 2.5° in going from the neutral NQ and MNQ molecules to their corresponding radical anions. A significant increase in angles which is approximately the same amount 2.5° is calculated for the angles C₂-C₁-O₁₁ and C₃-C₄-O₁₄ in going from the neutral to their corresponding radical anion of the NQ and MNQ molecules. It is found that the angle C₂-C₃-H₁₃ decreases by magnitude ~1.6° in going from the neutral NQ and MNQ molecules to their respective radical anions. The angle C₅-C₆-H₁₅ decreases by ~1.4° in going from the two neutral molecules to their corresponding radical anions. The angle C₄-C₃-H₁₃ also decreases in going from NQ^{•-} to MNQ^{•-} (by 0.5°) molecules. For the quiones ring and their corresponding radical anions, the calculations indicate that only minor change is observed in the C-H bond lengths.

A perusal of the Table -1 shows that all the dihedral angles of the aromatic ring moiety (consisting C₁ to H₁₈) are found to either $\pm 0^\circ$ or $\pm 180^\circ$ within $\pm 0.03^\circ$ for the both molecules and their radical anionic species. The values of the dihedral angles C₁-C₂-C₁₂-H₁₉/C₁-C₂-C₁₂-H₂₀ are almost identical with values of 58.6° and 58.7° , respectively, in the MNQ and MNQ⁻ molecules. Different bond lengths and bond angles along with their values for the two neutral molecules and their respective radical anions are shown in Figs.5 (a-b). It can be seen that there is a variation noticed for many cases in the bond lengths, bond angles (Figs.5 (a-b)).

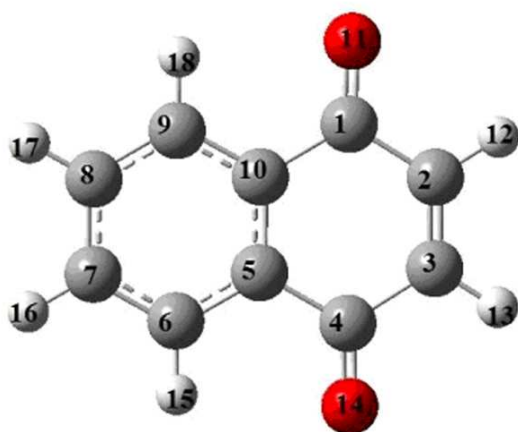


Fig.-1: Front View of NQ Molecule

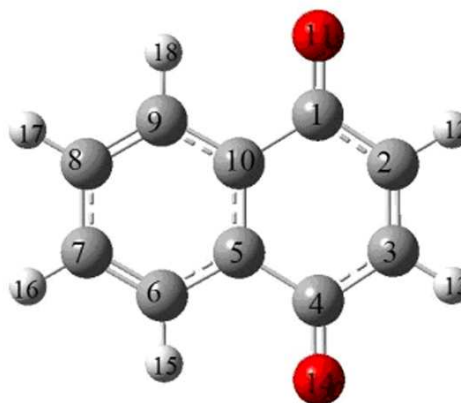


Fig.-2: Front View of NQ⁻ Molecule

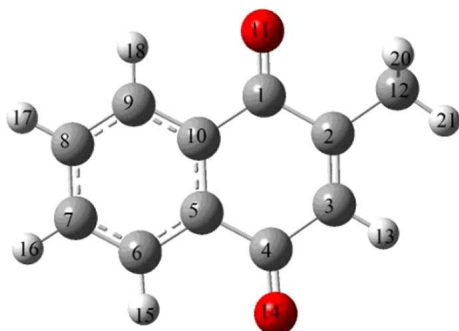


Fig.-3: Front View of MNQ Molecule

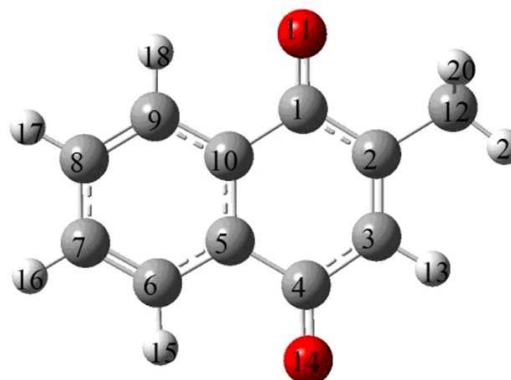


Fig.-4: Front View of MNQ⁻ Molecule

Figure 1-4. Numbering system adopted in this study (NQ, NQ⁻, MNQ and MNQ⁻ molecules).

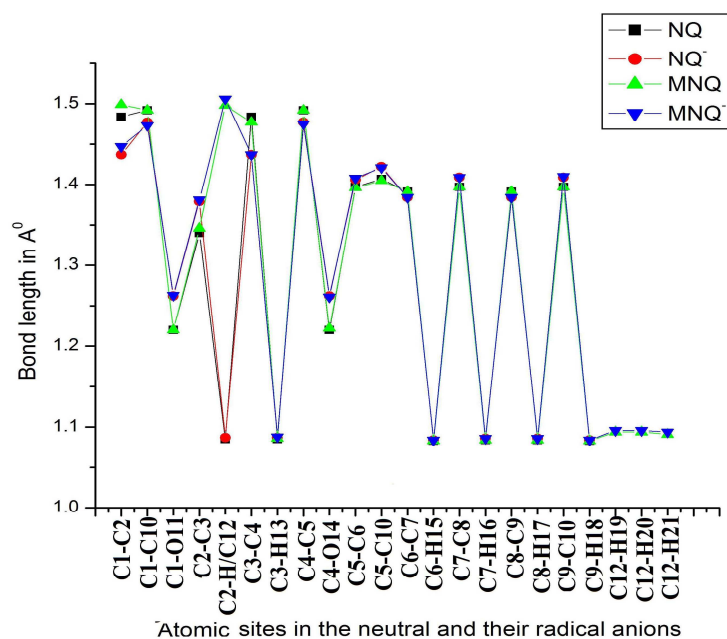


Fig.5(a)

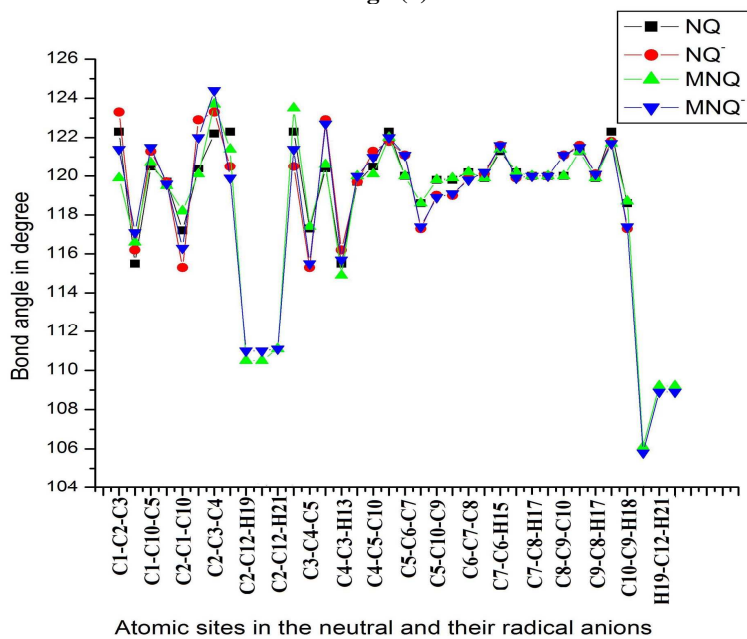


Fig.5(b)

Figure 5(a,b). The bond lengths and bond angles differences from the theoretical approaches of the NQ, NQ⁻, MNQ and MNQ⁻ molecules.

Table-1: Calculated Optimized Geometrical Parameters^a of the NQ, NQ⁺, MNQ and MNQ⁺ molecules

Definitions	NQ		NQ ⁺	MNQ	MNQ ⁺
	Cal.	Obs. ^b	Cal.	Cal.	Cal.
r(C ₁ -C ₂)	1.484	1.48	1.437	1.499	1.447
r(C ₁ -C ₁₀)	1.492	1.43	1.477	1.492	1.473
r(C ₁ -O ₁₁)	1.220	1.21	1.262	1.220	1.263
r(C ₂ -C ₃)	1.340	1.31	1.379	1.346	1.381
r(C ₂ -H ₁₂ /C ₁₂)	1.085	-	1.087	1.498	1.506
r(C ₃ -C ₄)	1.484	1.45	1.437	1.477	1.437
r(C ₃ -H ₁₃)	1.085	-	1.087	1.086	1.088
r(C ₄ -C ₅)	1.492	1.46	1.477	1.492	1.475
r(C ₄ -O ₁₄)	1.220	1.22	1.262	1.222	1.261
r(C ₅ -C ₆)	1.397	1.36	1.406	1.396	1.408
r(C ₅ -C ₁₀)	1.407	1.39	1.422	1.405	1.421
r(C ₆ -C ₇)	1.391	1.43	1.384	1.391	1.384
r(C ₆ -H ₁₅)	1.083	-	1.084	1.083	1.084
r(C ₇ -C ₈)	1.397	1.37	1.409	1.397	1.409
r(C ₇ -H ₁₆)	1.084	-	1.086	1.084	1.086
r(C ₈ -C ₉)	1.391	1.41	1.384	1.391	1.384
r(C ₈ -H ₁₇)	1.084	-	1.086	1.084	1.086
r(C ₉ -C ₁₀)	1.397	1.39	1.409	1.397	1.410
r(C ₉ -H ₁₈)	1.083	-	1.084	1.083	1.084
r(C ₁₂ -H ₁₉)	-	-	-	1.094	1.096
r(C ₁₂ -H ₂₀)	-	-	-	1.094	1.096
r(C ₁₂ -H ₂₁)	-	-	-	1.091	1.094
α(C ₁ -C ₂ -C ₃)	122.3	120.5	123.3	119.9	121.4
α(C ₁ -C ₂ -H ₁₂ /C ₁₂)	115.5	-	116.2	116.6	117.1
α(C ₁ -C ₁₀ -C ₅)	120.5	118.0	121.3	120.7	121.5
α(C ₁ -C ₁₀ -C ₉)	119.7	-	119.7	119.5	119.6
α(C ₂ -C ₁ -C ₁₀)	117.2	121.5	115.3	118.2	116.3
α(C ₂ -C ₁ -O ₁₁)	120.4	118.5	122.9	120.1	122.0
α(C ₂ -C ₃ -C ₄)	122.2	117.5	123.3	123.7	124.4
α(C ₂ -C ₃ -H ₁₃)	122.3	-	120.5	121.4	119.9
α(C ₂ -C ₁₂ -H ₁₉)	-	-	-	110.5	111.0
α(C ₂ -C ₁₂ -H ₂₀)	-	-	-	110.5	111.0
α(C ₂ -C ₁₂ -H ₂₁)	-	-	-	111.1	111.1
α(C ₃ -C ₂ -H ₁₂ /C ₁₂)	122.3	-	120.5	123.5	121.4
α(C ₃ -C ₄ -C ₅)	117.3	123.0	115.3	117.4	115.5
α(C ₃ -C ₄ -O ₁₄)	120.4	118.0	122.9	120.6	122.7
α(C ₄ -C ₃ -H ₁₃)	115.5	-	116.2	114.9	115.7
α(C ₄ -C ₅ -C ₆)	119.7	-	119.7	120.0	120.0
α(C ₄ -C ₅ -C ₁₀)	120.5	117.5	121.3	120.1	121.0
α(C ₅ -C ₄ -O ₁₄)	122.3	118.5	121.8	122.0	122.0
α(C ₅ -C ₆ -C ₇)	120.0	121.5	121.1	120.0	121.1
α(C ₅ -C ₆ -H ₁₅)	118.6	-	117.3	118.6	117.4
α(C ₅ -C ₁₀ -C ₉)	119.8	119.0	119.0	119.8	118.9
α(C ₆ -C ₅ -C ₁₀)	119.8	119.0	119.0	119.9	119.1
α(C ₆ -C ₇ -C ₈)	120.2	118.5	119.9	120.2	119.8
α(C ₆ -C ₇ -H ₁₆)	119.9	-	120.1	119.9	120.2
α(C ₇ -C ₆ -H ₁₅)	121.3	-	121.6	121.4	121.6
α(C ₇ -C ₈ -C ₉)	120.2	119.0	119.9	120.2	119.9
α(C ₇ -C ₈ -H ₁₇)	120.0	-	120.0	120.0	120.0

$\alpha(\text{C}_8\text{-C}_7\text{-H}_{16})$	120.0	-	120.0	120.0	120.0
$\alpha(\text{C}_8\text{-C}_9\text{-C}_{10})$	120.0	121.0	121.1	120.0	121.1
$\alpha(\text{C}_8\text{-C}_9\text{-H}_{18})$	121.3	-	121.6	121.3	121.5
$\alpha(\text{C}_9\text{-C}_8\text{-H}_{17})$	119.9	-	120.1	119.9	120.1
$\alpha(\text{C}_{10}\text{-C}_1\text{-O}_{11})$	122.3	119.0	121.8	121.7	121.7
$\alpha(\text{C}_{10}\text{-C}_9\text{-H}_{18})$	118.6	-	117.3	118.7	117.4
$\alpha(\text{H}_{19}\text{-C}_{12}\text{-H}_{20})$	-	-	-	106.1	105.8
$\alpha(\text{H}_{19}\text{-C}_{12}\text{-H}_{21})$	-	-	-	109.2	108.9
$\alpha(\text{H}_{20}\text{-C}_{12}\text{-H}_{21})$	-	-	-	109.2	108.9
$\delta(\text{C}_1\text{-C}_2\text{-C}_{12}\text{-H}_{19})$	-	-	-	58.6	58.7
$\delta(\text{C}_1\text{-C}_2\text{-C}_{12}\text{-H}_{20})$	-	-	-	58.6	58.7
$\delta(\text{C}_3\text{-C}_2\text{-C}_{12}\text{-H}_{19})$	-	-	-	121.4	121.3
$\delta(\text{C}_3\text{-C}_2\text{-C}_{12}\text{-H}_{20})$	-	-	-	121.4	121.3

a: Bond lengths in Å, bond angles and dihedral angles in °. b: [14].

3.2. Atomic Charges

The atomic charges for the neutral NQ and MNQ molecules and their radical anions are collected in Table-2. The calculated atomic charges are found between neutral and their radical anions that are plotted (Fig. 6). For the neutral NQ molecule and its radical anions, the magnitude of the atomic charges at the atoms C₁ and C₄ are almost identical and possess more positive charge due to the attachment of O atom at the sites C₁ and C₄. But in the case of MNQ and its radical anions are found to be not identical due to the electron withdrawing nature of CH₃ group attached at the sites C₂. The magnitudes of the charge on the site C₁ and C₄ are found to decrease by 0.013 and 0.055 respectively, for the radical anion NQ species as compared to the neutral molecule; it is due to the O atom(s) are more electronegativity. At the sites O₁₁ and O₁₄ (-0.731 and -0.861) are almost identical for the neutral NQ molecule and its radical anion. But in the case of MNQ and its radical anion, the magnitude of atomic charge at the site of O₁₄ is found to be greater than that of the O₁₁ due to attachment of an electron releasing alkyl (CH₃) group at the site C₂. It is interesting to note that the charges on the three pairs of hydrogen atom(s) H_{12/13}, H_{15/18} and H_{16/17} are almost identical and the atomic charges of the hydrogen atoms decrease with respect to their corresponding radical anion due to the radicalization. The magnitude of the charge on the C₇/C₈, C₅/C₁₀ and C₆/C₉ are found to be nearly same for the neutral NQ molecule and its radical anions (Fig.6), but at the sites C₅/C₇ are greater than C₁₀/C₈ for the neutral MNQ molecule whereas the reverse of this above site are found for the radical anion MNQ species. The magnitudes of the negative charges are increased by ~0.238, ~0.025 and ~0.006 at the sites C₆ and C₉ whereas the sites C₇ and C₈ are also increased by ~0.074, ~0.043 and ~0.058 of the NQ and MNQ molecules due to the radicalization(s). It is also found that the atomic charges on the C₁ increase in going from NQ⁻ to neutral MNQ (by -0.104) to MNQ⁻ (by 0.033) due to attachment of an electron releasing alkyl group (CH₃) at the site C₂. The local environment at C₆ and C₉ atoms of the neutral NQ and MNQ molecules are nearly same. In going from the NQ molecule to NQ⁻ species and the MNQ molecule to MNQ⁻ species the negative charge on the C₆ and C₉ atoms are found to be increased (Fig. 6).

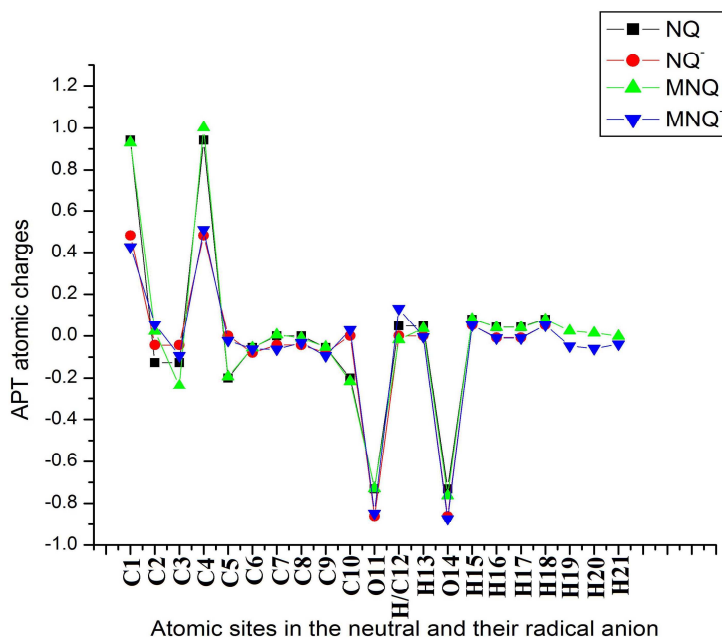


Figure 6. APT atomic charges at various atoms of the NQ, NQ⁻, MNQ and MNQ⁻ molecules.

Table-2: Calculated APT Charges at various atomic sites of the NQ, NQ⁻, MNQ and MNQ⁻ molecules

Atoms	Charges			
	NQ	NQ ⁻	MNQ	MNQ ⁻
C ₁	0.942	0.483	0.930	0.428
C ₂	-0.127	-0.044	0.023	0.056
C ₃	-0.127	-0.044	-0.237	-0.094
C ₄	0.942	0.483	1.001	0.511
C ₅	-0.200	0.001	-0.193	-0.022
C ₆	-0.055	-0.080	-0.056	-0.062
C ₇	-0.00009	-0.043	0.005	-0.063
C ₈	-0.00004	-0.043	-0.010	-0.032
C ₉	-0.055	-0.080	-0.053	-0.094
C ₁₀	-0.200	0.001	-0.215	0.029
O ₁₁	-0.731	-0.861	-0.729	-0.847
H ₁₂ /C ₁₂	0.048	0.0002	-0.017	0.132
H ₁₃	0.048	0.0002	0.036	-0.004
O ₁₄	-0.731	-0.861	-0.763	-0.874
H ₁₅	0.080	0.052	0.081	0.052
H ₁₆	0.043	-0.008	0.041	-0.010
H ₁₇	0.043	-0.008	0.041	-0.010
H ₁₈	0.080	0.052	0.079	0.052
H ₁₉	-	-	0.024	-0.048
H ₂₀	-	-	0.014	-0.060
H ₂₁	-	-	-0.001	-0.039

3.3. Vibrational assignments

The neutral NQ molecule to the point group C_{2v}. The 48 normal modes of vibration would be divided among the symmetry species as 17A₁+7A₂+8B₁+16B₂. The vibrations of species A₁, B₁ and B₂ are infra-red active while all the vibrations are Raman active. The neutral MNQ molecule

to the point group C_s . The 57 normal modes of vibration would be divided among the symmetry species as $37A' + 20A''$. The radical anions (NQ^- and MNQ^-) correspond to C_{2v} and C_s symmetry respectively. All the modes under both the species are IR as well as Raman active. The calculated vibrational frequencies, IR intensities, Raman activities and depolarization ratios of the Raman bands for the neutral and anionic species of the NQ and MNQ molecules. The calculated IR and Raman spectra for the neutral NQ and MNQ molecules and their corresponding radical anions are shown in Figs.7-14. The calculated harmonic vibrational frequencies and observed IR and Raman frequencies for the neutral NQ, MNQ and their radical anionic species at B3LYP level using the triple split valence basis sets along with diffuse 'd' and polarization 'p' functions, (6-311++G(d,p)) have been collected in Table-3. The assignments of the calculated frequency (Table-3) of normal modes under a given species have been made with the help of the Gauss View software. In addition, the corresponding observed fundamentals vibrational frequencies are taken from the literatures [15, 17, 18].

3.3.1. Neutral molecules

3.3.1.1. Ring Modes

For the neutral NQ and MNQ molecules, we found eleven C-C ring stretching mode from 1230–1670 cm^{-1} and to one vibration at 650–770 cm^{-1} region for the ring. The vibrational characteristics for the ring stretching modes (ν_{52} , ν_{51} , ν_{50} , ν_{49} , ν_{44} , ν_{43} and ν_{41}) are found to be nearly the same for the both neutral molecules. Some vibrations are localized on one of the rings, and some vibrations involve, to a great extent in the vibrations of the C-C bonds of the fused ring. The calculated frequency of the ring stretching mode (ν_{53}) decreases by $\sim 15 \text{ cm}^{-1}$ for MNQ as compared to NQ. The calculated vibrational frequencies of C-C ring stretching mode (ν_{45} , ν_{42} and ν_{18}) are shifted to the lower frequencies by 22, 27 and 42 cm^{-1} in going from the neutral NQ to MNQ molecules. The planar-ring deformations modes (ν_{19} , ν_{14} and ν_{12}) frequencies are found to be 45, 35 and 45 cm^{-1} in going from the neutral NQ to MNQ molecules. It is found that in going from the neutral NQ to MNQ molecules, the magnitude of the calculated of the planar-ring deformations modes (ν_{32} , ν_{22} and ν_{11}) frequencies decrease by 17, 10 and 11 cm^{-1} . The three non-planar deformation modes (ν_{16} , ν_{13} and ν_{10}) frequencies increase by 70, 8 and 10 cm^{-1} in going from the neutral NQ to MNQ molecules. It is found that in going from the neutral NQ to MNQ molecules, the (ν_6 and ν_1) modes are found to be decrease $\sim 55/20 \text{ cm}^{-1}$ with the measurement of the depolarization ratio of this Raman band 0.75.

3.3.1.3. C=O Modes

The 2 C=O group give rise to six normal modes of vibration as 2 C=O stretching (ν), 2 C=O in-plane bending (β) and 2 C=O out-of-plane bending (γ) modes. The C=O stretching mode is easily assigned on account of its characteristic magnitude and intensity. In the region 1530-1730 cm^{-1} , we identify two fundamental vibrations of the neutral and their corresponding radical anions: 2 C=O stretches. The C=O stretching mode easily assigned on account of its characteristic magnitude and intensity. Of the C=O stretches, the density functional theory using B3LYP/6-311++g** level predicts that the $\nu(C_1=O_{11})$ and $\nu(C_4=O_{14})$ mode (ν_{55} and ν_{54}) are found to be almost similar in the magnitudes. The calculation shows that the ($C_1=O_{11}$) and ($C_4=O_{14}$) stretching modes (ν_{55} and ν_{54}) are strongly coupled with $\nu(C_4=O_{14})/\nu(C_1=O_{11})$ mode, respectively, but for the $\nu(C_4=O_{14})$ mode is also strongly coupled with $\nu(C=C)$ mode. The C=O stretching vibrations are observed in the region 1700-1600 cm^{-1} [15, 17-19]. The C=O out-of-plane bending mode (γ) (ν_{23} and ν_{17}) are found to have calculated frequencies $\sim 800 \text{ cm}^{-1}$ and 700

cm^{-1} with the depolarization ratio 0.75 and are strongly coupled with the $\gamma(\text{C}_4=\text{O}_{14})/\gamma(\text{C}_1=\text{O}_{11})$ modes for both the neutral NQ and MNQ molecules respectively. This mode also appears to be highly localized modes. The modes (ν_{23} and ν_{17}) corresponding to the out-of-plane C=O deformation modes is observed in the region $750\text{--}650\text{ cm}^{-1}$ [15, 18] for the neutral NQ molecule. The frequency of the two in-plane bending mode of the C=O bonds for one (ν_9) of the $\beta(\text{C}_1=\text{O}_{11})$ are found to be almost similar ($\sim 380\text{ cm}^{-1}$) which strongly coupled $\beta(\text{C}_4=\text{O}_{14})$ with the mode while the other mode ν_{75} of the $\beta(\text{C}_4=\text{O}_{14})$ is upward by $\sim 35\text{ cm}^{-1}$ and are strongly coupled $\beta(\text{C}_4=\text{O}_{14})$ with the mode with weak intensity in the both spectra for both the neutral NQ and MNQ molecules. The present C=O in-plane bending frequencies for the neutral NQ molecule, is found to be in agreement with the earlier work [15, 18].

3.3.1.4. C-H Modes

Ab initio calculations give the $\nu(\text{C-H})$ mode in the region 3100 cm^{-1} – 3250 cm^{-1} . On account of their characteristic frequencies the C-H modes are easily assigned. Shanker et al. [27] observed C-H in-plane and out-of-plane bending modes for naphthalene appear in the region $1050\text{--}1450\text{ cm}^{-1}$ and $700\text{--}1000\text{ cm}^{-1}$ respectively, and observed only five C-H stretching modes for α -naphthylamine. The C-H stretching modes in the neutral NQ molecule are observed in the range $3200\text{--}3000\text{ cm}^{-1}$ [15, 18]. The magnitude of the frequency of the C-H stretching modes ν_{66} , ν_{65} , ν_{63} and ν_{60} are found to be almost similar to those of the both neutral molecules. The magnitude of the C-H stretching modes ν_{64} decreases by 21 cm^{-1} with decreases in the Raman activity in going from NQ to MNQ molecules. For the above mode, the Raman band is calculated to be more strongly polarized. It is found in going from NQ to MNQ, the magnitude of the $\gamma(\text{C-H})$ modes (ν_{37} , ν_{35} and ν_{15}) frequencies increases by 45, 33 and 652 cm^{-1} . The magnitude of the C-H in-plane-bending mode ν_{38} frequency decreases by 38 cm^{-1} with decreased IR intensity and Raman activity. The vibrational characteristics of the C-H out-of-plane deformation mode (ν_{30} , ν_{28} and ν_{25}) are found to be nearly same magnitude ~ 1020 , 1000 and 920 cm^{-1} for the both neutral molecules. The calculated magnitude of the $\gamma(\text{C-H})$ modes frequencies shifts towards the higher wavenumber side by $\sim 100\text{ cm}^{-1}$ (ν_{29}) for NQ while but the lower wavenumber side by $\sim 15\text{ cm}^{-1}$ (ν_{21}) for MNQ.

3.4. Neutral molecules and their radical anions

Table-3 shows the frequencies and assignments of the radical anions of naphthoquinone and their methylated derivatives have been fully investigated with the theoretical (B3LYP) methods and compare them to the previous experimental data. In the following we discuss the changes noticed in the vibrational characteristics of the anionic radicals with respect to their corresponding neutral molecules. It is found that the most of the vibrational characteristics of the anionic radicals are similar to their corresponding neutral molecules, but for some of the modes significant changes are noticed. Balakrishnan and Grafton et al. [16-17] reported several vibrational frequencies of NQ^- , and assigned them based on UHF/6-31G and B3LYP/6-31G (d) respectively and Clark et al. [19] reported C=O stretching frequencies for the radical anion (NQ^-). MNQ and its radical anion have been the subject of several experimental studies which focused especially on the C=O stretching frequencies.

3.4.1. Ring Modes

The conversion of the neutral NQ and MNQ molecules into their corresponding radical anions leads to significant increase in the IR intensities for the two ring stretching mode (ν_{51} and ν_{49}) while Raman activities increase for the five ring stretching mode (ν_{53} , ν_{51} , ν_{50} , ν_{44} and ν_{43}). Moreover, the calculated frequencies for the ring stretching mode (ν_{53} , ν_{51} , ν_{50} , ν_{49} and ν_{41}) shifts towards the lower wavenumber side in going from the neutral molecules to their radical anionic species. The observed frequencies for the ring stretching mode (ν_{51}) is found to be in agreement with the work of Balakrishnan et al. [17] for both the radical anionic species. In light of the present computation (ν_{50}), the observed frequencies 1441 cm^{-1} for NQ^- and 1468 cm^{-1} for MNQ^- could be correlated to the mode under the species A_1 and A' respectively. The calculated frequencies for the ring stretching modes ν_{44} and ν_{43} decrease in going from the NQ to NQ^- species, but further increase in going from the MNQ to MNQ^- species. The present $\nu(\text{ring})$ mode (ν_{44} and ν_{43}) frequencies for the NQ^- and MNQ^- species, respectively, are found to be in agreement with the earlier work [15,17-18]. It is also observed that the magnitude of the frequency for the ring stretching modes ν_{45} and ν_{42} slightly increase by $\sim 25/15\text{ cm}^{-1}$ in going from the NQ to NQ^- species while in going from the MNQ to MNQ^- species the calculated frequency decrease by $\sim 75/40\text{ cm}^{-1}$. The magnitudes of the frequencies for the in-plane ring deformation modes ν_{32} shift towards the lower wavenumber side towards the merely changes upto $\sim 3/15\text{ cm}^{-1}$ in radical NQ^- and MNQ^- species respectively as compared to their corresponding neutral molecules. The magnitudes of the frequencies for the in-plane ring deformation modes ν_{22} , ν_{19} , ν_{14} , ν_{12} and ν_{11} shift towards the upward wavenumber side towards the merely changes in radical NQ^- and MNQ^- species as compared to their corresponding neutral molecules. It is found that in going from NQ to NQ^- the magnitude of the out-of-plane ring deformation mode ν_{16} frequency decrease by $\sim 10\text{ cm}^{-1}$ while in going from MNQ to MNQ^- the magnitude of the frequency increases by $\sim 20\text{ cm}^{-1}$. The out-of-plane ring deformation mode ν_{13} , ν_{10} , ν_6 , ν_2 and ν_1 are found to be increase by $\sim 5, 10, 110, 20, 30\text{ cm}^{-1}$ for NQ^- and by $\sim 10, 15, 25, 20, 25\text{ cm}^{-1}$ for MNQ^- as compared to their neutral molecules with the depolarization ratios of the Raman bands.

3.4.2. C-H Modes

As a result of the anionic radicalization of the NQ and MNQ molecules, the magnitudes of the C-H stretching modes (ν_{66} , ν_{65} , ν_{64} , ν_{63} , ν_{62} , ν_{61} and ν_{60}) frequencies decrease considerably. For the above modes (ν_{66} , ν_{64} , ν_{63} , ν_{62} , ν_{61} and ν_{60}), in going from the both neutral molecule to the anionic species the IR intensity and Raman activity is found to increase. The magnitude of the calculated frequencies for the $\beta(\text{C-H})$ modes ν_{39} and ν_{38} decrease by $\sim 15/25\text{ cm}^{-1}$ for the NQ^- species while the magnitude of the corresponding frequencies increase by $\sim 45/10\text{ cm}^{-1}$ for the MNQ^- species. The Raman band frequency (ν_{39}) observed at 1158 cm^{-1} by Balakrishnan et al. [17] agrees with the present finding mode. The calculation show that the frequencies ν_{37} and ν_{35} decrease for the NQ^- and MNQ^- species as compared to their respective neutral molecules. The C-H in-plane bending mode ν_{36} by $\sim 10\text{ cm}^{-1}$ for the radical NQ^- ion (upward) as compared to the neutral molecule. The present calculations shows that the frequencies for the $\gamma(\text{C-H})$ modes ν_{30} , ν_{29} , ν_{28} , ν_{25} , ν_{24} and ν_{21} decrease for the singly charged NQ^- and MNQ^- species as compared to their respective neutral molecules. For the above modes, the Raman band is found to be depolarized for the both NQ and MNQ radical species.

3.4.3. C=O Modes

As a result of anionic radicalization of the NQ and MNQ molecules, strong downward shift of $\sim 105\text{ cm}^{-1}$ is noticed for the C=O stretching frequency (ν_{55}) with decrease drastically in the IR intensity and increase in the Raman activity. The mode ν_{55} is strongly coupled with the $\nu(\text{C}_4=\text{O}_{14})$ vibration. It is found that in going from NQ to NQ^- and MNQ to MNQ^- the magnitude of the C=O stretching frequency (ν_{54}) drastic decrease by $\sim 185\text{ cm}^{-1}$ with increase drastically in IR intensity and decrease in Raman activity which is strongly coupled with the $\nu(\text{C}_1=\text{O}_{11})$ mode. For the above mode, the Raman band is found to be depolarized for the radical NQ species while polarized for the radical MNQ species. For the both radical anionic species, these assignments would suggest that the modes determined experimentally Balakrishnan *et al.* [17] at 1603 and 1605 cm^{-1} Raman band be reassigned to $\nu_{\text{as}}(\text{C}=\text{O})$ stretching mode while 1515 and 1505 cm^{-1} could be reassigned as $\nu_{\text{s}}(\text{C}=\text{O})$ stretching mode. It can be seen from the Table-4 that the C=O out-of-plane (γ) bending modes are found to be (ν_{23}) decrease from $798 - 786\text{ cm}^{-1}$ in going from the neutral NQ molecule to the radical NQ^- anion species and $797 - 790\text{ cm}^{-1}$ in going from the neutral MNQ molecule to the radical anion MNQ^- species. As a result of anionic radicalization, the C=O out-of-plane bending frequency (ν_{17}) of the NQ and MNQ molecules decrease by 25 and 15 cm^{-1} with polarized Raman band. The C=O in-plane bending frequency mode (ν_9) frequency decrease by $\sim 11\text{ cm}^{-1}$ in going from both the neutral molecule to the radical anionic species. The vibrational characteristics of the C=O in-plane bending frequency (ν_7) is found to be nearly same wavenumber in going from NQ to NQ^- as well as in going from MNQ to MNQ^- respectively, as a result of radicalization. For the above mode, the Raman band is found to be depolarized for the NQ molecule while polarized for the MNQ species.

3.4.4. C-CH₃ Modes

The MNQ molecule and its radical anion possess one CH₃ group in the second position of the quinonoid ring. Vibrations of the each C-CH₃ system in MNQ and its radical anion species should be described by 12 normal modes. These are three stretching; 2 $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{s}}(\text{CH}_3)$; three deformation; 2 $\delta_{\text{as}}(\text{CH}_3)$ and $\delta_{\text{s}}(\text{CH}_3)$; 2 rocking $\rho(\text{CH}_3)$ and one torsional mode of the CH₃ group; $\tau(\text{CH}_3)$. Moreover, there are three modes describing vibrations of the whole C-CH₃ group. These are one in-plane and one out-of-plane bending and one stretching modes of the C-CH₃ bond. Methyl group generally referred as electron donating substituents in the aromatic ring system. The methyl hydrogen atoms in naphthoquinone and their methylated derivatives are subjected simultaneously to hyperconjugation and backdonation, which cause the decrease of stretching wavenumbers and IR intensities as reported in literature [28] for similar molecular systems. An absorption arising from the C-H stretching in the methyl group vibrations occurs [29–31] in the region $3000\text{--}2840\text{ cm}^{-1}$. Absorption intensities, the infrared spectrum, clearly indicate that methyl hydrogens are directly involved in the donation of electronic charge, which is confirmed by the large q_H^0 values.

The A' and A'' CH₃ antisymmetric stretching modes (ν_{58} , ν_{57}) at 3123 and 3088 cm^{-1} respectively, which shifts downward of the both modes by about 45 cm^{-1} for the MNQ^- species as compared to the neutral MNQ molecule. The magnitude of the frequency CH₃ symmetric stretching mode (ν_{56}) under A' species is found at 3037 cm^{-1} in the neutral MNQ molecule shifts downward to 3006 cm^{-1} in the radical anionic species. The infrared intensity and the Raman activity increases in going from the neutral molecule to the radical anionic species for the above

mode (ν_{56}). In our calculations, the antisymmetric and symmetric stretching deformations vibrations are predicted in the range 1500-1400 cm^{-1} by B3LYP/6-311++G(d,p). Balakrishnan et al. [17] have assigned quinonoid ring stretching (1447 cm^{-1}) and symmetric C=O stretching (1442 cm^{-1}) modes for the MNQ and MNQ⁻ respectively, which could be better reassigned as $\delta_{\text{as}}(\text{CH}_3)$ mode (ν_{47}).

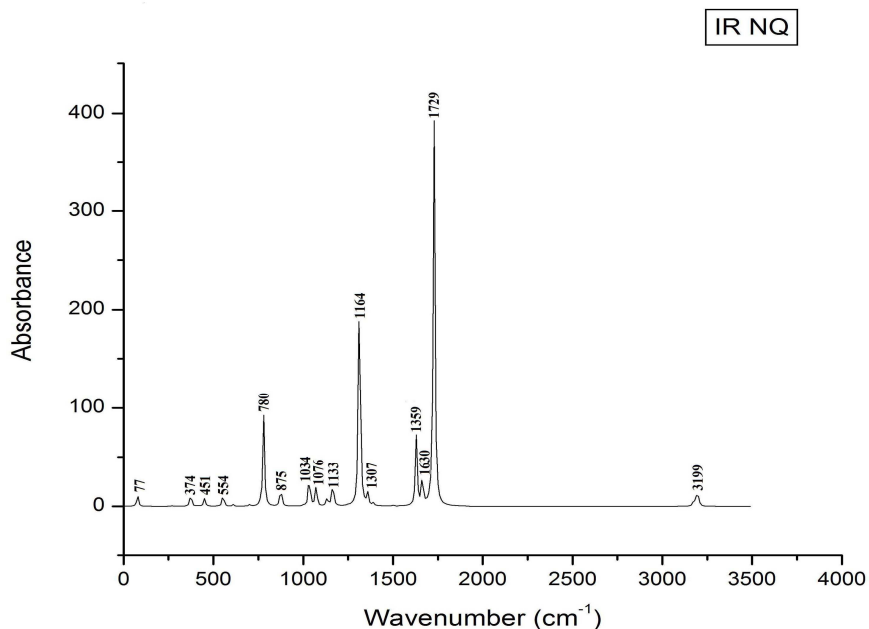


Fig.-7: Calculated IR spectrum of neutral NQ molecule

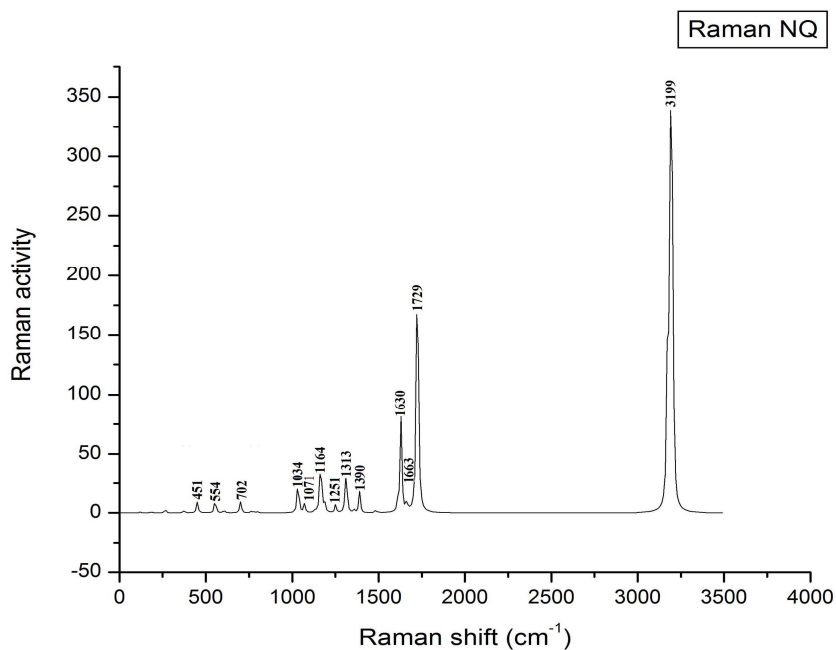
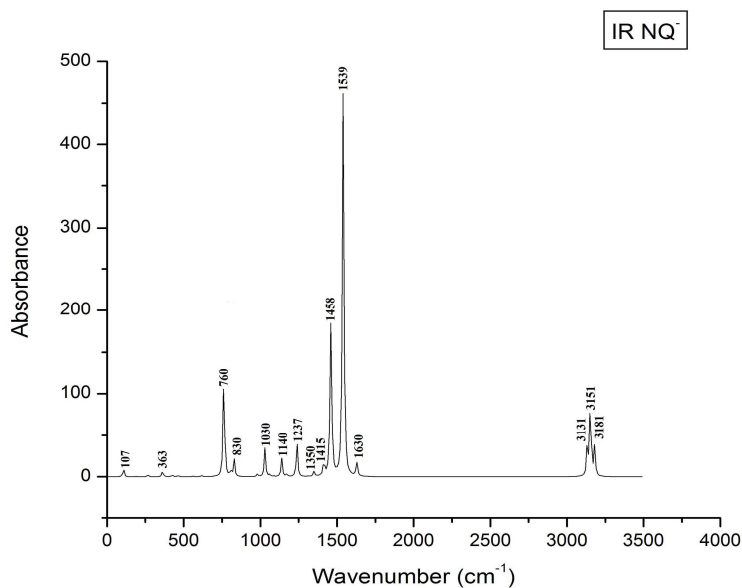
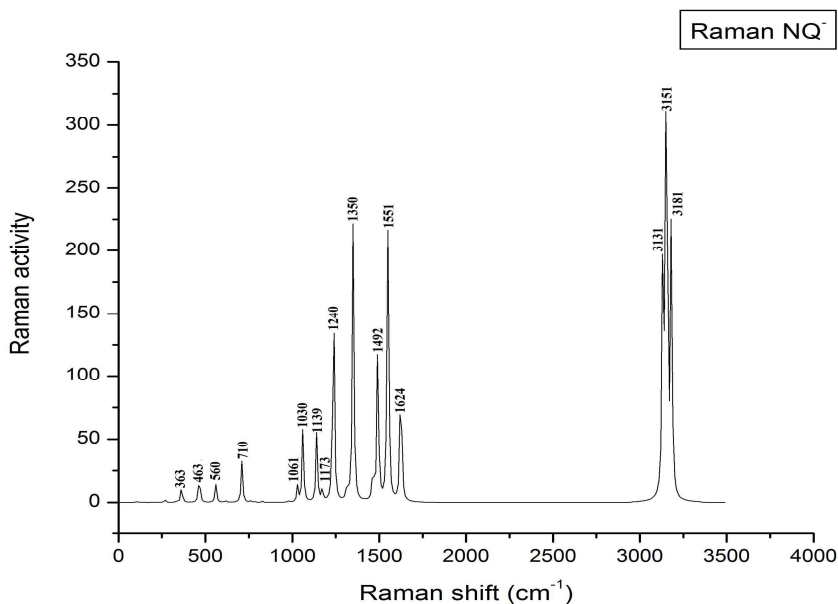


Fig.-8: Calculated Raman spectrum of neutral NQ molecule

**Fig.-9: Calculated IR spectrum of anion NQ molecule****Fig.-10: Calculated Raman spectrum of anion NQ molecule**

The frequency observed at 1385 cm^{-1} in Raman band [17] need to be reassigned as $\delta_{\text{as}}(\text{CH}_3)$ mode (ν_{46}). Conversion of the MNQ molecule to the radical anionic species shifts to the magnitude of the frequencies of the CH_3 rocking modes (ν_{33} , ν_{31}) are found to be same value $\sim 10\text{ cm}^{-1}$ (downward). The frequency of the CH_3 torsional mode ν_5 under the A'' species decreases by $\sim 35\text{ cm}^{-1}$ for the MNQ^- as compared to the neutral molecule. It is found that in MNQ molecule one of the $\rho(\text{CH}_3)$ modes have polarized Raman band and the other one has depolarized Raman band. The stretching and in-plane bending modes (ν_{26} , ν_4) associated with the C- CH_3 bond have

nearly same magnitudes in the MNQ molecule as compared to the radical anion molecule (Table-3). The out-of-plane bending vibrations of C-CH₃ bond (ν_6) shifted upward (by 20 cm⁻¹) with the depolarization ratio 0.75 in going from the MNQ to MNQ⁻ species.

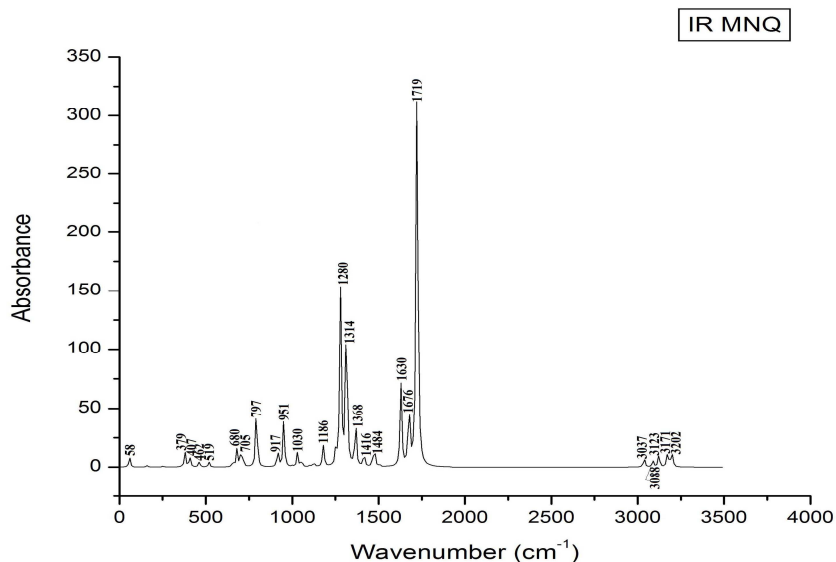


Fig.-11: Calculated IR spectrum of neutral MNQ molecule

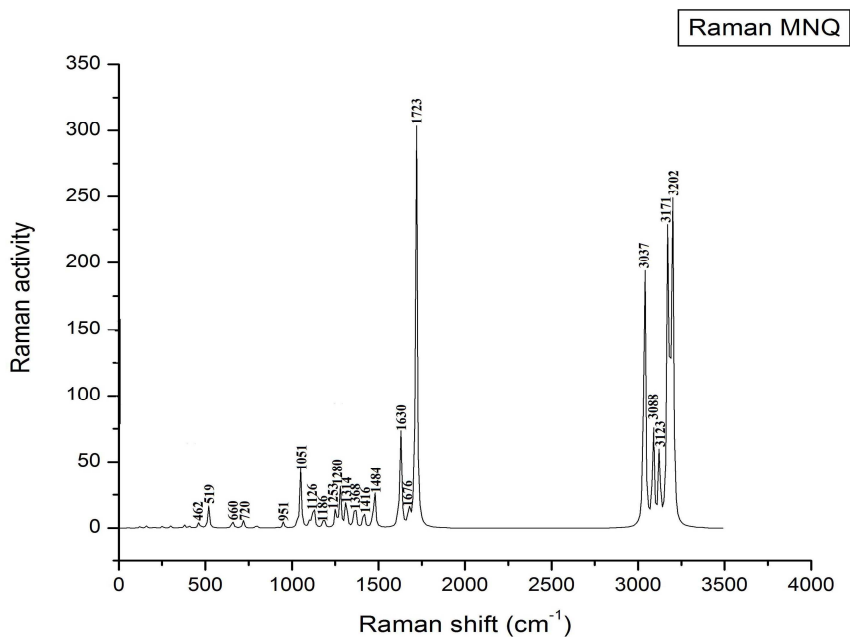


Fig.-12: Calculated Raman spectrum of neutral MNQ molecule

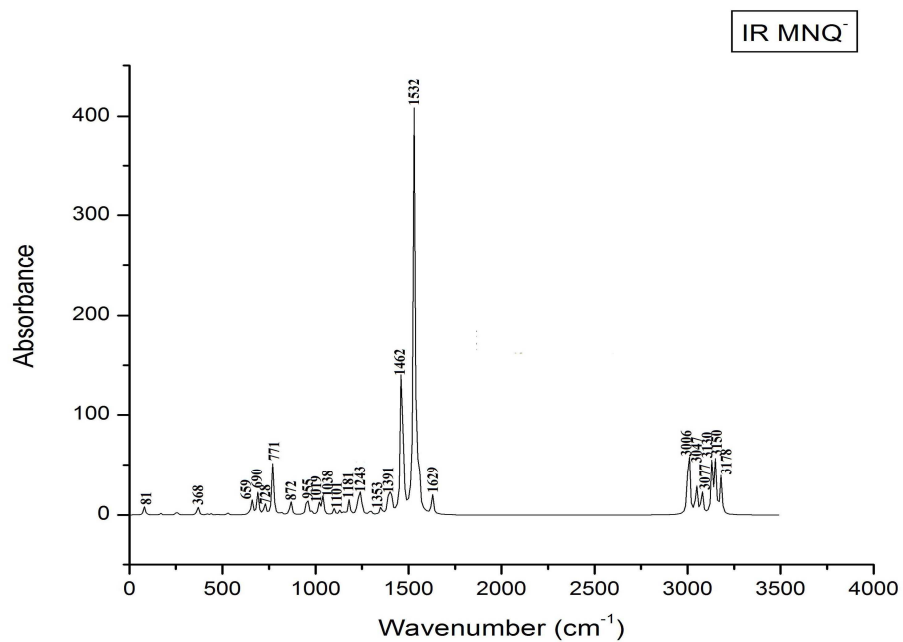


Fig.-13: Calculated IR spectrum of anion MNQ molecule

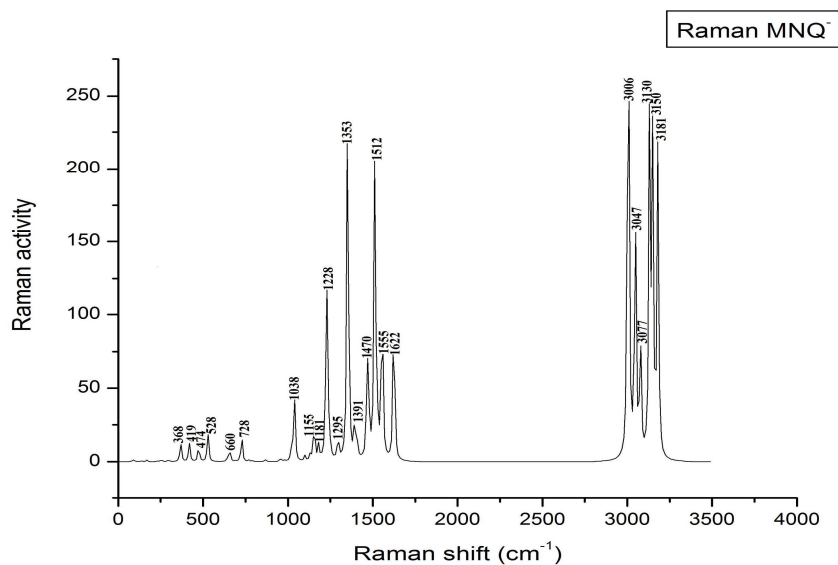


Fig.-14: Calculated Raman spectrum of anion MNQ molecule

Figures.7-14 : The calculated vibrational frequencies, IR intensity and Raman activity of the NQ, NQ⁻, MNQ and MNQ⁻ molecules.

Table-3: Comparison of the Calculated and observed^c vibrational frequencies of the NQ, NQ⁻, MNQ and MNQ⁻ Molecules

S.No.	NQ			NQ ⁻			MNQ			MNQ ⁻			Modes ^d
	Cal.	Obs.		Cal	Obs.		Cal.	Obs.		Cal.	Obs.		
		IR	R		IR	R		IR	R		IR	R	
v ₁	77 B₁ (12,0.03) 0.75	-	65 ⁱ _w	107 B₁ (10,0.82) 0.75	-	-	58 A^{''} (9,0.13) 0.75	-	-	81 A^{''} (8,0.34) 0.75	-	-	ϕ(ring)
v ₂	119 A₂ (0,0.83) 0.75	104 ^k	85 ⁱ	135 A₂ (0,0.33) 0.75	-	-	120 A^{''} (0,0.81) 0.75	-	-	137 A^{''} (0.22,0.68) 0.75	-	-	ϕ(ring)
v ₃	-	-	-	-	-	-	127 A^{''} (0.02,0.39) 0.75	-	-	93 A^{''} (0.51,1) 0.75	-	-	τ(CH ₃)
v ₄	185 B₁ (0.01,1) 0.75	158 ^k	152 ⁱ	193 B₁ (0.26,0.20) 0.75	-	-	159 A^{''} (1,2) 0.75	-	-	93 A^{''} (0.51,1) 0.75	-	-	butterfly
v ₅	-	-	-	-	-	-	253 A['] (1,2) 0.71	-	-	255 A['] (4,2) 0.72	-	-	β(C ₂ -C ₁₂)
v ₆	262 A₂ (0,0.71) 0.75	260 ⁱ	258 ⁱ	336 A₂ (0,0.83) 0.75	-	-	206 A^{''} (0.32,0.59) 0.75	-	-	231 A^{''} (0.04,0.38) 0.75	-	-	ϕ(ring)
v ₇	267 B₂ (0.44,2) 0.75	267 ^k	-	267 B₂ (3,2) 0.75	-	-	300 A['] (0.08,2) 0.62	-	-	295 A['] (0.11,1) 0.59	-	-	β(C ₄ =O ₁₄)+ β(C ₁ =O ₁₁)
v ₈	-	-	-	-	-	-	355 A^{''} (0.39,0.46) 0.75	-	-	372 A^{''} (0.40,0.63) 0.75	-	-	γ(C ₂ -C ₁₂)
v ₉	374 A₁ (14,2) 0.25	378 ^k	370 ⁱ	363 A₁ (7,13) 0.23	-	-	379 A['] (12,2) 0.34	-	-	368 A['] (9,13) 0.26	-	-	β(C ₁ =O ₁₁)+ β(C ₄ =O ₁₄)
v ₁₀	416 B₁ (0.82,0.07) 0.75	410 ^k	410 ⁱ	426 B₁ (2,0.09) 0.7497	-	-	426 A^{''} (0.26,0.01) 0.75	-	-	439 A^{''} (1,0.10) 0.75	-	-	ϕ(ring)
v ₁₁	451 A₁ (8,9) 0.18	-	-	463 A₁ (0.90,12) 0.66	-	-	462 A['] (5,5) 0.22	-	-	474 A['] (0.85,12) 0.73	-	-	α(ring)

v ₁₂	452 B₂ (0.07,0.39) 0.7492	450 ^k	450 ⁱ	467 B₂ (1,10) 0.75	-	-	407 A' (10,2) 0.61	-	-	419 A' (1,13) 0.53	-	-	α(ring)
v ₁₃	472 A₂ (0,0.36) 0.75	-	470 ⁱ	475 A₂ (0,0.11) 0.75	-	-	480 A'' (0.003,0.44) 0.75	-	-	490 A'' (0.001,0.07) 0.75	-	-	φ(ring)
v ₁₄	554 A₁ (14,13) 0.23	545 ^k	540 ⁱ	560 A₁ (0.82,14) 0.33	-	-	519 A' (5,18) 0.09	-	-	528 A' (2,20) 0.08	-	-	α(ring)
v ₁₅	600 B₂ (0.01,0.72) 0.75	598 ^k _w	563 ⁱ _w	603 B₂ (0.16,0.11) 0.7484	-	-	652 A' (2,3) 0.28	-	-	647 A' (3,5) 0.23	-	-	β(C-H)
v ₁₆	610 B₁ (2,1) 0.75	611 ^k _w	-	618 B₁ (1,1) 0.7499	-	-	680 A'' (15,0.28) 0.75	-	-	659 A'' (7,0.95) 0.75	-	-	φ(ring)
v ₁₇	692 A₂ (0,0.23) 0.75	690 ⁱ _w	690 ⁱ _w	667 A₂ (0,0.01) 0.75	-	-	705 A'' (17,0.46) 0.75	-	-	690 A'' (22,0.47) 0.75	-	-	γ(C ₄ =O ₁₄)+ γ(C ₁ =O ₁₁)
v ₁₈	702 A₁ (2,11) 0.09	693 ^k _w	-	710 A₁ (0.14,33) 0.04	-	-	660 A' (2,4) 0.37	-	-	660 A' (7,4) 0.09	-	-	v(ring) +α(ring)
v ₁₉	765 B₂ (3, 2) 0.75	-	-	767 B₂ (30,0.23) 0.7481	-	-	720 A' (3,5) 0.12	-	-	728 A' (12,18) 0.05	-	-	α(ring)
v ₂₁	780 B₁ (92,0.70) 0.75	762 ^k _s	755 ⁱ _s	760 B₁ (96,0.90) 0.75	-	-	792 A'' (42,0.68) 0.75	-	-	771 A'' (53,1) 0.75	-	-	γ(C-H)
v ₂₂	792 B₂ (0.01,0.08) 0.7499	-	-	807 B₂ (8,0.02) 0.74	-	-	802 A' (1,0.12) 0.49	-	-	816 A' (2,0.09) 0.7471	-	-	α(ring)
v ₂₃	798 A₂ (0,1) 0.75	774 ^k _w	780 ⁱ _w	786 A₂ (0,0.57) 0.75	-	-	797 A'' (8,1) 0.75	-	-	790 A'' (0.06,0.69) 0.75	-	-	γ(C ₁ =O ₁₁)+ γ(C ₄ =O ₁₄)

V ₂₄	875 B₁ (22,0.19) 0.75	865 ^k _w	-	830 B₁ (21,0.88) 0.7499	-	-	-	-	-	-	-	-	γ(C-H)
V ₂₅	918 A₂ (0,0.09) 0.7500	915 ^k _w	914 ⁱ _w	872 A₂ (0,0.02) 0.75	-	-	916 A'' (4,0.22) 0.75	-	-	872 A'' (1,0.15) 0.75	-	-	γ(C-H)
V ₂₆	-	-	-	-	-	-	951 A' (940,5) 0.35	-	-	955 A' (24,3) 0.73	-	-	ν(C ₂ -C ₁₂)
V ₂₈	1004 B₁ (1,0.005) 0.75	998 ^k _w	-	980 B₁ (3,0.75) 0.75	-	-	1002 A'' (1,0.01) 0.75	-	-	979 A'' (3,0.63) 0.75	-	-	γ(C-H)
V ₂₉	1016 A₂ (0,0.62) 0.75	-	-	928 A₂ (0,0) 0.75	-	-	917 A'' (11,0.22) 0.75	-	-	867 A'' (16,2) 0.75	-	-	γ(C-H)
V ₃₀	1021 A₂ (0,0.06) 0.75	1007 ^k _w	-	982 A₂ (0,0.05) 0.75	-	-	1020 A'' (0.01,0.07) 0.75	-	-	982 A'' (0.03,0.07) 0.75	-	-	γ(C-H)
V ₃₁	-	-	-	-	-	-	1030 A' (12,3) 0.41	-	-	1019 A' (11,7) 0.30	-	-	ρ(CH ₃)
V ₃₂	1034 A₁ (36,32) 0.07	1020 ^k _m	1018 ⁱ _m	1030 A₁ (35,12) 0.13	-	-	1051 A' (3,45) 0.08	-	-	1038 A' (21,49) 0.17	-	-	α(ring)
V ₃₃	-	-	-	-	-	-	1058 A'' (3,0.48) 0.75	-	-	1046 A'' (0.98,0.14) 0.75	-	-	ρ(CH ₃)
V ₃₅	1071 B₂ (16,7) 0.07	1057 ^k _m	1050 ⁱ _w	1061 B₂ (2,58) 0.14	-	-	1104 A' (2,8) 0.15	-	-	1101 A' (6,4) 0.74	-	-	β(C-H)
V ₃₆	1076 A₁ (5,0.33) 0.7495	1082 ⁱ _w	-	1088 A₁ (0.84,0.01) 0.68	-	-	-	-	-	-	-	-	β(C-H) +α(ring)

V ₃₇	1133 B₂ (10,2) 0.75	-	-	1139 B₂ (23,7) 0.7490	-	-	1179 A' (16,1) 0.32	-	-	1155 A' (3,29) 0.31	-	1139 ^j	β(C-H)
V ₃₈	1164 A₁ (29,59) 0.12	1157 ^k _m	1177 ^j _m	1140 A₁ (1,48) 0.10	-	-	1126 A' (4,23) 0.17	-	1109 ^j _w	1132 A' (5,5) 0.36	-	-	β(C-H)
V ₃₉	1187 A₁ (0.24,9) 0.44	-	1187 ^j _w	1173 A₁ (3,10) 0.56	-	1158 ^j _w	1186 A' (4,9) 0.73	-	1171 ^j _w	1228 A' (16,141) 0.27	-	-	β(C-H)
V ₄₁	1251 B₂ (0.56,7) 0.75	1230 ⁱ _{vw}	1235 ⁱ _w	1240 B₂ (25,0.07) 0.73	-	-	1253 A' (16,17) 0.25	-	1240 ^j _w	1181 A' (15,11) 0.15	-	-	v(ring)
V ₄₂	1307 B₂ (3,7) 0.7498	-	-	1315 B₂ (0.69,13) 0.75	-	-	1280 A' (150,30) 0.17	-	1267 ^j	1243 A' (29,22) 0.62	-	-	v(ring)
V ₄₃	1313 A₁ (266,36) 0.47	1301 ^k _{ms}	1300 ⁱ _m	1237 A₁ (19,181) 0.41	-	-	1314 A' (156,28) 0.58	-	1305 ^j _w	1353 A' (8,277) 0.25	-	1339 ^j _s	v(ring)
V ₄₄	1359 A₁ (13,2) 0.16	1331 ^k _m	1335 ⁱ _w	1350 A₁ (6,221) 0.27	-	1327 ^j _{ms}	1358 A' (2,9) 0.60	-	1328 ^j	1405 A' (34,20) 0.62	-	-	v(ring)
V ₄₅	1390 B₂ (2,18) 0.75	1378 ^k _w	1380 ⁱ _w	1415 B₂ (21,0.75) 0.7497	-	-	1368 A' (38,14) 0.72	-	1362 ^j	1295 A' (6,17) 0.7470	-	-	v(ring)
V ₄₆	-	-	-	-	-	-	1416 A' (13,17) 0.56	-	1385 ^j	1391 A' (14,17) 0.33	-	-	δ _s (CH ₃)
V ₄₇	-	-	-	-	-	-	1467 A'' (9,9) 0.75	-	1447 ^j	1464 A'' (4,14) 0.75	-	1442 ^j	δ _{as} (CH ₃)
V ₄₈	-	-	-	-	-	-	1479 A' (10,25) 0.43	-	-	1470 A' (32,55) 0.13	-	-	δ _{as} (CH ₃)
V ₄₉	1484 B₂ (0.03,3) 0.75	1456 ^k	1453 ⁱ	1458 B₂ (181,4) 0.7499	-	-	1484 A' (0.27,3) 0.72	-	-	1462 A' (159,6) 0.72	-	-	v(ring)
V ₅₀	1504 A₁ (1,0.48) 0.74	1510 ^k _{vw}	1510 ⁱ _{vw}	1465 A₁ (45,22) 0.18	-	1441 ^j _w	1506 A' (2,0.64) 0.7472	-	-	1481 A' (2,14) 0.73	-	1468 ^j _w	v(ring) _c
V ₅₁	1611 A₁ (0.23,8) 0.45	1607 ^k _w	1605 ⁱ _w	1551 A₁ (39,223) 0.7495	-	1537 ^j _{ms}	1614 A' (0.70,11) 0.42	1600 ^l _w	1599 ^j _w	1555 A' (54,129) 0.7488	-	1539 ^j _{ms}	v(ring)

V ₅₂	1630 B₂ (71,81) 0.75	-	-	1630 B₂ (15,1) 0.7494	-	-	1630 A'' (70,72) 0.75	1624 ^l _m	1624 ^j _m	1629 A'' (20,31) 0.23	-	-	v(ring)
V ₅₃	1663 A₁ (32,8) 0.02	1632 ^k _w	1660 ^j _w	1492 A₁ (0.52,129) 0.69	-	-	1676 A' (63,17) 0.15	-	1672 ^j _w	1512 A' (5,250) 0.7467	-	-	v(ring)
V ₅₄	1725 A₁ (20,303) 0.15	1686 ^k _{vs}	1678 ⁱ _{vs}	1539 A₁ (473,12) 0.75	1515 ^l _s	1515 ^j _s	1719 A' (40,317) 0.14	-	-	1532 A' (443,13) 0.62	1505 ^l _s	-	v(C ₄ =O ₁₄) + v(C ₁ =O ₁₁)
V ₅₅	1729 B₂ (408,2) 0.54	1665 ⁱ _{vs}	1663 ⁱ _{vs}	1624 B₂ (3,122) 0.36	1610 ^l _{mbr}	1603 ^j _m	1723 A' (385,6) 0.15	1669 ^m _s	1669 ^j _m	1622 A' (0.61,78) 0.38	-	1605 ^j _m	v(C ₁ =O ₁₁) + v(C ₄ =O ₁₄)
V ₅₆	-	-	-	-	-	-	3037 A' (8,261) 0.05	-	-	3006 A' (97,408) 0.09	-	-	v _s (CH ₃)
V ₅₇	-	-	-	-	-	-	3088 A'' (6,87) 0.75	-	-	3047 A'' (35,196) 0.75	-	-	v _{as} (CH ₃)
V ₅₈	-	-	-	-	-	-	3123 A' (12,70) 0.7485	-	-	3077 A' (26,87) 0.61	-	-	v _{as} (CH ₃)
V ₆₀	3172 B₂ (3,53) 0.75	3018 ⁱ _w	3020 ⁱ _w	3131 B₂ (21,78) 0.75	-	-	3171 A' (3,74) 0.7495	-	-	3130 A' (19,93) 0.74	-	-	v(C-H)
V ₆₂	3173 B₂ (0.72,101) 0.7486	3076 ^k _w	3070 ⁱ _w	3134 B₂ (20,156) 0.75	-	-	-	-	-	-	-	-	v(C-H)
V ₆₃	3186 A₁ (7,132) 0.40	-	3120 ⁱ _w	3151 A₁ (54,181) 0.32	-	-	3185 A' (8,141) 0.39	-	-	3150 A' (51,211) 0.32	-	-	v(C-H)
V ₆₄	3191 A₁ (5,215) 0.17	3065 ⁱ _m	3062 ⁱ _m	3155 A₁ (44,245) 0.20	-	-	3170 A' (7,137) 0.27	-	-	3132 A' (40,169) 0.39	-	-	v(C-H)
V ₆₅	3199 B₂ (0.35,22) 0.7482	3093 ⁱ _w	3085 ⁱ _w	3179 B₂ (13,24) 0.75	-	-	3199 A' (0.65,29) 0.57	-	-	3178 A' (14,41) 0.47	-	-	v(C-H)
V ₆₆	3202 A₁ (9,229) 0.11	3185 ⁱ _w	3183 ⁱ _w	3181 A₁ (25,197) 0.14	-	-	3202 A' (10,220) 0.11	-	-	3181 A' (26,179) 0.15	-	-	v(C-H)

c: The first and second numbers within each bracket represent IR intensity(Km/mol) and Raman activity($\text{\AA}^4/\text{amu}$) while the number above and below each bracket represent the corresponding calculated frequency (cm^{-1}) and depolarization ratios of the Raman band respectively. The letters following the brackets (in the red colour) corresponds the species of the mode.

d: ν = stretching, τ = twisting, ρ = rocking, γ = out-of-plane deformation, β = in-plane deformation, α = planar ring deformation,

ϕ = non-planar ring deformation, ν_{as} = antisymmetric stretching, ν_s = symmetric stretching, δ_{as} = antisymmetric deformation, δ_s = symmetric deformation.
i: [15], j: [18] and k: [17]

4. Thermo-dynamical properties

Basic thermodynamic parameters such as total energy (E), zero-point vibrational energy (ZPVE), dipole moment (μ), constant volume molar heat capacity (CV), entropy (S), thermal energy (TE) and rotational constant (RC) have been calculated for the neutral NQ and MNQ molecules and their corresponding radical anions. The results are presented in Table-4. The present calculations predict that the thermodynamical stability order based on the total energy E increases in the following orders: $NQ^- > NQ$ and $MNQ^- > MNQ$, thus, anionic form is more stable as compared to their neutral form. The magnitude of zero-point vibrational energy (ZPVE) and thermal energy correction (E) decreases slightly in going from NA to NA^- (by 4.127/3.609), NQ to NQ^- (by 1.396/1.492) and MNQ to MNQ^- (by 2.536/1.569) (in Kcal/Mol) respectively.

The constant volume molar heat capacity of a molecule defined as the amount of heat required to change the temperature of that molecule by 1° C. The molecules with the larger molecular mass will need more heat capacity than the smaller one [32]. The addition of electron for all the radical anion (NQ and MNQ) increases the magnitude of molar heat capacity as compared to their neutral molecules. According to the similarity principle [33], the higher the similarity among the components, higher the value of entropy will be and the higher the stability will be. The calculated entropy (S) value in the anion form is higher than the neutral form. The calculated rotational constant a, b, c for the neutral and their corresponding radical anionic molecules are shown in Table-4.

Table – 4: Calculated Thermo-dynamical Properties^e for the NQ, NQ^- , MNQ and MNQ^- molecules

S.No	Species	Total energies E	Zero-point vibrational energy ZPVE	Dipole Moment μ	Constant volume molar heat capacity CV	Entropy S	Thermal energy TE	Rotational Constant RC		
								a	b	c
1	NQ	-535.259	82.851	1.520	34.538	92.295	88.327	1.326	1.092	0.599
2	NQ^-	-535.332	81.455	3.404	34.790	92.400	86.835	1.285	1.116	0.597
3	MNQ	-574.591	100.151	1.167	40.427	100.172	106.686	1.288	0.768	0.483
4	MNQ^-	-574.661	98.615	2.033	40.733	100.930	105.117	1.256	0.780	0.483

e: E is measured in Hartrees, ZPVE & TE are measured in Kcal/Mol, CV & S are measured in Cal/Mol-Kelvin, μ is measured in Debye and RC is measured in GHZ.

CONCLUSION

The C₁-C₂ bond length in the enedione part falls in the single bond increases by 0.015 Å in going from the neutral NQ to MNQ molecule which is strongly affected by the methyl group. The bond angle C₁-C₂-C₃ decreases by 2.4° in going from NQ to MNQ molecules due to the enedione part presence of the CH₃ group at the site C₂ for the neutral MNQ molecule. The C=O and C₂=C₃ bonds are elongated by 0.042 Å and 0.035 Å, respectively, for the radical anions as compared to those of the neutral NQ and MNQ molecules. The other bond distances in the benzenoid part such as C₅-C₆, C₇-C₈ and C₉-C₁₀ are found to be increases in magnitude by ~0.012 Å in going from the three neutral molecules to their respective radical anions. The values of the dihedral

angles $C_1-C_2-C_{12}-H_{19}/C_1-C_2-C_{12}-H_{20}$ are almost identical with values of 58.6° and 58.7° , respectively, in the MNQ and MNQ^- molecules.

For the neutral NQ molecule and its radical anions, the magnitude of the atomic charges at the atoms C_1 and C_4 are almost identical seen to possess more positive charge due to the electronegative O atom attached at the sites C_1 and C_4 . But in the case of MNQ and its radical anions are not identical due to the electron withdrawing nature of CH_3 group attached at the sites C_2 . The magnitudes of the charge on the site C_1 and C_4 are found decreases by 0.013 and 0.055 respectively, for the radical anion NQ species as compared their neutral molecules due to the O atom(s) are seen to possess negative charge due to their electron-withdrawing nature. At the sites O_{11} and O_{14} (-0.731 and -0.861) are almost identical for the neutral NQ molecule and its radical anion. But in the case of MNQ and its radical anion, the magnitude of atomic charge at the site O_{14} are found to be greater than that of the O_{11} due to attachment of an electron releasing alkyl (CH_3) group at the site C_2 .

The calculated frequency of the ring stretching mode (ν_{53}) decreases by $\sim 15\text{ cm}^{-1}$ for MNQ as compared to NQ. The calculated vibrational frequencies of C-C ring stretching mode (ν_{45} , ν_{42} and ν_{18}) are shifted to the lower frequencies by 22, 27 and 42 cm^{-1} in going from the neutral NQ to MNQ molecules. The planar-ring deformations modes (ν_{19} , ν_{14} and ν_{12}) frequencies are found to be 45, 35 and 45 cm^{-1} in going from the neutral NQ to MNQ molecules. The calculated frequencies for the ring stretching modes ν_{44} and ν_{43} decrease in going from the NQ to NQ^- species, but further increase in going from the MNQ to MNQ^- species. It is also observed that the magnitude of the frequency for the ring stretching modes ν_{45} and ν_{42} slightly increase by $\sim 25/15\text{ cm}^{-1}$ in going from the NQ to NQ^- species while in going from the MNQ to MNQ^- species the calculated frequency decrease by $\sim 75/40\text{ cm}^{-1}$. The magnitude of the frequency CH_3 symmetric stretching mode (ν_{56}) under A' species is found at 3037 cm^{-1} in the neutral MNQ molecule shifts downward to 3006 cm^{-1} in the radical anionic species. The infrared intensity and the Raman activity increases in going from the neutral molecule to the radical anionic species for the above mode (ν_{56}).

The present calculations predict that the thermodynamical stability order based on the total energy E increases in the following orders: $NQ^- > NQ$ and $MNQ^- > MNQ$, thus, anionic form is more stable as compared to their neutral form. The magnitude of zero-point vibrational energy (ZPVE) and thermal energy correction (E) decreases slightly in going from NA to NA^- (by 4.127/3.609), NQ to NQ^- (by 1.396/1.492) and MNQ to MNQ^- (by 2.536/1.569) (in Kcal/Mol) respectively.

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